ATTACHMENT B

LABORATORY STANDARD OPERATING PROCEDURES

FILES ON ENCLOSED CD

AMERICAN WEST ANALYTICAL LABORATORIES
STANDARD OPERATING PROCEDURES

Alkalinity by SM 2320B (20th Edition)

1.0 Applicable matrix

1.1 This method is applicable to water samples.

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratory PQL is 10ppm

3.0 Scope and Application

3.1 This method may be used for all concentration ranges.

3.2 Titrating volumes greater than 50mL should be avoided by taking smaller volumes of sample.

3.3 This method may be used to determine the Total Alkalinity, Bicarbonate, Carbonate, Hydroxide and Carbon Dioxide concentrations of a water sample.

4.0 Summary of test method

4.1 A sample aliquot is titrated with 0.02N sulfuric acid to a pH of 8.3 to determine the carbonate concentration, and then to an endpoint of pH 4.5 to determine the total alkalinity. Bicarbonate may be determined by subtracting the carbonate value from the total alkalinity value.

5.0 Definitions

5.1 Alkalinity is defined as a waters capacity to neutralize acid.

5.2 MB: Method Blank

5.3 LCS: Laboratory Control Sample

5.4 MS: Matrix Spike

5.5 MSD: Matrix Spike Duplicate

5.6 Phenolphthalein alkalinity: traditional term for the quantity measured by titration to pH 8.3.

6.0 Interference

6.1 High concentrations of salts in the form of weak acids may interfere with pH measurements.

6.2 Samples containing Oil/grease, soaps, suspended material, and precipitates may coat the pH probe creating a slow response.

7.0 Safety

7.1 Samples from wastewater treatment plants may pose a potential biological hazard. Handle samples while wearing a lab coat, safety glasses, and proper gloves.

7.2 Reagents used in this procedure are caustic and acidic. Handle chemicals while wearing a lab coat, safety glasses and proper gloves.

8.0 Equipment and supplies

8.1 Orion Expandable Ion Analyzer EA940

8.2 Orion sure flow Ross combination electrode

8.3 Temperature compensator: ATC probe

8.4 Stir plate

8.5 Stir bar

8.6 Disposable beakers

8.7 150mL beaker

8.8 50mL buret, class A

9.0 Reagents and standards

9.1 pH Buffers: 4, 7, 9 and 10 purchased from a certified vendor.

9.1.1 The pH 9 buffer is purchased from a separate vendor than the 4, 7, and 10 to assure a second source standard is always available.

9.1.2 The vendors must supply a Certificate of Analysis (C of A) with the buffers. This C of A must be logged into the LIMS, labeled with the receiving person's initials, Laboratory ID, and expiration date. All C of A's must be delivered to the QAO.

9.2 pH filling solution, purchased from a certified vendor.

9.3 1N Sodium Carbonate Solution purchased from Fisher is equivalent to 50,000 mg/L.

9.3.1 A 0.005N solution is utilized for titrant standardization. Prepare this solution by diluting 0.1mL of the 1N sodium carbonate solution to 20mL with Di water.

9.3.2 2 separate lots of 1N sodium carbonate are purchased to provide a LCS and a spike.

9.3.3 Varying concentrations of the standard may be made by performing a dilution. The most common dilution is 5mL standard diluted to 1L with DI water producing a 250mg/L standard.

9.4 0.02N Sulfuric Acid titrant: Dilute 2 mL concentrated H_2SO_4 to 4L with DI water.

9.5 DI Water

10.0 Sample collection

10.1 Samples should be collected in a plastic container (HDPE) and refrigerate at >0 to 6°C until analysis.

10.2 Samples must be analyzed within 14 days of collection.

11.0 Quality control

11.1 A MB must be analyzed per batch of 20 samples or fewer.

11.2 A LCS must be analyzed per batch of 20 samples or fewer.

11.3 A MS/MSD must be analyzed per batch of 20 samples or fewer

12.0 Calibration and standardization

12.1 Calibrate the pH meter by following the directions below:

Display	**Action**
Operator Menu?	Press "**No**" If the instrument was used for another type of analysis Press "**Yes**".
Calibrate 1: pH?	Press "**Yes**"
Enter Number of Buffers (1-3)	Press "**3**"
Do Automatic Calibration?	Press "**Yes**"
1: pH Electrode in Buffer 1?	Place electrode in first buffer (pH4)
Buffer 1 = 4.35 Not Ready	None. Wait for stable reading
Buffer 1 = 4.05 Cal as 4.01	Press "**Yes**", if cal as value is correct
Repeat steps for 2nd and 3rd buffer	
Slope = 98% Yes to Continue	Press "**Yes"**
Measure 1: pH?	Place electrode in pH Buffer 9 and press "**Yes**"

1: pH = 9.03
Ready Record pH value

12.2 Standardize the titrant as follows:

12.2.1 Fill buret with titrant and place the meniscus on zero.

12.2.2 Place 0.1 mL of the 1N sodium carbonate solution in a beaker with a small stir bar, and add 20 mL of DI water.

12.2.3 Place sample on a stir plate and measure initial pH

12.2.4 Record the initial pH in the Alkalinity logbook.

12.2.5 Titrate sample slowly to a pH of 4.5 +/- 0.2.

12.2.6 Record volume of titrant delivered in the Alkalinity logbook and calculate results.

$$\text{Normality} = \frac{\text{mL } Na_2CO_3 \text{ used}}{\text{mL acid used}}$$

13.0 Procedure

13.1 Sample Analysis

13.1.1 Fill buret with titrant and place the meniscus on zero.

13.1.2 Place an aliquot of sample in a 150mL beaker with a stir bar. Record sample volume in Alkalinity log-book.

13.1.3 Place sample on a stir plate and measure initial pH.

13.1.4 Document the initial pH in the Alkalinity log-book.

13.1.5 Titrate sample slowly to a pH of 8.3 +/- 0.2.

13.1.6 Document the volume of titrant used in the Alkalinity logbook.

13.1.7 Titrate sample slowly to a pH of 4.5 +/- 0.2.

13.1.8 Document volume of titrant used in the Alkalinity logbook and calculate result.

13.2 Standard Normality

13.2.1 Fill buret with titrant and place the meniscus on zero.

13.2.2 Place 0.1 mL of the 1N sodium carbonate solution in a beaker and add 20 mL of DI water.

13.2.3 Place sample on a stir plate and measure initial pH.

13.2.4 Document the initial pH in the Alkalinity logbook.

13.2.5 Titrate sample slowly to a pH of 4.5 (4.3 – 4.7 is acceptable).

13.2.6 Document volume of titrant used in the Alkalinity logbook and calculate results.

14.0 Calculations

14.1

Result of Titration	**Hydroxide Alkalinity as $CaCO_3$**	**Carbonate Alkalinity as $CaCO_3$**	**Bicarbonate concentration as $CaCO_3$**
P = 0	0	0	T
P < ½ T	0	2P	T – 2P
P= ½ T	0	2P	0
P > ½ T	2P – T	2(T-P)	0
P = T	T	0	0

P = phenolphthalein alkalinity (8.3 titration)
T = Total alkalinity

The above calculations are handled by the AWAL Alkalinity Spreadsheet

14.2 Total Alkalinity (mg/L $CaCO_3$) = $\frac{A * N * 50{,}000}{\text{mL of sample}}$

Where:
A = mL standard acid used to achieve a pH of 8.3 & 4.5
N = normality standard acid

Note: This calculation only works when the pH is less than 8 when pH is above 8 use the spread sheet.

14.3 Carbonate Alkalinity in $\frac{\text{mg } CaCO_3}{1} = \frac{B * N * 50{,}000 * 2}{\text{mL Sample}}$

Where:
B = mL H_2SO_4 titrant used (8.3pH)
N = Normality of H_2SO_4 titrant

Note: The AWAL spreadsheet will perform this calculation.

14.4 Bicarbonate in mg $CaCO_3$ = Total Alkalinity – Carbonate

Note: The AWAL spreadsheet will perform this calculation.

14.5 Free Carbon Dioxide mg/L (mg CO_2/L) = $2.0 * C * 10^{(6 - pH)}$

Where:
C = Bicarbonate in mg $CaCO_3$

Note: The AWAL spreadsheet will perform this calculation.

14.6 Total Carbon Dioxide mg/L = D + 0.44 (2C + E)

Where:
D = mg free carbon dioxide
C = Bicarbonate alkalinity
E = Carbonate alkalinity

Note: The AWAL spreadsheet will perform this calculation.

14.7 Standard Acid Normality

14.7.1 Place 0.1 mL of 1N sodium carbonate solution in a beaker and dilute to 20 mL with DI water.

$$\text{Normality} = \frac{\text{mL } Na_2CO_3 \text{ used}}{\text{mL acid used}}$$

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated semi annually.

15.2 Current limits are listed in section 17.

16.0 Pollution prevention

16.1 To minimize the generation of waste, the pH buffers are purchased in 4L containers to avoid expiration of buffers before use.

16.2 Inorganic spill kits are available in the laboratory in case of spills. Baking soda is used for acid spills and Spill-X-C is used for caustic spills.

16.3 The samples analyzed in this procedure are typically drinking, surface, ground waters as well as industrial and domestic discharge waters that are not considered hazardous and may be disposed through the laboratory sink.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The MB must be less than the laboratory PQL.

17.2 The LCS must recover within 10% of its true value

17.3 The MS/MSD must recover within 20% and have an RPD within 10%.

17.4 The pH meter slope determined during pH calibration must be between 92 and 102% for acceptance.

18.0 Corrective actions for out of control data.

18.1 If the MB fails, make a fresh MB and re-analyze. If re-analysis fails, re-clean glassware and re-analyze the batch

18.2 If the LCS fails, make a fresh LCS and re-analyze. If re-analysis fails, re-standardize the titrant and re-analyze the batch.

18.3 If the RPD is extremely out of limits, reanalyze batch making sure samples are mixed well.

19.0 Contingencies for handling out of control data.

19.1 If reanalysis of samples cannot be performed within 14 days of collection, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a MS/MSD or its RPD fails due to matrix issues flag the final report with the appropriate qualifier.

20.0 Waste management

20.1 Excess sample may be disposed down the laboratory sink

20.2 Excess buffer may be neutralized and disposed down the laboratory sink.

20.3 Refer to the laboratory Waste Management and Sample Disposal SOP

21.0 References

21.1 Methods and Guidance for Analysis of Water, Alkalinity Method 310.1 Revised 1978.

21.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, p 2-27, Method 2320B.

21.3 Standard Methods for the Examination of Water and Wastewater, 20th Edition, p 4-32, Method 4500-CO_2D.

21.4 American West Analytical Laboratory Waste Management and Sample Disposal SOP, latest revision.

22.0 Tables, diagrams

22.1 Not Applicable

23.0 Clarification/Modifications of the method

23.1 The laboratory uses 0.005N Sodium Carbonate solution and not 0.05N to determine the normality of the titrant.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

1.0 Applicable matrix

1.1 This method is applicable to drinking water, ground water, surface waters industrial wastewater, domestic wastewater, water-extracted soils and non acetic acid leachates.

2.0 Detection Limit

2.1 The laboratory method detection limit (MDL) is determined semi-annually as specified by method 300.0 in accordance to 40CFR Part 136 Appendix B. The actual MDL study is located in the QAO files.

2.2 The laboratory practical quantitation limit (PQL) is based on the MDL study.

2.3 The laboratories PQLs and MDLs are found in the LIMS under the specified analyte group

2.3.1 The laboratories PQL's may be extended by sample dilution, if the sample exceeds the instruments linear calibration range.

3.0 Scope and Application

3.1 This method is designed to analyze the following inorganic anions by ion chromatography sequentially in an aqueous or aqueous extracted sample:

Chloride	Nitrite (as N)
Fluoride	Nitrate/Nitrite (as N)
Bromide	Ortho-Phosphate (as P)
Nitrate (as N)	Sulfate

4.0 Summary of test method

4.1 A small volume of sample is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system composed of a guard column, separation column, suppressor device, and a conductivity detector.

An extraction procedure must be performed to use this method for solid samples.

5.0 Definitions

5.1 Deionized water (DI): laboratory feedwater that is passed through an ion exchange system, consisting of a carbon bed, cation bed, anion bed and filters.

5.2 Double deionized water (DDI): laboratory feedwater that is re-circulated through the DI system more than once.

5.3 Method blank (MB): an aliquot of DDI that is treated exactly like a sample. One MB must be analyzed per batch.

5.4 Batch: is the term for samples and quality control samples analyzed together. A batch is composed of a MB, LCS, MS, MSD and no more than 20 samples.

5.5 Laboratory control sample (LCS): an aliquot of DDI that has been spiked with known analytes. This solution is made from the same source as the calibration standards.

5.6 Matrix spike/Matrix spike duplicate (MS/MSD): an analytical sample that is spiked with a known and analyzed. The MSD is a second aliquot of the analytical sample spiked just like the MS. The spiking solution used is the same as the calibration standards.

5.7 Initial calibration verification (ICV): this is a mid-range standard prepared from a separate source than the calibration standards. In method 300.0 this standards is referred to as an instrument performance check standard (IPC).

5.8 Continuing calibration verification (CCV): this is a mid-range standard prepared from the same source as the calibration standards.

5.9 Instrument performance check solution (IPC) – A solution of one or more method analytes used to test the performance of the instrument system. This solution is to be made from the same source as the calibration standards.

5.10 Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.

5.11 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified measured and reported with 99% confidence that the analyte concentration is greater than zero.

6.0 Interference

6.1 Positive interferences; can be caused by substances with similar retention time windows as the anion of interest. If this is suspected sample dilution and/or the method of standard addition can help separate peaks.

6.2 Interferences may be caused by samples with large anion concentrations masking adjacent anions. If this is suspected sample dilution and/or the method of standard addition can help separate peaks.

6.3 The negative peak that elutes near the fluoride peak can interfere with the base line used to measure the fluoride peak. This interference can be eliminated with the addition of 1 mL concentrated eluent to 100 mL of standard and sample.

6.4 Samples with particulates greater than 0.45 μm and reagents greater than 0.2 μm will stop your flow. Filter all samples and reagents through a 0.2 μm filter before pumping into the instrument.

6.4.1 The instrument has several filters one at 0.45 μm and three at 0.2 μm.

6.5 Acetic acid or acetate elutes somewhere between fluoride and chloride depending on its concentration. This method is not recommended for analysis of samples containing acetic acid such as leachates.

7.0 Safety

7.1 Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses. Samples should be considered hazardous. Avoid exposure, skin contact, inhalation, or ingestion.

7.1.1 Most of the standards and reagents are listed as skin irritants, if contact occurs wash well with water.

7.2 MSDSs for laboratory chemicals are located in notebooks near their area of use. These are for employee reference purposes.

8.0 Equipment and supplies

8.1 Analytical balance capable of weighing to the nearest 0.0001g.

8.2 Metrohm Advanced IC System

8.3 Centrifuge tubes, 50 mL capacity.

8.4 Pipettors different capacities

9.0 Reagents and standards

9.1 Reagent water: deionized water, laboratory system double deionized water (DDI) must be used.

9.2 Eluent solution: purchased pre-made from Methrom Peak, part number M.PAK.0050.

9.2.1 Shelf life of this reagent is 3 years or manufacturer expiration date, which ever is sooner.

9.3 Eluent solution laboratory made: Add 0.678 g of Sodium Carbonate and 0.168 g of Sodium Bicarbonate to 2 L of DDI. This may be stored for 6 months.

9.4 Regeneration solution: (Sulfuric acid 100mM and 100mM Oxalic acid and 1% MeOH), dilute 5.5 mL concentrated sulfuric acid, 12.6g oxalic acid and 10 mL MeOH to 1 L DDI water.

9.4.1 Shelf life of this reagent is 6 months.

9.5 Stock standard solutions purchased from Inorganic Ventures:

9.5.1 Sodium Fluoride, 1000 µg/mL;

9.5.2 Sodium Nitrate, 1000 µg/ml;

9.5.3 Potassium Sulfate, 1000 µg/ml;

9.5.4 Ammonium Dihydrogen Phosphate, 1000 µg/ml;

9.5.5 Potassium Chloride, 1000 µg/ml;

9.5.6 Sodium Nitrite, 1000 µg/ml;

9.5.7 Potassium Bromide, 1000 µg/ml.

Note: Expiration dates for the above stock standards are provided by the manufacturer per container.

9.6 Stock standard solutions purchased from Ultra Scientific:

9.6.1 Sodium Nitrate, 1000 µg/ml;

9.6.2 Potassium Chloride, 1000 µg/ml;

9.6.3 Potassium Sulfate, 1000 µg/ml;

9.6.4 Sodium Fluoride, 1000 µg/ml;

9.6.5 Potassium (ortho) Phosphate, 1000 µg/ml;

9.6.6 Potassium Bromide, 1000 µg/ml;

9.6.7 Sodium Nitrite, 1000 µg/ml.

Note: Expiration dates for the above stock standards are provided by the manufacturer per container.

9.7 Intermediate Standards:

9.7.1 100 mg/L from Inorganic Ventures: weigh 10 grams, of each 1000 µg/ml Inorganic Ventures stock solution (bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate) and dilute to 100.0 grams with DDI.

9.7.2 100 mg/L from Ultra Scientific: weigh 10 grams, of each 1000 µg/ml Inorganic Ventures stock solution (bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate) and dilute to 100.0 grams with DDI.

9.7.3 Intermediate standards are assigned a 6 month expiration date.

9.8 Calibration standards:

9.8.1 10 mg/L Cal STD: weigh 10 grams, of the 100 mg/L Inorganic Ventures intermediate standard solution and dilute to 100.0 grams with DDI.

9.8.2 5 mg/L Cal STD: weigh 5 grams, of the 100 mg/L Inorganic Ventures stock solution and dilute to 100.0 grams with DDI.

9.8.3 1 mg/L Cal STD: weigh 1 gram, of the 100 mg/L Inorganic Ventures stock solution and dilute to 100.0 grams with DDI.

9.8.4 0.05 mg/L Cal STD: weigh 1 gram, of the 5 mg/L Cal STD and dilute to 100.0 grams with DDI.

9.8.5 0.01 mg/L Cal STD: weigh 1 gram, of the 1 mg/L Cal STD and dilute to 100.0 grams with DDI.

Note: Calibration standards need to be prepared daily.

9.9 CCV, LCS solution

9.9.1 5 mg/L Cal STD from section 9.7.2. If analysis is being performed for NO_2, NO_3 or Ortho PO_4 the expiration date is 1 day otherwise the expiration date is 6 months.

9.10 MS/MSD Solution

9.8.1 100 mg/L spiking solution: place 10 mL of each 1000 mg/L Inorganic Venture's standard (Br, F, Cl, NO_2, NO_3, O-PO_4, and SO_4) in a container and dilute to a final weight of 100 grams with DDI.

9.11 ICV/IPC

9.11.1 5 mg/L ICV solution: weigh 5 grams of the 100 mg/L Ultra Scientific intermediate standard solution and dilute to 100.0 grams with DDI. If analysis is being performed for NO_2, NO_3 or Ortho PO_4 the expiration date is 1 day otherwise the expiration date is 6 months.

10.0 Sample collection

10.1 Sample should be collected in plastic or glass bottles.

10.2 100 mL of sample should be collected for this analysis.

10.3 Analyte preservation and holding time:

Analyte	Preservative Liquid	Preservative soils	Holding Time
Bromide	4°C	4°C	28 days
Chloride	4°C	4°C	28 days
Fluoride	4°C	4°C	28 days
Nitrate-N	4°C	4°C	48 hours
Nitrite-N	4°C	4°C	48 hours
O-Phosphate	4°C	4°C	48 hours
Sulfate	4°C	4°C	28 days
Nitrate/Nitrite	4°C	4°C	48 hours

10.4 Nitrate/Nitrite combined is achieved by adding the individual concentrations of nitrate and nitrite together.

10.5 The holding time of a sample requiring multiple anions is the anion with the shortest holding time.

11.0 Quality control

11.1 A method blank must be analyzed per batch of 20 or fewer samples.

11.1 A mid range IPC/ICV and ICB must be analyzed immediately following calibration or at the beginning of each analytical run.

11.2 A LCS must be analyzed per batch of 20 samples or fewer.

11.3 Analyze a sample duplicate or MS/MSD every 10 samples.

11.3.1 Each batch of 20 samples or fewer will contain a minimum of one sample duplicate (for method 9056 only) and two MS/MSD's to meet the every tenth requirement.

11.4 A CCB and a CCV must be analyzed every 10 samples and at the end of the run.

12.0 Calibration and standardization

12.1 Chromatographic conditions are set according to manufacturer's recommendations.

12.2 A calibration curve will consist of at least three (3) standards. Since a blank cannot be included in the calibration curve the lowest standard will be at or below the analyte PQL. The following standards will be used in the calibration curve: 0.10 mg/L, 1.0 mg/L, 5.0 mg/L 2.5mg/L and 10.0 mg/L. Additional standards may be used for analytes that have broader linear ranges.

12.2.1 Calibration must be performed in descending order, meaning analyze from high to low.

12.3 When calculating the curves coefficient, utilize a quadratic fit that does not force through zero.

12.4 The correlation coefficient for each curve must be 0.995 or better.

12.5 Update retention time windows after each new calibration.

13.0 Procedure

13.1 Aqueous sample prep

13.1.1 Shake all samples well to homogenize and filter through a 0.2 µm filter.

13.1.1.1 Samples requiring chloride or sulfate must start with a 1:10 dilution with DDI.

13.1.1.2 Check samples historical before analysis to assure the proper dilutions are started with. Some clients may require a 2000 or higher dilution.

13.1.2 Fill auto sampler vials with 10 mL of filtered sample and label the vial with the laboratory ID.

13.2 Solid sample prep

13.2.1 Weigh 5 grams of well mixed sample into a centrifuge tube and add 50 mL of DDI.

13.2.1.1 Label the centrifuge tube with the laboratory ID.

13.2.2 Cap and mix this solution for 10 minutes.

13.2.3 Centrifuge and filter through a 0.2 µm filter

13.2.4 Place 10 mL of filtered sample in a labeled auto sampler vial.

13.3 Sample analysis

13.3.1 Chromatographic conditions are set according to manufacturer's recommendations.

13.3.2 Refer to the manufacturer's Metrodata instruction manual for operating procedures.

13.3.3 Load samples in the auto sampler.

13.3.3.1 The MB/CCB, pour 10 mL of DDI into an auto sampler vial.

13.3.3.2 The LCS/CCV, pour 10 mL of the 5 mg/L Inorganic Ventures spiking solution into an auto sampler vial.

13.3.3.3 The MS/MSDs are prepared by adding 0.5 mL of the Inorganic Ventures 100 mg/L spiking solution to 9.5 mL of sample in an auto sampler tube (mix well before analyzing).

13.3.3.4 The ICV/IPC, pour 10 mL of the 5 mg/L Ultra Scientific spiking solution into an auto sampler vial.

13.3.3.5 Samples, mix well by shaking in their sample containers and pour 10 mL into an auto sampler vial.

13.3.3.5.1 If samples are turbid pre filter with a syringe filter (Whatman 1.6µm) before dispensing into auto sampler vial.

13.3.4 Each analytical run must include the following:

ICV/ IPC
ICB
CCV
CCB
MB
LCS
MS
MSD
6 Samples
CCV
CCB
9 Samples
Sample Duplicate
CCV
CCB

14.0 Calculations

14.1 Sample results are reported in mg/L directly by the IC Metrodata software.

14.2 Sample dilutions are entered into the sample information file and calculated by the instrument.

14.3 Manual integrations may **only** be performed when necessary.

14.3.1 The manual integration must take in the full peak (tails and all).

14.3.2 The manual integration when performed must be documented on the raw data (pdf) in the form of a text box.

14.3.2.1 The analyst must initial and date the manual dilution on the raw data.

14.3.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Current limits are specified in section 17.

16.0 Pollution prevention

16.1 Use care in handling standards for this analysis and glassware. Several analytes in this method are also analytes in the following areas:

Lachat area: chloride, sulfate, o-phosphate, nitrate and nitrite;

Wet Chem Area: Turbidmetric sulfate and ion selective fluoride

17.0 Data assessment and acceptance criteria for quality control measures

17.1 The MB, ICB and CCB result must be less than the laboratory PQL.

17.2 The ICV (IPC) and CCV must recover within 10% of its true value

17.3 An LCS (QCS) must recover within 10% of its true value.

17.4 Matrix spikes must recover within 10%, and have a RPD within 20%.

17.5 A ICB and ICV must be analyzed immediately following calibration and/or the beginning of every run.

17.6 A CCB and a CCV must be analyzed following every 10 samples and at the end of the run.

18.0 Corrective actions for out of control data

18.1 If one of the blanks fails, pour a fresh aliquot and re-analyze.

18.1.1 If the instrument blank fails a second time stop analysis and trouble shoot the cause.

18.1.2 If the batch MB fails a second time the batch needs to be re-prepped.

18.2 If an ICV, CCV or LCS fails, pour a fresh aliquot and re-analyze.

18.2.1 If re-analysis does not work for the ICV or CCV stop analysis, make a new standard, recalibrate and re-analyze the batch.

18.2.2 If the LCS fails a second time, the batch must be reanalyzed.

18.3 If the MS or MSD fails, and the LCS is acceptable, the sample results must be flagged matrix interference.

18.4 If the MS or MSD fails, and the LCS fails the batch must be reanalyzed.

18.4 If the MS and MSD RPD is the out, and the cause is not due to low analyte concentration (under spiking for the sample concentration) or non-homogeneity due to matrix the batch must be reanalyzed.

19.0 Contingencies for handling out of control data or unacceptable data

19.1 If reanalysis of samples cannot be performed within the expiration dates listed in section 10.0, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails due to a matrix problem the final report must be flagged with the appropriate qualifier.

20.0 Waste management

20.1 The Regeneration solution (sulfuric acid/oxalic acid solution) may be disposed through the laboratory sink, after neutralization with baking soda.

20.2 Expired Eluent may be disposed through the laboratory sink.

20.3 Unused portions of ground water, wastewater and drinking water samples may be disposed through the laboratory sink.

20.4 Standards, reagents and stock chemicals are only to be purchased in amounts reasonable for use within the substance expiration date.

20.4.1 1000 mg/L stock standards should only be purchased in a single container of 100 mL.

20.4.2 All unused or expired stock solutions are to be collected in the metal contaminated bin in sample archiving.

21.0 References

21.1 Methods and Guidance for Analysis of Water. Method 300.0, Determination of inorganic anions by ion chromatography, Environmental monitoring systems laboratory office of research and development, US Environmental Protection Agency. Revision 2.1 August 1993

21.2 Test Methods For Evaluating Solid Waste Physical/Chemical Methods (SW-846). Method 9056A, Determination Of Inorganic Anions By Ion Chromatography, Revision 1

22.0 Tables, diagrams

22.1 Not Applicable.

23.0 Clarification/Modifications of the method

23.1 The IC software is incapable of calibrating with a blank as part of the calibration curve. For this reason the instrument is not calibrated with a blank as specified by both method 300.0 and 9056.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

Chloride by 9251 (Revision 0, September 1986) SM4500-Cl E (20TH ED)

1.0 Applicable matrix

1.1 This method is applicable to water samples, drinking, ground, surface, industrial and domestic waste.

1.2 The method may be modified to accommodate the analysis of soil, based on a DI water extraction.

2.0 Detection Limit

2.1 See LIMS test groups for Detection limits.

2.2 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.3 The laboratory PQL is 5 ppm.

3.0 Scope and Application

3.1 This procedure utilizes one calibration curve with a range of 5 to 100ppm.

4.0 Summary of test method

4.1 A sample aliquot is poured into an 8mL test tube and mixed with a color reagent containing mercuric thiocyanate and ferric nitrate via the Lachat System. Thiocyanate is liberated from mercuric thiocyanate and the thiocyanate reacts with ferric nitrate to form ferric thiocyanate. This reaction produces a highly colored sample that is proportional to the samples chloride content.

5.0 Definitions

5.1 A listing of general laboratory terminology is located in the laboratory QAP.

6.0 Interference

6.1 Turbidity may cause false positives and instrumentation clogs, filter or centrifuge samples before analysis.

6.2 Method interferences can be caused by contaminated glassware and reagents. Assure glassware used is clean and maintain good laboratory practiced to avoid reagent contamination.

7.0 Safety

7.1 Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses. Samples should be considered hazardous. Avoid exposure, skin contact, inhalation, or ingestion.

7.2 The color reagent and analysis by product contain a form of mercury. Mercury is highly toxic if swallowed, inhaled or absorbed through the skin.

8.0 Equipment and supplies

8.1 Lachat, Quikchem FIA 8500 with reagent pump, and autosampler.

8.2 480 nm wavelength cell

8.3 10 mL disposable pipettes

8.4 Pipettors, various sizes.

8.5 8 mL poly propylene test tubes

8.6 50 mL centrifuge tubes

8.7 Volumetric glassware (flasks and pipettes) various sizes.

9.0 Reagents and standards

9.1 DI Water

9.2 The color reagent: 0.06% mercuric thiocyanate solution is purchased prepared from GFS Chemicals through Fisher Scientific. Expiration date 3 years after received.

9.3 1000ppm, chloride calibration standard and LCS standard are purchased prepared from Labchem through Fisher Scientific. The calibration standard and LCS standard must be from a separate lot. Solution must be refrigerated. Expiration date provided by vendor.

9.4 100ppm chloride calibration standard: dilute 5mL of the 1000ppm chloride calibration standard to 50mL with DI water. Solution must be refrigerated. Expiration date one month after preparation.

9.5 50ppm chloride calibration standard: dilute 2.5mL of the 1000ppm chloride calibration standard to 50mL with DI water. Solution must be refrigerated. Expiration date one month after preparation.

9.6 25ppm chloride calibration standard: dilute 1.25mL of the 1000ppm chloride calibration standard to 50mL with DI water. Solution must be refrigerated. Expiration date one month after preparation.

9.7 10ppm chloride calibration standard: dilute 0.5mL of the 1000ppm chloride calibration standard to 50mL with DI water. Solution must be refrigerated. Expiration date one month after preparation.

9.8 5ppm chloride calibration standard: dilute 0.25mL of the 1000ppm chloride calibration standard to 50mL with DI water. Solution must be refrigerated. Expiration date one month after preparation.

9.9 50ppm chloride LCS standard: dilute 2.5mL of the 1000ppm chloride LCS standard to 50mL with DI water. Solution must be refrigerated. Expiration date one month after preparation.

10.0 Sample collection

10.1 Samples should be collected in a clean, high density, polyethylene container.

10.2 Samples must be chilled at >0 to 6°C and analyzed within 28 days of sampling.

10.3 The method requires 50 mL of sample as a minimum.

11.0 Quality control

11.1 A method blank must be analyzed per batch of 20 or fewer samples.

11.2 A mid range ICV and ICB must be analyzed immediately following calibration.

11.3 A LCS must be analyzed every 10 samples or fewer.

11.4 A MS/MSD must be analyzed every 10 samples or fewer.

11.5 A CCB and a CCV must be analyzed every 10 samples and at the end of the run.

12.0 Calibration and standardization

12.1 The instrument is calibrated with 6 points: 0, 5 ppm, 10 ppm, 25 ppm, 50 ppm, and 100 ppm standard.

12.2 The calibration coefficient for acceptance must be equal to or better than 0.995.

12.2.1 This coefficient may be derived from a linear or quadratic (first or second order) calibration.

12.2.2 Higher order calibrations, forcing through zero, and/or point-to-point calibrations are not allowed.

12.3 To start calibration click the open button on the top of the screen and select the method desired (CHLORIDE TEMPLATE.omn for waters and CHLORIDE SOIL TEMPLATE.omn for soils).

12.3.1 The soil method uses two manifolds while water only uses one.

12.4 In the tray, list the calibration standards to be analyzed and the samples to be analyzed. Also include the CCV, CCB, ICV, and ICB

12.4.1 Calibration standards are entered and analyzed in reverse order. They will be analyzed in the following order: 100, 50, 25, 10, 5 and 0.

12.5 Enter the cup number for each standard and sample. The cup number is their position on the automated sampler.

12.6 Label the calibration standard samples as “calibration standard” and the ICV, ICB, CCV, and CCB as “check standard” on the sample type column

12.7 Reps, is always listed as one.

12.8 Manual dilution documents the manual dilution factor and weight records the prep factor.

13.0 Procedure

13.1 Lachat Analysis

13.1.1 Pour sample aliquots into 8mL tubes and position them in the cup number assigned in section 12.

13.1.1.1 Soil Samples

13.1.1.1.1 Weigh 25 g of soil into a ½ pint container.

13.1.1.1.2 Add 25 mL of DI water to the ½ pint.

13.1.1.1.3 Place the ½ pint container with sample and DI water on the shaker.

13.1.1.1.4 Secure the sample with the shaker clamps and rubber bands.

13.1.1.1.5 Set the shaker timer for five minutes.

13.1.1.1.6 Place on the centrifuge until solids are settled to the bottom.

13.1.1.1.7 Pour extracted sample or an aliquot into 10mL tubes and position them in the cup number assigned in section 12.

13.1.1.1.8 For shared sampled weigh 100 g of soil into the pint container and add 100 mL of DI water and follow directions above.

Note: Different prep factor (5 g to 50 mL) may be performed if not enough sample was provided to make a 1:1 soil prep.

13.1.2 Second check the positions

13.1.3 Push the “start” button to start analysis. A file name will be automatically given when a run is finished.

14.0 Calculations

14.1 Sample results are reported in mg/L directly by the Lachat software.

14.2 Manual dilution factor must be hand entered into the Lachat spreadsheet; this will multiply the raw data and multiplied by the factor.

14.3 Soil results are reported as mg/kg- wet directly by the Lachat through the LIMs

14.3.1 Soil results must be multiplied by the extraction ratio. Example the sample results must be multiplied by 10 if a 10:100 extraction was performed. Extraction ratio must be hand entered into the Lachat spreadsheet under the weight column.

14.3.2 The data must be flagged analysis performed on a 1:1 DI water extraction.

14.3.3 Samples must be corrected for color interference. The instrument is set up so that both a normal run and color blank is run at the same time. These results are then used to find the correct value.

Chloride Result – Chloride Color Blank = Color Corrected Chloride Result

14.4 Samples requiring results on a dry weight basis must have a percent moisture analysis performed.

14.4.1 The results of the percent moisture are entered into the LIMS and the LIMS calculates the dry weight basis calculation.

14.5 Manual integrations may **only** be performed when necessary.

14.5.1 The manual integration must take in the full peak (tails and all).

14.5.2 The manual integration when performed must be documented on the raw data.

14.5.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Current limits are listed in section 17.

16.0 Pollution prevention

16.1 The color reagent used in this procedure contains a form of mercury and a form of cyanide. Both of these forms are analyzed in the laboratory. Use glassware or disposable glassware that is specific to this method to avoid cross contamination with mercury and cyanide analysis.

16.2 Since the color reagent contains a form of mercury and cyanide. All waste from the test must be treated as hazardous waste. Place this waste in a sealed container, mark it as mercury and cyanide contaminant and place in the cyanide waste collection barrel for disposal through a hazardous contamination firm. Do not pour down the sink.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The method blank, ICB and CCB result must be below the laboratory PQL of 5 ppm.

17.2 The ICV and CCV must recovery within 10% of its true value.

17.3 A LCS must recovery within 10% of its true value for waters and 15% for soils.

17.4 MS/MSD recovery must be ≤ 10% with an RPD ≤ 10% for waters, and MS/MSD recovery must be ≤ 20% with an RPD ≤ 20% for soils.

18.0 Corrective actions for out of control data.

18.1 If one of the blanks fails, pour a fresh aliquot and re-analyze.

18.2 If an ICV, CCV or LCS fails, pour a fresh aliquot and re-analyze. If re-analysis does not work, make a new standard if it is the ICV or CCV, recalibrate and re-analyze the batch. If the LCS fails a second time, the batch must be re-prepped.

18.3 If the MS or MSD fails and the instrument QC look good the sample results must be flagged matrix interference.

18.4 If the MS and MSD RPD is out re-prep the samples and re-analyze.

19.0 Contingencies for handling out of control data or unacceptable data.

19.1 If reanalysis of samples cannot be performed within 28 days of collection, have supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails due to matrix interference issues flag the final report with the appropriate qualifier.

20.0 Waste management

20.1 Unused portions of ground water, wastewater and drinking water samples may be disposed through the laboratory sink.

20.2 Unused or expired portions of color reagent are considered hazardous and must be disposed properly. Place this waste in a sealed container, mark it as mercury and cyanide contaminant and place in the cyanide waste collection barrel for disposal through a hazardous contamination firm.

21.0 References

21.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 9251, Chloride (Colorimetric, Automated Ferricyanide AAII), Revision 0, September 1986.

21.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Automated Ferricyanide Method, 4500-Cl E, page 4-70.

21.3 Methods and Guidance for Analysis of Water. Method 325.2, Chloride (Colorimetric, Automated Ferricyanide AAII), Revision March 1983.

21.4 Lachat Instruments QuikChem Method 10-117-07-1-I, 08/15/01.

22.0 Tables, diagrams

22.1 Not Applicable

23.0 Clarification/Modifications of the method

23.1 LCS recovery is 100 ± 15% instead of 100 ± 10% due to interferences on the instrument when correcting for color.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

Total Cyanide by 335.4 (Revision 1.0)

1.0 Applicable matrix

1.1 This method is applicable to the analysis of water samples.

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratory PQL is 0.005ppm.

3.0 Scope and Application

3.1 This method measures the presence of inorganic cyanides (soluble salts or complexes) in samples.

3.2 The analytical range is from 0.005 to 0.2 mg/L.

4.0 Summary of test method

4.1 Cyanide in released from samples under acidic conditions in the form of HCN, in a heated distillation unit. The HCN is passed through and trapped into a basic solution. This solution is then analyzed on the Lachat, trapped cyanide is hydrolyzed with Chloramine T to form CNCl and mixing with a color indicator pyridine barbituric acid reagent.

5.0 Definitions

5.1 Cyanide by definition is: cyanide ion and complex cyanides converted to hydrocyanic acids (HCN), through a reflux system reaction of mineral acids in the presence of magnesium ion.

5.2 CNCl: Cyanogen chloride.

6.0 Interference

6.1 Nitrates and nitrites if present will create a positive interference. This interference is eliminated by the addition of sulfamic acid, to the sample prior to distilling.

6.2 Chlorine and other oxidizing agents will create a negative interference. The presence of this type of interference may be identified with the use of KI paper. If present, the paper will turn blue. If this occurs add ascorbic acid until the paper is unchanging in color.

6.3 The presence of sulfide in a sample will create a negative interference by forming hydrogen sulfide versus hydrogen cyanide. Its presence is detected with lead acetate paper. If the paper darkens when contacted, with sample sulfides are present. Add cadmium carbonate until a yellow precipitate is formed and the acetate paper does not darken.

6.4 The following are known interferences that cannot be chemically corrected: aldehydes, thiocyanate and thiosulfate. The analysis of a matrix spike is the only way to detect these interferences.

7.0 Safety

7.1 Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses. Samples should be considered hazardous: avoid exposure, skin contact, inhalation or ingestion.

7.2 This method test for and uses cyanide a toxic substance. The acidification and chlorination of samples may produce a toxic gas. Perform all preps and distillations in a fume hood.

7.3 Do not dispose of cyanide containing substances through the laboratory sink. High quantities of acid are used through out the laboratory and this may cause hydrogen cyanide to form in the drains.

7.4 This procedure uses corrosive substances (NaOH and HCL) that will burn skin on contact. Always wear a lab coat, safety glasses and laboratory supplied gloves when handling.

8.0 Equipment and supplies

8.1 Micro Dist block

8.2 Fume hood

8.3 Lachat, Quikchem FIA 8500 with reagent pump and autosampler.

8.4 10mL disposable pipettes

8.5 Pipettor, various sizes

8.6 8 mL poly propylene test tubes

8.7 Volumetric glassware various sizes

8.8 Pre-filled collector tubes

8.9 Press

8.10 Heat resistant gloves

8.11 Rack

9.0 Reagents and standards

9.1 DI Water

9.2 Ascorbic acid

9.3 Cadmium carbonate

9.4 Sulfamic acid

9.5 Carrier (Sodium Hydroxide solution, 0.25N purchased or prepared): dissolve 20g of sodium hydroxide pellets in DI water and dilute to 2L with DI water when cool (or 10g/1L).

Note: This solution will get extremely hot, prepare in a cool water bath.

9.6 1:1Sulfuric acid: gently add 400mL of concentrated sulfuric acid into 400mL of DI water.

Note: This solution will get extremely warm. If the acid is added to fast the solution will spit/boil.

9.7 Magnesium chloride: dissolve 510g in DI water and dilute to 1L with DI water.

9.8 Cyanide Buffer solution, purchased or prepared: dissolve 48.5g of potassium phosphate, mono basic anhydrous in DI water and dilute to 500mL with DI water.

9.9 Chloramine T solution purchased or prepared: dissolve 1g of chloramine-T in DI water and dilute to 250mL with DI water.

Note: prepare fresh each day if prepared.

9.10 Color reagent, purchased or prepared: place 15g barbituric acid, 75mL pyridine in 100 mL of DI water and stir. Add 15mL concentrated hydrochloric acid in DI water and swril to dissolve. When solution has cooled, dilute to 1L with DI water. Prepare this reagent in a hood or well ventilated area. Exp. one month if prepared.

9.11 Releasing reagent: To a 100mL beaker add 7.52 of magnesium chloride hexahydrate to 20mL if DI water, dissolve completely. Next slowly add 40mL of sulfuric acid. Dilute to mark. Solution is good for six months.

Note: HCl will be produces and fumes will be released make in a hood.

9.12 1000ppm cyanide calibration standard is purchased prepared from certified vendor.

9.13 10ppm, calibration standard: dilute 0.5mL of the 1000ppm calibration standard to 50mL with carrier (0.025N NaOH). 2 day expiration date.

9.14 0.2ppm, calibration standard: dilute 1mL of the 10ppm calibration standard to 50mL with carrier (0.025N NaOH). 2 day expiration date.

Note: All standards are distilled.

9.15 0.1ppm, calibration standard: dilute 05mL of the 10ppm calibration standard to 50mL with carrier (0.025N NaOH). 2 day expiration date.

9.16 0.05ppm, calibration standard: dilute 0.25mL of the 10ppm calibration standard to 50mL with carrier (0.025N NaOH). 2 day expiration date.

9.17 0.01ppm, calibration standard: dilute 5mL of the 0.1ppm calibration standard to 50mL with carrier (0.025N NaOH). 2 day expiration date.

9.18 0.005ppm, calibration standard: dilute 2.5mL of the 0.1ppm calibration standard to 50mL with carrier (0.025N NaOH). 2 day expiration date.

9.19 1000ppm cyanide LCS standard: dissolve 0.2509g ± 0.002g of potassium cyanide and 0.2g potassium hydroxide in DI water and dilute to 100mL with DI Water. 1 week expiration date.

9.20 10ppm, LCS standard: dilute 0.5mL of the 1000ppm LCS standard to 50mL with carrier (0.25N NaOH). 2 day expiration date.

9.21 0.1ppm, LCS standard: dilute 0.5mL of the 10ppm LCS standard to 50mL with carrier (0.25N NaOH). 2 day expiration date.

10.0 Sample collection

10.1 Samples should be collected as per standard EPA guidelines for the analysis of water 40 CFR pt 136 Table 1-1.

10.2 Samples should be collected in a plastic container, preserved to a pH of 12 with NaOH, refrigerated to >0 - 6°C and analyzed within 14 days.

11.0 Quality control

11.1 A method blank must be analyzed per batch of 20 or fewer samples.

11.2 A mid range ICV and ICB must be analyzed immediately following calibration.

11.3 A LCS must be analyzed per batch of 20 samples or fewer.

11.4 A MS/MSD must be analyzed every 10 samples. A batch of twenty samples must have two MS/MSDs prepared and analyzed.

11.5 A CCB and a CCV must be analyzed every 10 samples and at the end of the run.

11.5.1 The CCV must be at a mid range concentration.

12.0 Calibration and standardization

12.1 The instrument is calibrated with 5 points: 0, 0.005 ppm, 0.01 ppm, 0.05 ppm, 0.1 ppm and a 0.2 ppm standard.

12.2 The calibration coefficient for acceptance must be equal to or better than 0.995.

12.2.1 This coefficient may be derived from a linear, first order calibration.

12.2.2 A second and third order, calibration is not allowed.

12.2.3 Forcing through zero is not allowed.

12.2.4 Point-to-point calibration is not allowed.

12.3 To start calibration Push the open button on the top of the screen and select the method desired (CYANIDE TEMPLATE.omn).

12.4 In the tray, list the calibration standards and the samples to be analyzed, include the ICV, ICB, CCV, and CCB.

12.4.1 Calibration standards are entered and analyzed in reverse order. They will be analyzed in the following order: 0.2, 0.1, 0.05, 0.01, 0.005 and 0.

12.5 Enter the cup number for each standard and sample. The cup number is their position on the automated sampler.

12.6 On sample type column change the label based on the type of sample: calibration standard, sample, and check standard (ICV, ICB, CCV, and CCB).

12.7 Reps, is always listed as one.

12.8 Manual dilution documents the manual dilution factor and weight records the prep factor.

12.9 Sample analysis is located in section 13.2.

13.0 Procedure

13.1 Distillation

13.1.1 Test sample for the presence of sulfide with lead acetate paper. If the paper turns dark add cadmium carbonate to sample until the paper is unchanging.

13.1.2 Test sample for the presence of chlorine with KI paper. A blue color indicates the presence of chlorine. Add ascorbic acid in small amounts until the KI paper is unchanging.

13.1.3 Set the controller of the Micro Dist to 120°C. Allow heater block to warm up, this will take approximately 40 minutes.

13.1.4 Put required number of collector tubes into rack, M end up, up to 21 for one block.

13.1.5 Add required amount of sample tubes into sample rack. Pipette 6mL of sample or standard into each tube, fill and cap tubes before using. For the MS/MSD and LCS spike 0.3mL of 2mg/L solution. This gives a spike value of 0.1mg/L.

13.1.6 For soils add 0.5 to 1g of sample to 5mL of DI water.

13.1.7 Add 0.75mL of 7.11 M sulfuric acid/0.79M magnesium chloride solution to the sample tube.

13.1.8 Immediately push the D end of the collector tube over the open end od each sample tube to start the seal.

13.1.9 Place tube into press, putting sample tube into hole in white base. Grip collector tube firmly at breakaway point, Press down smoothly on handle until stop ring on sample tube hits the end of the D on the collector tube.

13.1.10 Put on heat resistant gloves and then push fully assembled tube at the D end into the preheated block.

13.1.11 Set timed for 30 minutes.

13.1.12 After 30 minutes put the heat resistant gloves back on. Remove first tube from block and immediately pull off its sample tube using a downward twisting motion and dispose of sample tube. Repeat for each of the tubes. Take no longer than 4 seconds to remove each sample tube.

13.1.13 Invert each collector tube and place into rack with D end up. Allow tubes to cool for at least 10 minutes.

13.1.14 For each tube hold it horizontally and rinse the walls with distillate. Roll the distillate around the tube to gather all droplets. Return to upright position so D end is up.

13.1.15 Break the collector tube in half by pulling the D end hard towards the user to break it, then twisting and tearing off the D end. Discard the D end.

13.1.16 In the M end of collector tube dilute to 6mL with DI water.

13.1.17 Swirl tube to mix, seal both ends with parafilm if sample is not immediately determined by the Lachat.

13.2 Lachat analysis

13.2.1 Pour sample aliquots into, 10 mL, tubes and position them in the cup number assigned in section 12

13.2.2 Second check the positions

13.2.3 Push the start button to start analysis. A file name will be automatically given when a run is run.

14.0 Calculations

14.1 Sample results are reported in mg/L directly for both the chlorinated and un-chlorinated samples by the Lachat software.

14.2 Manual dilutions and the dilution factor are calculated by the Lachat program.

14.3 Manual integrations may **only** be performed when necessary.

14.3.1 The manual integration must take in the full peak (tails and all).

14.3.2 The manual integration when performed must be documented on the raw data.

14.3.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Refer to section 17 for quality samples' current limits.

16.0 Pollution prevention

16.1 Care must be used in handling samples and standards exposure to acid could produce HCN. Procedure should be performed in a hood or well ventilated area.

16.2 Sulfide is a known interferent and a common analyte analyzed in the laboratory. Glassware and cyanide analysis should remain in separate areas to avoid cross contamination.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The method blank, ICB and CCB result must be below the laboratory PQL.

17.2 The ICV and CCV must recovery within 10% of its true value.

17.3 A LCS must recovery within 10% of its true value.

17.4 Matrix spikes must recover within 10%, and have a RPD within 10%.

18.0 Corrective actions for out of control data.

18.1 If one of the blanks fails, pour a fresh aliquot and re-analyze.

18.2 If an ICV, CCV or LCS fails, pour a fresh aliquot and re-analyze. If re-analysis does not work, make a new standard if it is the ICV or CCV, recalibrate and re-analyze the batch. If the LCS fails a second time, the batch must be re-prepped.

18.3 If the MS or MSD fails and the instrument QC look good the sample results must be flagged matrix interference.

18.4 If the MS and MSD RPD is out re-prep the samples and re-analyze.

19.0 Contingencies for handling out of control data or unacceptable data.

19.1 If reanalysis of samples cannot be performed within 14 days of collection, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails due to matrix interference issues flag the final report with the appropriate qualifier.

20.0 Waste management

20.1 Cyanide is an extremely hazardous substance. The hazardous materials substances & waste compliance guide states more than 1kg of material must be disposed through a hazardous collection firm.

20.2 Samples and standards containing cyanide must be stored in the cyanide collection bin in the rear of the sample archive room.

20.3 Unused portions of samples and reagents not containing cyanide may be disposed through the laboratory sink after neutralization.

20.4 All acidified reagents may be disposed through the laboratory sink after neutralization.

21.0 References

21.1 Methods and Guidance for Analysis of Water Method 335.2, Cyanide, Total, Titrimetric, Spectrophotometric, March 1983.

21.2 Methods and Guidance for Analysis of Water Method 335.3, Cyanide, Total, Colorimetric, Automated UV, March 1983.

21.3 Methods and Guidance for Analysis of Water Method 335.4, Determination of Total Cyanide by Semi-Automated Colorimetry, Rev. 1, August 1993.

21.4 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Cyanide Methods, 4500-CN A, B, C, E and I page 4-32 – 4-45.

21.5 Lachat Instruments, QuikChem Method 10-204-00-1-A, June 6 1996.

21.6 Determination of Cyanide by flow injection analysis, Method 10-204-00-1-X, March 29, 2001.

22.0 Tables, diagrams

22.1 Not Applicable

23.0 Clarification/Modifications of the method

23.1 The Color reagent used in this procedure is four times more diluted then the method reagent as per Lachat instructions.

23.2 Potassium phosphate, mono basic anhydrous is used in place of the regulatory method sodium dihydrogenphosphate as per Lachat instructions.

23.3 Sulfamic acid is added to all samples and blanks.

23.4 Chloramine-T solution is made 1g/250 mL instead of 1g/100 mL as per Lachat instructions.

23.5 Stock standards are not titrated with silver nitrate solution. One is purchased certified and the other is compared against the certified standard for accuracy

23.6 Standards are distilled as per Micro Dist method.

23.7 Pyridne is made 30g barbituric acid , 150mL of pyridine and 30mL concentrated HCl acid to the flask and dilute to 1L per Lachat instructions.

23.8 Less sample volume is used in distillation per Micro Dist method.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date _____
QA/QC Officer

Fluoride by 340.2 (EPA Revision 1983) & SM 4500 F- C & B

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1.0 Applicable matrix

1.1 This method is applicable to the analysis of fluoride in water matrices (drinking industrial and ground).

2.0 Detection Limit

2.1 The laboratory PQL is 0.1ppm.

2.2 The laboratory MDL is determined annually in accordance to 40CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

3.0 Scope and Application

3.1 This procedure is capable of detecting fluoride in the range of 0.1ppm to 1000ppm.

3.2 Distillation is not required for drinking water samples.

3.3 Ground water samples as in monitoring wells do not require distillation.

3.4 NPDES samples require distillation

4.0 Summary of test method

4.1 The fluoride concentration is determined with the use of an ion select probe and a millivolt scale ion meter that has been calibrated with a series of fluoride standards.

4.1.1 Samples requiring distillation are distilled with sulfuric acid prior to analysis with the ion select probe.

5.0 Definitions

5.1 LCS: Laboratory Control Sample

5.2 MB: Method Blank

5.3 MS: Matrix Spike

5.4 MSD: Matrix Spike Duplicate

5.2 ISE: Ion Select Electrode

5.3 NPDES: National Pollutant Discharge Elimination System

6.0 Interference

6.1 If the pH is extremely acidic or basic a fluoride complex with aluminum, iron and silica may be formed creating a low fluoride basis. The pH of all samples should be adjusted to be between 5 and 9 to eliminate this interference.

6.2 Ion select electrodes are affected by temperature. They should be used with an ATC temperature probe. All samples and standards should be brought to the same temperature before analysis.

7.0 Safety

7.1 Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses. Samples should be considered hazardous. Avoid exposure, skin contact, inhalation or ingestion.

7.2 The acidification of samples containing reactive material may result in the release of toxic gases such as cyanide or sulfides.

7.3 When working with acidic reagents always add acid to water.

8.0 Equipment and supplies

8.1 Orion 940 Ion Analyzer

8.2 Fluoride Electrode

8.3 Reference Electrode

8.4 Stir Plate

8.5 Stir bars, Teflon coated

8.6 Plastic beakers, 150mL

8.7 Volumetric Flask: 1L and 100mL

8.8 Volumetric pipettes, various sizes.

8.9 Distillation equipment

8.9.1 Heating mantel

8.9.2 Condenser

8.9.3 Glass beads

8.9.4 Thermometer

8.9.5 Boiling flask (1L)

9.0 Reagents and standards

9.1 DI Water

9.2 Sulfuric Acid, concentrated

9.3 Silver sulfate (Ag_2SO_4), crystals

9.4 100ppm Fluoride standard. This solution is purchased from one of the laboratories vendors. The laboratory must have two standards from separate sources. One will be used for calibration (labeled ICV/CCV) and the other for verification (labeled LCS/SPK).

9.4.1 1 ppm standard; dilute 0.5 mL of the 100 ppm standard to 50 mL with DI water.

9.4.2 10 ppm standard; dilute 5 mL of the 100 ppm standard to 50 mL with DI water.

9.4.3 0.1 ppm standard; dilute 0.5 mL of the 10 ppm standard to 50 mL with DI water.

9.5 TISAB III, purchased from an approved laboratory vendor.

9.6 Hydrochloric Acid (HCl), 1N: place 500mL of DI water in a1L volumetric flask, add 83mL of concentrated HCl while stirring and dilute to volume with DI water.

Note: Concentrated HCl is an irritant to the eyes and throat, handle in a fume hood when making solutions.

10.0 Sample collection

10.1 Samples should be collected in a clean plastic or glass container and stored at > 0 to 4°C and analyzed within 28 days from collection.

11.0 Quality control

11.1 A method blank and laboratory control sample (LCS) should be analyzed following calibration.

11.1.1 The LCS (1 ppm standard) should be prepared from a separate source than the calibration standards.

11.2 A continuing calibration verification (CCV) should be analyzed every 10 samples and at the end of each batch. The concentration of the CCV should be varied throughout the run.

11.2.1 The CCV (0.1ppm standard) is made from the same source as the calibration standards.

11.3 A matrix spike and matrix spike sample must be performed on a sample in the batch.

11.4 All Quality control is based on a batch of 20 samples or fewer. If the amount of samples to be analyzed is greater than 20 samples after the 20th sample analyze the CCV, method blank, LCS and continue analyzing the new batch of samples.

12.0 Calibration and standardization

12.1 The instrument is calibrated using a minimum of a blank and two standards (1, and 10 ppm). The slope is calculated from the best straight line of all points used in calibrating

12.2 Instrument Calibration

12.2.1 Press 2nd function key then the "2"

12.2.2 Press speed key then the "0"

12.2.3 Meter reads "calibrate?" Press the "Yes" key

12.2.4 Meter reads "Calibrate direct?" Press the "Yes" key

12.2.5 Meter reads "enter number of standards" Press the "2" key

12.2.6 Meter reads "Do blank correction?" Press the "No" key

12.2.7 Meter reads electrode in 1?" Place electrode in the 1 ppm standard and press the "Yes" key

12.2.7.1 When instrument reads ready press the "Yes" key

12.2.8 Repeat last two steps for the 10 ppm standard.

12.2.9 After the instrument reads the 10 ppm standard it will display the Slope. Write this information down on your bench sheet.

12.2.10 Meter reads “Measure F?" Press the "Yes" key. You are now ready to analyze samples.

12.3 The acceptable slope for Fluoride is a –54 to –60.

13.0 Procedure

13.1 Place 50mL of sample or standard in a 150mL beaker, and check the pH of the sample. Sample pH should be between 5 and 9 for this analysis.

13.1.1 If pH is greater than 9, adjust to 8.3 with 1N HCl before adding buffer solution.

13.1.2 If pH is less than 5, adjust to between 5 and 9 with 5N sodium hydroxide before adding buffer solution.

13.2 Prepare MB with 50mL DI water.

13.3 Prepare the LCS with 50mL of DI water and 0.5mL of spiking solution.

13.4 Prepare the CCV with 50mL of DI water and 0.05ml of spiking solution.

13.5 Prepare a MS/MSD with 50mL of sample and 0.5mL of spiking solution.

13.6 Add 5 mL of TISAB III

13.7 Place beaker on stir plate and mix at a medium speed.

13.8 Immerse Fluoride electrode and reference electrode in solution.

13.9 Press the "**Yes"** key to start instrument to measure.

13.10 When the instrument displays "**READY"**, the instrument is stable and the number shown may be documented.

Note: Concentration below 0.5ppm will take longer to stabilize. 5 minute wait is not unusual.

14.0 Calculations

14.1 The instrument reports results directly in mg/L, when the instrument has been calibrated.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The laboratory does not update its limits based on control charts. The laboratory utilizes set limits defined by the method.

15.2 Limits utilized by the laboratory are listed in section 17.

16.0 Pollution prevention

16.1 The buffer solution is slightly basic and should be neutralized before disposal to the sewer system.

16.2 Inorganic spill kits are available in the preparation labs in case of acid and corrosive spills.

16.3 Fluoride solutions greater than 4ppm should not be disposed through the sewer system.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The LCS must recover within ±15% of its true value.

17.2 The CCV must recover within ± 20% of its true value,

17.3 The method blank must not read greater than 0.1ppm Fluoride.

17.4 Matrix spike and matrix spike duplicate recoveries must be within 20% of their true value, with a 10% RPD limit.

18.0 Corrective actions for out of control data.

18.1 If the blank is above acceptance, stop analysis and locate the contamination point. Once found begin analysis again. It may be necessary to recalibrate.

18.2 If a LCS is out of acceptance, stop analysis, make a new LCS and try again. If it is still out, recalibrate the instrument and attempt analysis again.

18.3 If the CCV is outside acceptance, pour a fresh CCV and analyze. If it is still outside limits, make new standards and recalibrate the instrument.

18.4 If a matrix spike falls outside the 20 % acceptance limit and instrument QC is acceptable, the sample matrix is cause for concern. The sample should be diluted and spiked again to see if the interference may be diluted out. If the recovery is still outside acceptance limits the field sample report must be flagged.

18.5 If the matrix spike duplicate RPD is outside acceptance limits, sample homogeneity is suspect. Reanalyze sample spike and spike duplicate again.

18.6 If any of the above suggestions do not work, refer to the electrode instruction manual and perform the electrode check and suggested maintenance.

19.0 Contingineiecs for handling out of control data or unacceptable data.

19.1 The field sample report must be flagged to indicate any QC deficiency or other deficiency of the QC for that set or sample. If data is unacceptable the client must be notified immediately.

20.0 Waste management

20.1 The sample waste, remaining from this test is acidic and must be neutralized before disposal through a laboratory sink.

20.2 Refer to the laboratory Waste Management and Sample Disposal SOP for more information.

21.0 References

21.1 Standard Methods 20th Edition, Method 4500 F- C & B, pages 4-80 through 4-82.

21.2 Methods and Guidance for Analysis of Water. Method 340.2, Fluoride Potentiometric, Ion Select Electrode, Revision 1974.

21.3 Test Methods for Evaluating Solid Waste Physical/Chemical Method (SW-846), Method 9214, Potentiometric Determination of Fluoride in Aqueous Samples with Ion Select Electrode, Revision 0, December 1996.

21.4 American West Analytical Laboratory Waste Management and Sample Disposal SOP, Revision 2.0.

22.0 Tables, diagrams

Fluoride ISE Interferences

Analyte Concentration mg/L	Interferences	Measured Concentration mg/L	RSD %
1.00	None	0.95	2.0
1.00	1 mg/L Al^{+3}	0.97	3.1
1.00	5 mg/L Al^{+3}	0.86	3.9
1.00	25 mg/L Al^{+3}	0.51	Single measurement
1.00	50 mg/L Al^{+3}	0.41	4.9
1.00	1 mg/L Fe^{+3}	1.00	3.9
1.00	5 mg/L Fe^{+3}	1.02	3.8
1.00	50 mg/L Fe^{+3}	0.92	3.2

23.0 Clarification/Modifications of the method

23.1 The laboratory does not make the standards or buffer solution. These are purchased.

23.2 The buffer solution is concentrated requiring less volume used than the 50mL stated in EPA methods 340.2 & 4500 F.

_____ Date_____
Inorganic Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

Mercury by 7470A (SW846 Rev. 1) and EPA 245.1 (EPA Rev. 3)

1.0 Applicable matrix

1.1 This method is applicable to the analysis of mercury in liquid waste and extracts.

2.0 Detection Limit

2.1 PQL's are based on an annual method detection limit study (MDL). This study is performed in accordance to CFR40, Part 136, and Appendix B. A minimum of seven standards are analyzed, and calculated for a mean; a standard deviation, and then multiplied by the associated student t factor. An acceptable MDL study is where the spiking concentration is not more than ten times the calculated MDL.

2.2 The laboratory's current PQL is located in the LIMS.

3.0 Scope and Application

3.1 This procedure measures total mercury (organic and inorganic forms) present in a liquid sample through a chemical and thermal reaction if the sample is capable of being digested.

4.0 Summary of test method

4.1 A liquid waste or extract sample is digested with acids and an oxidizer at a controlled temperature and vaporized in a closed system to measure absorption of radiation at a particular wavelength (253.7nm). This measurement is performed on a CETAC Measuring System.

5.0 Definitions

5.1 Chemical reaction: a change in chemistry that may occur with the combining, decomposition, or replacement of chemicals. A chemical reaction breaks the bonds holding molecule together.

5.2 Organic: A carbon based substance

5.3 PDS: Post Digestion Spike

5.4 SD: Serial Dilution

5.5 Thermal reaction: exciting bonds with heat to release their molecule

6.0 Interference

6.1 Sulfide is known to interfere at concentrations of 20ppm and greater. The method reduces this interference with the addition of potassium permanganate.

6.2 The method lists copper as a known interference, but states "concentrations as high as 10ppm had no effect on recovery of mercury from spiked samples".

6.3 Samples high in chloride will require additional permanganate (no more than 25mL) for complete oxidation. The sample must remain purple in color for a minimum of 15 minutes.

6.4 The presence of free chlorine will create a positive interference during vaporization. Therefore, it is extremely important to remove free chlorine before analysis; the addition of sodium chloride-hydroxylamine hydrochloride should dispel the free chlorine.

7.0 Safety

7.1 Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses. Samples should be considered hazardous. Avoid exposure, skin contact, inhalation, or ingestion.

7.2 The addition of sodium chloride-hydroxylamine hydrochloride could release chlorine gas in the sample container. This step should be performed under a hood to minimize exposure.

7.3 The addition of acids to the sample can release nitrous oxide fumes. This procedure should be performed under a hood to minimize exposure.

7.4 Mercury samples are highly toxic if swallowed, inhaled, or absorbed through the skin. The mercury analyst should use chemical resistant gloves when handling mercury standards and assure the instrument is ventilated into a hood.

8.0 Equipment and supplies

8.1 A hot plate and metal tub with cover, to create a water bath capable of maintaining a temperature of 86 – 96 ^{o}C. Temperature should be documented and verified against a NIST calibrated thermometer.

8.2 Volumetric flasks: 100 mL and 1L

8.3 Calibrated Pipettes

8.4 50mL centrifuge tubes

8.5 CETAC with autosampler

8.6 Analytical balance, capable of reading three places

8.7 Assorted containers

9.0 Reagents and standards

9.1 Sulfuric acid, concentrated (trace metal or Omni trace grade). Expiration date assigned by supplier.

9.2 DI Water

9.3 Hydrochloric acid, concentrated (trace metal or Omni trace grade). Expiration date assigned by supplier.

9.4 Nitric acid, concentrated (trace metal or Omni trace grade). Expiration date assigned by supplier.

9.5 Stannous Chloride, crystals (SnCl2 • 2H20). Expiration date assigned by supplier.

9.6 Stannous Chloride solution: Weigh 100 grams into a 1 L bottle place add 70 mL of concentrated HCl. Dissolve and dilute to the 1 L mark with DI water. Expiration date 6 months.

9.7 Sodium Chloride-Hydroxylamine hydrochloride Solution. Place 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride in a 2.0 L bottle. Add enough DI water to dissolve and then dilute to the 2.0 L mark with DI water. Expiration date 6 months.

9.8 5% Potassium Permanganate solution, w/v. Place 100 g of $KMNO_4$ in a 2 L bottle, dissolve and dilute to the 2.0 L mark with DI water. Expiration date 6 months.

9.9 5% Potassium Persulfate solution w/v. Place 100 g $K_2S_2O_7$ in a 2 L bottle, dissolve and dilute to the 2 L mark with DI water. Expiration date 6 months.

9.10 Calibration Stock Mercury Solution: 1,000 ppm purchased standard from certified vendor. Expiration date provided by vendor.

9.10.1 10 ppm Calibration Solution: dilute 1.0 mL of the stock solution and 7 mL of concentrated HCl to 100 mL with DI water. Expiration date 2 weeks.

9.10.2 100 ppb calibration solution: dilute 1 mL of the 10 ppm standard and 7 mL of concentrated HCl to 100 mL with DI water. Expiration date 2 weeks.

9.10.3 ICV/CCV 2 ppb: dilute 1 mL of the 100 ppb to 50 mL with DI water. Expiration date 2 weeks.

9.11 LCS Stock Mercury Solution: 1,000 ppm purchased from certified vendor. Expiration date assigned by supplier.

9.11.1 10 ppm Calibration Solution: dilute 1.0 mL of the stock solution and 7 mL of concentrated HCl to 100 mL with DI water. Expiration date 2 weeks.

9.11.2 100 ppb calibration solution: dilute 1 mL of the 10 ppm standard and 7 mL of concentrated HCl to 100 mL with DI water. Expiration date 2 weeks.

10.0 Sample collection

10.1 Samples must be collected in cleaned plastic or glass containers, acidified to a pH<2 with HNO_3, and analyzed within 28 days from collection.

11.0 Quality control

11.1 Analyze an ICB/CCB following calibration, every 10 samples, and at the end of the run.

11.2 Analyze an ICV following calibration, and CCVs every 10 samples, and at the end of the run.

11.3 Analyze one method blank per sample batch to determine if contamination or any memory effects are occurring.

Note: Do not exceed more than 20 samples per batch.

11.4 Analyze a LCS per batch of 20 or fewer samples.

11.5 Analyze a matrix spike and a matrix spike duplicate per batch of 20 or fewer samples.

11.6 Perform a dilution test on one sample per batch. Dilute a sample 5X and analyzed.

11.6.1 Perform the Dilution test on the same sample as the MS/MSD.

11.7 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of the calibration curve.

11.8 Perform a PDS per batch of 20 samples. Spike 9.8 mL of sample with 0.2 mL of the LCS 100 ppb standard.

12.0 Calibration and standardization

12.1 A calibration curve must be composed of a minimum of a blank and five standards. The calibration correlation coefficient must be ≥ .995.

12.1.1 Calibration curves are made with a blank, 0.2 ppb, 0.5 ppb, 1 ppb, 2 ppb, 4 ppb, and 10 ppb standards.

12.1.2 The above standards are made in the following manner:

100 ppb Standard	Diluted To	Final Concentration
0.10 mL	50 mL	0.2 ppb
0.25 mL	50 mL	0.5 ppb
0.5 mL	50 mL	1.0 ppb
1.0 mL	50 mL	2.0 ppb
2.0 mL	50 mL	4.0 ppb
5.0 mL	50 mL	10 ppb

12.2 The laboratory LDR and MDL will be determined annually. LDR and MDL results are maintained in the QAO's files.

12.3 When the continuing calibration results obtained are outside the established acceptance criteria, Corrective action must be performed. If routine preventative maintenance (corrective action) fails to produce a second consecutive (immediate) CCV within acceptance criteria, then the analyst must demonstrate performance after corrective action with two successful CCV or a new initial calibration must be performed. Sample data associated with unacceptable calibration verification may be reported if qualified for the following condition: CCV Acceptance criteria was exceeded high and the samples are non-detects. Other wise the samples affected will be re-analyzed after a new calibration curve has been established and accepted.

13.0 Procedure

13.1 Transferred approximately 30 mL DI water to 50 mL centrifuges tubes assigned for the standards. Add 1.50 mL of concentrated sulfuric acid and 0.75 mL of concentrated nitric acid. Spiked 0, 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0 aliquots of the 100 ppb Hg standard. The concentrations of these prepared standards are 0, 0.2 ppb, 0.5 ppb, 1 ppb, 2 ppb, 4 ppb, and 10 ppb.

13.2 Transfer 30mL of sample into a 50mL centrifuge tube.

13.3 Add 1.50mL of concentrated sulfuric acid to each tube and swirl to mix.

13.4 Add 0.75mL of concentrated nitric acid to each tube and swirl to mix.

13.5 Add 4.50mL of potassium permanganate solution and mix. If the sample does not maintain a purple color for 15 minutes, more potassium permanganate solution must be added.

> **Note:** Ensure that equal amounts of permanganate are added to standards and blanks.

13.6 Add 2.40mL of potassium persulfate solution and swirl to mix.

13.7 Place all centrifuge tubes in a water-bath for 2 hours; maintain temperature between 86 – 96 ^{o}C.

13.8 Remove samples from the water-bath and allow too cool.

13.9 Add 1.80mL of sodium chloride-hydroxylamine hydrochloride solution to each centrifuge tube and swirl to mix.

13.10 Bring samples and standards to 50 mL with DI water

13.11 Standards and samples are now ready to be analyzed on the CETAC.

14.0 Calculations

14.1 A linear regression calibration curve is generated with a correlation coefficient ≥ 0.995.

14.2 The instrument compares the sample concentration against the calibration curve.

14.3 Results are transferred into the LIMS electronically.

15.0 Method performance

15.1 The LIMS tracks precision and accuracy through the plotting of quality control recoveries. The lab does not update its limits for this method based on the LIMS calculations. Set limits from the regulatory method are utilized.

15.2 See section 17 for the laboratory limits.

16.0 Pollution prevention

16.1 The laboratory minimizes waste through reduction of sample, standard, ASTM water, and reagent volumes.

16.2 Inorganic spill kits are available in the preparation labs in case of acid spills.

16.3 The water-bath temperature should be verified with a non-mercury filled thermometer. In case of breakage the analysis will not be contaminated.

16.4 Preparation and analysis are performed in 50mL disposable centrifuge tubes to avoid cross contamination through the washing and reuse of glassware.

16.5 Volumetric glassware used to make mercury standards are not to go through the laboratory washing station, and are not to be used for any other purpose than the preparation of mercury standards.

17.0 Data assessment and acceptance criteria for quality control measures

17.1 Blanks results must be lower than the laboratory PQL;

17.2 ICV must recover between 90 - 110% for 7470A; 95 – 105% for method 245.1

17.3 CCV must recover between 80 - 120% for 7470A; 90 – 110% for method 245.1

17.4 LCS must recover between 80 – 120% for 7470A; 85 – 115% for method 245.1

17.5 Matrix spikes must recover between 80 – 120% with and RPD of 20% or less;

17.6 Dilution test must agree within 90 - 110% of the undiluted sample.

17.7 PDS must recover between 85 – 115%.

18.0 Corrective actions for out of control data

18.1 If one of the Standards (ICV, LCS, and CCV) is not within limits, make a new standard and re-analyze batch prior to sample expiration.

Note: If initial CCV fails, immediate routine corrective action may be performed and a second CCV analyzed if this passes analysis may continue.

18.2 If the method blank is not within limits, the batch is deemed unacceptable and must be reanalyzed prior to sample expiration.

18.3 If the duplicate is not within limits, a sample prep error is assumed. Sample should be re-prepped and analyzed prior to sample expiration.

18.4 If a matrix spike fails evaluate the dilution test and the post digestion spike.

19.0 Contingencies for handling out of control data or unacceptable data.

19.1 If re-analysis of samples cannot be performed within 28 days of collection, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If the initial CCV fails and routine corrective action fails to produce a second consecutive (immediate) CCV within acceptance criteria, the analyst must demonstrate performance after corrective action with two successful CCV or a new initial calibration must be performed.

19.4 If a matrix spike, serial dilution and or post digestion spike fail. The sample report must be flagged matrix interference.

20.0 Waste management

20.1 All samples, reagents, and by products not containing mercury may be disposed through the laboratory sink after neutralization with baking soda.

20.2 Solutions and solid materials containing mercury must be disposed through a hazardous collection firm.

20.2.1 The laboratory maintains a 16 gallon drum for liquid Hg waste in the sample archiving area.

21.0 References

21.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846) Method 7470A, revision 1, September 1994.

21.2 Methods and Guidance for Analysis of Water, Method 245.1, Revision 3.

21.3 Quick Trace M-7500 Mercury Analyzer Operator Manual Version 1.0.3

22.0 Tables, diagrams

22.1 Not Applicable

23.0 Clarification/modifications of the method

23.1 A 30ml sample volume is utilized instead of 100mL specified by the method. Because sample volume is reduced, the amount of reagents added is also reduced to remain proportional to the method.

23.2 The stannous chloride solution utilized by the laboratory varies slightly from the method stated recipe. CETAC developed and recommends a lower higher concentration of the method stated reagent due to type of system recommends the use of HCL over H_2SO_4. The use of H_2SO_4 forms a suspension that builds up in instrument lines.

23.3 The laboratory interprets 95°C to be 86 – 96 ^{o}C based on the regulatory method (7470A) section 4.10: A hotplate or equivalent adjustable and capable of maintaining a temperature of 86 – 96 ^{o}C.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

1.0 Applicable matrix

1.1 These methods are applicable to the analysis of CWA and SDWA requirements, water, industrial waste, soil, sediment, sludge, organic waste, and TCLP extracts that have been solubilized or digested.

2.0 Detection limit

2.1 See Omega V9 LIMS test groups for detection limits. Note detection limit is defined as PQL in the LIMS.

2.2 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.3 Linear dynamic range (LDR) determinations are performed every six months. This determination is documented with the MDLs. Values above the LDR must be diluted.

2.4 The laboratory lowest PQLs for the following elements in mg/L are:

Element	Water	Soil	Element	Water	Soil	Element	Water	Soil
Ag	0.01	1	Cu	0.004	0.5	Se	0.05	5
Al	0.1	10	Fe	0.05	5	Si	0.05	50
As	0.05	5	K	1	100	Sn	0.5	50
B	0.5	50	Mg	1	100	Sr	0.005	10
Ba	0.002	0.2	Mn	0.005	0.5	Ti	0.005	0.5
Be	0.001	0.1	Mo	0.04	4	Tl	0.5	50
Ca	1	100	Na	1	100	V	0.005	0.5
Cd	0.004	0.4	Ni	0.005	0.5	Zn	0.005	0.5
Co	0.01	1	Pb	0.01	5			
Cr	0.01	1	Sb	0.1	10			

2.5 Inter-element correction factors (IECs) are calculated and adjusted annually.

2.6 Instrument detection limits (IDLs) are calculated quarterly.

3.0 Scope and application

3.1 This procedure is capable of analyzing 29 elements at once. An elements detection limit, sensitivity, and range of detection will vary on the wavelength, matrix, operating conditions, and spectrometer. The manufacturer/EPA recommended wavelengths are:

Ag	328.068	Cu	324.754	Se	196.026
Al	308.215	Fe	259.940	Si	251.611
As	193.696	K	766.491	Sn	189.927
B	249.678	Mg	279.079	Sr	407.771
Ba	455.403	Mn	257.610	Ti	334.941

Be	313.042	Mo	202.030	Tl	190.864
Ca	317.933	Na	588.995	V	292.402
Cd	226.502	Ni	231.604	Zn	213.856
Co	228.616	Pb	220.353	Zr	339.197
Cr	267.716	Sb	206.833		

NOTE: Sr and Zr are not typical analytes analyzed in this laboratory and are not in the laboratory standards. If these analytes are requested they must be added to the laboratory standards.

4.0 Summary of test method

4.1 Samples are first solubilized or digested by one of the following methods: 3005A, 3051, 3015, or 200.7. Following sample prep, samples are analyzed via the ICP. In the ICP, a sample is forced through a nebulizer, converted into an aerosol, and forced through a plasma. As the aerosol passes through the plasma, atoms become excited producing emission spectra, specific for each element. The spectra are monitored by photosensitive devices.

5.0 Definitions

5.1 CCV (Continuing Calibration Verification): a solution containing a known concentration of elements. Made from the same source as the calibration standards.

5.2 CCB/ICB (Continuing Calibration Blank/Initial Calibration Blank): DDI water containing 10% nitric acid. The difference between CCB and ICB is the placement during an analytical run.

5.3 ICV (Initial Calibration Verification): a solution containing a known concentration of elements. Made from a different source than the calibration standards.

5.4 ICSA (Interference Check Solution A): a solution containing potentially interfering elements and zero concentration of potentially affected elements.

5.5 ICSAB (Interference Check Solution AB): a solution containing potentially interfering elements and known concentrations of potentially affected elements.

5.6 ICP (Inductively Coupled Plasma): the instrument used for analysis of metals by 6010B.

5.7 PECAL: solutions used in calibrating the instrument. Made from diluting purchased stock standards.

5.8 MB (Method Blank): DDI water that follows the digestion process with the samples. There is one MB for each batch of 20 or fewer samples.

5.9 LCS (Laboratory Control Standard): DDI spiked with elements of known concentration that follows the digestion process with the samples. There is one LCS for each batch of 20 or fewer samples.

5.10 MS/MSD (Matrix Spike/Matrix Spike Duplicate): a sample spiked and duplicated with elements of a known concentration. There is at least one MS and one MSD for each batch of 20 samples or fewer.

5.11 PDS (Post Dilution Spike): a sample spiked with elements of known concentration after the digestion process. This is a second QC check. There is one PDS for each batch of 20 samples or fewer.

5.12 SD (Serial Dilution): a sample diluted, usually 1:5, after the digestion process. This is a second QC check. There is one SD for each batch of 20 samples or fewer.

5.13 LLOQ (Lower Limit of Quantitation): a solution containing elements at concentrations equal to the laboratory PQL. This standard is used to both establish and confirm the lowest quantitation.

5.14 LLCCV (Low-Level Continuing Calibration Verification). A standard prepared using the same source as the initial calibration standards, at the stablished lower limit of quantitation.

5.15 LLICV (Low-Level Initial Calibration Verification). A standard prepared using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation.

6.0 Interference

6.1 Spectral interferences are the major interferent with analysis by ICP. There are three types of spectral interferences: background emission, stray light, and overlapping of other spectral lines.

6.1.1 Background emission and stray light may usually be corrected for by determining the adjacent background emissions and subtracting from the analyte wavelength peak.

6.1.2 Spectral overlaps should be avoided by the use of alternative lines. A table of recommended wavelengths is provided in section 22.

6.1.3 IEC factors are used to eliminate the effects of neighboring (on-line, off-line) elements on the wavelength chosen. Correction factors will vary per instrument. They will be verified with an ICSA and ICSAB solution every calibration.

6.2 Physical effects caused by the sample matrix may also pose analytical inaccuracies. Physical effects may be caused by sample viscosity, acid concentration, and dissolved solid content. To overcome these types of

interferences, the laboratory uses a high solids nebulizer, a peristaltic pump, sample dilution (when necessary), and an internal standard.

6.3 Chemical effects are sample specific. Typically, a substance within a sample will inhibit recoveries of analytes requested. Matrix problems of this nature are screened for with the use of matrix spikes. If recoveries of matrix spikes are below required limits, matrix interferences are suspected. The use of additional standards may overcome matrix effects.

6.4 Memory effects occur when sample concentrations are higher than the instrument can rinse through the system before the next sample is introduced. This can cause a false positive for the second sample. The method requires a 60 second rinse time between samples. The rinse time can be lengthened to reduce memory effects.

7.0 Safety

7.1 Wear approved gloves while handling chemicals. Additionally, always wear a lab coat and safety glasses. Samples should be considered hazardous. Avoid exposure, skin contact, inhalation, or ingestion.

7.2 The acidification of samples containing reactive material may result in the release of toxic gases such as cyanide or sulfides. The acidification of samples should only occur under a hood.

7.3 The ICP should only be viewed with proper eye protection that protects from ultra violet light.

7.4 The plasma generates a great deal of heat, making the surrounding torch hot. Allow the torch to cool before handling.

7.5 The instrument must be vented to avoid exposure to toxic fumes produced during atomization.

8.0 Equipment and supplies

8.1 Perkin Elmer Optima 3300 ICP with WinLab 32 software

8.2 Perkin Elmer Optima 5300 ICP with WinLab 32 software

8.3 15 mL disposable test tubes

8.4 Calibrated pipettes of various sizes

9.0 Reagents and standards

9.1 DDI water

9.2 CCB/ICB: dilute 100 mL concentrated nitric acid to 1000 mL with DDI water. **NOTE:** always add acid to water.

9.3 ICV: dilute 10 mL QCS-26 standard and 1.0 mL Sn 1000 mg/L standard to 500 mL with 10% nitric acid.

9.3.1 QCS-26 contains: 100 mg/L Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, Ti, V, and Zn; 50 mg/L Si; and 1000 mg/L K.

9.4 CCV: dilute 10 mL QCS-7 standard, 10 mL QCS-21 standard, and 0.1 mL Sn 10,000 mg/L standard to 500 mL with 10% nitric acid.

9.4.1 QCS-7 contains: 1000 mg/L K; 100 mg/L Ag, Al, B, Ba, Na; and 50 mg/L Si.

9.4.2 QCS-21 contains: 100 mg/L As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V, and Zn.

9.5 ICSA: dilute 12.5 mL Interferents A standard to 500 mL with 10% nitric acid.

9.5.1 Interferents A contains: 5000 mg/L Al, Ca, and Mg; 2000 mg/L Fe.

9.6 ICSAB: dilute 12.5 mL Interferents A standard, 10 mL QCS-26 standard, and 0.1 mL Sn 10,000 mg/L standard to 500 mL with 10% nitric acid.

9.7 PECAL 1: dilute 25 mL QCS-21 standard and 0.25 mL Sn 10,000 mg/L standard to 500 mL with 10% nitric acid.

9.8 PECAL 2: dilute 25 mL QCS-7 standard to 500 mL with 10% nitric acid.

9.9 PECAL 3: dilute 0.125 mL Ag 1000 mg/L standard to 500 mL with 10% nitric acid.

9.10 Internal Standard: dilute 2 mL Lu 10,000 mg/L standard to 1000 mL with 10% nitric acid.

9.11 PDS standard: dilute 0.5 mL Sn 10,000 mg/L standard to 50 mL with QCS-26.

9.12 Radial alignment standard: dilute 5 mL Mn 1000 mg/L standard to 500 mL with DDI water.

9.13 Axial alignment standard: dilute 50 mL of radial alignment standard to 500 mL with DDI water.

9.14 LLOQ: dilute 0.5 mL LLOQ standard to 500 mL with 10% nitric acid.

9.15 LLCCV: dilute 5 mL QCS-7 standard, 5 mL QCS-21 standard, and 0.05 mL Sn 10,000 mg/L standard to 500 mL with 10% nitric acid.

9.16 LLICV: dilute 5 mL QCS-26 standard and 0.5 mL Sn 1000 mg/L standard to 500 mL with 10% nitric acid.

10.0 Sample collection

10.1 Liquid samples must be collected in a clean plastic or glass container (no metal), acidified to pH<2 with nitric acid, and analyzed within 6 months of collection. If samples are received unpreserved, add up to 4 mL of nitric acid and document preservation with a footnote. Analysis can proceed at any time.

NOTE: Refrigeration is not required for preserved liquid samples.

10.2 Solid samples must be collected in a clean plastic or glass container (no metal), and refrigerated at 0° to 6° C, and analyzed within 6 months of collection.

10.3 Samples to be analyzed for dissolved metals are either filtered and preserved in the field by the client, or should be filtered and preserved immediately upon receipt.

11.0 Quality control

11.1 The quality control for this procedure is broken into two types: batch and instrument.

11.1.1 Each batch for 6010 analysis must contain 20 or fewer samples, a MB, an LCS, and an MS/MSD. TCLP batches must also contain a TCLP prep batch MB. These are incorporated into the batch during the digestion process. Each batch for 200.7 analysis must contain 20 or fewer samples, a MB, an LCS, and an MS/MSD for every 10 samples.

11.1.2 Each batch must contain one PDS and one SD. These are incorporated after the digestion process.

11.1.2.1 PDS: this is run on the parent sample in the batch. 0.1 mL of PDS solution is diluted to 10 mL with sample.

11.1.2.2 SD: this is run on the parent sample. A 1:5 dilution is analyzed.

11.1.3 The instrument must analyze the following QC at the stated interval:

11.1.3.1 The three IPC standards must be analyzed immediately following the calibration. They must pass for every analyte requested for 200.7 analysis to continue. Each standard may be run two times before a new calibration is required.

11.1.3.2 An ICV, LLICV, and ICB must be analyzed immediately following the IPCs. They must pass for every analyte the client requests to continue. Each standard may be run two times before a new calibration is required.

11.1.3.3 A CCV, LLCCV, and CCB must be analyzed every 10 samples and at the end of the run. The CCV, LLCCV, and CCB must pass for each analyte requested for preceding data to be valid. They can each be run two times before a new calibration is required.

11.1.3.4 An ICSA and ICSAB must be analyzed at the end of each calibration following the ICV and ICB. The ICSA must pass for each analyte spike in (Al, Ca, Fe, Mg) regardless if requested by client. The ICSAB must pass for ICSA analytes (Al, Ca, Fe, Mg), as well as all analytes requested to continue. Each standard may be run two times before a new calibration is required.

11.2 A typical run would look like the following:

CAL BLANK	*ICV*	*LLCCV*	*MS*
PECAL 1	*ICB*	*CCV*	*MSD*
PECAL 2	*LLOQ*	*CCB*	*SAMPLE*
PECAL 3	*LLCCV*	*MB*	*SAMPLE*
IPC 1	*CCV*	*LCS*	*SAMPLE*
IPC 2	*CCB*	*5X (SD)*	*LLCCV*
IPC 3	*ICSA*	*SAMPLE*	*CCV*
LLICV	*ICSAB*	*PDS*	*CCB*

12.0 Instrument start-up

12.1 Before the instrument is started, the following maintenance must be performed and documented in the maintenance logbook. Monthly maintenance and any other instrument maintenance or repairs must also be documented in the maintenance logbook.

12.2 Change pump tubing

12.2.1 Replace the two red-red tubes once a month.

12.2.2 Replace the black-black sample introduction tube daily.

12.2.3 Replace the red-orange internal standard tube daily.

12.3 Change torch

12.3.1 The torch should be cleaned and replaced daily at a minimum. The frequency of torch changes depends on the samples that are analyzed. The laboratory maintains several torches to avoid lengthy downtimes.

12.3.2 The torch and injector should be cleaned by soaking in 3% nitric acid solution for at least one hour. Do not use solvents.

12.3.3 Rinse the torch well with DI water and carefully shake to dry.

12.4 Igniting the torch

12.4.1 In the main screen of the WinLab 32 software, click the “on” button located in the lower left-hand corner of the screen.

12.4.2 Allow the instrument to warm-up for a minimum of 30 minutes to one hour.

12.5 Aligning the torch

12.5.1 A torch alignment must be performed every time the torch is changed.

12.5.1.1 The axial alignment is performed first. The axial alignment standard is used and the intensity is recorded in the maintenance logbook.

12.5.1.2 The radial alignment is performed second. The radial alignment standard is used and the intensity is recorded in the maintenance logbook.

12.5.1.3 The mercury alignment is performed last. The rinse water solution is used and the intensity is recorded in the maintenance logbook.

13.0 Calibration

13.1 A new calibration is performed every time the torch is changed or if analytes fail to pass. The calibration is performed per manufacturer's instructions and RCRA guidelines, with one blank and one standard per analyte.

13.2 Following each calibration, quality control standards are run to verify calibration. The following limits are required:

13.2.1 ICV: must recover ± 10% of the true value.

13.2.2 CCV: must recover ± 10% of the true value.

13.2.3 ICSA: must recover ± 20% for spiked analytes and ± 3 times the PQL for non-spiked analytes for 6010, and ± 10% for spiked analytes for 200.7.

13.2.4 ICSAB: must recover ± 20% of the true value.

13.2.5 ICB/CCB: must be ± the laboratory PQL.

13.2.6 IPC: must recover ± 5% of true value.

13.2.7 LLOQ/LLICV/LLCCV: must recover ± 30% of true value.

14.0 Samples

14.1 The samples are prepped for analysis and loaded into the auto-sampler tray. The information is input into the Sample Info file in the WinLab32 software.

14.1.1 Enter the initial volume or weight and final volume.

14.1.2 Enter any dilutions, including for the SD.

14.1.3 Enter correct units, mg/L or mg/kg.

14.1.4 Enter correct tray location.

14.1.5 Analyze samples.

15.0 Calculations

15.1 Sample results are reported in mg/L or mg/kg directly from the WinLab32 to the laboratory database, Data Manager.

15.2 If the correct dilutions are entered, the software will automatically calculate the results.

15.3 If sample results are requested on a dry weight basis, the percent moisture of the sample must be entered in the LIMS.

16.0 Method performance

16.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

16.2 The following limits are required:

16.2.1 MB: must recover ± laboratory PQL.

16.2.2 LCS: must recover ± 25% of the true value for 6010 anlaysis and ± 15% for 200.7 analysis.

16.2.3 MS/MSD: must recover ± 25% of the spiked value for 6010 analysis and ± 30% for 200.7 analysis, and have an RPD ± 20% for either analysis.

16.2.4 PDS: must recover ± 25% of the spiked value for 6010 analysis and ± 15% for 200.7 analysis.

16.2.5 SD: must recover ± 10% of the undiluted portion.

NOTE: MB and LCS must recover within specified limits. MS/MSD, PDS, and SD can sometimes be footnoted if they are out, depending on the sample.

17.0 Pollution prevention

17.1 The laboratory uses reduced volumes to eliminate the production of excessive processed waste.

17.2 Reagents used in this procedure are very corrosive. Care must be used in handling to prevent spills that might attack surrounding equipment.

17.3 All acid spills should be neutralized with baking soda and disposed of in the laboratory sink or trash.

17.4 Disposable test tubes are used in the instrument sampling tray to prevent cross-contamination.

18.0 Corrective actions for out of control data

18.1 If a MB or LCS fails, pour a fresh aliquot and re-analyze. If it fails a second time, return batch for a re-prep.

18.2 If any calibration QC standards fail, pour a fresh aliquot and re-analyze. If it continues to fail, make a new standard and re-analyze. If it continues to fail, re-evaluate the IEC or MSD.

18.3 If the MS/MSD fails and the instrument QC is passing, the sample can be flagged for matrix interference.

18.4 If the MS/MSD RPD fails the sample may be flagged non-homogenous.

19.0 Contingencies for handling out of control data or unacceptable data

19.1 If re-analysis of samples cannot be performed within 6 months of collection, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

20.0 Waste management

20.1 All waste generated from this procedure is extremely corrosive and must be neutralized with baking soda before disposal through the laboratory sink.

20.2 Some TCLP waste must be disposed of in a TCLP hazardous waste barrel.

20.3 Refer to the laboratory “Waste Management and Sample Disposal SOP”.

21.0 References

21.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846) Method 6010B, Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 2, December 1996.

21.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846) Method 7000A, Atomic Absorption Methods, Revision 1, July 1992.

21.3 Perkin Elmer ICP, Emission Spectroscopy, Optima 3000 Family, Hardware Guide, 1997.

21.4 Perkin Elmer ICP, Emission Spectroscopy, Optima 3000 Family, Wavelength Tables, 1998.

21.5 Perkin Elmer, ICP Optical Emission, WinLab32, Data Management Software, 1999.

21.6 Perkin Elmer, ICP Optical Emission, WinLab32, Instrument Control Software, 1999.

22.0 Tables

22.1 Potential interferences

	λ(nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Al	308.215							0.21			1.4
Sb	206.833	0.47		2.9		0.08				0.25	0.45
As	193.696	1.3		0.44							1.1
Ba	455.403										
Be	313.042									0.04	0.05
Cd	226.502					0.03			0.02		
Ca	317.933			0.08		0.01	0.01	0.04		0.03	0.03
Cr	267.716					0.003		0.04			0.04
Co	228.616			0.03		0.005			0.03	0.15	
Cu	324.754					0.003				0.05	0.02
Fe	259.940							0.12			
Pb	220.353	0.17									
Mg	279.079		0.02	0.11		0.13		0.25		0.07	0.12
Mn	257.610	0.005	------	0.01		0.002	0.002				
Mo	202.030	0.05				0.03					
Ni	231.604										
Se	196.026	0.23				0.09					
Na	588.995									0.08	
Tl	190.864	0.30									
V	292.402			0.05		0.005				0.02	
Zn	213.856				0.14				0.29		

_____ Date _____
Inorganic Dept. Supervisor

_____ Date _____
Laboratory Director

_____ Date _____
QAO

1.0 Applicable Matrix

1.1. This method is applicable to the analysis of: water, industrial waste, soil, sediment, sludge, organic waste and TCLP extracts that have been digested.

2.0 Detection Limit

The laboratory MDL is determined annually in accordance with 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL. The PQL is normally higher than the MDL and never lower than the MDL.

2.1. Linear range determinations should be performed annually. This determination should be documented with the MDLs.

2.1.1 To perform the LDR make a series of standards: 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100ppm.

2.1.1.1 Analyze each standard for every element listed below in section 2.3.

2.1.1.2 Evaluate each analysis for accuracy. The first standard/element that does not recover within 10% of its true value is the stopping point for that standard/element.

2.1.1.3 The LDR is the highest standard that recovered within 10%.

2.2. The PQLs for this method are found on the LIMS.

2.2.1 The laboratory PQLs are derived from the MDLs. The PQLs for a sample are calculated by multiplying the raw PQLs listed above by the dilution factors for the sample.

2.2.1.1 The analyst must be aware of the instruments current MDLs and laboratory PQLs.

3.0 Scope and Application

3.1. This method is capable of analyzing 23 elements at once. The masses listed in table 22.3 are used to either quantitate or provide qualitative confirmation of the element's presence. The bold masses are used for quantitation.

3.2. Other elements are possible to analyze by this instrumentation e.g., uranium, thorium and others.

3.2.1. These elements would require additional IDL, MDL, and internal blind sample checks.

3.2.2. Check with the quality assurance department to see if additional measures are required before analysis of these elements.

4.0 Summary of Test Method

4.1. Samples are first digested with a HNO_3 & HCL acid mixture. HCl is absolutely required if either silver or antimony is to be determined. Following sample preparation the

samples are analyzed via the ICP/MS. In the ICP/MS a sample is forced through a nebulizer, where it is converted into an aerosol. The resultant aerosol is then forced through a plasma. Once the aerosol passes through the plasma atoms become ionized. The ionized atoms are extracted from the plasma by a vacuum interface and directed through a quadrupole. The quadrupole separates the ions by mass to charge ratio.

5.0 Definitions

5.1. **IDL**: Instrument detection limit. The IDL is calculated from a repeated analysis (7 minimum) of the calibration blank.

5.2. **MDL**: Method detection limit. The MDL is calculated from a repeated analysis (7 minimum) of known concentration standard that has gone through the digestion process identical to routine samples. See 40 CFR Part 136 Appendix B.

5.3. **PQL**: Practical quantitation limit. Normally 5 times the concentration of the MDL. Allows for “real world” sample interferences.

5.4. **QCS**: Quality control sample. AWAL uses the acronym ICV (Initial Calibration Verification) for this protocol.

5.5. **LCS**: Laboratory Control Sample. This is a fortified (from the same source as the calibration standards) blank.

5.6. **LDR**: Linear dynamic range. Upper concentration limit for reporting a particular element. Calculated by increasing the concentration of an element until the reported value is <90% of the true value and using the highest concentration that is >/=90% of the true value as the upper report limit.

5.7. **LRB**: Laboratory reagent blank. AWAL uses the acronym MB (method blank) for this protocol. See MB.

5.8. **MB**: Method blank. The method blank goes through all processes as the samples, including filtering, digesting etc.

5.9. **FB**: Field blank. Deionized water placed in the same bottles as regular samples by the field sampler <u>at the time of field collection</u>.

5.10. **TB**: Trip blank. Deionized water placed in the same bottles as regular samples by the laboratory before the bottles are taken into the field. The TB follows along with the samples at all times through analysis.

5.11. **ICSA**: Interference Check Solution A. Contains potentially interfering elements and zero concentration of potentially affected elements. This solution is used to ensure that the instrument is correcting for interferences properly.

5.12. **ICSAB**: Interference Check Solution AB. Contains potentially interfering elements and a known concentration of potentially affected elements. This solution is used to ensure that the instrument is correcting for interferences properly.

5.13. **CCV**: Continuing Calibration Verification. Contains a mid-range concentration of all elements to be reported. This is made from the same source as the calibration standards.

5.14. **CCB**: Continuing Calibration Blank. Contains deionized water and all acids contained in samples.

5.15. **ICV**: Initial Calibration Verification. Analyzed immediately after the initial calibration to confirm that the calibration is accurate. This is made from a separate source than the calibration standards.

5.16. **ICB**: Initial Calibration Blank. Same as the CCV except analyzed immediately after the initial calibration to confirm that the zero point is within limits.

5.17. **LLOQ**: Lower Limit of Quantitation. Contains all elements to be reported at concentrations ≤ the reporting limit. This is made from a separate source than the calibration standards.

5.18. **MS**: Matrix spike

5.19. **MSD**: Matrix spike duplicate

5.20. **LFB**: Laboratory Fortified Blank. AWAL uses the acronym LCS (Laboratory Control Sample) for this protocol.

5.21. **LD1** or **LD2**: Laboratory Duplicate Sample #1 and Sample #2. AWAL simply uses the sample ID and sample ID dup for sample duplicate analyses.

6.0 Interferences (see table 22.5)

6.1. Isobaric elemental interferences: These are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference with the exception of Se-78 and Se-82. Selenium has krypton as an interferent and is corrected mathematically by monitoring the concentration of krypton in the system.

Selenium-78 analysis by DRC-Oxygen has a positive interference from nickel-62. Ni-62 in the presence of oxygen forms NiO-78 which is the same mass as Se-78. Therefore, the two cannot be differentiated. To correct this interference the concentration of Ni-62 must be calculated. According to "Isotopic Compositions of the Elements 1989," from Pure Applied Chemistry, Volume 63, No7, pp. 991-1002, 1991, the percentage of Ni-62 is 3.634% of the entire isotope concentration of nickel. Since the ICP/MS is calibrated for Ni-60 (26.223% of the total nickel concentration) it assumes that Ni-60 is 100% of the reference standard concentration. In other words, the reference standard provides a given concentration for nickel which is really 68.077% Ni-58, 26.223% Ni-60, 1.14% Ni-61, 3.634% Ni-62, and 0.926% Ni-64. As long as the 26.223% Ni-60 is given the total concentration during calibration, the fact that in actuality it is only measuring 26.223% does not matter since this process corrects for that difference. While the references report that 3.634% of nickel is Ni-62 it is critical that the actual percentage that interferes with Se-78 by DRC-O is determined empirically. This was determined by running 4 standards (10, 20, 50, 100

µg/L) of nickel with no other elements present and then noting the Se-78 concentration by DRC-O. Based on these results the concentration of interference is 0.07083 or 7.083% (RSD of 1.2%) of the total Ni-60 concentration. This number must be confirmed or modified with a new empirical study every 6 months, as well as any time the DRC-O RPQ (0.6) or the cell gas flow (0.8) is changed. All Se-78 results above the PQL are manually corrected by multiplying the concentration of Ni-60 in the sample by 0.07083 and subtracting this value from the Se-78 DRC-O result.

6.2. Abundance sensitivity: This is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. It must be recognized that large concentrations of an element adjacent to another mass of interest may overflow into the adjacent mass. This is reduced or eliminated by ensuring that the peak width meets method criteria during the mass calibration procedure.

6.3. Isobaric polyatomic ion interferences: These are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest. These ions are commonly formed in the plasma or interface system from support gases or sample components. The dynamic reaction cell (DRC) can significantly reduce if not eliminate these interferences.

6.4. Physical interferences: These are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. Two major concerns are viscosity effects and surface tension. Dissolved solids levels not exceeding 0.2% (w/v) are recommended. The use of internal standards significantly reduces these effects.

6.5. Memory interferences: This interference results when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Proper rinse times will eliminate this problem. AWAL will not run mercury by this method and therefore will not need to correct for this most difficult element to reduce memory effect. The rinse times are calculated by analyzing a standard at 10 times the LDR and noting how long is required to reduce the concentration to 10 times the MDL.

7.0 Safety

7.1. The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

7.1.1 Always wear safety glasses or a shield for eye protection and protective clothing.

7.1.2 Observe proper mixing (add acid to water) when working with these reagents.

7.1.3 The acidification of samples containing reactive material may result in the release of toxic gases such as cyanide or sulfides. Prepare samples in a fume hood.

8.0 Equipment and supplies

8.1. Inductively coupled plasma mass spectrometer (ICP/MS), Perkin-Elmer DRC II

8.2. Gas supply

8.2.1 Argon gas, high purity grade >/= 99.99%. Low krypton content.

8.2.2 Oxygen, compressed

8.2.3 Ammonia, anhydrous

8.3 Meinhart nebulizer.

8.4 Cyclonic spray chamber.

8.5 Vacuum pump

8.5.1 Mechanical vacuum pump oil

8.6 Analytical balance accurate to 0.1 mg.

8.7 Teflon 100 ml volumetric flasks for preparation of standards.

8.8 Various calibrated pipetters with tips.

8.9 Various pump tubing.

8.10 Plastic test tubes, 15mL

8.11 Test tube racks

8.12 Plastic containers, ½ gallon, 1L, pint and ½ pint.

8.13 Syringe, 20mL

8.14 Syringe filter, 0.7μm

8.15 Centrifuge tubes, 50mL, with clear caps.

8.16 Centrifuge.

9.0 Reagents and standards

9.1 Hydrochloric acid (HCl), concentrated, Optima grade

9.2 Hydrochloric acid, concentrated, trace grade

9.3 Nitric acid (HNO_3), concentrated, Optima grade

9.4 Nitric acid, concentrated, trace grade

9.5 Deionized water, resistance of >/= 18 Mega Ohms. Available only in the TCLP preparation laboratory (A.K.A. Double DI).

9.6 Mixed element primary standard (Spex CL-CAL-2) containing 100 mg/L of: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn

9.7 Mixed element secondary source standard (Inorganic Ventures QCP-QCS-3) 50 mg/L Se, 10 mg/L remaining elements Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Ag, Na, Tl, Th, U, V, Zn in 5% HNO_3

9.8 Tuning solution: (Spex CL-Tune-1) contains 10 mg/L of Ba, Be, Ce, Co, In, Li, Mg, Pb, Rh, Tl, U, Y in 2% HNO_3 & 5% HCl.

9.9 Multi-element internal standard: (Spex CLISS-1): 10 mg/L of Bi, Ho, In, Li-6, Sc, Tb, And Y in 2% HNO_3.

9.10 Rhodium Internal Standard: (Spex CLRH1-1AY): 10 mg/L of Rh in 2% HCl

9.11 Gallium Internal Standard: (Inorganic V. CGGA1-1): 1000 mg/L of Ga in H_2O

9.12 ICP/MS Interference Check Solution A (ICSA): (Spex CL-INT-A2): 10000 mg/L of Cl, 2000 mg/L C, 1000 mg/L Al, Ca, Fe, K, Mg, Na, P, S, 20 mg/L Mo, Ti in 5% HNO_3 and trace of HF.

9.12.1 When prepared as in Table 22.7 the end concentration of the ICSA is:
Al and Fe at 25ppm;
Ti and Mo at 0.5ppm.

9.13 ICP/MS Interference Check Solution B (ICSB): (Spex CL-INT-B3N): 2 mg/L Sb, As, Ba, Be, Cd, Cr, Co, Pb, Mn, Ni, Se, Ag, Tl, V, Zn in 2% HNO_3 and trace of HF.

9.14 ICSAB: See table 22.7 for preparation.

9.14.1 When prepared as in Table 22.7 the end concentration of the ICSAB is:
Al 25ppm
Mo and Tl are at 0.5ppm
Be, B, Ti, Mn, Co, Cu, Zn, Sr, Ag, Cd, Sn, Sb, Ba, Pb, As, Se, Cr, Fe and V are at 0.02ppm

9.15 Boron Primary Standard: (Spex ZAWAUT-1-100 custom standard) 1000 mg/L

9.16 Boron Secondary Standard: (Inorganic Ventures CGB1-1) 1000 mg/L

9.17 Strontium Secondary Standard: (Inorganic Ventures CGSR1-1) 1000 mg/L

9.18 Tin Secondary Standard: (Inorganic Ventures CGSN1-1): 1000 mg/L

9.19 Titanium Secondary Standard: (Inorganic Ventures CGTI1-1) 1000 mg/L

9.20 Custom Claritas standard for LCS, MS, MSD (Spex ZAWAUT-3) containing:1000mg/L Na, K, Ca, Mg, 100mg/L Al, B. Sn, Fe, Ti Zn, Si, 20mg/L Ag, Pg, As, Sb, Ba, Se, Be, Cd, Sr, Co, Cr, Tl Cu, V, Mn, Mo, Ni

9.21 Dual Detector Calibration Solution: 250 ppb of all elements including internal standards. Prepare by taking 250 µl of mixed primary standard (9.6), 2.5 mL of multi-

element internal standard (9.9), 2.5 mL of both Rh (9.10) & Ga (9.11), and 25 µl of boron standard (9.14).

9.22 Primary standard calibration working solution: see table 22.6.

9.23 Continuing Calibration Verification (CCV) Standard: see table 22.6.

9.24 Continuing Calibration Blank (CCB) Standard: see table 22.7.

9.25 Initial Calibration Verification (ICV) Standard: see table 22.7.

9.26 Initial Calibration Blank (ICB) Standard: see table 22.7.

9.27 Internal Standard Working Solution: see table 22.7.

9.28 Rinse water: Deionized water that contains 2% trace quality HNO_3 and 1% trace quality HCL.

9.29 Instrument tuning working solution: see table 22.7.

9.30 Mass calibration solution: use the instrument tuning solution (9.8)

9.31 PDS spiking solution: combine 2.5mL CL-CAL-2 (9.6) and 0.5mL ZAWAUT-1-100 (9.14) and dilute up to 50mL.

9.32 Salt matrix: place 22.28mg potassium sulfate (k_2SO_4), 33.24mg calcium chloride ($CaCl_2$), 762.4 mg sodium chloride (NaCl) in a 2 L flask. Add DDI water, 40mL Ultra pure nitric acid (HNO_3) and 20mL ultra pure hydrochloric acid (HCL). Mix to dissolve and dilute to volume with DDI water.

9.32.1 Working salt matrix: place 100 mL of the salt matrix in a 1L volumetric flask, Add 18mL of ultra pure HNO_3 and 9 mL of HCL. Dilute to volume with DDI water.

9.33 Salt matrix calibration standards. These are prepared as listed in section 9.21 through 9.25 replacing the DDI water with the working salt matrix.

9.34 ICP/MS Lower Limit of Quantitation (LLOQ) Standard: (Elements CS-AWA01): 100 µg/mL Al, Fe; 50 µg/mL B; 20 µg/mL V, Zn; 5 µg/mL Ti; 2 µg/mL Be, Mn, Co, Ni, Cu, Sr, Ag, Sn, Sb, Ba, Tl, Pb, As, Se, Cr, Mo; 0.9 µg/mL Cd in 2% HNO_3 and trace of HF.

9.35 Multi-Element LLOQ Standard: see table 22.7.

9.36 Ti LLOQ Standard: see table 22.7.

9.37 Sn LLOQ Standard: see table 22.7.

10.0 Sample Collection

10.1 Aqueous or aqueous compatible samples must be collected in a clean plastic container (no metal lids), acidified to a pH<2 with HNO_3 and analyzed within 6 months of the collection date.

Note: Refrigeration is not required for samples preserved pH<2.

10.2 Solid or non-aqueous compatible samples (e.g., oil) must be collected in a clean glass or plastic container (no metal lids), and refrigerated to >0°C to 6°C, and analyzed within 6 months of the collection date.

11.0 Quality Control

11.1 The quality control for this procedure is broken into two types: batch and instrument.

11.1.1 Batch QC: The batch (20 or fewer samples prepared at the same time) must contain: a method blank, a LCS, an MS/MSD, post digestion spike, and a serial dilution.

Note: Projects requiring QC level 2+ or higher must have samples from that project used for the MS/MSD.

11.1.1.1 Post digestion spike: Spike one sample in the batch (preferably the sample with the MS/MSD) with 0.1mL of PDS spiking solution (final volume 10 ml) for a 5 µg/L effective final concentration, and analyze.

11.1.1.2 Serial dilution: if a sample concentration is > or = 100 times the detection limit a 1:5 dilution should recover within 10% of the undiluted portion. If not, matrix interference is indicated.

11.1.2 Instrument QC: The instrument QC consists of the following analyses: tuning, ICSA, ICSAB, ICV, ICB, CCV, CCB, LLOQ, MB, LCS, MS, MSD, Serial dilution, post digestion spike and internal standard. The criteria for these analyses can be found in *Table 22.4*.

12.0 Calibration and standardization

12.1 The analysis schedule is as follows:

- Calibration Blank
- Calibration Standard 0.02 µg/L
- Calibration Standard 0.1 µg/L
- Calibration Standard 1.0 µg/L
- Calibration Standard 10 µg/L
- Calibration Standard 20 µg/L
- Calibration Standard 100 µg/L
- ICV (QC Std 1)
- ICB (QC Std 2)
- CCV (QC Std 3)
- CCB (QC Std 4)
- ICSA (QC Std 5)
- ICSAB (QC Std 6)
- Multi-Element LLOQ (QC Std 7)
- Ti LLOQ (QC Std 8)
- Sn LLOQ (QC Std 9)

- 5 samples (may include ICSA, ICSAB, MB, LCS, MS, MSD, Post Dig. Spike, Serial dilution, or simple samples)
- CCV
- CCB
- 10 samples
- CCV
- CCB

  Repeat CCV/CCB, 10 sample, CCV/CCB loop as necessary as long as all criteria are met.
  The ICSA and ICSAB must be analyzed once every 12 hours.
  Only three calibration standards are required. Therefore, points may be dropped if necessary as long as there are at least three remaining points and the points bracket the sample concentration.

13.0 ICP/MS Analysis

13.1 Daily Maintenance – Before Plasma Startup (Record all maintenance):

13.1.1 Rinse water reservoir is filled.

13.1.2 Waste container is sufficiently empty.

13.1.3 Water chiller is running at the correct pressure (55 psi) and temperature ($18^{o}C$).

13.1.4 Check argon tank pressure: 51 +/- 1psi.

13.1.5 Check the ammonia gas pressure (7 +/- 2psi)

13.1.6 Check vacuum pump oil level and color.

13.1.7 Check cone cleanliness/orifice size. Clean as necessary with a cotton swab or KimWipe moistened with 0.2% HNO_3.

13.1.8 Inspect injector, support adapter, torch and coil. Clean or replace as necessary.

13.1.9 Check the instrument status menu to determine that the vacuum is sufficiently low. This is indicated by the color green.

13.1.10 Check pump tubing and replace if it has been used for more than 8 hours.

13.1.11 Inspect drain tubing. Replace as necessary.

13.2 ICP/MS Weekly Maintenance (Record all maintenance)

13.2.1 Inspect the condition of the cones and replace with new or cleaned cones.

13.2.2 Install clean spray chamber, injector, and injector support.

13.2.3 Clean autosampler probe. Check for clogging in fitting at top of probe.

13.2.4 Check nebulizer spray. Replace or clean nebulizer as needed.

13.2.5 Replace peristaltic pump sample tubing.

13.2.6 Record “done” for the nebulizer and final values for autolens.

13.2.7 The run daily performance section is not performed on a daily basis. It is performed as necessary. When performed document the values for DRC Mode neb gas, lens voltage, cell gas, DRC mode CPV, DRC mode CRO, and DRC mode QRO.

Note: Necessary is defined as nothing works.

13.3 ICP/MS Monthly Maintenance (Record all maintenance)

13.3.1 Inspect Air Filters

13.3.1.1 Inspect and clean or replace the “QPS” filter (wire mesh) on the backside of the vacuum chamber, under the turbo pumps.

13.3.1.2 Inspect and clean or replace the “RF Generator” filter (wire mesh) on the left rear panel.

13.3.1.3 Inspect and clean or replace the “Torch Box” front and back filter (wire mesh) behind the start/stop buttons on the front panel.

13.3.1.4 Inspect and clean or replace the “Main Filters” on the rear panel covers.

13.3.2 Water Chiller

13.3.2.1 Check the water level.

13.3.2.2 Clean the air intake grill.

13.3.2.3 Clean the filter. Replace as necessary.

13.3.2.4 Check strainer after 6 months. Clean if necessary.

13.3.3 Rough Pumps

13.3.3.1 Inspect the roughing pump oil. Change if dark brown or every 3 months whichever comes first. (Recommend changing once a month).

13.3.3.2 Check the mist eliminator. Drain or replace as needed.

13.3.4 Dynamic Reaction Cell

13.3.4.1 Set the ammonia flow to 1.5 mL/minute and record the running vacuum pressure.

13.3.5 Tuning

13.3.5.1 Record the resolutions for; C, Mg, Ar_2, In, Ce, Pb, and U.

13.4 Instrument Startup

13.4.1 Go to instrument panel in the software and click on start plasma. The plasma should start after the blue status bar on the screen reaches the end. If the plasma does not start after three attempts, check for problems with introduction apparatus.

13.4.2 Start peristaltic pump at a rate of 22 rpm.

13.4.3 Allow the plasma to warm up for at least 30 minutes before performing a daily tune.

13.5 Daily Performance Check and Tune

13.5.1 Check running vacuum pressure. (record)

13.5.2 If the torch, cones or other internal hardware has been modified perform an X-Y calibration by aspirating the tuning solution (9.29) and optimizing for In.

13.5.3 See section 13.2 for instrument tuning requirements that must be performed before the daily tuning can proceed.

13.5.4 Perform a nebulizer optimization by aspirating the tuning solution (9.29). (record)

13.5.4.1 Open the workspace “AWAL nebulizer optimization.wrk”

13.5.4.2 In the parameter description list box, click nebulizer gas flow (NEB).

13.5.4.3 Click “Get analyte list”.

13.5.4.4 Ensure that In 114.904 appears in the analyte field.

13.5.4.5 In the optimization criteria group choose the “maximum intensity” option.

13.5.4.6 Click “get defaults”.

13.5.4.7 Click “optimize”

13.5.4.8 If the CeO/Ce ratio is too high in the daily tune, lower the nebulizer setting by 0.1 – 0.2 to lower this ratio.

13.5.5 Perform an auto-lens voltage optimization by aspirating the tuning solution. (record)

13.5.5.1 Open the workspace “AWAL auto lens.wrk”.

13.5.5.2 In the optimization window, click the “Auto Lens” tab and click “Clear Calibration”. Click “OK” to confirm.

13.5.5.3 Click “Get analyte list”.

13.5.5.4 Click “Get defaults”

13.5.5.5 In the “Auto Lens” tab, click “Calibrate”.

13.5.5.6 Save the optimization file.

13.5.6 Perform a daily performance check by aspirating the tuning solution (9.29). Record the Mg, In, and U sensitivity. Also, record the CeO/Ce and Ba++/Ba percentage. Finally, record the background intensities for masses 8.5 and 220.

13.5.7 Perform a DRC check by aspirating a 1µg/L standard containing Fe-56 (Table 22.7). An older (previous calibration curve standard used within the last 2 weeks) may be used for this procedure. Compare and record the Fe-56 sensitivity and the Ar-40+O-16 (56) sensitivity. (Do this only as necessary).

13.5.8 If the calibration has a linearity problem particularly in the higher concentration range a dual detector calibration should be performed. Aspirate the dual detector calibration solution (9.19) and perform a “cross calibrating the dual detector” optimization. Choose “open workspace” from the menu and select the dual calibration workspace.

13.5.9 Repeat the daily performance check (13.5.6) after any changes to the system and record this information. If the daily performance check does not meet the following minimum criteria additional optimization may be necessary. See section 13.2 for more intensive optimization.

13.6 Weekly and less often Instrument Tuning

13.6.1 The following items are not required on a daily basis but must be completed satisfactorily before the daily tuning can proceed.

13.6.1.1 Performing a Mass Calibration

13.6.1.1.1 Aspirate the tuning solution (Table 22.7).

13.6.1.1.2 Open the workspace “tuning.wrk”.

13.6.1.1.3 In the tuning window, click “tune mass spec” to perform an automatic tune.

13.6.1.1.4 Check the results of the elements against table 22.2.

13.6.1.1.5 If the results are acceptable, review the peak resolution values. The peak resolution must be 0.7 +/- 0.1 amu. If not manually change the

"Resolution DAC Value". To decrease the peak width, increase the DAC value by 30 units for an approximate change of 0.1 amu. Do the reverse to increase the peak width.

13.6.1.2 Performing a pulse stage voltage optimization

13.6.1.2.1 Aspirate de-ionized water.

13.6.1.2.2 Open workspace "optimizing the detector.wrk".

13.6.1.2.3 In the optimization window, click the "auto optimize" tab and click "pulse stage" voltage in the parameter description list box.

13.6.1.2.4 Ensure that "pulse 76" appears in the analyte field.

13.6.1.2.5 Click "get defaults".

13.6.1.2.6 In the optimization criteria group, click the "intensity change percent" option. Ensure that the value is "15".

13.6.1.2.7 Click "optimize".

13.6.1.3 Performing an analog stage voltage.

13.6.1.3.1 Aspirate de-ionized water.

13.6.1.3.2 Open the same software setup as in 13.6.1.2.2 (pulse stage).

13.6.1.3.3 In the parameter description list box, click "analog stage voltage".

13.6.1.3.4 Click "get analyte list"

13.6.1.3.5 Ensure that the "analog 80" appears in the analyte field.

13.6.1.3.6 Click auto, then full.

13.6.1.3.7 Make sure that the "Use N (max)" box is cleared and type 10000 for the target gain.

13.6.1.3.8 Click details button.

13.6.1.3.9 Click "get defaults".

13.6.1.3.10 Click "optimize".

13.6.1.4 Perform the pulse stage voltage optimization (see 13.6.1.2)

13.6.1.4.1 This must be performed after the analog stage.

13.6.1.5 Checking the dead time correction

13.6.1.5.1 The dead time correction should be set to approximately 50-60 ns at the time of instrument installation by the manufacturer.

13.6.1.5.2 If not consult the procedure on page 3-65 in the Perkin-Elmer software manual.

13.6.1.6 Performing a cross calibration of the dual detector

13.6.1.6.1 Aspirate the Dual detector solution (9.20).

13.6.1.6.2 Open the workspace “cross calibrating the dual detector.wrk”.

13.6.1.6.3 In the optimization window, click the “dual detector calibration” tab.

13.6.1.6.4 Click “clear calibration”.

13.6.1.6.5 Click “get analyte list”

13.6.1.6.6 Click “get defaults”

13.6.1.6.7 Click “calibrate”

13.6.1.6.8 Perform this calibration at least once each week.

13.6.1.6.9 The cell rod offset and cell path voltage should be set up properly at installation by the manufacturer. If optimization is required, see pages 3-68 and 3-69 in the Perkin-Elmer Elan Version 2.4 manual.

13.7 Instrument calibration

13.7.1 Load the calibration standards on the autosampler in the order: Standard Blank, Standard 0.02, Standard 0.1, Standard 1, Standard 10, Standard 20, and Standard 100.

13.7.2 Set up a new data set in the software and make sure the correct method and “DAC” files are selected.

13.7.3 Set up the autosampler sequence in the software and initiate the run.

13.7.4 Evaluate the calibration for each element. The minimum correlation coefficient is 0.995. However, for elements other than Na, Ca, K, and Mg the correlation coefficient should be at least 0.999. If not, the calibration should be reviewed for possible problems. Points may be dropped as long as there

are at least three points and the remaining points bracket the sample concentration.

13.8 Sample Analysis

13.8.1 Follow the calibration and sample analysis schedule in section 12.1.

13.8.2 Samples must contain </= 0.2% TDS. Solid samples are diluted 5x in addition to the standard 100x prep factor. Water samples are diluted 20x, or up to 100x for those with high TDS or other matrix interferences. Higher dilutions are generally done only to compensate for high analyte concentrations; however, if matrix interferences dictate a higher dilution, the PQLs must be checked beforehand to ensure the client's needs are still met.

13.8.3 Prepare Samples

13.8.3.1 **Autosampler tubes must be labeled** with a sample identification to prevent sample mix up.

13.8.3.2 Pipette 0.1mL Internal Standard spiking solution into each tube.

13.8.3.3 Pipette 0.1mL PDS spiking solution into the tube labeled PDS.

13.8.3.4 Carefully pipette 10mL sample into the properly designated tube. Make dilutions, if necessary.

13.8.3.5 The sample information, including dilution factor, is entered into the software as appropriate. The sample header must identify the dilution factor.

13.8.3.6 Using the mouse, highlight all the samples desired for analysis.

13.8.3.7 Click the "Analyze Batch" button.

13.8.3.8 All required quality control samples (ICSA, ICSAB, ICV, ICB, CCV, CCB, LLOQ, MB, & LCS) must pass the criteria outlined in Table 8. If these criteria are not met, analysis must be terminated and no sample results may be reported after the last passing QC.

13.9 Salt matrix analysis differences

13.9.1 Prior to calibration prime the instrument for ten minutes with the working salt matrix solution.

13.9.2 Change the instruments rinse water to the working salt matrix solution

13.9.3 Calibrate the instrument utilizing the salt matrix calibration standards.

13.9.4 Perform an additional 20x to 100x dilution on all samples prior to analysis.

13.9.4.1 The following elements can handle a 100x dilution

before PQL adjustment must occur: As, Ba, Cd, Cr, Pb, Mo, Se and Ag.

14.0 Calculations

14.1 The sample results are calculated by the software using a "linear through zero" calibration.

14.2 Results by default should be reported in mg/L for water samples and mg/kg for soil or solid samples.

14.3 Correction for ^{78}Se du to ^{60}Ni. This correction must be performed manually.

^{60}Ni * 0.07083 = X

^{78}Se DRC – X = Corrected ^{78}Se

All samples, the LCS and the MS/MSD must be corrected.

14.4 Wipe samples or paint chips based on an area instead of sample volume or weight are calculated as follows:

$$\frac{(C)\ (V)}{\text{Area}}$$

Where: C = sample concentration in mg/L
V = total sample volume (assumes entire sample is in solution)
Area = area wiped or area paint was removed. Report in mg/area.
The area is usually reported in cm^2 so the final result would be mg/cm^2.

14.5 If solid or soil samples are required to be reported in dry weight, use the following calculation to convert from wet weight to dry weight:

$$\frac{\text{Concentration in mg/kg}}{\text{Total solids (fractional)}}$$

Example: if the concentration of a sample is 10.0 mg/kg-wet weight and the total solid is 75.0% (0.750), the final result is 13.3 mg/kg-dry weight.

14.6 Matrix spike and Matrix spike duplicate recovery calculations:

$$\text{\% Recovery} = \frac{(SSR-SR) \times 100}{SA}$$

Where:
SSR = Spiked Sample Results
SR = Sample Result
SA = Spike Added

14.7 Relative percent difference calculations:

$$RPD = \frac{(S-D) \times 100}{(S+D)/2}$$

Where:
S = First sample value (original sample)
D = Second sample value (duplicate) Method Performance

14.8 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum. See Table 22.4 for current limits.

14.9 Some client projects may require specific project limits. Project limits are followed (unless AWAL limits are more stringent) when this condition exists.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The lab does not update its acceptance limits based on these calculations. Set limits dictated by the method are utilized.

15.2 Current limits are listed in table 22.4.

16.0 Pollution Prevention

16.1 The laboratory uses reduced volumes (appropriately proportioned) to reduce the production of excessive processed waste.

16.2 Reagents used in this procedure are very corrosive. Care must be used in handling to prevent spills that might attack surrounding equipment through rusting that could potentially contaminate samples.

16.3 All acid spills should be neutralized with baking soda, prior to picking up and disposal into the trash or through the laboratory sink.

16.4 Disposable test tubes are used in the instrument-sampling tray to prevent cross contamination through re-use.

17.0 Data assessment and acceptance criteria for quality control measures

17.1 The criteria have been placed in a table to ease confusion. Please refer to table 22.4.

18.0 Corrective action for out of control data

18.1 See Table 22.4. Failure to take corrective action while reporting data is a major violation of the method and may result in data rejection.

19.0 Contingencies for handling out of control data or unacceptable data

19.1 If it is necessary to report any data that does not entirely meet the criteria in Table 22.4, all deviations must be clearly noted on the final report along with the reason why compliance could not be met.

20.0 Waste management

20.1 Drinking water, wastewater and soil digestates must be neutralized with baking soda before disposal through the laboratory sink.

20.2 Digestates from TCLP analysis must be poured into the waste barrel labeled "TCLP acid waste" in sample archiving.

20.3 Expired stock standards must be poured in the waste barrel, labeled "metal waste" in sample archiving.

21.0 References

21.1 USEPA, SW-846 Method 6020A, Revision 1, "Inductively Coupled Plasma-Mass Spectrometry", February 2007.

21.2 USEPA, Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry", Revision 5.4, EMMC Version

21.3 USEPA, Contract Laboratory Program (CLP), "CLP Statement of Work (SOW) for Multi-Media, Multi-Concentration Inorganic Analysis (ILM05.2), September 2002.

21.4 Perkin-Elmer, Elan Version 2.4 Software Guide, 2001

21.5 USEPA, SW-846 Method 3015, Revision 0, "Microwave Assisted Acid Digestion of Aqueous Samples and Extracts", September 1994.

21.6 USEPA, SW-846 Method 3051, Revision 0, "Microwave Assisted Acid Digestion of Sediments Sludges, Soils and Oils", September 1994.

22.0 Tables

22.1 ICPMS minimum performance requirements

Element or Mass	1 µg/L Tuning Standard
Mg	>6000 cps, RSD <5%
In	>30000 cps, RSD <5%
U	>20000 cps, RSD <5%
Ba++/Ba	<3%
CeO/Ce	<3%
220	<2 cps

22.2 Mass calibration criteria

Analyte	Acceptable Measured Mass
C	11.950 – 12.050
Mg	23.935 – 24.035
$^{76}Ar_2$	75.880 – 76.980
In	114.854 – 114.954
Ce	139.855 – 139.955
Pb	207.988 – 232.088

22.3 Element masses

Analyte	ICP/MS Mode	Quantitation Mass	Additional Masses	Comments
Silver (Ag)	Standard	**107**	109	Carryover when > 100 PPB
Aluminum (Al)	Standard	**27**		Watch for contamination
Arsenic (As)	Standard		75	
Arsenic (As)	DRC-NH_3		75	
Arsenic (As)	DRC-O_2	**91 (AsO)**		Best arsenic result
Boron (B)	Standard	**11**	10	Watch for contamination
Barium (Ba)	Standard	**137**	135	Watch for contamination
Beryllium (Be)	Standard	**9**		
Calcium (Ca)	Standard	**44**		
Cadmium (Cd)	Standard	**114**	111	
Cobalt (Co)	Standard	**59**		
Chromium (Cr)	DRC-NH_3	**52**	53	
Copper (Cu)	Standard	**65**	63	
Iron (Fe)	DRC-NH_3	**56**	57	Watch for contamination
Potassium (K)	Standard	**39**		
Magnesium (Mg)	Standard	**24**		
Manganese (Mn)	Standard	**55**		
Molybdenum (Mo)	Standard		98	
Molybdenum (Mo)	DRC-NH_3	**98**	95	
Sodium (Na)	Standard	**23**		
Nickel (Ni)	Standard	**60**		
Lead (Pb)	Standard	**(208+207+206)**		
Antimony (Sb)	Standard	**121**	123	
Selenium (Se)	Standard		82	
Selenium (Se)	DRC-NH_3		78	
Selenium (Se)	DRC-O_2	**78**		Best selenium result
Tin (Sn)	Standard	**120**	118	Pump tube carryover
Strontium (Sr)	Standard	**88**		
Titanium (Ti)	Standard	**47**	48	
Thallium (Tl)	Standard	**203**	205	Watch for memory problems
Vanadium (V)	DRC-NH_3	**51**		
Zinc (Zn)	Standard	**66**	68	Watch for contamination
Zirconium (Zr)	Standard	**90**	91	

22.4 Daily assessment and acceptance criteria for quality control

Quality Control Item	Criteria	Corrective Action
Tuning RSD	5 replicate analysis <5% RSD	Fix problem, don't start
ICSA	+/-20% or +/- 3X PQL whichever is greater[3]	Advisory, review for gross problems
ICSAB	+/-20% or +/- 3X PQL whichever is greater[3]	Advisory, review for gross problems
ICV	+/- 10% of true value[1,2,3]	Stop analysis, check for error, and then recalibrate.
ICB	+/- Reporting limit (PQL)	Stop analysis & fix problem
CCV	+/- 10% of true value[1,2,3,10]	Stop analysis & fix problem
CCB	+/- Reporting limit (PQL)	Stop analysis & fix problem
MB	+/- Reporting limit (PQL)[6] or the sample must be >10X the concentration of the blank	Reanalyze. If still fails and CCBs acceptable re-digest the sample batch.
LCS	85-115% recovery[1,7] Laboratory must maintain the tightest limits between both method 200.8 & 6020.	Reanalyze. If still fails and CCVs acceptable re-digest the sample batch.
MS	75-125% recovery[2], Limits apply only if spike concentration is >30% of sample concentration.	Note on final report if spike concentration is >30% of sample concentration.
MSD	75-125% recovery[2], Limits apply only if spike concentration is >30% of sample concentration. 20% RPD (RPD can be a sample duplicate)	Note on final report if spike concentration is >30% of sample concentration.
Serial Dilution	+/- 10% of undiluted value[2,3]	Note on final report
Post Digestion Spike	80-120% recovery[2,9]	Dilute sample and rerun
Internal standard	70-120% of the calibration blank[1,2,4]	Dilute sample 5x and rerun
LLOQ	70-130% recovery[2]	Stop analysis, check for error, and then recalibrate.

[1] – USEPA Method 200.8
[2] – USEPA SW-846 Method 6020A
[3] – USEPA CLP SOW ILM05.2
[5] – Method 6020A notes +/- 3X IDL
[6] – Method 200.8 notes 2.2X MDL or 10% sample concentration whichever is greater.
[7] – Method 6020A and ILM05.2 limits are 80-120%.
[8] – Method ILM05.2 has tighter limits 75-125%
[9] – Method LIM05.2 only requires a post digestion spike if the MS fails. There is no requirement for method 200.8.
[10] – Method 200.8 could be interpreted as +/- 15%.

22.5 Elemental interference table

Element	Mass	Interferent			Element	Mass	Interferent		
		#1	#2	#3			#1	#2	#3
Be	9				Zn	68			
B	10				As	75	$Ar^{35}Cl^{+}$		
B	11				Se	78	$^{40}Ar^{38}Ar^{+}$	^{78}Kr	^{60}Ni
Na	23				Se	82	$^{81}BrH^{+}$		
Mg	24	C_2^{+}			Sr	88			
Al	27				Zr	90			
K	39	$^{38}ArH^{+}$			Zr	91			
Ca	44	CO_2^{+}			Mo	95	$^{79}BrO^{+}$		
Ti	47	PO^{+}			Mo	98	^{98}Ru	$^{81}BrOH^{+}$	
Ti	48	^{48}Ca	$^{32}SO^{+}$	POH^{+}	Ag	107	ZrO		
V	51	$^{35}ClO^{+}$	$^{34}SOH^{+}$		Ag	109	ZrO	MoO	
Cr	52	ArC^{+}	ArO^{+}	$^{35}ClOH^{+}$	Cd	111	ZrO	MoO	
Cr	53	$^{37}ClO^{+}$			Cd	114	^{114}Sn	MoO	
Mn	55	$ArNH^{+}$			Sn	118			
Fe	56	ArO^{+}			Sn	120	^{120}Te		
Fe	57	$ArOH^{+}$			Sb	121	$Ar^{81}Br^{+}$		
Co	59				Sb	123	^{123}Te		
Ni	60				Ba	135			
Ni	62	TiO			Ba	137			
Cu	63	PO_2^{+}	$ArNa^{+}$	TiO	Tl	203			
Cu	65	TiO			Tl	205			
Zn	66	TiO			Pb	206/207/208			

22.6 Working calibration standard preparation table

Standard ID (µg/L)	Starting Solution	Starting Conc.	Volume Taken	Final Volume	Final Conc. (µg/L)	Milliliters of HNO_3/HCl*
Standard Blank	Deionized water (9.5)	0 mg/L	100 ml	100 mL	0.00	2/1
Standard 100	Spex CL-CAL-2 (9.6) & Spex ZAWAUT-1-100 (Boron) (9.14)	100 mg/L 1000 mg/L	100 µl 20 µl	100 mL	100 B = 200	2/1
Standard 20	Standard 100 from above	100 µg/L B = 200 µg/L	20 mL	100 mL	20.0 B = 40.0	1.6/0.8
Standard 10 or CCV	Standard 100 from above	100 µg/L B = 200 µg/L	10 mL	100 mL	10.0 B = 20.0	1.8/0.9
Standard 1	Standard 100 from above	100 µg/L B = 200 µg/L	1000 µL	100 mL	1.00 B = 2.00	1.98/0.99
Standard 0.1	Standard 100 from above	100 µg/L B = 200 µg/L	100 µL	100 mL	0.10 B = 0.200	2/1
Standard 0.02	Standard 100 from above	100 µg/L B = 200 µg/L	20 µL	100 mL	0.020 B = 0.040	2/1

* Use ultrapure acids (sections 9.1 & 9.3) and dilute to the mark with deionized water (section 9.5).

22.7 Quality control sample preparation table

Standard ID (µg/L)	Starting Solution	Starting Conc.	Volume Taken	Final Volume	Final Conc.	Milliliters of HNO_3/HCl*
ICV	Inorganic Ventures QCP-QCS-3 (9.7), B, Sr, Sn, Ti Intermediates from below	10 (50 Se)mg/L 10 mg/L	500 µL 500 µL	500 mL	10 µg/L	10/5
I.S. Spiking Solution	Spex CLISS-1 (9.9) Spex CLRH1-1AY (9.10) Inorganic Ventures CGGA1-1 (9.11)	10 mg/L 10 mg/L 1000 mg/L	5 mL 5 mL 50 µL	50 mL**	1000 µg/L 1000 µg/L 1000 µg/L	10/0 No HCL
B, Sr, Sn Intermediate	Inorganic Ventures (B) CGB1-1 (9.15) Inorganic Ventures (Sr) CGSR1-1 (9.16) Inorganic Ventures (Sn) CGSN1-1 (9.17)	1000 mg/L 1000 mg/L 1000 mg/L	1000 µL 1000 µL 1000 µL	100 mL combine	10 mg/L	2/0 No HCL
Ti Intermediate	Inorganic Ventures (Ti) CGTI1-1 (9.18)	1000 mg/L	1000 µL	100 mL	10 mg/L	2/1
ICB or CCB	Deionized water (9.5)	NA		100 mL	0.0 µg/L	2/1
MS & LCS solution	Spex CL-CAL-2 (9.6) & Spex ZAWAUT-1-100 (Boron) (9.14)	100 mg/L 1000 mg/L	1000 µL 100 µL	100 mL	1 mg/L	2 No HCl
Working tuning solution	Spex CL-TUNE-1 (9.8)	10 mg/L	100 µL	1 L	1 µg/L	20
ICSA	Spex CL-INT-A2 (9.12)	Various	10 mL	100 mL	various	1.5/1
ICSAB	Spex CL-INT-A2 (9.12) Spex CL-INT-B3N (9.13) B, Sr, Sn, intermediate from above	Various 2 mg/L 10 mg/L	10 mL 1000 µL 200 µL	100 mL	A = various B = 20 µg/L	1.5/1
Sn LLOQ	Elements CS-AWA01 (9.34)	various	40 µL	1 L	various	20/10
Ti LLOQ	Sn LLOQ from above	various	50 mL	100 mL	various	1/0.5
Multi-Element LLOQ	Sn LLOQ from above	various	25 mL	100 mL	various	1.5/0.75

* Use ultrapure acids (sections 9.1 & 9.3) and dilute to the mark with deionized water (section 9.5).
** Final volume is not critical since concentration may be approximate as long as the same I.S. solution is used for the entire run.

23.0 Clarifications/Clarifications of the method

23.1 This method has been written to comply with all requirements of both methods 200.8 and 6020A. Where no criteria was available in either of these methods (e.g., ICSA & ICSAB), the Contact Laboratory Program (CLP) Statement of Work (SOW) ILM05.2 was employed.

_____ Date_____

Inorganic Dept. Supervisor

_____ Date_____

Laboratory Director

_____ Date_____

QA/QC Officer

Nitrate/Nitrite by 353.2 and Nitrite by 353.2 (EPA Revision 2.0 1993)

1.0 Applicable matrix

1.1 This method is applicable to the analysis of waters (ground, surface, drinking, and wastewaters) and extracted soil samples.

1.2 Soil samples are extracted with deionized (DI) water before analysis.

1.3 The applicable range is 0.01 to 2.0 mg/L

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratory PQL is 0.01ppm.

3.0 Scope and Application

3.1 This method measures nitrite alone or total nitrate plus nitrite within an aqueous sample. Nitrate may be determined by subtracting nitrite from the nitrate/nitrite result.

4.0 Summary of test method

4.1 A sample is placed through a cadmium-copper reduction column to reduce nitrate to nitrite. Method reagents added react with nitrite to form a colored azo dye that can be measured colorimetrically at wavelength of 520 nm.

4.2 Nitrite is determined independently by analyzing the sample without the cadmium-copper reduction column.

5.0 Definitions

5.1 LCS: Laboratory Control Sample

5.2 MB: Method Blank

5.3 MS: Matrix Spike

5.4 MSD: Matrix Spike Duplicate

5.5 NO_3: Nitrate

5.6 NO_2: Nitrite

6.0 Interference

6.1 Turbidity may interfere with the analysis. Filtration through a 0.45 μm porosity membrane will remove this interference.

6.2 Samples that have color may produce a positive bias; analysis and subtraction of a sample without color reagents may compensate for this interference.

6.3 Sample containing high concentrations of metals, specifically iron and copper may create a negative bias; EDTA in the buffer solution prevents this bias.

6.4 Residual chlorine in samples will create a negative bias; the addition of sodium thiosulfate to the samples will eliminate this bias.

6.5 Oil & Grease will coat the cadmium column. Samples suspected to contain oil & grease should be extracted with Hexane before analysis.

7.0 Safety

7.1 Samples should be considered hazardous. Avoid exposure, skin contact, inhalation, or ingestion.

7.2 Several chemicals used in this procedure (sodium hydroxide and phosphoric acid) are corrosives. They will get hot when mixed with water, and burn skin on contact. Handle chemicals while wearing a lab coat, safety glasses and proper gloves.

8.0 Equipment and supplies

8.1 Lachat, Quikchem FIA 8500 with reagent pump, autosampler and a wavelength cell of 520nm.

8.2 10 mL disposable pipettes

8.3 pipetters with tips, various sizes

8.4 8 mL poly propylene test tubes

8.5 50mL centrifuge tubes

8.6 Volumetric glassware various sizes.

9.0 Reagents and standards

9.1 DI Water

9.2 Ammonium Chloride Buffer: dissolve 212.5g ammonium chloride and 2.5g EDTA (disodium ethylenediamine tetraacetate) in 900mL of DI water. Adjust to a pH of 8.5 with 50% NaOH and dilute to 2.5L with DI water (or 2340g). Expiration 6 months.

9.3 Color Reagent: to 800mL of DI water add 250mL concentrated Phosphoric acid while stirring, 100g sulfanilamide, 5.0g N-1-naphthylethylenediamine dihydrochloride (NED), stir until dissolved and dilute to 2.5L with DI water (or 2190g). Store in a brown bottle, and away from light. Expiration 6 months.

9.4 50% NaOH: dissolve 150g of sodium hydroxide pellets into 250mL DI water while stirring. **Caution solution will get very hot**. Expiration 6 months.

9.5 Cadmium column for nitrate determination is purchased through Lachat instruments. Part no. 50237A.

9.6 NO_2 calibration standard, 1000ppm purchased prepared from Spex. The expiration date of this solution is dictated by the manufacturer.

9.7 NO_2 calibration standard, 100ppm: dilute 5mL of the 1000ppm NO_2 calibration standard and dilute to 50mL with DI water. Expiration 6 months.

9.8 NO_2 calibration standard, 2ppm: dilute 1mL of the 100ppm NO_2 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.9 NO_2 calibration standard, 0.5ppm: dilute 0.25mL of the 100ppm NO_2 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.10 NO_2 calibration standard, 0.1ppm: dilute 2.5mL of the 2ppm NO_2 calibration standard and dilute to 50mL. Expiration 2 days.

9.11 NO_2 calibration standard, 0.05ppm: dilute 5mL of the 0.5ppm NO_2 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.12 NO_2 calibration standard, 0.01ppm: dilute 1mL of the 0.5ppm NO_2 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.13 NO_2 LCS standard,1000ppm: dissolve 0.493g of sodium nitrate in DI water and dilute to 100mL with DI water. Add 0.2mL of chloroform as a preservative. Expiration 6 months.

9.14 NO_2 LCS standard, 100ppm: dilute 5mL of the 1000ppm NO_2 LCS standard to 50mL with DI water. Add 0.2mL of chloroform as a preservative. Expiration 6 months.

9.15 NO_2 LCS standard, 1ppm: dilute 0.5mL of the 100ppm LCS standard to 50mL with DI water. Expiration 2 days.

9.16 NO_3 calibration standard, 100ppm: purchased prepared from HACH. The expiration date of this solution is dictated by the manufacturer.

9.17 NO_3 calibration standard, 2ppm: dilute 1mL of the 100ppm NO_3 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.18 NO_3 calibration standard, 0.5ppm: dilute 0.25mL of the 100ppm NO_3 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.19 NO_3 calibration standard, 0.1ppm: dilute 2.5mL of the 2ppm NO_3 calibration standard and dilute to 50mL. Expiration 2 days.

9.20 NO_3 calibration standard, 0.05ppm: dilute 5mL of the 0.5ppm NO_3 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.21 NO_3 calibration standard, 0.01ppm: dilute 1mL of the 0.5ppm NO_3 calibration standard and dilute to 50mL with DI water. Expiration 2 days.

9.22 NO_3 LCS standard, 1000ppm: dissolve 0.722g of potassium nitrate in DI water and dilute to 100mL with DI water. Add 0.2mL of chloroform as a preservative. Expiration 6 months.

9.23 NO_3 LCS standard, 100ppm: dilute 5mL of the 1000ppm NO_3 LCS standard 50mL with DI water. Add 0.2mL of chloroform as a preservative. May be stored Expiration 6 months.

9.24 NO_3 LCS standard, 1ppm: dilute 0.5mL of the 100ppm NO_3 LCS standard 50mL with DI water. Expiration 2 days.

10.0 Sample collection

10.1 Nitrate, nitrite and nitrate/nitrite samples (liquid and soil) are chilled to > 0 - 6°C and analyzed within 48 hours.

10.2 200mL of sample is required to perform the analysis.

10.3 If only the combined nitrate/nitrite result is requested, the sample may be preserved to a pH<2 with sulfuric acid and held up to 28 days before analysis.

11.0 Quality control

11.1 An ICB and midrange ICV must be analyzed immediately following the calibration.

11.2 A MB and LCS must be analyzed per batch of 20 or fewer.

11.3 A MS/MSD must be analyzed every 10 samples. A batch of 20 samples must have two MS/MSDs prepared and analyzed.

11.4 A CCB and a mid range CCV must be analyzed every 10 samples and at the end of the run.

12.0 Calibration and standardization

12.1 The instrument has two calibrations for this method (NO_2 and NO_2/NO_3). Both are composed of 6 points: 0, 0.01ppm, 0.05ppm, 0.1ppm, 0.5ppm and a 2ppm standard.

12.2 The calibration coefficient for acceptance must be equal to or better than 0.995. Only linear or first order calibrations are allowed. Second or third calibrations, forcing through zero and point-to-point calibration are not allowed.

12.3 To start calibration push the open button on the top of the screen and select the method desired (NO2_NO3 TEMPLATE.omn for NO_2, NO_2/NO_3 and NO_3, NO2_ONLY.omn for NO_2 only or NO_2/NO_3 COMBO_ONLY.omn).

12.4 In the tray, list the calibration standards to be analyzed and the samples to be analyzed. They need to be analyzed in the following order: 2, 0.5, 0.1, 0.05, 0.01 and 0. Also include the CCV, CCV, ICV and ICB.

12.5 Enter the cup number for each standard and sample. The cup number is the position on the autosampler tray.

12.6 Sample type is an automatic function; do not change this column for field samples. For calibration standard samples change it to Calibration standard; for ICV, ICB, CCV and CCB it is labeled as check standard.

12.7 Reps, is always listed as one.

12.8 Enter the manual dilution as the manual dilution and the preparation factor as the weight.

13.0 Procedure

13.1 Water Matrices:

13.1.1 Pour sample aliquots into 8mL tubes and position them in the cup number assigned in section 12.

13.1.1.1 Acidified samples do not need to be pH adjusted, the ammonium chloride buffer solution is sufficient to perform this task. If it is not, a negative peak will precede the sample peak indicating a pH problem.

13.1.2 Second check the positions

13.1.3 Push the start button to start analysis. A file name will be automatically given when a run is finished.

13.2 Soil Matrices:

13.2.1 Weigh 10g of soil into a ½ pint container.

13.2.2 Add 100mL of DI water to the ½ pint.

13.2.3 Place the ½ pint container with sample and DI water on the shaker.

13.2.3.1 Secure the sample with the shaker clamps and rubber bands.

13.2.3.2 Set the shaker timer for five minutes.

13.2.4 Transfer extracted sample into two 50mL centrifuge tubes.

13.2.4.1 Place on the centrifuge until solids are settled to the bottom.

13.2.5 Pour extracted sample or an aliquot into 10mL tubes and position them in the cup number assigned in section 12.

13.2.6 Second check the positions

13.2.7 Push the start button to start analysis. A file name will be automatically given when a run is finished.

14.0 Calculations

14.1 Sample results are reported in mg/L directly by the Lachat software.

14.2 Manual dilutions must be hand calculated. The analyst must document the dilution made on the raw data and multiply the dilution factor by the result.

14.3 Soil results are reported as mg/kg- wet directly by the Lachat through the LIMS

14.3.1 Soil results must be multiplied by the extraction ratio. Enter the prep factor in the weight column. The Lachat software will perform the calculation.

14.3.2 The data must be flagged analysis performed on a 1:1 DI water extraction.

14.4 Samples requiring results on a dry weight basis must have a percent moisture analysis performed. Enter the percent moisture results into the LIMS and the LIMS performs the dry weight calculation.

14.5 Manual integrations are allowed only when necessary.

14.5.1 The manual integration must take in the full peak (tails and all).

14.5.2 The manual integration must be documented on the raw data.

14.5.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate; for example the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The lab does not update its limits based on these recoveries. The lab utilizes set limits defined by the regulatory method

15.2 Current limits are listed in section 17.0.

16.0 Pollution prevention

16.1 Pollution prevention relies upon minimizing standard and reagent surplus.

16.2 If spills occur they must be cleaned up and disposed of properly. Inorganic spill kits (such as baking soda) are available in the laboratory in case of acid spills.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The method blank, ICB and CCB result must be below the laboratory PQL.

17.2 The ICV and CCV must recover within 10% of its true value.

17.3 The LCS must recover within 10% of its true value.

17.4 The MS/MSD must recover within 10% on water matrices and 20% on soil matrices, and have a RPD within 10% for water matrices and 20% for soil matrices.

18.0 Corrective actions for out of control data.

18.1 If one of the blanks fails, pour a fresh aliquot and re-analyze.

18.2 If an ICV, CCV or LCS fails, pour a fresh aliquot and re-analyze. If re-analysis does not work, make a new standard if it is the ICV or CCV, recalibrate and re-analyze the batch. If the LCS fails a second time, the batch must be re-prepped.

18.3 If the MS or MSD fails and the instrument QC passes, the sample results must be flagged for matrix interference.

18.4 If the MS, MSD or RPD is extremely out (Zero spike recovery or double recovery), re-prep the samples and re-analyze.

19.0 Contingencies for handling out of control data or unacceptable data.

19.1 If reanalysis of samples cannot be performed within 48 hours (unpreserved samples) or 28 days (preserved samples) of collection, ask the supervisor to contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails due to matrix interference issues, flag the final report with the appropriate qualifiers.

20.0 Waste management

20.1 Unused portions of non-acidified samples may be disposed through the laboratory sink.

20.2 Acidified reagents and samples may be disposed through the laboratory sink after neutralization with baking soda.

21.0 References

21.1 Methods and Guidance for Analysis of Water, Method 353.2, Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry, Revision 2.0, August 1993.

21.2 Methods and Guidance for Analysis of Water, Method 353.3, Nitrate-Nitrite Colorimetric Manual Cadmium Reduction, Revision March 1983.

21.3 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Nitrogen Method, 4500-N, page 4-123.

21.4 Lachat Instruments QuikChem Method 10-107-04-1-C, 04/23/1999.

22.0 Tables, diagrams

22.1 Not Applicable

23.0 Clarification/Modifications of the method

23.1 Do not add Brij-35, Brij-35 is a Technicon specific reagent.

23.2 Adjust pH only if it is >2. (Negative peaks preceding sample peaks indicate a pH problem.) The Lachat reagents are designed to handle samples with a pH<2.

23.3 The Lachat needs no warm up period for this method.

_____ Date _____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date _____
QA/QC Officer

1.0 Applicable matrix

1.1 This procedure is designed for the analysis of waters prepared by method 3510C, soils method 3550C or 3545A, and oils by method 3580A

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratory PQLs are located in the LIMS

3.0 Scope and Application

Method 8082A is used to determine the concentrations of polychlorinated biphenyls as Aroclors in extracts from solid and liquid matrices using capillary columns with electron capture detectors (ECD). The compounds listed below are determined by either single or dual column analysis.

Compound	CAS Registry No.
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1268	11100-14-4

4.0 Summary of test method

4.1 Method 3510C is utilized for the extraction of water samples by measuring 1 L of sample, spiking with surrogates, and extracting with 50 ml of methylene chloride three times. The extract is concentrated to a final volume of 5ml in hexane and then acid cleaned.

4.2 Method 3545A is utilized for the extraction of soil samples by weighing 12 grams of sample, mixing with the appropriate amount of Hydromatrix, spiking with surrogates, and loading on the ASE and extracting with hexane-acetone (1:1). The extract is dried using sodium sulfate and concentrated to a final volume of 2ml in hexane and then acid cleaned.

4.3 Method 3580A is utilized for the extraction of oil samples by weighing 1gram of sample, spiking with appropriate surrogates matrix spikes, and diluting to a final volume of 10mL. This is then shaken for 2 minutes and then acid cleaned with 2 to 5 mL of sulfuric acid.

4.3.1 Use an uncontaminated mineral oil base matrix (PCB free transformer oil) for the MB, LCS, and LCS duplicates.

5.0 Definitions

5.1 TCMX: Tetrachloro-m-xylene

5.2 DCB: Decachlorobiphenyl

5.3 ICV: Initial Calibration Verification, separate source from the calibration standard.

5.4 CCV: Continuing Calibration Verification, same source as the calibration standards.

5.5 LCS: Laboratory Control Sample

5.6 MB: Method Blank

5.7 MS: Matrix Spike

5.8 MSD: Matrix Spike Duplicate

6.0 Interference

6.1 Method interferences may be caused by contaminants in the solvents, reagents, glassware, and processing hardware utilized by the laboratory. The analysis of a reagent blank will demonstrate these substances are free from interferences.

6.1.1 The use of high purity reagents and solvents is required. Pesticide grade solvents are used for the extraction and dilution of all samples and standards.

6.2 Glassware is cleaned as discussed in the organic prep SOP.

6.3 Phthalate esters are a major interference in the analysis of pesticides. To avoid this problem do not allow samples to contact plastic materials during preparation.

6.4 Sulfur (common in sediment samples) will create broad peaks, interfering with early eluting organochlorine pesticides.

7.0 Safety

7.1 Samples should be considered hazardous: avoid exposure, skin contact, inhalation or ingestion.

7.2 Many of the compounds analyzed by this method are carcinogenic. Hexane, methanol, and methylene chloride are toxic and should be considered dangerous. Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses.

7.3 Perform extractions, filtrations and evaporations under a fume hood.

8.0 Equipment and supplies

8.1 A HP 5890 Gas chromatograph with dual ECD's, injection ports, and towers is employed to analyze all samples and standards. Signal A is detector C and signal B is detector D and are labeled under GC interface #5. The oven program

is as follows: 110°C for .5 min. Rate A = 20°C/min. to 140°C. Rate B = 11°C/min to 300°C hold for 2.46 min.

8.2 The following table describes GC columns and parameters:

	Front (primary) Column (C)	Rear (secondary) Column (D)
Signal Range	0	1
Injection volume	3 µL	3 µL
Detector temperature	300	300
Injector temperature	200, 300 for oil	200, 300 for oil
Column name	DB-17	Varian factor 4
Manufacturer	J & W	Varian
Size	30m x .32mm x .25µm	30m x .32mm x .25µm

8.3 Volumetric flasks are used for the preparation of standards.

8.4 Only glass and Teflon containers are used for samples and standards.

8.5 Syringes are calibrated by the manufacturer and are used for all standards preparation.

8.6 Septa funnels

8.7 Zymark turbo vap with evaporation tubes

8.8 40 and 7 mL vials

9.0 Reagents and standards

9.1 Pesticide grade hexane.

9.2 Methylene Chloride

9.3 Sodium Sulfate

9.4 All standards are prepared in PTFE sealed containers and are stored at >0 to 6°C. Working standards are replaced every 6 months or sooner. All stock standards are stored as per vendor specifications.

9.5 Standards preparation

9.5.1 All standards are prepared using calibrated class “A” volumetric flasks and pipettes at room temperature. All standards are written in the Standards Logbook as well as entered electronically into the LIMS Analytical Standards Database.

9.5.2 Exercise extreme care when preparing and storing stock solutions.

9.5.3 When a neat standard is being used, a four-place analytical balance is required to prepare the primary standard gravimetrically.

9.5.4 See the Calculations section for preparing standards volumetrically.

9.6 Pesticide Surrogate Spiking Solution from Supelco containing, 200 µg/mL of TCMX and DCB.

9.7 Aroclor 1016, 1000ug/mL purchased from Supelco.

9.8 Aroclor 1260, 1000uig/mL purchased from Supelco.

9.9 1660 10ppm intermediate standard: dilute 0.1mL of 1000ug/mL Aroclor 1260, 1000 µg/mL Aroclor 1016 and 0.025 mL pesticide surrogate spiking solution to 10 mL with Hexane.

9.10 100ppm 1660 matrix spiking solution: dilute 0.2ml of 1000ug/ml Aroclor 1016 and 1260 to 2mL with acetone.

9.11 0.1ppm 1660: dilute 0.05mL of the 10ppm 1660 intermediate standard intermediate standard to 5 mL with hexane.

9.12 0.2ppm 1660: dilute 0.1mL of the 10ppm 1660 intermediate standard to 5 mL with hexane.

9.13 0.5ppm 1660: dilute 0.25mL of the 10ppm 1660 intermediate standard to 5 mL with hexane.

9.14 1ppm 1660: dilute 0.5mL of the 10ppm 1660 intermediate standard to 5 mL with hexane.

9.15 2ppm 1660: dilute 1mL of the 10ppm 1660 intermediate standard to 5 mL with hexane.

9.16 3ppm 1660: dilute 1.5mL of the 10ppm 1660 intermediate standard to 5 mL with hexane.

9.17 5ppm 1660: dilute 2.5mL of the 10ppm 1660 intermediate standard to 5 mL with hexane.

9.18 0.3ppm 1660: dilute 0.15mL of the 10ppm 1660 intermediate standard to 5mL hexane.

10.0 Sample collection

10.1 Liquid samples should be collected in a 1L amber Boston Round container.

10.2 Solid samples should be collected in an 8-oz. clear wide mouth container.

10.3 Both liquid and solid samples should be refrigerated (>0 to 6°C) from the time of collection to the time of extraction. Following extraction, the extracts must be refrigerated at the same temperature until analysis.

10.4 Extractions for liquid sample matrices must occur within 7 days of collection, and all solid sample matrices (soils and oils) must occur within 14 days of collection. Analysis of all extracts must occur within 40 days from extraction.

11.0 Quality control

11.1 All new analysts will demonstrate initial proficiency with the method by analyzing 4 LCS's for precision and accuracy (P&A) for each matrix. Method performance will be evaluated based on pre-established LCS control limits for surrogates and matrix spike compounds.

11.1.1 The LCS must contain 1016/1260 unless the samples are known to contain another Aroclor.

11.2 All field samples should be prepared and analyzed with a method blank, laboratory control sample, matrix spike and matrix spike duplicate. If there is insufficient sample to perform a MS/MSD, then an LCSD should be included in the analysis.

11.3 Surrogates are to be spiked into all field samples and quality control samples. The analytical batch contains no more than 20 field samples.

11.4 An initial calibration standard (ICV) is run right after each curve, but before any sample extracts (batch QC included) to prove integrity of the calibration curve being used. The recovery for each analyte should be ±20% of the curve calibration.

11.5 A calibration standard (CCV) is included after each group of 10 samples to check calibration and minimize the number of repeat injections. The recovery for each analyte should be ±20% of the curve calibration. When this falls outside 20% analysis should be stopped and all samples after the last passing CCV will be re-analyzed.

11.6 However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, since the verification standard has demonstrated that the analyte would have been detected if it were present.

11.6.1 Verify calibration each 12-hour shift or every 10 samples by injecting a calibration verification standard before analyzing any samples. This standard is a mixture of Aroclor 1016 and Aroclor 1260, unless the samples are known to contain another Aroclor, along with two surrogates, TCMX and DCB, at a mid-range calibration level.

11.7 Surrogate recoveries are evaluated versus the surrogate control limits developed by AWAL for every sample and all QC.

11.7 A low level 1660 standard is included with every batch to demonstrate confirmation column sensitivity. A clearly recognizable 1260 pattern must be observed on the rear column before any Aroclor hits in samples can be confirmed.

12.0 Calibration and standardization

12.1 Prepare Aroclor 1660 (or other Aroclor) calibration standards at 0.1, 0.2, 0.3. 0.5, 1.0, 2.0, 3.0 and 5.0 ppm using intermediate standard prepared at 10.0 ppm using Supelco standards containing the analytes of interest at 1000ppm. Add surrogate standards, TCMX and DCB from Ultra mix into the intermediate at the same final concentration. Prepare a PCB ICV using a second source standard containing the appropriate analytes. All standards are prepared in Hexane.

12.2 Curve acceptance criteria consists of an R-squared value of .995 or higher. A quadratic curve may be used to establish a calibration curve if a minimum of six standards is included in the curve.

12.3 Prepare single point pattern identification standards for the Aroclors not in the calibration standards: 1221, 1232, 1248, 1242, 1268, and 1254 at 1.0 ppm which corresponds to the laboratory reporting limit and mid-point of the linear range of the detector. These standards are to be analyzed before any samples but may be analyzed before or after the calibration standards.

12.3.1 If a pattern for one of these aroclors is identified in a sample a curve will be run to quantitate the actual amount.

13.0 Procedure

13.1 Daily routine startup

13.1.1 Check that there is adequate pressure in both the carrier gas cylinder (helium) and the make-up gas cylinder (nitrogen). Less than 200-psi warrants changing the tank, if tank pressure is acceptable proceed to 13.1.2.

13.1.1.1 Turn tanks valve off and remove regulator. Place cap on tank and move tank to empty tank storage area. Choose a new tank of the same gas and replace regulator. Open the valve and check for leaks.

13.1.1.2 Do not bump the delivery pressure adjustment screw, this will cause instrument flows to change. Mark the pressure gauge in order to return flows to normal if the screw is bumped.

13.1.2 Verify oven program and check ECD signals.

13.1.3 Check columns head pressure using the gauges on the GC control panel.

13.1.4 Check injection tower lights and Nelson interfaces box lights are on and green. Red lights indicate a problem or fault. No lights indicate there is no power to the peripheral.

13.2 Routine maintenance

13.2.1 All maintenance is to be written in the maintenance logbook. There is to be no maintenance done during an analytical clock. Basic maintenance is usually required after running PCB samples (especially oils).

13.2.2 Always cool ECD's before replacing the column or performing maintenance where the ECD would or could be subjected to the atmosphere.

13.2.3 Basic maintenance includes:

Cooling the injection ports and oven to <80°C.
Replacing injection port liner and o-ring ferrule.
Replacing septa (every 50-100 injections).
Replacing gold seal.
Cutting a minimum 6'' of column.
Returning oven to normal operating temperatures.
Checking for leaks
Check and clean autosampler syringe every 200 injections

13.2.4 Required maintenance

Performing ECD wipe test every 6 months on each ECD
Replacing gas traps and filters as indicated by manufacturer.

13.2.5 Drastic maintenance includes:

Replacing column (every 6 months is suggested)
Replacing ECD

13.3 Sample analysis

13.3.1 All samples are transported to the GC via the autosampler tray. Once the tower is started, the analysis will continue until the control arm is unable to pick up another vial or it is manually stopped. The data is only collected from these runs if a valid sequence is produced. See sec. 13.4.

13.3.2 The order of sample analysis is as follows:

PATTERN IDENTIFICATION STANDARDS
CALIBRATION STANDARDS
INITIAL CALIBRATION VERIFICATION STANDARD (ICV)
0.05 PPM 1660 RESPONSE STANDARD
METHOD BLANK (MB)
LABORATORY CONTROL SAMPLE (LCS)
FIELD SAMPLES
MATRIX SPIKE SAMPLE (MS)
MATRIX SPIKE DUPLICATE SAMPLES (MSD)
CONTINUING CALIBRATION VERIFICATION STD (every 10 samples)
FIELD SAMPLES
END-RUN CALIBRATION VERIFICATION STANDARD

13.3.3 Pipette approximately 0.5ml of each sample into labeled 2-ml GC vials and position vials in the above order on the sample tray. Type in sample names in the sequence order and print this sequence for future reference.

13.4 Software setup

13.4.1 Turbochrom Navigator 6.1.0.1:F04 is used to collect, store, and analyze chromatographic data. The software is controlled through the main Turbochrom Navigator screen where there are various icons for building an instrument sequence, setting up the instrument, building methods, processing data, viewing real time analysis and details of the current analysis, reprocessing data and batch reprocessing as well as comparing chromatograms.

13.4.2 The sequence is the software's blueprint telling the system what to do next, with what method, and what adjustments are necessary to arrive at the final result. The sequence should be set up prior to analysis; saving an existing sequence to the next consecutive lower number with a pest distinction using the "save-as" command can do this. Renumber the "Data" column to reflect the new sequence number for each column or channel. It is not necessary to fill out the names of the samples before

starting a run, but it is highly recommended, as it will have to be done before processing the samples. Click on actions in the menu options, then click on Set-up, to set-up a run. The set-up instrument window appears click “OK” to start. The software is now ready for data acquisition. Check rinse vials in GC tower, fill with toluene if they are below the half volume line, then press the start button on the GC tower to initiate the automated analysis.

NOTE: The autosampler will always start with position 1. If the system is halted the vials that did not run need to be moved up or the first samples will be run over again when the autosampler is restarted.

13.5 Running and processing samples

13.5.1 Run samples.

13.5.2 Process samples by going into graphic editor. Choose mid-range standard. Save new method as new name correlating to the sequence number. Make adjustments to retention time windows (RTW) save and exit. A minimum of 3 peaks must be chosen for each Aroclor and preferably 5 peaks. Choose peaks that are at least 25% of the height of the largest Aroclor peak and at least one that is unique to that Aroclor.

13.5.3 Return to the sequence; make sure all names and methods are correct. Change calibration and process methods to recently updated method by double clicking on cell with method and choosing new method. Batch process whole sequence from peak identification to quantitation to create result file with name association.

13.5.4 Go to Results, reprocess and scroll through each file, looking for proper peak integration.

13.5.5 Go to build method and choose “load method stored on disk”, then choose recently named method. Click on “components” in the menu options then go to “calibration” to load curve. De-click “identify peaks before calibrating” and click open files icon. Highlight all files in curve and click “open.” One by one highlight the selected file, highlight the calibration level associated with that file number, and then click on ADD. Repeat for each calibration level and click OK when finished. The curve is now updated. If an error message appears this is most likely due to a compound not being identified at one or more calibration levels. Go to OTHER in menu options and click on graphic editor to check if ICV passes the recently updated curve. Print file and return to method, OTHER, and FIT ANALYSIS to modify curve parameters for analytes outside ± 20% window. Once an acceptable curve has been identified for each, change component curve in method component list. If no combination of curve parameters results in passing criteria, perform instrument maintenance and re-analyze curve.

13.5.6 Batch reprocess from QUANTITATION to REPORT GENERATION to create a TXO file. Choose Acrobat PDF Writer as the batch printer to print a portable document format (PDF) file. Choose a folder and unique name for each file as they are produced. At this point print the sequence file to a PDF and include in the same folder for identification purposes.

13.5.7 When samples contain Aroclors, single column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern both on the primary and the rear (confirmation) column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a Response standard run at the lowest concentration level used on the curve, usually 0.05 ppm. Once this qualitative confirmation has been established, the analyst will document the comparable peaks in the sample and the Aroclor standard, the absence of other major Aroclor peaks, and information indicating Aroclors were anticipated in the sample.

13.5.8 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks and the calibration model established from the calibration curve. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

13.5.8.1 If an Aroclor has been identified, another way to quantify it would be to run a 5 point curve for the specific Aroclor and re-run the sample containing that Aroclor.

13.6 Adobe Acrobat 8.0

13.6.1 Processing of data files is done mainly in Adobe as PDF files. To create PDF sets see section 13.7.

13.6.2 Batch QC consists of MB, LCS, MS, and MSD. Highlight all surrogate and matrix spike recoveries.

13.6.3 Instrument QC consists of ICV, CCV's, and end-run CCV's. Check that instrument QC passes the method-specified recoveries.

13.6.4 Field samples must be evaluated for surrogate recoveries, and multi-component analytes. The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be make as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCB's in the sample. Sample chromatogram comparisons must be included in the PDF.

13.7 Creating PDF sets

13.7.1 Enter Adobe Acrobat 8.0.

13.7.2 Click on open file icon. Look in the C drive for file folder AA. This file contains a COVERSHEET to be used with every set. Typing CNTL+SHIFT+I will insert the desired page into the PDF folder. Typing CNTL+B will allow you to name the page you are currently on. In this way you can create an entire file and save it under ADATASETS with a unique name.

13.7.3 Page layout should be as follows:

COVERSHEET
PREP BATCH
MB
LCS
FIELD SAMPLES + MS/MSD
DAILY PACKAGE (WHEN APPLICABLE)
CURVE PACKAGE: Run sequence, all pattern ID's, calibration standards, ICV, CCV(s), end-run CCV's, curves

13.8 LIMS

13.8.1 All field samples and batch QC is transferred into the AWAL database or Laboratory Information Management System (LIMS).

13.8.2 Click on OMEGA icon and enter name and password. Click on DATA ENTRY BY RUN. Click on ADD. Enter instrument ID as GC, date and analyst. Click on DATA IMPORT. Find Turbochrom under specifications and enter test code and sample type, method blank (MBLK). Click OK. Open GC#5 and find desired file to import. Repeat for LCS, MS, MSD, and all field samples (SAMP). Enter in percent moisture for all soil samples. Check BATCH ID and Pfac values are correct according to the prep batch prepared by the Extractionist. Go to view data, and calculate sequence. Check all values are correct and delete any false positives. Check for flags and add qualifiers and comments to data as necessary.

13.8.3 Check that the MB is less than the PQL for all target compounds.

13.8.4 Check that the LCS, MS and MSD pass all current control limits.

13.8.5 Check the RPD is within current control limits on MSD.

13.8.6 One of two surrogates must pass in all samples. If not include a re-run or re-extract of data and a comment.

13.8.7 Check that the Analysis and prep date are correct.

13.8.8 Check that the data is entered for the correct method as requested by the client.

13.8.9 Check the dilution factor is correct.

13.8.10 Check that the PQL's are adjusted for DF and % moisture.

13.8.11 Check that the units are correct.

13.8.12 At this point the analyst must decide if the data is acceptable or if it requires a re-extraction. Therefore, all this must be completed before the hold time expires.

14.0 Calculations

14.1 When preparing dilution of stock standards use the equation:

$$C_1V_1 = C_2V_2$$

Where,

C_1= concentration of stock
V_1 = volume of stock
C_2 = concentration of working standard
V_2 = volume of working standard

Note: When preparing stock chemicals it is important to take into account the purity and the density of the solution. The purity of the compound will be listed on the C of A. The density will be located in the Handbook of Chemistry and Physics.

When weighing the dilution the density is no longer an issue, but purity is. If the C of A states purity is less than 100%, that percentage must be accounted.

Example calculation: 93% pure want 1g = 1/0.93 = 1.075g

14.2 The instrument calculates results directly in ppb based on criteria mentioned in the labs instrument calibration SOP.

14.3 The Extractionist is responsible for entering the correct extraction specifications into the PREP BATCH REPORT in the LIMS. A unique prep batch number is created for each analytical batch. The Extractionist includes the initial volume used, the spike amount, and the final volume, which the LIMS uses to calculate the extraction factor for each sample. When importing data, the LIMS automatically transfers this information and uses it to calculate the final result in ppb.

14.4 Calculate the raw spike target or MS targets to check if LIMS is correct:

Target = (amount spiked) (spike concentration) ÷ (initial volume or weight)

14.5 Manual integrations may **only** be performed when necessary.

14.5.1 The manual integration must take in the full peak (tails and all).

14.5.2 The manual integration when performed must be documented on the raw data.

14.5.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Current limits for all matrixes and both methods are located in the LIMs.

16.0 Pollution prevention

16.1 Samples, reagents and standards containing PCBs require special disposal. Place these items in the waste container labeled PCB waste in the sample archive room.

16.2 Methylene chloride, acetone, and hexane are all 8260C analytes and the following precautions should be taken to prevent cross contamination: 1) Only store all three in the organic extraction area or in a well ventilated area away from the Volatile Analysis room, 2) Only use all three in the organic extraction area in a well ventilated area away from the Volatile Analysis room, and 3) Do not enter the Volatile Analysis room if you have been in the extraction room or any other part of the lab that may be contaminated with these solvents.

16.3 All standards and samples are disposed of according section 20 of this SOP.

16.3.1 Solvents must not be thrown down the drain or evaporated in a hood to dispose.

17.0 Data assessment and acceptance criteria for quality control measures

17.1 The method blank result must be below the laboratory MDL,

17.1.1 Less than 5% of the regulatory limit,

17.1.2 or less than 5% of the sample results.

17.1.3 Blank subtraction is not allowed.

17.2 The ICV and CCV must recover within +/- 20% of its true value.

17.3 The LCS must recover within the laboratory control limits, listed in the LIMS.

17.3.1 The Laboratory generates in-house limits that define the acceptance of the LCS. These limits are updated several times per year, utilizing a minimum of 20 points and 3 standard deviations. The laboratory's LIMS performs this function.

17.4 The matrix spikes must recover within the laboratory control limits, listed in the LIMS.

17.4.1 The MS recovery limits are generated like the LCS in section 17.3.1.

17.5 The matrix spike and matrix spike duplicate RPD must be below the established laboratory limits listed in the LIMS.

17.5.1 The RPD recovery limits are generated like the LCS in section 17.3.1.

17.6 Surrogate recoveries must be within laboratory limits on both columns.

18.0 Corrective actions for out of control data

18.1 If one of the blanks (ICB, CCB, MB) fails, re-analyze. If the blank still fails perform one of the following corrective actions:

18.1.1 If the ICB or CCB fails, contamination is suspect. The contamination could be coming from the instrument (column, detector) or the vials.

Systematically eliminate the problem. If the problem is found to be, column or detector oriented recalibrate.

18.1.1.1 All instrument maintenance must be recorded in the instruments maintenance log with a calibration reference if applicable.

18.1.2 If the MB fails, contamination during preparation is assumed and the batch must be re-extracted.

18.2 If an ICV or a CCV fails, re-analyze a second time. If the standard still fails, make new standards, recalibrate the instrument and reanalyze the batch.

18.3 If the LCS fails, re-analyze a second time. If the standard still fails the entire batch must be re-prepped.

18.4 If the MS or MSD fails and the instrument QC look good the sample matrix is suspected and the final results must be flagged matrix interference.

19.0 Contingencies for handling out of control or unacceptable data

19.1 If re-analysis of samples cannot be performed within 7 days (14 days for soils/solids) of collection or 40 days after extraction, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails, due to matrix interference issues, flag the final report with the appropriate qualifier.

20.0 Waste management

20.1 All solvent waste generated during extraction must be collected in a safety can as temporary storage. When the safety can is full, it is then emptied into the 30 gallon, waste solvent container in the waste storage area.

20.1.1 Solvent waste must be free of water and non acidic before disposing in the waste container.

20.2 Samples that are pure (gas, paint thinners, oil, etc.) may be disposed in the solvent waste container.

20.3 Samples that are not pure but are heavily contaminated with a volatile or semi volatile should be left in their sample container and placed in the bin marked suspicious samples for disposal.

20.3.1 Samples that contain PCBs should be placed in the PCB contaminated 30 gallon waste barrel.

20.4 Standards and spiking solutions are disposed in their vials in the non PCB or PCB 30 gallon waste barrel in the waste storage area.

21.0 References

21.1 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 8082A, Revision 1, February 2007.

21.2 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

21.3 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

21.4 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3545A, Pressurized Fluid Extraction, Revision 1, February 2007.

21.5 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

21.6 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3580A, Waste Dilution, Revision 1, July 1992.

21.7 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3500B, Organic Extraction and sample Preparation, Revision 2, December 1996.

21.8 HP 5890 Series II and Series II Plus Reference Manual, Hewlett-Packard Company, 1994.

21.9 HP 5890 Series II and Series II Plus Operating Manual, Hewlett-Packard Company, 1994.

21.10 Turbochrom Workstation User's Guide, Perkin-Elmer Corporation, May 1998.

22.0 Tables, diagrams

22.1 Trouble shooting

Instrument	Problem	Action	Comment
GC and peripherals	CCV failure	Stop run, do basic main.	Run and check Daily.
	Breakdown fails	Stop, do basic main.	Check for leaks.
	Tower error	Press stop	Count blinks and check fault guide inside tower door.
	Controller error	Power off/ power on	Check tower and tray
	PE Nelson ADD error	Power off/power on	Check data, power off computer if data is stuck in Nelson interface.
	Tray stops run	Check tray belts	Check correct connection to controller
Chromatographic symptoms	Baseline drift	Check septum, change inlet liner.	Suspect leak
	Noise	Consider all recent changes to the system	Suspect carrier gas
	Retention time drift	Check carrier gas level	Check oven setpoints, inlet for leak

	No peaks	Check syringe, and system parameters.	Check columns exit flow.
	Extra or ghost peaks	Clean inlet and change septa	Possible carryover!? Inlet too hot.
	Peak tailing	Check for leaks or contamination with inlet	Do basic maintenance. Cold spot? Co-elution?
	Peak fronting	Dilute sample and rerun	Overloaded column or poor installation.
	Deformed peak or split apex of peak	Dilute and re-analyze	Column overload. Check sensitivity.
	System leak	Check all connections, tighten fittings, replace ferrules	Check flows and suspect contaminated carrier gas.
	Excessive column bleed	Check final temp.	Caused by oxygen, thermal or chemical damage
	Broad solvent front	Check injector temp. lower injection volume	Split ratio too low. Possible inlet leak
	Loss of resolution	Lower head pressure	Possible contamination, check carrier gas velocity
	Column breakage	Use connector	Replace column
	Mass discrimination/ poor resolution	Increase split flow, lower injection vol.	Increase inlet temperature
ECD Detector	High background	Isolate and evaluate	Dirty detector
	Low response	Increase background current	
	Negative peaks	Normal for ECD. Bake-out cell.	Dirty or old cell if negative peak follows large peak.
	Large drift or bleed	Lower ECD temp.	

23.0 Clarification/modifications of the method

23.1 Primary column is a DB-17. Secondary column is a DB-XLB.

23.2 Curve acceptance criteria is a R-squared value of .995 or higher. A quadratic curve may be used to establish the calibration curve if, a minimum of six standards are included in the curve.

23.3 Any sample exceeding the high standard concentration must be diluted and re-analyzed or the data must be flagged with an “E” qualifier.

23.4 Temperature program: Temp1=110 deg. C. T1=0.5 min. Rate 1=20 deg C./min. Rate 2= 11deg C./min. final time 2.46 min.

23.5 This procedure may use the same extracts as the 8081B method. An aliquot is split off without performing the sulfuric acid clean up. An Acid clean up will cause degradation of the pesticide analytes.

_____ Date_____
Organic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

Pesticides by 8081B (SW846 Revision 2, February 2007)

1.0 Applicable matrix

1.1 This method is capable of determining pesticide concentrations in water, waste, and solid matrices

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratory PQLs are:

Analyte	Water Matrix	Soil Matrix	CAS No.
Aldrin	0.1	1.0	309-00-2
α-BHC	0.1	1.0	319-84-6
β-BHC	0.1	1.0	319-85-7
γ-BHC	0.1	1.0	58-89-9
δ-BHC	0.1	1.0	319-86-8
Chlorobenzilate	Not Analyzed By Lab		510-15-6
α-Chlordane	0.1	1.0	5103-71-9
γ-Chlordane	0.1	1.0	5103-74-2
Chlordane	0.25	5.0	57-74-9
DBCP	Not Analyzed By Lab		96-12-8
4,4'-DDD	0.1	1.0	72-54-8
4,4'-DDE	0.1	1.0	72-55-9
4,4'-DDT	0.1	1.0	50-29-3
Diallate	Not Analyzed By Lab		2303-16-4
Dieldrin	0.1	1.0	60-57-1
Endosulfan I	0.1	1.0	959-98-8
Endosulfan II	0.1	1.0	33213-65-9
Endosulfan sulfate	0.1	1.0	1031-07-8
Endrin	0.1	1.0	72-20-8
Endrin aldehyde	0.1	1.0	7421-93-4
Endrin ketone	0.1	1.0	53494-70-5
Heptachlor	0.1	1.0	76-44-8
Heptachlor epoxide	0.1	1.0	1024-57-3
Hexachlorobenzene	Not Analyzed By Lab		118-74-1
Hexachlorocyclopentadiene	Not Analyzed By Lab		77-47-4
Isodrin	0.1	Not Analyzed	465-73-5
Methoxychlor	0.5	5.0	72-43-5
Toxaphene	0.25	10.0	8001-35-2

3.0 Scope and Application

3.1 Method 8081A is used to determine the concentration of the above organochlorine pesticides in an extracted sample. The analysis of Aroclors (PCBs) is not performed by this method refer to method 8082A for further details.

4.0 Summary of test method

4.1 A liter water sample is extracted using Method 3510C at a neutral pH (7). If a cleanup step is not necessary, 3 uL of extracted sample is injected into a GC with a capillary

column and an ECD. If a cleanup step is necessary, perform Method 3620B and then inject the sample into the GC.

4.2 Soil samples are extracted using Method 3545A. Following extraction, the extract is injected into a GC with a capillary column and an ECD.

5.0 Definitions

5.1 ECD: Electron Capture Detector

5.2 PTFE: Polytetrafluoroethylene

5.3 ICV: Initial Calibration Verification, separate source from the calibration standards.

5.4 CCV: Continuing Calibration Verification, same source as the calibration standards.

5.5 LCS: Laboratory Control Sample

5.6 MB: Method Blank

5.7 MS: Matrix Spike

5.8 MSD: Matrix Spike Duplicate

6.0 Interferences

6.1 Method interferences may be caused by contaminants in the solvents, reagents, glassware, and processing hardware utilized by the laboratory. The analysis of a reagent blank will demonstrate these substances are free from interferences.

6.1.1 The use of high purity reagents and solvents is required. Pesticide grade solvents are used for the extraction and dilution of all samples and standards.

6.2 Carry-over is always a concern when dealing with high concentration samples. The analytical instrument may not be able to completely clean itself following a highly concentrated sample. When this happens, reanalysis of samples following the highly concentrated sample should occur if they show similar hits.

6.3 Glassware is cleaned using a definitive 6 step process:

6.3.1 This process is described in the sample prep SOP's where glassware is cleaned.

6.4 Phthalate esters are a major interference in the analysis of pesticides. To avoid this problem do not allow samples to contact plastic materials during preparation and do not use latex gloves (only use nitrile).

6.5 Sulfur (common in sediment samples) will create broad peaks, interfering with later eluting organochlorine pesticides.

6.6 Heavy molecular weight substances, wax and lipids, may create an interference that can be removed by gel permeation.

6.7 Co-elution problems may appear on the following columns:

Single column:

DB 608 Trfluralin / Diallate isomers & PCNP / Dichlone / Isodrin

DB 1701 Captafol / Mirex & Methoxychlor / Endosulfan sulfate & α-cldn/endosulfan-1

Dual Column:

DB-5 Permethrin / Heptachlor epoxide; Endosulfan I / α-Chlordane; Perthane / Endrin; Endosulfan II / Chloropropylate / Chlorobenzilate; 4,4'-DDT / Endosulfan sulfate; Methoxychlor / Dicofol

DB-1701 Chlorothalonil / β-BHC; δ-BHC / DCPA / Permethrin; α-Chlorodane / trans-Nonachlor.

7.0 Safety

7.1 Samples should be considered hazardous: avoid exposure, skin contact, inhalation or ingestion.

7.2 Many of the compounds analyzed by this method are carcinogenic. Hexane, methanol, Hydromix, and methylene chloride are toxic and should be considered dangerous. Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat and safety glasses.

7.3 Perform extractions, filtrations and evaporations under a fume hood.

8.0 Equipment and supplies

8.1 An Agilent 6890N Gas chromatograph with dual ECD's, injection ports, and towers (7683B) is employed to analyze all samples and standards. Signal A is detector A and signal B is detector B and are labeled under GC interface #1. The oven program is as follows: 110°C for 3 min. Rate A = 20°C/min. to 245°C. Rate B = 13°C/min to 300°C hold for 1.02 min.

8.1.1 The laboratory performs single column analysis

8.2 The following table describes GC columns and parameters:

	Front (primary) Column (A)	Rear (secondary) Column (B)
Signal Range	0	1
Injection volume	3 uL	3 uL
Detector temperature	310	310
Injector temperature	210	210
Column name	DB-17 or CLPesticides	Factor 4 or CLPesticides II
Manufacturer	J & W Scientific / Restek	Varian / Restek
Size	30m x .32mm x .5um	30m x .32mm x .25um

8.3 Volumetric flasks are used for the preparation of standards.

8.4 Only glass and Teflon containers are used for samples and standards.

8.5 Syringes are calibrated by the manufacturer and are used for all standards preparation.

9.0 Reagents and standards

9.1 Hexane, pesticide grade.

9.2 P-5, make up gas.

9.3 Helium, carrier gas

9.4 Standard Preparation

9.4.1 All standards are prepared in PTFE sealed containers and are stored at 4°C. Working standards are replaced every 6 months or sooner. All stock standards are stored as per vendor specifications.

9.4.2 All standards are prepared using calibrated class "A" volumetric flasks and pipettes at room temperature. All standards are written in the Standards Logbook as well as entered electronically into the LIMS system standards Database.

9.4.3 Exercise extreme care when preparing and storing stock solutions.

9.4.4 When a neat standard is being used, a four-place analytical balance is required to prepare the primary standard gravimetrically.

9.4.5 See the Calculations section for preparing standards volumetrically.

9.5 Standard Solutions

9.5.1 Matrix specific method detection limits (MDL) solutions

9.5.1.1 Waters: prepare a 0.5µg/ml spiking solution containing all target analytes. Spike 100 uL of this solution into each of 7 samples for a target of .05 µg/L per analyte, with the exception of Aldrin and Dieldrin where a .005µg/L target is required, a 10 µl spike is necessary.

9.5.1.1.1 Generally, the MDL's require two extractions, one set of eight for the .05 targets and eight more for the lower targets.

9.5.1.2 Soils, prepare a 0.1 µg/ml spiking solution containing all target analytes, spike 100 µl of this solution onto each of eight 12g samples for ASE extraction. The target will be .83 µg/kg per analyte.

9.5.2 Spiking, LCS and surrogate solutions are purchased prepared from Ultra scientific and Supelco.

9.5.2.1 Surrogate Spiking Solution: Supelco's Surrogate Spike Mix (200 ug/mL) contains Decachlorobiphenyl (dcb) and Tetrachloro-m-xylene (tcmx).

9.5.2.1.1 Dilute 0.75 mL of the Supelco mix to 30 mL with acetone. The final concentration is 5 ug/mL.

Or if you're feeling different and don't need 30 mL try the dilutions below:

Dilute 0.25 mL to 10mL or 0.125 mL to 5 mL

9.5.2.2 LCS, MS/MSD Spiking Solution: Supelco's 8081 Spiking Mix at 200ug/mL contains 23 analytes including tcmx and dcb.

9.5.2.2.1 Dilute-100 uL of the Supelco mix to 8 mL with acetone. The final concentration in the diluted mix is 2.5ug/mL.

9.5.3 100 ug/L toxaphene (stock) purchased prepared from Supelco.

9.5.4 200 ug/mL toxaphene (ICV) purchased from Protocol.

9.5.5 Toxaphene ICV at 10ppm; dilute 0.25 mL of the Protocol stock solution (200 ug/mL) to 5 mL with hexane.

9.5.6 Toxaphene ICV at 0.2 ppm: dilute 0.1 mL of the ICV 10 ppm to 5 mL with hexane.

9.5.7 Toxaphene intermediate standard at 10 ppm: dilute 0.5 mL of the 100 ug/L Supelco standard solution to 5 mL with hexane.

9.5.8 Toxaphene calibration standards:

9.5.8.1 1.0 ppm: dilute 0.5 mL of the intermediate to 5 mL with hexane.

9.5.8.2 0.5 ppm: dilute 0.25 mL of the intermediate to 5 mL with hexane

9.5.8.3 0.2 ppm: dilute 0.1 mL of the intermediate to 5 mL with hexane.

9.5.8.4 0.1 ppm: dilute 0.05 mL of the intermediate to 5 mL with hexane.

9.5.8.5 0.05 ppm: dilute 0.025 mL of the intermediate to 5 mL with hexane.

9.5.8.6 0.02 ppm: dilute 0.01 mL of the intermediate to 5 mL with hexane.

9.6 Pesticide intermediate ICV standard at 10 ppm: dilute 0.02 mL of Ultra's Method 8081A Organochlorine Pesticides; 0.1 mL of Ultra's Pesticide Surrogate Standard Spiking Solution; and 0.2 mL of Ultra's Isodrin Solution to 2 mL with hexane.

9.7 Pesticide ICV standard at 0.05 ppm: dilute 0.025 mL of the pesticide intermediate ICV standard at 10 ppm to 5 mL with hexane.

9.8 Pesticide intermediate Calibration standard at 1 ppm: dilute 0.025 mL of Supelco's Pesticide 8081 Standard Mix and 0.001 mL of Supelco's Isodrin Solution to 5 mL with hexane.

9.8.3 Supelco's pesticide 8081 standard mix contains the following analytes:

4,4-DDD	Dieldrin	Endrin Ketone
4,4-DDE	Endosulfan I	Gamma-BHC
4,4-DDT	Endosulfan II	Gamma chlordane
Aldrin	Endosulfan sulfate	Heptachlor
Alpha-BHC	Endrin	Heptachlor epoxide
Delta-BHC	Endrin Aldehyde	Methoxychlor
Alpha chlordane	Beta-BHC	

9.9 Pesticide calibration standards:

9.9.3 0.001 ppm: dilute 0.0025 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.3.1 Or dilute 0.0005 mL to 5 mL.

9.9.4 0.002 ppm: dilute 0.005 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.4.1 Or dilute 0.001 mL to 5 mL

9.9.5 0.005 ppm: dilute 0.0125 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.5.1 Or dilute 0.025 mL to 5 mL

9.9.6 0.01 ppm: dilute 0.025 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.6.1 Or dilute 0.005 mL to 5 mL

9.9.7 0.02 ppm: dilute 0.05 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.7.1 Or dilute 0.01mL to 5 mL

9.9.8 0.05 ppm: dilute 0.25 mL of the 10 ppm pesticide intermediate calibration standard to 50 mL with hexane.

9.9.8.1 Or dilute 0.1mL to 20 mL

9.9.9 0.1 ppm: dilute 0.25 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.9.1 Or dilute 0.05 mL to 5 mL

9.9.10 0.2 ppm: dilute 0.5 mL of the 10 ppm pesticide intermediate calibration standard to 25 mL with hexane.

9.9.10.1 Or dilute 0.1mL to 5 mL

9.10 Methylene Chloride

9.11 Hexane

9.12 Sodium sulfate

9.13 Hydromix

10.0 Sample collection

10.1 Liquid samples should be collected in 1L amber Boston Round container.

10.2 Solid samples should be collected in an 8 oz. clear wide mouth container.

10.3 Both liquid and solid samples should be refrigerated (>0 - 6°C) from the time of collection to the time of extraction. Following extraction, the extracts must be refrigerated at the same temperature until analysis.

10.4 Extractions for water matrices must occur within 7 days of collection, and analysis must occur within 40 days from extraction.

10.5 Extractions for soil/solid matrices must occur within 14 days of collection, and analysis must occur within 40 days from extraction.

11.0 Quality control

11.1 All new analysts will demonstrate initial proficiency with the method by analyzing 4 LCS's for a precision and accuracy (P&A) evaluation prior to analyzing samples.

11.2 Each analyst and extraction personnel must demonstrate continued proficiency as a work group annually by performing 4 LCS's. These LCS's do not have to be performed in the same batch they may be performed in one, two, three or four individual batches.

11.3 Quality control for this procedure is broken into two types: batch and instrument.

11.3.1 The batch must contain the following per 20 samples or fewer: a method blank; a LCS and a MS/MSD.

11.3.1.1 If insufficient sample is provided for an MS/MSD, analyze a LCSD. The results would have to flagged insufficient sample for batch QC (MS/MSD)

11.3.2 All samples and batch QC are spiked during extraction with the surrogate solution. See organic prep SOP for further information regarding extraction.

11.3.3 The instrument must analyze the following QC at the stated interval:

11.3.3.1 At the beginning of every 12-hour shift and before analyzing any samples a breakdown of DDT and Endrin is measured. Analyzing a standard prepared at 0.05 ug/ml of DDT and Endrin

does this. If the breakdown for either exceeds 15%, corrective action is taken by stopping analysis and cleaning the injection port. See calculations for Breakdown calculation.

11.3.3.2 A CCV is analyzed at the beginning of every 12-hour clock, after every 10 samples and at the end of an analytical run.

Note: Method 608 requires, a CCV every 10 samples this is the reason for the increased CCV frequency.

11.3.3.3 An ICV must be analyzed immediately following calibration.

12.0 Calibration and standardization

12.1 Prepare the pesticide calibration standards and the Toxaphene standards as described in section 9.0. While toxaphene contains a large number of compounds that will produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of this mixture. Although the resolved peaks are important for the identification of the mixture, the area of the unresolved complex mixture contributes a significant portion of the area of the total response. To measure total area, construct the baseline of toxaphene in the sample chromatogram between the retention times of the first and last eluting toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

12.2 The curve acceptance criteria consists of an R-squared value of .995 or higher. A quadratic curve may be used to establish a calibration curve, if a minimum of six standards are included in the curve.

12.2.1 The calibration may not be forced through the origin.

12.2.2 The calibration must be verified with an ICV.

13.0 Procedure

13.1 Daily routine startup

13.1.1 Check that there is adequate pressure in both the carrier gas cylinder (helium) and the make-up gas cylinder (P-5). Less than 200-psi warrants changing the tank, if tank pressure is acceptable proceed to 13.1.2.

13.1.1.1 Turn tank valve off and remove regulator. Place cap on tank and move tank to empty tank storage area. Choose a new tank of the same gas and replace regulator. Open the valve and check for leaks.

13.1.1.2 Do not bump the delivery pressure adjustment screw, this will cause instrument flows to change. Mark the pressure gauge in order to return flows to normal if the screw is bumped.

13.1.2 Verify oven program and check ECD signals.

13.1.3 Check column head pressure using the gauges on the GC control panel.

13.1.4 Check injection tower lights and Nelson interfaces box lights are on and green. Red lights indicate a problem or fault. No lights indicate there is no power to the peripheral.

13.2 Routine maintenance

13.2.1 All maintenance is to be written in the maintenance logbook. With each maintenance documentation, the analyst initials, date and reference to the next passing calibration or CCV must be documented. There is to be no maintenance done during an analytical clock, only before running a breakdown standard.

13.2.2 Always cool ECD's before replacing the column or performing maintenance were the ECD would or could be subjected to the atmosphere.

13.2.3 Basic maintenance includes:

Cooling the injection ports and oven to <80°C.
Replacing injection port liner and o-ring ferrule.
Replacing septa (every 50-100 injections).
Replacing or cleaning gold seal.
Cutting <6'' of column.
Returning oven to normal operating temperatures.
Checking for leaks
Check and clean autosampler syringe every 200 injections

13.2.4 Required maintenance

Performing ECD wipe test every 6 months on each ECD
Replacing gas traps and filters as indicated by manufacturer.

13.2.5 Drastic maintenance includes:

Replacing column (every 6 months is suggested)
Replacing ECD
Cutting 2 – 4 loops off the column first before replacing it.

13.3 Sample analysis

13.3.1 All samples are transported to the GC via the autosampler tray. Once the tower is started, the analysis will continue until the control arm is unable to pick up another vial or it is manually stopped. The data is only collected from these runs if a valid sequence is produced. See sec. 13.4.

13.3.2 The order of sample analysis is as follows:
Prime
BREAKDOWN
PATTERN IDENTIFICATION STANDARDS
CALIBRATION STANDARDS
INITIAL CALIBRATION VERIFICATION STANDARD (ICV)

METHOD BLANK (MB)
LABORATORY CONTROL SAMPLE (LCS)
FIELD SAMPLES
MATRIX SPIKE SAMPLE (MS)
MATRIX SPIKE DUPLICATE SAMPLES (MSD)
CONTINUING CALIBRATION VERIFICATION STD (every 10 samples)
FIELD SAMPLES
END-RUN CALIBRATION VERIFICATION STANDARD

13.3.3 Pipette approximately .5ml of each sample into labeled 2-ml GC vials and position vials in the above order on the sample tray. Type in sample names in the sequence order and print this sequence for future reference.

13.4 Software setup and processing

13.4.1 Turbochrom Navigator 6.1.0.1:F04 is used to collect, store, and analyze chromatographic data. The software is controlled through the main Turbochrom Navigator screen where there are various icons for building an instrument sequence, setting up the instrument, building methods, processing data, viewing real time analysis and details of the current analysis, reprocessing data and batch reprocessing as well as comparing chromatograms.

13.4.2 The sequence is the software's blueprint telling the system what to do next, with what method, and what adjustments are necessary to arrive at the final result. The sequence should be set up prior to analysis; saving an existing sequence to the next consecutive lower number with a pest distinction using the "save-as" command can do this. Renumber the "Data" column to reflect the new sequence number for each column or channel. It is not necessary to fill out the names of the samples before starting a run, but it is highly recommended, as it will have to be done before processing the samples. Click on actions in the menu options, and then click on Set-up, to set-up a run. The set-up instrument window appears click "OK" to start. The software is now ready for data acquisition. Check rinse vials in GC tower; fill with toluene if they are below the half volume line, then press the start button on the GC tower to initiate the automated analysis.

NOTE: The autosampler will always start with position 1. If the system is halted the vials that did not run need to be moved up or the first samples will be run over again when the autosampler is restarted.

13.4.3 Run samples.

13.4.4 Process samples by going into graphic editor. Choose mid-range standard. Save new method as new name correlating to the sequence number. Make adjustments to retention time windows (RTW) save and exit. Create the daily retention time windows using the daily standard for each column.

13.4.5 Return to the sequence and make sure all names and methods are correct. Only change calibration and process methods to recently updated method by double clicking on cell with method and choosing new method. Batch process whole sequence from peak identification to quantitation to create result file with name association.

13.4.6 Go to Results reprocess and scroll through each file, looking for proper peak integration.

13.4.7 Go to build method and choose “load method stored on disk”, then choose recently named method. Click on “components” in the menu options then go to “calibration” to load curve. De-click “identify peaks before calibrating” and click open files icon. Highlight all files in curve and click “open.” One by one highlight the selected file, highlight the calibration level associated with that file number, and then click on ADD. Repeat for each calibration level and click OK when finished. The curve is now updated. If an error message appears this is most likely due to a compound not being identified at one or more calibration levels. Go to OTHER in menu options and click on graphic editor to check if ICV passes the recently updated curve. Print file and return to method, OTHER, and FIT ANALYSIS to modify curve parameters for analytes outside ±15% window. Once an acceptable curve has been identified for each, change component curve in method component list. If no combination of curve parameters results in passing criteria, perform instrument maintenance and re-analyze curve.

13.4.8 Batch reprocess from QUANTITATION to REPORT GENERATION to create a TXO file. Choose Acrobat PDF Writer as the batch printer to print a portable document format (PDF) file. Choose a folder and unique name for each file as they are produced. At this point print the sequence file to a PDF and include in the same folder for identification purposes.

13.4.9 After .txo files have been created for all QC and sample data, import them into LIMS. Check quantities and flags in LIMS. If below MDL, report “<MDL” on the .pdf files. If below PQL and the client does not ask data to be reported be to MDL, report “<PQL” in the .pdf report and delete all raw values below PQL. If the client does ask data to be reported to MDL, treat all J flags in LIMS as hits. Check the retention times for all hits (and J flags if applicable). If they are not within the retention time window, report “oRTW” on the .pdf and erase the raw value from LIMS. If the hit is within the RTW, check the confirmation column data. There must be a hit for the same analyte that is within the conf column’s RTW. If the confirmation is not within the RTW, report “oRTW” on the .pdf conf page and report “U” for “unconfirmed” on the primary analysis page. If the conf data is within the RTW, check the raw value on the conf data to make sure it is within 5x of the primary raw value for that analyte. If it is not within 5x, report “>5x” or “<5x” depending on whether the conf is greater than or less than the primary, report “U” on the primary page, and erase the raw value from LIMS. If the conf raw value is within 5x of the primary raw value, highlight the conf raw value and report “C” for “confirmed” on the primary page and highlight the raw value as it *will* be reported in LIMS.

13.5 Adobe Acrobat

13.5.1 Processing of data files is done mainly in Adobe as PDF files. To create PDF sets see sec. 13.6.

13.5.2 Check all RTW’s for batch QC, Instrument QC and field samples by preparing a RTW from a midpoint standard and printing to PDF.

13.5.3 Batch QC consists of MB, LCS, MS, and MSD. Highlight all surrogate and matrix spike recoveries and their respective RT's.

13.5.4 Instrument QC consists of ICV, CCV's, end-run CCV's, and breakdown. Check that instrument QC passes the method-specified recoveries. Check RTW's.

13.5.5 Field samples must be evaluated for surrogate recoveries, target compounds, and multi-component analytes. Any compound identification above PQL and within RTW's must be verified by a confirmation analysis.

13.5.6 All outliers need a data qualifier and must be flagged.

13.6 Creating PDF sets

13.6.1 Enter Adobe Acrobat

13.6.2 Click on open file icon. Look in the C drive for file folder AA. This file contains a COVERSHEET. Typing CNTL+SHIFT+I will insert the desired page into the PDF folder. Typing CNTL+B will allow you to name the page you are currently on. In this way you can create an entire file and save it under ADATASETS with a unique name.

13.6.3 Page layout should be as follows:

COVERSHEET
PREP BATCH contains MB/LCS/Parent/MS/MSD
RETENTION TIME WINDOW
DAILY STANDARD
BREAKDOWN
MB
LCS
FIELD SAMPLES + MS/MSD
CONTINUING CALIBRATION STANDARDS (two every 10 samples)
END RUN CONTINUING CALIBRATION STANDARD
SEQUENCE contains retention time window sheet, and the daily stds, continuing std and end runs, and breakdown
CALIBRATION CURVE + PATTERN ID'S + curves for each analyte

13.6.4 When the primary data contains target analytes a confirmation sequence is required and should be included after primary sequence in this order.

SEQUENCE
RTW'S
DAILY STANDARD
BREAKDOWN
MB/LCS/FIELD SAMPLES THAT CONTAIN TARGET ANALYTES
CALIBRATION CURVE AND CURVES FOR EACH ANALYTE
END-RUN STANDARDS

13.7 LIMS

13.7.1 All field samples and batch QC is transferred into the AWAL database or Laboratory Information Management System (LIMS).

13.7.2 Click on the LIMs icon and enter name and password. Click on DATA ENTRY BY RUN. Click on ADD. Enter instrument ID as GC, date and analyst. Click on DATA IMPORT. Find Turbochrom under specifications and enter test code and sample type, method blank (MBLK). Click OK. Open GC#1 and find desired file to import. Repeat for LCS, MS, MSD, and all field samples (SAMP). Enter in percent moisture for all soil samples. Check BATCH ID and Pfac values are correct according to the prep batch prepared by the Extractionist. Go to view data, and calculate sequence. Check all values are correct and delete any false positives. Check for flags and add qualifiers and comments to data as necessary.

13.7.3 Check that the MB is less than the detection limit for all target compounds.

13.7.4 Check that the LCS, MS and MSD pass all current control limits.

13.7.5 Check the RPD is within current control limits on MSD. If the RPD is not within limits the LIMs will automatically flag with a “R”.

13.7.6 One of two surrogates must pass in all samples. If not include a re-run or re-extract of data and a comment.

13.7.7 Check that the Analysis and prep date are correct.

13.7.8 Check that the data is entered for the correct method as requested by the client.

13.7.9 Check the dilution factor is correct.

13.7.10 Check that the PQL’s are adjusted for DF and % moisture.

13.7.11 Check that the units are correct.

13.7.12 At this point, the analyst must decide if the data is acceptable or if it requires a re-extraction. Therefore, all this must be completed before the hold time expires.

14.0 Calculations

14.1 When preparing a dilution of the stock standards, use the following equation:

$$C_1V_1 = C_2V_2$$

Where,

C_1= concentration of stock
V_1 = volume of stock
C_2 = concentration of working standard
V_2 = volume of working standard

Note: When preparing stock chemicals it is important to take into account the purity and the density of the solution. The purity of the compound will be listed on the C of A. The density will be located in the Handbook of Chemistry and Physics.

When weighing the dilution the density is no longer an issue, but purity is. If the C of A states purity is less than 100%, that percentage must be accounted.

Example calculation: 93% pure want 1g 1/0.93 = 1.075g

14.2 Calculate percent breakdown using the peak area as follows:

% DDT = ((DDD + DDE) ÷ (DDT + DDE + DDD)) * 100

% Endrin = ((aldehyde + ketone) ÷ (Endrin + aldehyde + ketone)) * 100

14.3 The instrument calculates results directly in ppb based on sample information inputted into the system.

14.4 The Extractionist is responsible for entering the correct extraction specifications into the PREP BATCH REPORT in the LIMS. A unique prep batch number is created for each analytical batch. The Extractionist includes the initial volume used, the spike amount, and the final volume, which the LIMS uses to calculate the extraction factor for each sample. When importing data, the LIMS automatically transfers this information and uses it to calculate the final result in ppb.

Note: TCLP samples are setup at 200mL, for consistency the MB and LCS are documented based on 200mLs. This helps assure PQLs are calculated correctly for the samples.

14.5 Calculate the raw spike target or MS targets to check if LIMS is correct:

Target = (amount spiked)(spike concentration) ÷ (initial volume or weight)

14.6 The % moisture is performed and calculated by the inorganic section.

14.7 Absolute RTW's are calculated based on three injections of a mid-point standard over a 72-hour period. The RT values are entered into an Excel spreadsheet, which calculates the standard deviation for each analytes retention time. A ±3 standard deviation window is obtained and the daily RTW is updated using the daily standard. The absolute RTW's are updated annually.

14.8 Manual integrations may **only** be performed when necessary.

14.8.1 The manual integration must take in the full peak (tails and all).

14.8.2 The manual integration when performed must be documented on the raw data.

14.8.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Current limits for all matrices and both methods are located in the LIMs.

16.0 Pollution prevention

16.1 Samples, reagents and standards containing PCBs require special disposal. Place these items in the waste container labeled PCB waste in the sample archive room.

16.2 Methylene Chloride is an 8260C analyte and the following precautions should be taken to prevent cross contamination: Do not store $MeCl_2$ in an area close to the Volatile Analysis Laboratory. Do not enter the Volatile Analysis room if you have been in the extraction room or around any solvent or other volatile compound.

17.0 Data assessment and acceptance criteria for quality control measures

17.1 The method blank result must be below the laboratory MDL,

17.1.1 or less than 5% of the regulatory limit,

17.1.2 or less than 5% of the sample results.

17.1.3 Blank subtraction is not allowed.

17.2 The ICV and CCV must recover within 20% (+/-) of its true value for each analyte.

17.2.1 However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >20%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present.

17.3 The LCS must recover within the laboratory control limits, listed in the LIMs.

17.3.1 The Laboratory generates in-house limits that define the acceptance of the LCS. These limits are updated several times per year, utilizing a minimum of 20 points and 3 standard deviations. The laboratory's LIMs actually performs this function.

17.4 The matrix spikes must recover within the laboratory control limits, listed in the LIMS.

17.4.1 The MS recovery limits are generated like the LCS in section 17.3.1.

17.5 The matrix spike and matrix spike duplicate RPD must be below the established laboratory limits listed in the LIMs.

17.5.1 The RPD recovery limits are generated like the LCS in section 17.3.1.

17.6 Surrogate recoveries must be within 30-150% on both columns.

17.7 The Endrin/DDT breakdown must be ≤15% and evaluated using peak areas.

17.8 The CCV percent drift must be <15% from the calibration factors.

17.8.1 All analytes must fall within retention time windows.

18.0 Corrective actions for out of control data

18.1 If the MB fails contamination during preparation is assumed and the batch must be re-extracted.

18.2 If an ICV or a CCV fails, investigate, perform routine maintenance, re-analyze a second time. If the standard still fails, make new standards, recalibrate the instrument and reanalyze the batch.

18.3 If the LCS fails, re-analyze a second time. If the standard still fails the entire batch must be re-prepped.

18.4 If the MS or MSD fails and the instrument QC is within range, the sample matrix is suspected and the final results must be flagged matrix interference.

18.5 If the MS and MSD RPD is out and re-prepping is not an option the results must be flagged non-homogenous.

19.0 Contingencies for handling out of control or unacceptable data

19.1 If re-analysis of samples cannot be performed within 7 days of collection or 40 days after extraction, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails, due to matrix interference issues, flag the final report with the appropriate qualifier.

20.0 Contingencies for handling out of control or unacceptable data

20.1 If reanalysis of samples cannot be performed within 7 days of collection for waters and 14 days for soils/solids or 40 days after extraction, have your supervisor contact the client and request a new sample.

20.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

20.3 If a matrix spike fails, due to matrix interference, flag the final report with the appropriate qualifier.

21.0 Waste management

21.1 All solvent waste generated during extraction must be collected in a safety can as temporary storage. When the safety can is full, it is then emptied into the 30 gallon, waste solvent container in the waste storage area.

21.1.1 Solvent waste must be free of water and non acidic before disposing in the waste container.

21.2 Samples that are pure (gas, paint thinners, oil, etc.) may be disposed in the solvent waste container.

21.3 Samples that are not pure but are heavily contaminated with a volatile or semi volatile should be left in their sample container and placed in the bin marked suspicious samples for disposal.

20.3.1 Samples containing PCBs should be placed in the PCB contaminated 30 gallon waste barrel.

21.4 Standards and spiking solutions are disposed in their vials in the non-PCB or PCB 30 gallon waste barrel in the waste storage area.

22.0 References

22.1 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 8081B, Organchlorine Pesticides by Gas Chromatography, Revision 2, February 2007.

22.2 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

22.3 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

22.4 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3545A, Pressurized Fluid Extraction, Revision 1, February 2007.

22.5 Test method for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3500B, Organic Extraction and Sample Preparation, Revision 2, December 1996.

23.0 Tables and diagrams

23.1 Troubleshooting:

Instrument	**Problem**	**Action**	**Comment**
GC and peripherals	CCV failure	Stop run, do basic main.	Run and check Daily.
	Breakdown fails	Stop, do basic main.	Check for leaks.
	Tower error	Press stop	Count blinks and check fault guide inside tower door.
	Controller error	Power off/ power on	Check tower and tray
	PE Nelson ADD error	Power off/power on	Check data, power off computer if data is stuck in Nelson interface.
	Tray stops run	Check tray belts	Check correct connection to controller
Chromatographic symptoms	Baseline drift	Check septum, change inlet liner.	Suspect leak
	Noise	Consider all recent changes to the system	Suspect carrier gas
	Retention time drift	Check carrier gas level	Check oven set points, inlet for leak

	No peaks	Check syringe, and system parameters.	Check columns exit flow.
	Extra or ghost peaks	Clean inlet and change septa	Possible carryover!? Inlet too hot.
	Peak tailing	Check for leaks or contamination with inlet	Do basic maintenance. Cold spot? Co-elution?
	Peak fronting	Dilute sample and rerun	Overloaded column or poor installation.
	Deformed peak or split apex of peak	Dilute and re-analyze	Column overload. Check sensitivity.
	System leak	Check all connections, tighten fittings, replace ferrules	Check flows and suspect contaminated carrier gas.
	Excessive column bleed	Check final temp.	Caused by oxygen, thermal or chemical damage

Instrument	**Problem**	**Action**	**Comment**
	Broad solvent front	Check injector temp. lower injection volume	Split ratio too low. Possible inlet leak
	Loss of resolution	Lower head pressure	Possible contamination, check carrier gas velocity
	Column breakage	Use connector	Replace column
	Mass discrimination/ poor resolution	Increase split flow, lower injection vol.	Increase inlet temperature
ECD Detector	High background	Isolate and evaluate	Dirty detector
	Low response	Increase background current	
	Negative peaks	Normal for ECD. Bake-out cell.	Dirty or old cell if negative peak follows large peak.
	Large drift or bleed	Lower ECD temp.	

23.0 Clarification/Modifications of the method

23.1 Not Applicable

_____
Organic Dept. Supervisor

_____
Laboratory Director

_____
QA/QC Officer

Semivolatiles by 625 (40CFR July 1) and 8270D (Revision 4, February 2007)

1.0 Applicable matrix

1.1 This method is applicable to the analysis of waters prepared by method 3510C, soils/solids prepared by method 3545A and oils/waste materials by 3580A.

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratories PQLs are listed in the LIMS under tests. The LIMS currently has 19 separate active 8270D methods. There are 2 oil test codes, 1 soil test code and 3 water test codes. See the following tables that relates the test codes with their test groups:

Test Code	**8270-O**	**8270-O-TCLP**	**8270-S**
Test Group	8270-O-Custom	8270-O-TCLP	8270-S-Custom
Test Group	8270-O-D List	8270-O-TCLP-F&D List	8270-S-D List
Test Group	8270-O-F&D List		8270-S-F&D List
Test Group	8270-O-Frac		8270-S-Frac
Test Group	8270-O-TCL		8270-S-PNA
Test Group			8270-S-TCL

Test Code	**8270-W**	**8270-W-SPLP**	**8270-W-TCLP**
Test Group	8270-W-Custom	8270-W-SPLP	8270-W-TCLP
Test Group	8270-W-D List		8270-W-TCLP-F&D List
Test Group	8270-W-F&D List		
Test Group	8270-W-Frac		
Test Group	8270-W-PNA		
Test Group	8270-W-TCL		
Test Group	8270-W-X9		
Test Group	8270-W-X2 SIM		

2.3 For the 625 method there is one test code, 625-W with the following test groups: 625-W-Custom and 625-W-PP.

3.0 Scope and Application

3.1 The determination of semi volatile compounds in an extracted sample.

3.2 Analyte List

Analyte	**CAS No.**	**Analyte**	**CAS No.**
		Phenol-d6 (surr)	13127-88-3
1,2,4,5-Tetrachlorobenzene	95-94-3	Diallate	2303-16-4
1,2,4-Trichlorobenzene	120-82-1	Dibenz(a,h)anthracene	53-70-3
1,2-Dichlorobenzene	95-50-1	Benzoic Acid	65-85-0
1,3-Dichlorobenzene	541-73-1	n-Decane	124-18-5
1,4-Dichlorobenzene	106-46-7	Dibenzofuran	132-64-9
1,4-Naphthoquinone	130-15-4	Diethyl phthalate	84-66-2
1-Methylnaphthalene	90-12-0	Dimethoate	60-51-5

1-Naphthylamine	134-32-7	Dimethyl phthalate	131-11-3
2,3,4,6-Tetrachlorophenol	58-90-2	Dinoseb	88-85-7
2,4,5-Trichlorophenol	95-95-4	Diphenylamine	122-39-4
2,4,6-Trichlorophenol	88-06-2	Disulfoton	298-04-4
2,4-Dichlorophenol	120-83-2	Ethyl methanesulfonate	62-50-0
2,4-Dimethylphenol	105-67-9	Famphur	52-85-7
2,4-Dinitrophenol	51-28-5	Fluoranthene	206-44-0
2,4-Dinitrotoluene	121-14-2	Fluorene	86-73-7
2,6-Dichlorophenol	87-65-0	Hexachlorobenzene	118-74-1
2,6-Dinitrotoluene	606-20-2	Hexachlorobutadiene	87-68-3
2-Acetylaminofluorene	53-96-3	Hexachlorocyclopentadiene	77-47-4
2-Chloronaphthalene	91-58-7	Hexachloroethane	67-72-1
2-Chlorophenol	95-57-8	Hexachlorophene	70-30-4
2-Methylnaphthalene	91-57-6	Hexachloropropene	1888-71-7
2-Methylphenol	95-48-7	Indene	95-13-6
2-Naphthylamine	91-59-8	Indeno(1,2,3-cd)pyrene	193-39-5
2-Nitroaniline	88-74-4	Isodrin	465-73-6
2-Nitrophenol	88-75-5	Isophorone	78-59-1
2-Picoline	109-06-8	Isosafrole	120-58-1
3 & 4-Methylphenol	----------	Kepone	143-50-0
3-Nitroaniline	99-09-2	Methyl methanesulfonate	66-27-3
4,6-Dinitro-2-methylphenol	534-52-1	Methyl parathion	298-00-0
4-Aminobiphenyl	92-67-1	3-Methylchloanthrene	56-49-5
4-Bromophenyl phenyl ether	101-55-3	N-Nitroso-di-n-butylamine	925-16-3
4-Chloro-3-methylphenol	59-50-7	N-Nitrosodi-propylamine	621-64-7
4-Chloroaniline	106-47-8	N-Nitrosodiethylamine	55-18-5
4-Chlorophenyl phenyl ether	7005-72-3	N-Nitrosodimethylamine	62-75-9
4-Nitroaniline	100-01-6	N-Nitrosodiphenylamine	86-30-6
4-Nitrophenol	100-02-7	N-Nitrosomethylethylamine	10595-95-6
Nitroquinoline ,1-oxide	56-57-5	N-Nitrosomorpholine	59-89-2
5-Nitro-o-toluidine	99-55-8	N-Nitrosopiperidine	100-75-4
7,12-Dimethylbenz(a)anthracene	57-97-6	N-Nitrosopyrrolidine	930-55-2
a,a-Dimethylphenethylamine	122-09-8	Naphthalene	91-20-3
Acenaphthene	83-32-9	Nitrobenzene	98-95-3
Acenaphthylene	208-96-8	O,O,O-Triethylphosphorothioate	126-68-1
Acetophenone	98-86-2	o-Toluidine	95-53-4
Aniline	62-53-3	Dimethylaminoazobenzene	60-11-7
Anthracene	120-12-7	1,4-Phenylenediamine	106-50-3
Aramite	140-57-8	Parathion-ethyl	56-38-2
Azobenzene	103-33-3	Pentachlorobenzene	608-93-5
Benz(a)anthracene	56-55-3	Pentachloronitrobenzene	82-68-8
Benzidine	92-87-5	Pentachlorophenol	87-86-5
Benzo(a)pyrene	50-32-8	Phenacetin	62-44-2
Benzo(b)fluoranthene	205-99-2	Phenanthrene	85-01-8
Benzo(g,h,i)perylene	191-24-2	Phenol	108-95-2
Benzo(k)fluoranthene	207-08-9	Phorate	298-02-2
Benzyl alcohol	100-51-6	Pronamide	23950-58-5
Bis(2-chloroethoxy)methane	111-91-1	Pyrene	129-00-0
Bis(2-chloroethyl)ether	111-44-4	Pyridine	110-86-1
Bis(2-chloroisopropyl)ether	108-60-1	Safrole	94-59-7
Bis(2-ethylhexyl)phthalate	117-81-7	Sulfotepp	3689-24-5
Butyl benzyl phthalate	85-68-7	1,3,5-Trinitrobenzene	99-35-4

Carbazole	86-74-8	α-Terpineol	10482-56-1
Chlorobenzilate	510-15-6	2,4,6-Tribromophenol (Surr)	118-79-6
Chrysene	218-01-9	2-Fluorobiphenyl (surr)	321-60-8
Di-n-butyl phthalate	84-74-2	2-Fluorophenol (surr)	367-12-4
Di-n-octyl phthalate	117-84-0	4-Terphenyl-d14 (surr)	1718-51-0
n-Octadecane	593-45-3	Quinoline	91-22-5
Thionazine	297-97-2	Nitrobenzene-d5 (Surr)	4165-60-0
1,1'-Biphenyl	92-52-4	1-Chloronaphthalene	90-13-1
3,3´-Dichlorobenzidine	91-94-1	1,3-Dinitrobenzene	99-65-0
3,3´-Dimethylbenzidine	119-93-7	Methapyrilene	91-80-5

4.0 Summary of test method

4.1 Samples are extracted by one of the above prep methods and automatically injected into a capillary column subjected to an increasing heat program to separate numerous analytes that may be present in the extract. Once the analytes have been separated, they are transferred through a direct connection into the mass spectrometer. Where the analytes mass spectra are compared to the mass spectra of standards.

4.2 When TPH fractionation is performed, the same extraction and analytical procedures are followed with the exception of the target compound list and aliphatic hydrocarbon integration. The following table are the TPH soil fractionation constituents:

&Analyte	MDL	PQL
Acenaphthylene	0.5	100
Acenaphthene	0.5	100
Fluorene	0.5	100
Phenanthrene	0.5	100
Anthracene	0.5	100
Fluoranthene	0.5	100
Pyrene	0.5	100
Benz(a)anthracene	0.5	100
Chrysene	0.5	100
Benzo(b)fluoranthene	0.5	100
Benzo(k)fluoranthene	0.5	100
Benzo(a)pyrene	0.5	100
Indeno(1,2,3-cd)pyrene	0.5	100
Dibenz(a,h)anthracene	0.5	100
Benzo(g,h,i)perylene	0.5	100
C11 to C12 Aliphatics	0.5	170
C13 to C16 Aliphatics	0.5	170
C17 to C21 Aliphatics	0.5	170
C22 to C35 Aliphatics	0.5	170
Total C12 to C22 PAH**	0.5	100
C11 to C13 Alkyl Naphthalenes***	0.5	170

The same analytes are constituents for the 8270-W-Frac method but the MDL's and PQL's are 5 for all single component analytes and Total C12 to C22 PAH**, and 5 for the aliphatic hydrocarbons.

5.0 Definitions

5.1 System performance check compounds: SPCCs (N-nitroso-di-n-propylamine,

Hexachlorocyclopentadieine, 2,4-Dinitrophenol and 4-Nitrophenol)

5.2 Response factors: RFs

5.3 Decafluorotriphenylphosphine: DFTPP

6.0 Interference

6.1 Blanks, LCSs and spikes are extracted and analyzed with each extraction to check method performance and possible matrix effects of the samples. If quality control samples show signs of contamination re-extract and analyze if the samples show signs of matrix effects flag report.

6.2 The laboratory uses high purity reagents and solvents to minimize interference problems.

6.3 Carryover is always a concern when analyzing samples with high concentrations of semi compounds. To avoid carry over, rinse sample syringe with solvent between sample injections.

6.4 Contamination may also occur during extractions. The laboratory performs the following steps to prevent compounds from adhering to the glassware.

1. Immediately rinse the glassware with the last solvent used before placing in the wash station.
2. Wash with laboratory detergent (Alconox Liqui-Nox), hot water, and brushes.
3. Rinse with tap water (3 times minimum) and placed in the acid bath for a minimum of 2 minutes.
4. Rinse with DI water (3 times minimum).
5. Rinse twice with acetone then twice with methylene chloride
6. Store glassware inverted on aluminum foil
7. Prior to use rinse once with the extracting solvent.

6.5 The base-neutral extraction may produce reduced recovery of phenol, 2-methylphenol and 2,4-dimethylphenol.

6.6 The laboratory uses capillary columns to avoid known resolution problems with packed columns (Method 625 is written for packed columns).

6.7 Method 625 allows the use of chemical ionization mass spectrometry to support electron ionization mass spectrometry in samples exhibiting interferences.

6.8 Some sample analytes may become contaminated with its own matrix. AWAL has three general rules analysts should follow in regards to a questionable positive hit from a contaminated matrix.

1) RT & ion match: Primary, secondary & tertiary ions, when applicable, in addition to corresponding reporting-levels, are the main criteria. If the secondary or tertiary ion are just out of range (i.e. <1%) analyst judgment can be used. If the retention time (RT) is only slightly off (there is some shift in these runs. Try to keep it under 0.02 minutes), again analyst judgment should be used. If the RT is off by more than 0.04, proceed to next item.

2) Questionable hits (RT off and/or ion ratios off): Need supporting data as why called (subtractions / NIST comparisons. RT miss-matches caused by suspected matrix

effects need to be backed up with evidence such as relative IS & Spike analyte RT-shifts in MS/D samples, etc.). Highlight any RT shifts in the ISTD and check to see if it is comparable to the analyte hit in question. Include any subtractions that are of use in the final .pdf report.

3) **If a hit is still in question:** A second opinion should be supplied by another analyst or supervisor. Both the analyst & second opinion need to document why hit(s) were called. Sometimes this is simply a judgment call based on experience (i.e. the analyst experience should weigh heavily in the interpretation of the chromatographic evidence).

7.0 Safety

7.1 Some of the solvents and standards used in this method are considered carcinogenic. Avoid prolong exposure, use in a well-ventilated area, and ware proper attire when handling (safety glasses and gloves).

7.2 The solvents used in this procedure are also flammable, do not use near open flames, or hot surfaces (ovens / hotplates). Always store in a flammable cabinet and never have more then 10 gallons open and in use in the laboratory.

8.0 Equipment and supplies

8.1 Hewlett-Packard 5973D containing capillary column injection ports with septum purge.

8.1.1 Oven Program

Oven Ramp	°C/Min	Next °C	Hold Min	Run Time
Initial	N/A	40	1	1
Ramp 1	25	280	0.30	10.9
Ramp 2	8	330	0	17.15

Solvent Delay: from 3.4 back to 1.0 min. depending on length of column left in instrument.

Note: Oven program and solvent delay may vary depending on column length and condition, analyte list, etc. The oven program employed should ensure proper elution, resolution and separation of all analytes of interest.

8.1.2 Column

8.1.2.1 Zebron ZB-5MS; Length: 20m, ID: 0.18mm, Film: 0.32µm (with or without the 10m integrated guard column).

8.2 Hewlett Packard 5973 with quadrupole mass selective detector with turbo pumps.

8.3 Hewlett Packard 7683 injection tower/sampling arm

8.4 Software: Hp Chemstation, revision D.01.02

8.5 Syringes: 10 µL and 500 µL

8.6 Target ID vials with aluminum crimp tops

9.0 Reagents and standards

9.1 Helium

9.2 Semi volatile Internal Standard Mix purchased from Supleco, containing Acenaphthene-d10, Chrysene-d12, Naphthalene-d8, Perylene-d12, Phenanthrene-d10, and 1,4-Dichlorobenzene-d4 at a concentration of 2000 µg/mL.

9.3 8270 Surrogate Standard purchased from Supelco, containing Nitrobenzene-d5, p-Terphenyl-d14, Phenol-d6, 2-Fluorobiphenyl, 2-Fluorophenol and, 2,4,6-Tribromophenol at a concentration of 4000 µg/mL.

9.4 Semivolatile Surrogate Standard Spiking Solution from Ultra, containing Nitrobenzene-d5 (100 µg/mL); p-Terphenyl-d14 (100 µg/mL); Phenol-d6 (200 µg/mL); 2-Fluorobiphenyl (100 µg/mL); 2-Fluorophenol (200 µg/mL); 2,4,6-Tribromophenol (200 µg/mL).

9.5 EPA 8270 GC/MS Tuning Solution purchased from Supelco, containing Benzidine, DFTPP; Pentachlorophenol; 4,4-DDT.

9.6 8270 MegaMix purchased from Restek, containing semi-volatile analytes @ 1000 µg/L.

9.7 625 calibration kit from Supelco, containing all 625 analytes (except 1-Chloronaphthalene) in three mixes: 1)TCL Benzidine mix contains Benzidine and 3,3'-Dichlorobenzidine at 2,000 µg/mL, 2)N-nitroso-diphenylamine solution at 5,000 µg/mL, 3)625 Semi-volatile calibration mix containing all other analytes (except 1-Chloronaphthalene) at 1,000 µg/mL

9.7.1 625 semi-volatile calibration mix may need to be re-ordered separately, from Supelco.

9.8 1-Chloronaphthalene: from Ultra, neat, to make a 1-Chloronaphthalene 10,000 ppm mix for calibration.

9.9 1-Chloronaphthalene: from Supelco at a concentration of 2,000 µg/mL for the 625 spiking solution used for semi waters.

9.10 Methylene Chloride

9.11 Sodium Sulfate

9.12 Sulfuric Acid

9.13 Sodium Hydroxide

10.0 Sample collection

10.1 Collect samples in a 1 liter amber Boston Round container containing sodium thiosulfate ($Na_2S_2O_3$) (if samples contain chlorine) and refrigerate at a temperature between >0 to 6°C.

10.2 Extract water samples within 7 days of collection and soil & oil samples within 14 days of collection. Analyze all extracts within 40 days of extraction.

10.3 Store sample extracts in a freezer between –20 and -10°C, protected from light by storing in amber sealed vials equipped with unpierced PTFE-lined septa.

11.0 Quality control

11.1 Perform a tune with DFTPP in a full scan mode every 12 hours.

11.2 Perform a continuing calibration check every 12 hours.

11.3 Perform a method blank with every batch of 20 or fewer samples extracted.

11.4 Analyze a LCS with every batch of 20 or fewer samples extracted. The LCS is the laboratories second source standard. The acceptance criterion is listed in section 17.

11.4.1 The LCS for SIM Mode analysis is diluted (1:50) from the original extract to fall within the calibration range (2ppm).

11.5 Analyze a MS/MSD with every batch of 20 or fewer samples extracted

11.6 Inject 400µl for waters and soils of the following surrogates into samples and QC samples prior the extraction:

Base neutrals	Acids
Nitrobenzene-d5	Phenol-d6
2-Fluorobiphenyl	2-Fluorophenol
p-Terphenyl-d14	2,4,6-Tribromophenol

11.7 Inject 4µl of the following internal standards into 200µl of the extracted samples and extracted QC samples prior to analysis:

Acenaphthene-d10	Chrysene-d12
Naphthalene-d8	Perylene-d12
Phenanthrene-d10	1,4-Dichlorobenzene-d4

12.0 Calibration and standardization

12.1 The calibration is prepared with eleven standards: 200, 160, 130,100, 80, 60, 40, 20, 10, 5, and 2 µg/mL.

12.1.1 SIM Mode calibration is prepared with the following standards: 0.1, 0.2, 0.5, 1, 2, 3, and 5ppm.

12.2 The calibration must contain all target analytes.

12.3 The lowest calibration standard must be less than or equal to, the laboratory reporting limit.

12.4 The percent RSD must be ≤ 20% RSD or drift for all compounds except the CCC's (Method 8270D).

12.4.1 Method 625 requires all % RSD's be less than 35 %

12.4.2 If the RSD of all target analytes is ≤ 20% (or <35% for method 625), the calibration is considered linear and the average response factor is used for quantitation.

12.4.2.1 Average response assumes linearity through zero.

12.4.3 If the response for any target analyte is > 15% (or > 35% method 625), an alternative calibration model must be used to quantitate those analytes. The alternative mode could be regression or quadratic using percent drift (≤ 20% in the CCV) as the criteria. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.995) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

12.4.3.1 When linear regression is performed the correlation must be 0.995 or better, and the curve must not be forced through zero.

12.5 The CCC's RPD must also be ≤ 30% RSD for 8270D.

12.6 See section 21.0 of this SOP for 8270D and 625 method comparison tables.

13.0 Procedure

13.1 Sample preparation

13.1.1 Samples are prepared using one of the following AWAL SOP's:

Water preparation by 3510C and 625

Soil preparation by 3550C, with GPC cleanup step (3640A)

Oil/Waste Substances preparation by 3580A

13.2 Daily routine startup

13.2.1 Check that there is adequate pressure in all the gas cylinders (helium). Less than 200-psi warrants changing the tank, if tank pressure is acceptable proceed to 13.3.

13.2.1.1 Turn tanks valve off and remove regulator. Place cap on tank and move tank to empty tank storage area. Choose a new tank of the same gas and replace regulator. Open the valve and check for leaks.

13.2.1.2 Do not bump the delivery pressure adjustment screw, this will cause instrument flows to change. Mark the pressure gauge in order to return flows to normal if the screw is bumped.

13.2.2 Check columns head pressure using the gauges on the GC control panel.

13.3 Routine maintenance

13.3.1 All maintenance is to be written in the maintenance logbook. There is to be no maintenance done during an analytical clock.

13.3.2 Always cool the detector before replacing the column or performing maintenance where the MS would or could be subjected to the atmosphere.

13.3.3 Basic maintenance includes:

Cooling the injection ports and oven to <80°C.
Replacing injection port liner.
Cutting <6'' of column.
Returning oven to normal operating temperatures.
Checking for leaks

13.3.4 Required maintenance

Cleaning the MSD
Flushing and baking out transfer lines.

13.4 Software setup and processing

13.4.1 Chemstation is used to collect, store, and analyze GC/MS data. The software is controlled through the main Chemstation software screen where there are various icons for building an instrument sequence, setting up the instrument, building methods, processing data, viewing real time analysis and details of the current analysis, reprocessing data and batch reprocessing as well as comparing chromatograms.

13.4.2 The sequence is the software's blueprint telling the system what to do next, with what method, and what adjustments are necessary to arrive at the final result. The sequence contains the file names for acquisition of data, method for data acquisition, sample names/ID's, and any miscellaneous information that is relevant (i.e. matrix of sample, sample type, other comments). Once the appropriate information is entered into the sequence, the instrument is ready to run samples and acquire data.

13.4.3 Run samples.

13.4.3.1 Each analytical clock must be started with a tuning solution standard followed by a daily calibration check standard or a calibration curve. The criteria for evaluation of the tune (625 Table 9 & 8270D Table 3), daily standard, and curve (Section 7 625 & 8270D) are outlined in methods 625 and 8270D.

Injection log example:

DFTPP
Daily Standard
Method Blank
LCS
Samples (1 –20)
Matrix spike
Matrix Spike Duplicate

13.4.3.2 After the tune and calibration (curve or daily standard) have been evaluated and have met the necessary criteria, samples may

then be run for twelve hours following the time of acquisition of the tune. Run samples in the following order: MB, LCS, parent, MS/MSD and, other samples pertaining to preparation batch.

13.4.3.2.1 The injection amount is 1µL for all extracts, batch QC, and calibration standards.

13.4.3.3 Process samples by going into Environmental Data Analysis. Click on Quant then scroll to Qedit Quant Result.

13.4.3.3.1 In Qedit click on Spectrum then scroll down to Display reference spectra and click on it.

13.4.3.3.2 Go through the analytes, surrogates and internal standards, double-checking that the ion percents and the retention times match up. **Please review section 6.8.**

13.4.3.3.3 SVOA TPH Fractionation Procedure. SEMI fractionation is broken down into four fractions; C11-C12, C13-C16, C18-C21, and C22-C35 and uses ion 57 as the quantitating ion. The standard has C10, C12, C16, C21, and C35 in it. These hydrocarbons are used to set up the retention time windows for the entire range. For the C11-C12 fraction, the retention time window begins just after C10 and ends just after C12. For the C13-C16 fraction, the retention time window begins just after C12 and ends just after C16. For the C17-C21 fraction, the retention time window begins just after C16 and ends just after C21. For the C22-C35 fraction, the retention time window begins just after C21 and ends just after C35. When quantifying these fractions, everything with a 57 ion in it within the retention time window is integrated. The calibration uses C12, C16, C21, and C35 to calculate the individual fractions. Since the entire range is integrated, there is not an upper limit as there is with every other analyte. A sample is only diluted when one or more peaks within the retention time window have saturated the instrument and have flat topped.

13.4.3.3.4 After evaluating, click on Exit in the Quick Qedit box. Then click “Yes” to save changes.

13.4.3.3.5 Click on Quant then scroll to Generate Report. Generate Summary reports to file for transfer into the LIMS. Generate detailed reports to printer (Adobe PDF Writer) to generate .pdf files to put into the report format.

13.5 Adobe Acrobat

13.5.1 Processing of data files is done mainly in Adobe as PDF files. To create PDF sets see sec. 13.6.

13.5.2 Batch QC consists of MB, LCS, MS, and MSD. Highlight all surrogate and matrix spike recoveries.

13.5.3 Instrument QC consists of a tune and a continuing calibration standard. Check that instrument QC passes the method-specified recoveries.

13.5.4 Field samples must be evaluated for surrogate recoveries, and target compounds.

13.5.5 All outliers need a data qualifier and must be flagged.

13.6 Creating PDF sets

13.6.1 Enter Adobe Acrobat.

13.6.2 Click on open file icon. Look in the C drive for file folder AA. This file contains a COVERSHEET to be used with every set. Typing CRTL+SHIFT+I will insert the desired page into the PDF folder. Typing CRTL+B will allow you to name the page you are currently on. In this way you can create an entire file and save it under ADATASETS with a unique name.

13.6.3 Page layout should be as follows:

COVERSHEET
PREP BATCH
BATCH QC: MB, LCS, MS, and MSD
FIELD SAMPLE: RAW DATA
DAILY PACKAGE: TUNE, DAILY, REFC, QAQC, INJECTION LOG
CURVE PACKAGE: CALIBRATION STANDARDS, SRM, REFC, QAQC, INJECTION LOG

13.6.3.1 There may be multiple prep batches, batch QC's, etc. depending on if sample needed re-extracted, re-run, etc.

13.7 LIMS

13.7.1 All field samples and batch QC are transferred into the AWAL database or Laboratory Information Management System (LIMS).

13.7.2 Click on OMEGA icon and enter name and password. Click on DATA ENTRY BY RUN. Click on ADD. Enter instrument ID as 5973-B according to the correct instrument, date and analyst. Click on DATA IMPORT. Find 5973-B under specifications and enter test code. Click OK. Open and find desired file to import. Enter in percent moisture for all soil samples or check that one has imported with the soil sample. Check BATCH ID and Pfac values are correct if an extraction was performed. Go to view data, and calculate sequence. Check all values are correct. Check for flags and add qualifiers and comments to data as necessary.

13.7.3 Check that the MB is less than the detection limit for all target compounds.

13.7.4 Check that the LCS, MS and MSD pass all current control limits.

13.7.5 Check the RPD is within current control limits on MSD.

13.7.6 Check that the surrogates pass method control limits.

13.7.7 Check that the Analysis and prep date are correct.

13.7.8 Check that the data is entered for the correct method as requested by the client.

13.7.9 Check that the dilution factor is correct.

13.7.10 Check that the PQL's are adjusted for DF and % moisture.

13.7.11 Check that the units are correct.

13.7.12 At this point the analyst must decide if the data is acceptable or if it requires a re-run. Therefore, all this must be completed before the hold time expires.

14.0 Calculations

14.1 When preparing dilution of stock standards use the equation:

$C_1V_1 = C_2V_2$

Where,

C_1 = concentration of stock
V_1 = volume of stock
C_2 = concentration of working standard
V_2 = volume of working standard

Note: When preparing stock chemicals it is important to take into account the purity and the density of the solution. The purity of the compound will be listed on the C of A. The density will be located in the Handbook of Chemistry and Physics.

When weighing the dilution the density is no longer an issue, but purity is. If the C of A states that purity is less than 100%, that percentage must be accounted.

Example calculation: 93% pure want 1g = 1/0.93 = 1.075g

14.2 The instrument calculates results directly in ppb based on criteria mentioned in the labs instrument calibration SOP.

14.3 The Extractionist is responsible for entering the correct extraction specifications into the PREP BATCH REPORT in the LIMS. A unique prep batch number is created for each analytical batch. The Extractionist includes the initial volume used, the spike amount, and the final volume, which the LIMS uses to calculate the extraction factor for each sample. When importing data, the LIMS automatically transfers this information and uses it to calculate the final result in ppb.

14.4 Calculate the raw spike target or MS targets to check if LIMS is correct:

Target = (amount spiked)(spike concentration) / (initial volume or weight)

14.5 The % moisture is calculated by the inorganic section and entered into the LIMS.

14.6 Manual integrations may **only** be performed when necessary.

14.6.1 The manual integrations must take in the full peak (fronts, tails, and all).

14.6.2 The manual integrations when performed must be documented on the raw data.

14.6.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

14.7 Updating reference spectra:

14.7.1 When an analyte is added or removed from the method, The "SAV" file must be removed to avoid analyte misidentification. The steps for "SAV" removal are:

- From d:MSD/Methods/ <choose applicable method> / refspec.
- Delet the entire "refspec" folder
- Recalibrate standards and update ref specs

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Current limits for all matrixes and both methods are located in the LIMS.

16.0 Pollution prevention

16.1 All standards and samples are disposed of according section 20 of this SOP.

16.1.1 Solvents must not be thrown down the drain or evaporated in a hood to dispose.

16.2 Keep the GC door closed and utilize the hood when vials contain solvents.

16.3 Methylene Chloride and Hexane are 8260C analytes and the following precautions should be taken to prevent cross contamination: Do not store $MeCl_2$ in an area close to the VOA Lab or outside the organic extraction area. Do not enter Volatile Analysis room if you have entered extraction room. Do not enter volatile analysis area if you have been working with $MeCl_2$.

16.4 Acetone is also an 8260C analyte. Which, in the past, had wide spread use in the general chemistry section. Acetone is now banned from use except in the organic extraction lab. Standards that utilize Acetone as a dilutant may only be prepared in the organic extraction lab.

17.0 Data assessment and acceptance criteria for quality control measures

17.1 DFTPP acceptance criteria:

Ion	Abundance criteria

51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-80% of mass 198
365	> 1% of mass 198
441	Present but less than mass 442
442	> 50% of mass 198
443	15-24% of mass 442

17.2 The DDT breakdown should be <20%.

17.2.1 Peak tailing factors for benzidine and pentachlorophenol is < 2

17.3 Continuing calibration

17.3.1 Must have a concentration near the midpoint of the calibration curve.

17.3.2 Must contain all the target analytes.

17.3.3 8270D - The percent drift or RSD must be ≤20% for CCC's and a response of ≥ 0.05 for SPCC's

17.3.4 625 - The percent drift or RSD must be ≤20% for all reported analytes.

17.4 Method blank

17.4.1 The concentration of target analytes in the method blank must be less than or equal to the reporting limit.

17.5 LCS

17.5.1 Must be prepared from a different source than the calibration standards. This is the laboratory's second source standard.

17.5.2 The concentration should be between the low and midpoint standards.

17.5.3 The LCS must contain all the target analytes (for 625).

17.5.4 The Laboratory generates in-house limits that define the acceptance of the LCS. These limits are updated several times per year, utilizing a minimum of 20 points and 3 standard deviations. The laboratory's LIMS actually performs this function.

17.5.4.1 Therefore the current acceptance limits are not located in the SOP. But may be found in the LIMS where the data is evaluated for acceptance.

17.6 MS/MSD

17.6.1 Must be prepared form a different source that the calibration standards.

17.6.2 The concentration should be between the low and midpoint standards.

17.6.3 The spike must contain all the target analyte.

17.6.4 The laboratory generates in-house limits which are listed in the laboratory LIMs These limits are generated in the same manner as the LCS limits described in section 17.5.4.

17.7 Surrogates

17.7.1 Must analyze a minimum of three surrogates for both the base-neutrals and the basis.

17.7.2 The laboratory generates in-house limits, which are listed in the laboratory LIMs These limits are generated in the same manner as the LCS limits described in section 17.5.4.

17.8 Internal Standards

17.8.1 A minimum of 6 analytes at retention times across the GC run must be analyzed.

17.8.2 Area counts must be between 50-200% of the associated continuing calibration standard area counts.

17.8.3 Internal standard retention times must be within 30 seconds of the continuing calibration standard for waters and soils/solids.

17.8.3.1 An oil matrix may cause a great amount of shift in retention times of the internal standards, target analytes, and surrogates.

17.8.4 1,4 Dichlorobenzene-d4 ion utilized must be 152.

18.0 Corrective actions for out of control data

18.1 If the DFTPP fails perform instrument injection port maintenance and retune instrument.

18.1.1 Document injection port maintenance in the instruments maintenance log.

18.2 If one the blank (MB) fails, re-analyze. If the blank still fails perform one of the following corrective actions:

18.2.1 If the MB fails, contamination is suspect. The contamination could be coming from the instrument (column, detector) or the vials. Systematically eliminate the problem. If the problem is found to be, column or detector oriented recalibrate. If the failure is due to contamination during extraction, re-extract the sample batch.

18.2.2 All instrument maintenance must be recorded in the instruments maintenance log with a calibration reference if applicable.

18.3 If a continuing calibration fails, re-analyze a second time. If the standard still fails, make new standards, recalibrate the instrument and re-analyze the batch.

18.4 If the LCS fails, re-analyze a second time. If the standard still fails, the entire batch must be re-prepped.

18.5 If the MS or MSD fails and the instrument QC and LCS look good the sample matrix is suspected and the final results must be flagged matrix interference.

18.6 If the MS and MSD RPD's are out and re-prepping is not an option the results must be flagged non-homogenous.

18.7 If any surrogates fail in one fraction re-extract the sample.

18.7.1 If a surrogate is diluted below the lowest calibration standard, no corrective action is necessary.

18.8 If an internal standard falls outside the acceptance limits re-analyze the sample unless matrix effects are to blame.

18.8.1 Matrix effect in confirmed by re-analysis with similar resulting failures.

19.0 Contingencies for handling out of control or unacceptable data

19.1 If reanalysis of samples cannot be performed within 7 days of collection or 40 days after extraction, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails, due to matrix interference issues, flag the final report with the appropriate qualifier.

20.0 Waste management

20.1 All solvent waste generated during extraction must be collected in a safety can as temporary storage. When the safety can is full, it is then emptied into the 30 gallon, waste solvent container in waste storage area.

20.1.1 Solvent waste must be free of water and non acidic before disposing in the 30 gallon waste container.

20.2 Samples that are pure (gas, paint thinners, oil, etc.) may be disposed in the solvent waste container.

20.3 Samples that are not pure but are heavily contaminated with a volatile or semi volatile should be left in their sample container and placed in the bin marked suspicious samples for disposal.

20.4 Standards and spiking solutions are disposed in their vials in the non-PCB organic vial 16 gallon barrel in the waste storage area.

21 References

21.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 8270D, Semivolatiles, Revision 4, February 2007.

21.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3510C, Seperatory Funnel liquid-liquid Extraction, Revision 3, December 1996.

21.3 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

21.4 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3580A, Waste Dilution, Revision 1, July 1992.

21.5 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 3545A, Pressurized Fluid Extraction, Revision 1, February 2007.

21.6 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. Method 625, Base/Neutrals, 40 CFR, Appendix A, Part 136.

21.7 American West Analytical Laboratories, Laboratory Method Manual, Soil Preparation By 3550C, latest revision.

21.8 American West Analytical Laboratories, Laboratory Method Manual, Water Preparation By 3510C and 625.

22 Tables, diagrams

22.1 Method 625 and 8270D Differences

Method 625	Method 8270D
Calibration standards minimum of 3	Calibration standards minimum of 5
Calibration compounds RSD < 35%	Calibration compounds RSD < 20% CCCs RSD < 30%
Check standard every 20 samples	Check standard every 12 hours
Surrogates pick three from Table 8 of the regulatory method	The 6 listed in section 11.6 of this method
Internal standards select three that are of similar analytical behavior to analytes of interest	The 6 listed in section 11.7 of this method

22.2 Initial Calibration Criteria

8270D Calibration Criteria	625 Calibration Criteria
SPCC's must meet min response criteria as follows (8270D 7.3.4.2): N-nitroso-di-n-propylamine 0.05 Hexachlorocyclopentadieine 0.05 2,4-Dinitrophenol 0.05 4-Nitrophenol 0.05 SIM Mode must also meet these criteria for four SPCC's	All % RSD's must be less then 35% or a curve plot of response ratios may be used (625 7.2.2). Note: method 625 does not give specific criteria for coefficient of determination, but as default we will use method 8000B criteria (7.5.3) of greater then or equal to 0.99.
All % RSD's for each analyte must be less than or equal to 15% or avg. response factors may not be used for quantitation (8270D 7.3.7.1).	There is no minimum response criteria llisted in method 625 so again we will default to method 8270D (7.3.4.2) for minimum response criteria for the SPCC's as follows: N-nitroso-di-n-propylamine 0.05 Hexachlorocyclopentadieine 0.05 2,4-Dinitrophenol 0.05

	4-Nitrophenol 0.05 SIM Mode must also meet these criteria for four SPCC's
If the % RSD for any analyte exceeds 15% then a linear regression, or quadratic curve fit may be used with a min of 6 points for a quadratic as long as the coefficient of determination is greater then or equal to 0.995 (8000B 7.5.2/7.5.3).	
All CCC's regardless of curve fit must still have a % RSD less then or equal to 30%. Base/Neutrals — Acids Acenaphthene — 4-Chloro-3-methylphenol 1,4-Dichlorobenzene — 2,4-Dichlorophenol Hexachlorobutadiene — 2-Nitrophenol N-nitroso-diphenylamine — Phenol Di-n-octylphthalate — Pentachlorophenol Fluoranthene — 2,4,6-Trichlorophenol Benzo(a)pyrene	

22.3 Daily Standard Criteria

8270D Daily CCV Criteria	625 Daily CCV Criteria
A DFTPP solution of 50 ng must be run and meet the criteria in Table 3 (8270D 7.3.1). The mass spectra of the DFTPP is obtained by three scans (the peak apex and the scans immediately preceding and following the apex) and averaged (8270D 7.3.1.1)	A DFTPP solution of 50 ng must be run and meet the criteria in Table 9. No directions are given in 625 as to how the spectra of DFTPP should be obtained. By default 8270D recommendations will be used.
SPCC's must meet min response criteria as follows (8270D 7.4.4.1): N-nitroso-di-n-propylamine 0.05 Hexachlorocyclopentadieine 0.05 2,4-Dinitrophenol 0.05 4-Nitrophenol 0.05 SIM Mode must also meet these criteria for four SPCC's	All analytes reported must pass +/- 20% criteria for either the % RSD or % Drift (625 7.3). ☞ Use % RSD if avg. response factors are used to quantitate ☞ Use % Drift only if a regression fit was used to quantitate
All CCC's must have a % RSD or % Drift less then or equal to 20%. ☞ Use % RSD if avg. response factors are used to quantitate (8270D 7.4.5.1) ☞ Use % Drift only if a regression fit was used to quantitate (8270D 7.4.5.1) Base/Neutrals — Acids Acenaphthene — 4-Chloro-3-methylphenol 1,4-Dichlorobenzene — 2,4-Dichlorophenol Hexachlorobutadiene — 2-Nitrophenol N-nitroso-diphenylamine — Phenol Di-n-octylphthalate — Pentachlorophenol Fluoranthene — 2,4,6-Trichlorophenol Benzo(a)pyrene	There is no minimum response criteria listed in method 625 so again we will default method 8270D (7.4.4.1) for minimum response criteria for the SPCC's as follows: N-nitroso-di-n-propylamine 0.05 Hexachlorocyclopentadieine 0.05 2,4-Dinitrophenol 0.05 4-Nitrophenol 0.05 SIM Mode must also meet these criteria for four SPCC's

23 Clarification or modifications of the method

23.1 Not Applicable

_____ Date_____
Organic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

Sulfate by SM4500SO4^{-2}E (SM 20th), 375.4 (EPA Revision Date 1978) and 9038 (SW-846 Revision 0)

1.0 Applicable matrix

1.1 This method is applicable to water and extracted soil samples.

2.0 Detection Limit

2.1 The laboratory PQL is 5ppm.

2.2 The laboratory MDL is determined annually in accordance to 40CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

3.0 Scope and Application

3.1 The methods upper limit of detection is 40 mg/L. Samples and standards above 40 mg/L are diluted to a concentration below 40 mg/L.

3.2 The analysis of soil samples requires an extraction with DI water in accordance with SOP WC-001.

4.0 Summary of test method

4.1 A powder pillow containing barium chloride is added to a 25mL sample aliquot and allowed to stand for 5 minutes. During the 5 minute reaction sulfate ions react with the barium chloride forming a white barium sulfate cloud.

5.0 Definitions

5.1 Color, is defined as the color of water from which turbidity has been removed.

5.2 Turbidity is defined as suspended particulates.

6.0 Interference

6.1 Suspended material, color and silica over 500ppm will result in a positive interference. Suspended material and color can be corrected by first filtering the sample and then analyzing a sample blank.

6.2 The following elements will interfere with this procedure if found at certain levels: Calcium above 20,000 mg/L; Chloride above 40,000 mg/L; and Magnesium above 10,000 mg/L.

7.0 Safety

7.1 Handle chemicals while wearing approved gloves. Additionally, always wear a lab coat/apron and safety glasses. Samples should be considered hazardous: avoid exposure, skin contact, inhalation or ingestion.

8.0 Equipment and supplies

8.1 HACH DR 2800 spectrophotometer.

8.2 HACH 25 mL sample cells.

8.3 Various class A volumetric pipettes for dilutions.

8.4 100 mL volumetric class A flask.

8.5 Adjustable pipettes for dilutions.

8.6 KimWipe or similar.

9.0 Reagents and standards

9.1 DI Water.

9.2 SulfaVer 4 Sulfate Reagent Powder Pillows from HACH.

9.3 1000 ppm sulfate standard purchased from a certified supplier (Used to prepare calibration standards, ICVs, and CCVs).

9.3.1 40 ppm sulfate standard; dilute 20 mL of the 1000ppm standard to 500 mL with DI water.

9.3.2 20 ppm sulfate standard; dilute 10 mL of the 1000 ppm sulfate standard to 500 mL with DI water (this is also the CCV).

9.3.3 10 ppm sulfate standard; dilute 5 mL of the 1000 ppm sulfate standard to 500 mL with DI water.

9.3.4 5 ppm sulfate standard; dilute 2.5 of the 1000 ppm sulfate standard to 500 mL with DI water.

9.4 1000 ppm sulfate standard purchased from a second-source certified supplier (used to prepare the LCS and MS/MSDs).

10.0 Sample collection

10.1 Samples should be collected in a plastic container (HDPE) and refrigerated at >0 to 6°C until analysis.

10.2 Samples must be analyzed within 28 days of collection.

11.0 Quality control

11.1 An ICV must be analyzed prior to analyzing samples. The ICV is 0.5 mL of the 1000 ppm calibration standard, diluted to 25 mL with DI water, equivalent to 20 ppm.

11.2 A LCS must be analyzed every 10 samples. The LCS is 1.0 mL of the second-source 1000 ppm standard, diluted to 25 mL with DI water, equivalent to 40 ppm.

11.3 A MB must be analyzed per batch of 20 or fewer samples. The MB is 25 mL DI water.

11.4 A MS/MSD must be analyzed per batch of 20 samples or fewer. The MS/MSD is a sample spiked with 0.50 mL of the second-source 1000 ppm standard, diluted to 25 mL with DI water. This equals a 20 ppm spike

11.5 A DI water CCB must be analyzed every 10 samples and at the end of the run.

11.6 A CCV must be analyzed every fourth sample and at the end of the run. The CCV may be any or the calibration standards listed in section 9.3.1 – 9.3.4

12.0 Calibration and standardization

12.1 Adjustable pipettes must be calibrated quarterly.

12.2 The instrument maintains a pre-calibrated non-linear curve. The following known standards are analyzed against this curve for calibration verification: 5 ppm, 10 ppm, 20 ppm, 40 ppm

13.0 Procedure

13.1 Sample and sample blank analysis

13.1.1 Turn on the HACH DR 2800. Press the "On/Off" button on the back of the instrument.

13.1.2 Using the touch screen, press "User Programs." The next screen should have "950 Sulfate" pre-selected.

13.1.3 Press "**Start**."

13.1.4 The display will read "**mg/L SO_4^{2-}**".

13.1.5 To analyze a sample, fill two cells with 25mL of sample or an aliquot diluted to 25 mL.

13.1.5.1 Colored or turbid samples should be filtered before analysis. Repeat the same procedure for the QC samples.

13.1.6 Add one Sulfa Ver Powder pillow packet to the second sample cell. Cover the cell with a piece of parafilm and shake to dissolve.

13.1.7 Press the **"Timer"** icon, 🕑, and then **"OK."** This will measure a 5 minute time period needed for the reaction to occur.

13.1.8 The timer will sound at the end of five minutes and the display will read"**mg/L SO_4^{2-}**".

13.1.9 Wipe the outside of all cells to be used with a KimWipe to remove water droplets, dust, or spots before placing them in the instrument.

13.1.10 Place the cell without the powder pillow in the instrument first and cover with the black shield.

13.1.10.1 Note: Place all sample cells into the instrument with the fill line facing right.

13.1.11 Press **"Zero"**, the display will show **"Zeroing"** then **0 mg/L SO_4^{2-}**

13.1.12 Place the second sample cell containing the sample with the powder pillow in the instrument and cover with the black shield.

13.1.13 Press **"READ"** the display will show **"Reading"** followed by the results in **mg/L SO_4^{2-}.**

13.1.14 Write the sample results in the sulfate log-book.

13.1.15 Repeat steps 13.1.5 through 13.1.14 for all calibration checks, samples, and quality controls.

14.0 Calculations

14.1 The instrument reads mg/L directly.

14.2 If a dilution was made multiply the instrument mg/L reading by the dilution factor for the sample result.

14.2.1 Dilution factors are calculated by dividing 25 mL by the actual volume of sample used.

14.3 Enter the results for the zero, 5 ppm, 10 ppm, 20 ppm, and 40 ppm standards into the Sulfate Excel spreadsheet and print the "r" value on the bench sheet.

14.3.1 The "r" value must be at least 0.995 for acceptance.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. AWAL does not update its limits based on the tracking. It utilizes the limits defined by the method.

15.2 Current limits are listed in section 17.

16.0 Pollution prevention

16.1 Because these samples are taken from drinking and ground waters or domestic and industrial discharges, they do not pose a pollution risk to the environment if disposed through the laboratory sink.

16.2 The powder pillow used in this analysis contains barium chloride. Do not store or use glassware that might be used in chloride or barium analysis.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The ICV and LCS recoveries must be 100 ± 10% in all batches.

17.2 The MB and CCB recoveries must be lower than the PQL in all batches.

17.3 The MS/MSD recoveries must be 100± 20% in all batches.

17.4 The MSD RPD must be not greater than10% in water batches and 20% in extracted soil batches.

17.5 The CCV recovery must be 100 ± 10% in water batches and ± 25% in extracted soil batches.

17.6 Adjustable pipettes calibration must be accurate within 3.0%.

17.7 A calibration coefficient "r" at least 0.995.

18.0 Corrective actions for out of control data.

18.1 If one of the Standards (ICV, LCS, and CCV) are not within limits, make a new standard and re-analyze batch.

18.2 If the method blank is not within limits, the 25mL cells might be contaminated. Clean the cells and re-analyze the batch.

18.3 If the duplicate is not within limits, re-analyze batch making sure samples are shaken well.

19.0 Contingencies for handling out of control data or unacceptable data.

19.1 If re-analysis of samples cannot be performed within 28 days of collection, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, reported values must be flagged with the appropriate qualifiers.

20.0 Waste management

20.1 The samples are typically drinking water, ground water or wastewater treatment plant influents/effluents. If samples are from one of the above mentioned sources, unused sample may be disposed through the laboratory sink.

20.2 Soil samples if not associated with a waste site may be disposed in the laboratory trash.

21.0 References

21.1 Methods and Guidance for Analysis of Water, Sulfate Method 375.4 Revised 1978.

21.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, p 4-178, Method 4500-SO_4^{2-} E.

21.3 HACH Water Analysis Handbook, Third Edition, Method 8051, p 1138.

21.4 Det. of Sulfate in waters by Flow Injection Analysis Colorimetry Method 10-116-10-2-C Rev. date 28 August 2003

22.0 Tables, diagrams

22.1 Not Applicable.

23.0 Clarification/Modifications of the method

23.1 The 1000 ppm sulfate standards are purchased from certified suppliers and are not prepared by AWAL.

23.2 SulfaVer 4 Sulfate Reagent Powder Pillows, by HACH, are used in place of all other reagents. The HACH sulfate method has been approved by the EPA as an acceptable method. EPA method 375.4, section 3.0, comments.

23.3 When the soil procedure is performed, the analytical report must reflect that the method has been modified.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QAO

Total dissolved solids by 160.1 (EPA Revision Date 1971) and SM 2540C (20th Edition)

1.0 Applicable matrix

1.0 This method is applicable to drinking, surface, saline waters, and domestic and industrial wastewaters.

2.0 Detection Limit

2.1 The laboratory PQL is 10ppm.

2.2 The laboratory MDL is determined annually in accordance to 40CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

3.0 Scope and Application

3.1 The method stated range of detection is 10mg/L to 20,000mg/L.

3.2 TDS may be performed on the filtrate remaining from a TSS analysis.

4.0 Summary of test method

4.1 A well-mixed sample aliquot is filtered through a glass fiber filter. The filtrate is transferred into a vessel, evaporated to dryness at 103°C and dried to a constant weight at 180°C.

5.0 Definitions

5.1 Filterable residue: solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

5.2 Hygroscopic: the ability of an ion to pull moisture from the surrounding atmosphere.

5.3 LCS: Laboratory control standard

5.4 MB: Method blank

6.0 Interference

6.1 Waters with high concentrations of calcium, magnesium, chloride and sulfate will be hygroscopic and require additional drying, desiccation and rapid weighing to prevent false positives.

6.2 Waters with high concentrations of bicarbonate will require prolonged drying at 180°C to convert the bicarbonate to carbonate.

6.3 Using too much, sample will create excessive residue in the beaker. Forming a surface crust and trapping water underneath. The total residue derived at the end of the test should not exceed 200 mg.

6.4 Refrigeration of the sample should occur ASAP to minimize micro-biological decomposition of solids.

7.0 Safety

7.1 Samples from wastewater treatment plants pose a potential biological hazard (total & fecal coliforms, salmonella, and hepatitis), laboratory attire should be worn (gloves, glasses and lab coat/apron) when handling.

8.0 Equipment and supplies

8.1 Whatman 934-AH Glass fiber filter discs.

8.2 300mL magnetic filter funnel

8.3 Suction flask, 500 mL

8.4 Evaporating dishes, 100 mL beakers.

8.5 Drying oven, 103 - 180°C ± 2°C

8.6 Desiccator

8.7 Analytical balance, capable of weighing to 0.1 mg

8.8 Graduated cylinders, 50mL

9.0 Reagents and standards

9.1 Potassium Chloride, KCL: dissolve 0.2050g of KCL in DI water and dilute to 1L. This standard equals 205ppm.

9.2 DI Water

10.0 Sample collection

10.1 Samples should be collected in a plastic container (HDPE) and refrigerate at >0 to 6°C until analysis.

10.2 Samples must be analyzed within 7 days of collection.

11.0 Quality control

11.1 A method blank must be analyzed per batch of 20 samples or fewer.

11.2 An LCS must be analyzed per batch of 20 samples or fewer.

11.3 A sample duplicate must be analyzed per batch of 20 samples or fewer.

12.0 Calibration and standardization

12.1 The drying oven must be calibrated with a NIST traceable thermometer. The temperature of the ovens must be monitored and documented each business day.

12.2 The analytical balance must be calibrated each business day with Class S weights that have been verified against NIST.

13.0 Procedure

13.1 Preparation of evaporating beakers: Heat the beakers in the oven for a minimum of 2 hours at 180 ± 2°C. Cool and store in a desiccator until needed. Weigh immediately before use. Document beaker tare weight in the TDS logbook.

13.2 Preparation of filters: Place the filter on the magnetic filter bottom, attach the filter assembly top and apply vacuum.

13.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer an aliquot of sample into the funnel with the graduated cylinder. Document sample volume in the TDS logbook.

13.3.1 Filter 50mL of standard for the LCS.

13.3.2 Filter 50mL of DI waster for the blank.

13.3.2 The general sample size taken is 25mL diluted to 50mL with DI water. If the sample residue is greater than 200mg a smaller portion of sample must be used.

13.3.3 Occasionally a TDS is requested on treatment plant compost. A 1:1 extraction is performed on the sample with DI water. 10mL of the extracted liquid diluted to 50mL with DI water is filtered.

13.4 Rinse the filter and the graduated cylinder three times with 10mL portions of DI water.

13.5 Apply vacuum for approximately 3 minutes after filtration is complete to remove water droplets.

13.6 Transfer the filtrate (50mL) and rinse into a weighed beaker and evaporate to dryness, in the TDS oven overnight at 103°C. Document, the evaporation temperature on the TDS oven temperature chart.

13.7 In the morning increase the TDS oven temperature to 180°C ± 2°C

13.8 Dry the evaporated samples for a minimum of 2 hours at 180°C ± 2°C. Document oven's temperature on temperature table.

13.9 Cool samples and quality control samples in a desiccator and weigh, Document weight in logbook.

13.9.1 If sample result is greater than 2500 mg/L, place sample back in oven for another drying cycle and re-weigh. Continue this step until the sample weight loss is within 0.0005 mg.

14.0 Calculations

14.1 TDS mg/L = ((A-B)1000)/C Dilution Factor = 1000/C

Where: A= Final weight (g)
B= Initial weight (g)
C= mL of sample (g)

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated semi annually.

15.2 Current limits are ± 20% on the standard and ± 20% on the sample RPD.

16.0 Pollution prevention

16.1 Because the samples analyzed are from sewage lines or ground water monitoring wells, disposal through the laboratory sink is acceptable.

17.0 Data assessment and acceptance criteria for quality control measures.

17.1 The method blank must not record a TDS value greater than the PQL, which is 10ppm.

17.2 The LCS must recover 80 – 120% of its true value.

17.3 The sample duplicate must produce an RPD of ± 20%.

17.3 The sample residue cannot exceed 200mg.

17.4 If results are greater than 2500 mg/L (TDS) the sample must be reheated and cooled to check for further weight loss.

17.5 Oven drying temperature must be within 178 - 182°C

17.6 Balance calibration must be within the following:

100g must weigh between 99.9000 – 100.1000g
10g must weigh between 9.9900 - 10.0100g
0.2g must weigh between 0.1998 - 0.2002g
0.1g must weigh between 0.0997 - 0.1030g

18.0 Corrective actions for out of control data.

18.1 If the method blank is not within limits, prepare new beakers and re-analyze batch.

18.2 If the Standard is not within limits, make a new standard and re-analyze batch.

18.3 If the duplicate is not within limits, reanalyze batch making sure samples are shaken well.

18.4 If the sample residue exceeds 200mg, re-analyze a smaller volume of sample.

18.5 If the oven is not within limits, adjust it to within limits and cook samples for a minimum of 2 hours.

18.6 If the balance is not within limits, calibrate the balance and re-weigh samples.

19.0 Contingencies for handling out of control data or unacceptable data.

19.1 If re-analysis of samples cannot be performed within 7 days of collection, have your supervisor contact the client and request a new sample.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

20.0 Waste management

20.1 This procedure does not deal with caustic or corrosive materials. Unused portions of sample may be disposed through the laboratory sink.

20.2 Refer to the laboratory Waste Management and Sample Disposal SOP.

21.0 References

21.1 Methods and Guidance for Analysis of Water, TDS Method 160.1 Revised March 1971.

21.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, p 2-56, Method 2540C.

21.3 American West Analytical Laboratory Waste Management and Sample Disposal SOP, Revision 2.0

22.0 Tables, diagrams

22.1 Not Applicable

23.0 Clarification/Modifications of the method

23.1 Use 100mL beakers in place of porcelain.

23.2 The laboratory does not pre-wash the filters used in this method. They do not contain lint material that would exhibit a positive interference in the analysis as proven by the method blank.

23.3 A re-weigh study was performed in 2004 in response to an on-site audit. This re-weigh study found only samples exceeding 2500 mg/L TDS had a potential to further loose weight during an additional heating and cooling cycle. Therefore only samples with TDSs greater than 2500 mg/L will be put through an additional heating and cooling cycle.

_____ Date_____
Inorganic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

VOC by 624 (40 CFR July 1, 1995) and 8260C (SW846 Rev. 3, 2006).
Purge and Trap for Volatiles by 5030C (SW846 Revision 3 May, 2002)
Purge Trap for Volatiles by 5035A (SW846 Revision 1 July 2002)

1.0 Applicable matrix

1.1 This method is used for the determination of volatile organic compounds by gas chromatography/mass spectrometry (GC/MS) for aqueous, soil and waste matrices and low level analysis of ground water.

2.0 Detection Limit

2.1 The laboratory MDL is determined annually in accordance to 40 CFR Part 136 Appendix B. The laboratory PQL is based on the MDL.

2.2 The laboratory PQLs are listed in the LIMS under tests. All active volatile organic methods are name “8260-matrix-analyte list” or “624-matrix-analyte list”.

3.0 Scope and Application

3.1 The determination of purgeable compounds with boiling points below 200˚C. in samples.

3.2 Analyte list

Analyte	CAS No.	Method 624	Method 8260C
Acetone	67-64-1		X
Acetonitrile	75-05-8		X
Acrolein	107-02-8	X	X
Acrylonitrile	107-13-1	X	X
Allyl alcohol	107-18-6		X
Allyl chloride	107-05-1		X
Benzene	71-43-2	X	X
Benzyl chloride	100-44-7		X
Bis(2-chloroethyl)sulfide	505-60-2		X
Bromoacetone	598-31-2		X
Bromochloromethane	74-97-5		X
Bromodichloromethane	75-27-4	X	X
4-Bromofluorobenzene (surr)	460-00-4	X	x
Bromoform	75-25-2	X	X
Bromomethane	74-83-9	X	X
n-Butanol	71-36-3		X
2-Butanone (MEK)	78-93-3		X
t-Butyl alcohol	75-65-0		X
Carbon disulfide	75-15-0		X
Carbon tetrachloride	56-23-5	X	X
Chloral hydrate	302-17-0		X
Chlorobenzene	108-90-7	X	X
Chlorobenzene-d_5 (IS)			
Chlorodibromomethane	124-48-1	X	X
Chloroethane	75-00-3	X	X
2-Chloroethanol	107-07-3		X
2-Chloroethyl vinyl ether	110-75-8	X	X

Analyte	CAS No.	Method 624	Method 8260C
Chloroform	67-66-3	X	X
Chloromethane	74-87-3	X	X
Chloroprene	126-99-8		X
Crotonaldehyde	4170-30-3		X
Cyclohexanone			X
1,2-Dibromo-3-chloropropane	96-12-8		X
1,2-Dibromoethane	106-93-4		X
Dibromomethane	74-95-3		X
1,2-Dichlorobenzene	95-50-1	X	X
1,3-Dichlorobenzene	541-73-1	X	X
1,4-Dichlorobenzene	106-46-7	X	X
1,4-Dichlorobenzene-d_4 (IS)			
Cis-1,4-Dichloro-2-butene	1476-11-5		X
Trans-1,4-Dichloro-2-butene	110-57-6		X
Dichlorodifluoromethane	75-71-8		X
1,1-Dichloroethane	75-34-3	X	X
1,2-Dichloroethane	107-06-2	X	X
1,2-Dichloroethane-d_4 (surr)		X	x
1,1-Dichloroethene	75-35-4	X	X
Trans-1,2-Dichloroethene	156-60-5	X	X
1,2-Dichlororpropane	78-87-5	X	X
1,3-Dichloro-2-propanol	96-23-1		X
Cis-1,3-Dichloropropene	10061-01-5	X	X
Trans-1,3-Dichloropropene	10061-02-6	X	X
1,2,3,4-Diepoxybutane	1464-53-5		X
Diethyl ether	60-29-7		X
1,4-Difluorobenzene (IS)	540-36-3		X
1,4-Dioxane	123-91-1		X
Ethyl acetate	141-78-6		X
Ethylbenzene	100-41-4	X	X
Ethyl ether	60-29-7		
Ethylene oxide	75-21-8		X
Ethyl methacrylate	97-63-2		X
Fluorobenzene (IS)	462-06-6		
Hexachlorobutadiene	87-68-3		X
2-Hexanone	591-78-6		X
Iodomethane	74-88-4		X
Isobutyl alcohol	78-83-1		X
Isopropylbenzene	98-82-8		X
Malononitrile	109-77-3		X
Methacrylonitrile	126-98-7		X
Methylene chloride	75-09-2	X	X
Methyl methacrylate	80-62-6		X
4-Methyl-2-pentanone (MIBK)	108-10-1		X
Naphthalene	91-20-3	X	X
Nitrobenzene	98-95-3		X
2-Nitropropane	79-46-9		X
N-Nitroso-di-n-butylamine	924-16-3		X

Analyte	CAS No.	Method 624	Method 8260C
Paraldehyde	123-63-7		X
2-Pentanone	107-87-9		X
2-Picoline	109-06-8		X
1-Propanol	71-23-8		X
2-Propanol	67-63-0		X
Propargyl alcohol	107-19-7		X
B-Propiolactone	57-57-8		X
Propionitrile	107-12-0		X
n-Propylamine	107-10-8		X
Styrene	100-42-5		X
1,1,1,2-Tetrachloroethane	630-20-6		X
1,1,2,2-Tetrachloroethane	79-34-5	X	X
Tetrachloroethene	127-18-4	X	X
Toluene	108-88-3	X	X
Toluene-d_8 (surr)	2037-26-5	X	x
O-Toluidine	95-53-4		X
1,2,4-Trichlorobenzene	120-82-1		X
1,1,1-Trichloroethane	71-55-6	X	X
1,1,2-Trichloroethane	79-00-5	X	X
Trichloroethene	79-01-6	X	X
Trichlorofluoromethane	75-69-4	X	X
1,2,3-Trichloropropane	96-18-4		X
Vinyl acetate	108-05-4		X
Vinyl chloride	75-01-4	X	X
o-Xylene	95-47-6		X
m-Xylene	108-38-3		X
p-Xylene	106-42-3		X

3.3 TPH regions reported.

3.3.1 Aliphatic Hydrocarbons: C6, C7 through C8, C9 through C10, and C11 through C15.

3.3.2 Alkyl Benzenes: C9 through C10

4.0 Summary of test method

4.1 Samples are placed in an automatic sampler where they are injected into the purge and trap. The purge and trap bubbles helium through the sample to release the volatile organic analytes which are then collected on a trap. The trap is heated to release the analytes where the volatile analytes collected and directly transfer into the MS. Compound identification occurs using relative retention time windows and a comparison of the mass spectra to spectra of authentic standards.

5.0 Definitions

5.1 IS: Internal Standard, a known amount of a standard added to a sample as a reference point for evaluating and controlling the precision and bias of the analytical method.

5.2 GC/MS: Gas Chromatography/Mass Detector

5.3 MS/MSD: Matrix Spike / Matrix Spike Duplicate

5.4 Surr: Surrogate, a substance not likely found in the environment and is added to samples by the laboratory for quality control purposes.

5.5 SRM: Standard Reference Material

5.6 VOA: Volatile Organic Analysis

5.7 VOC: Volatile Organic Compound.

5.8 Purge and Trap means the sample introduction system that operates by purging a sample with Helium gas. The gas transports the volatile analytes onto a trap that is then baked. This process delivers the volatile analytes into the injection port of the gas chromatograph where they undergo separation in the capillary column.

5.9 LL: Low Level, 25mL of water sample is purged.

5.10 POD: A cluster of six tanks of gas connected to each other that function off one regulator.

6.0 Interferences

6.1 Contaminants that may cause interferences are non-pure chemicals/reagents, gases and dirty syringes. The laboratory prepares and analyzes a method blank in every sample batch to monitor this type of contamination.

6.1.1 The laboratory only purchases purge and trap grade solvents to use in this procedure.

6.1.2 Common laboratory solvents are monitored closely and are stored away from the VOA lab. See section 16.2 for specific solvents.

6.1.3 The use of non-polytetrafluoroethylene components is not allowed.

6.2 Contaminants may diffuse through the sample septum during shipping and storage. To monitor contamination from transportation trip blanks are supplied to clients when sample containers are requested. To monitor contamination during laboratory storage refrigerator blanks are analyzed.

6.3 Contamination from carry over is reduced by rinsing the purging device and syringe with DI water between samples and subjecting the purging vessel to a heated cycle between samples. If the purging device becomes contaminated it will need to be disassembled and baked out in an oven set at 105°C.

7.0 Safety

7.1 Samples should be considered hazardous. Avoid exposure, skin contact, inhalation, or ingestion.

7.2 Always handle chemicals while wearing approved gloves, safety glasses and laboratory coat.

8.0 Equipment and supplies

8.1 There are three GC/MS systems in the VOA lab.

8.1.1 System "A" utilizes a Tekmar-Dohrman Solotek 72 autosampler with a Tekmar-Dohrman 3100 concentrator linked to a 6890 HP GC interfaced with the 5973 MSD. The autosampler run conditions are as follows:

Instrument "A"	Waters	Soils	LL Waters
Purge time and temp	7.5 min @ 40°C	7.0 min @ 40°C	11.00 min @ 40°C
Desorbed time and temp	1.5 min @ 255°C	1.5 min @ 250°C	4 min @ 255°C
Bake time and temp	7.5 min @ 295°C	7 min @ 290°C	8 min @ 295°C
Injector temperature	250°C	250°C	250°C
Transfer line temp.	150°C	150°C	150°C
Column	RTX-VMS	RTX-VMS	RTX-VMS
Size	30m x .25mm x 1.4um	30m x .25mm x 1.4um	30m x .25mm x 1.4um
Cup temp	40°C	50°C	40°C
Needle temp	40°C	50°C	40°C

8.1.1.1 The GC and MS program is the same for waters and soils. The GC initial temp. is 45°C held for 3.00 minutes, then ramped at 25°C/min to 100°C and held for 0.00 minutes, then ramped at 40°C/min to 225°C and held for 3.40 minutes. The MSD has a solvent delay start with a constant source temperature of 230°C and a constant quadrapole temperature of 150°C with a mass range of 35 to 300 AMU.

8.1.1.2 The 3100 concentrator utilizes a K trap.

8.1.2 System "C" utilizes Tekmar-Dohrman Precept II autosampler with a Tekmar-Dohrman 3100 concentrator linked to a 6890 HP GC interfaced with the 5973 MSD. The autosampler run conditions are as follows:

Instrument "C"	Waters	soils
Purge time and temp	7.0 min @ 40°C	THE "C"
Desorb time and temp	1.5 min @250°C	INSTRUMENT
Bake time and temp	7.5 min @ 295°C	DOES
Column	RTX-VMS	NOT
Size	30m x .25mm x 1.4um	RUN
Transfer line temp.	150°C	SOILS

8.1.2.1 The GC and MS program for waters is as follows: The GC initial temperature is 45°C held for 3 minutes, then ramped at

25°C/min to 100°C and held for 0 minutes, then ramped at 40°C/min to 225°C and held for 3.40 minutes. The MSD has a solvent delay start with a constant source temperature of 230°C and a constant quadrapole temperature of 150°C with a mass range of 35 to 300 AMU.

8.1.2.2 The 3100 concentrator utilizes a K trap.

8.1.3 System "D" utilizes a Tekmar-Dohrman Solotek 72 autosampler with a Tekmar-Dohrman Velocity XPT concentrator linked to a 6890N Agilent GC interfaced with the 5973N Agilent MSD. The autosampler run conditions are as follows:

Instrument "D"	Waters	Soils	LL Waters
Purge time and temp	8.5 min @ 40°C	8.5 min @ 40°C	10 min @ 40°C
Desorb time and temp	1.5 min @ 250°C	1.5 min @ 250°C	1.5 min @ 250°C
Bake time and temp	2.2 min @ 295°C	4.4 min @ 295°C	5.5 min @ 295°C
Injector temperature	250°C	250°C	250°C
Transfer line temp.	150°C	150°C	150°C
Column	RX-VMS	RX-VMS	RX-VMS
Size	30m x .25mm x 1.4um	30m x .25mm x 1.4um	30m x .25mm x 1.4um
Cup temp	40°C	40°C	40°C
Needle temp	35°C	40°C	40°C

8.1.3.1 The GC and MS program is: GC initial temp. is 45°C held for 3.00 minutes, then ramped at 25°C/min to 100°C and held for 0.0 minutes, then ramped 40°C/min to 235°C and held for 3.40 minutes. The MSD has a solvent delay start with a constant source temperature of 230°C and a constant quadrapole temperature of 150°C with a mass range of 35 to 300 AMU.

8.1.3.2 The XPT concentrator utilizes a K trap (VOC CARB 3000). This trap has a female connector

8.2 Volumetric flasks are used for the preparation of standards.

8.3 Only glass and Teflon containers are used for samples and standards.

8.4 Syringes are calibrated by the manufacturer and are used for all standards preparation.

8.5 40 ml vials with Teflon septa.

8.6 A balance capable of measuring to three places.

9.0 Reagents and standards

9.1 Purge and Trap grade methanol.

9.2 RO water

9.3 Spiking Solution: Spiking solutions are prepared separately for the Solotek (instrument A & D) and the Precept II (instrument C) and are loaded directly to standard vessels on the respective auto-samplers. The Solotek spikes 5 µl of the internal/surrogate spike into the samples. This standard is prepared using 500 µl of mix STM-540 to a final volume of 25 ml of P&T methanol. The Precept spikes 1 µl into each sample; therefore a 250 µg/ml standard is prepared using 1 ml of Mix STM-540 to a final volume of 10 ml of P&T methanol.

9.4 All standards are logged into the LIMS and written in the standards log book where a detailed log is available for reference about past standards.

9.5 Standard storage and shelf life:

9.5.1 All standards are prepared in 2 mL amber vials and are stored at >0 to 6°C

9.5.2 Working standards are replaced every 6 months or sooner if needed.

9.5.3 All stock standards are stored per vendor specifications, which is typically protect from light and maintain at –10 to -20°C

9.6 Standards preparation:

9.6.1 All standards are prepared using calibrated class “A” volumetric flask and syringes at room temperature.

9.6.2 Exercise extreme care when preparing and storing stock solutions.

9.6.3 When a neat standard is being used, a three place analytical balance is required to prepare the primary standard gravimetrically.

9.7 Internal and Surrogate Standards:

9.7.1 Stock Solution “Internal & Surrogate Standard Mixture” purchased from certified vendor at a concentration of 2500 µg/mL. This mix contains: chlorobenzene-d5; 1,4-dichlorobenzene-d4; Fluorobenzene; 4-bromofluorobenzene; dibromofluoromethane; 1,2-dichloroethane-d4 and toluene-d8

9.7.1.1 Precept: dilute 1000µL of the Internal & Surrogate Standard Mixture to 10mL with P&T methanol.

9.7.1.2 Solotek 72: dilute 500µL of the Internal & Surrogate Standard Mixture to 25mL with methanol.

9.7.2 BFB Tuning Solution (50µg/mL): dilute 100µL of the Internal & Surrogate Standard Mixture to 5mL with P&T methanol.

9.7.3 SRM Standards purchased from certified vendors:

9.7.3.1 Stock solution: “VOC mixture (DWM-589N)” at a concentration of 2000µg/mL.

9.7.3.2 Stock solution: “VOC mixture (DWM-592)” at a concentration of 2000µg/mL.

9.7.3.3 Stock solution: “Custom STD mix” at a concentration range of 2000ug/mL – 4000µg/ml. It comes with 2 ampules, Cyclohexanone in one ampule and other analytes in the second one.

9.7.3.4 Stock solution: “Bis(2-chloroisopropyl)ether” at a concentration of 5000µg/mL.

9.7.3.5 Stock solution: “VOC mixture (DWM-584)” at a concentration of 200µg/mL

9.7.3.6 Stock solution: “Chloroprene Solution” at a concentration of 100µg/mL.

9.7.3.7 Stock solution: “2-Chloroethylvinylether” at a concentration of 200µg/mL.

9.7.3.8 Stock solution: “1,4-Dioxane” at a concentration of 2000µg/mL.

9.7.3.9 Stock solution: “Acrolein” at a concentration of neat.

9.7.3.10 VCM 1(250µg/mL): dilute 625uL of the VOC mixture (DWM-589N) to 5mL with Methanol.

9.7.3.11 VCM 2 (250µg/mL): dilute 625µL of the VOC mixture (DWM-592) Mix to 5mL with methanol.

9.7.3.12 VCM 3 (250µg/mL): dilute 625uL of the Custom STD mix to 5mL with methanol.

9.7.3.13 VCMX (500µg/mL): dilute 625 µL of the Custom Cyclohexanone STD to 5 mL with methanol.

9.7.3.14 VCM B (250µg/mL): dilute 250µL of the Bis(2-Chloroisopropyl) ether 5 mL with methanol.

9.7.3.15 VCM A (500µg/mL): dilute neat STD (0.100g to 10ml of Methanol) of Acrolein for an intermediate STD at 10,000µg/ml. Use 250µl of the intermediate STD to 5mL with methanol.

9.7.3.16 VCM G (200µg/L): inject stock solution VOC mixture (DWM-584) directly.

9.7.3.17 VCM D (2000µg/L): inject stock solution 1,4-Dioxane directly.

9.7.3.18 VCM C (200µg/L): inject stock solution 2-Chloroethylvinylether directly.

9.7.3.19 VCM P (100µg/L): inject stock solution Chloroprene directly.

9.7.4 Calibration Standards:

9.7.4.1 Stock solution: “8260B Cal Mix at a concentration of 2,000 µg/mL

9.7.4.2 Stock solution: “VOA Cal Mix #1” at a concentration of 5,000 µg/mL

9.7.4.3 Stock solution: “8260B Acetates Mix” at a concentration of 2,000 µg/mL

9.7.4.4 Stock solution: “Custom Mix” at a concentration of 2,000µg/mL comes with 2 ampules, Cyclohexanone in one ampule and other analytes in the second one.

9.7.4.5 Stock solution: “502.2 Cal Mix #1A” at a concentration of 200 µg/mL

9.7.4.6 Stock solution: “1,4-Dioxane” at a concentration of 2,000 µg/mL

9.7.4.7 Stock solution: “Acrolein” at a concentration of 10,000 µg/mL

9.7.4.8 Stock solution: “n-Pentadecane” purchased from Restek neat.

9.7.4.9 TPH Stock solution: dilute 0.1g of each Aldrich neat Solution, pentane, hexane, octane, decane, and dodecane to 10mL with methanol.

9.7.4.10 NCM1: direct inject of the stock 8260C Cal Mix.

9.7.4.11 NCM2 (1,000µg/mL): dilute 1000uL of VOA cal mix #1 to 5ml with methanol.

9.7.4.12 NCM3: direct inject of 8260C Acetates mix.

9.7.4.13 NCM4: direct inject of Restek custom mix.

9.7.4.14 NCMX: direct inject Restek custom Cyclohexanone

9.7.4.15 NCMG: direct inject of 502.2 Cal ix #1A.

9.7.4.16 NCMD: direct inject of 1,4-Dioxane

9.7.4.17 NCMC: direct inject of 8260C Cal mix #1B.

9.7.4.18 NCMA: dilute 1000 µL of the 10000 µg/L Acrolein stock solution to 5 mL with methanol. This makes a 2000 µg/mL Acrolein standard.

9.7.4.19 NCMT (2,000µg/mL): dilute 1000ul of TPH stock to 5mL with methanol.

9.7.4.20 NCMP (10,000µg/mL): dilute 0.10g of n-Pentadecane to 10mL with methanol.

10.0 Sample collection

10.1 Liquid samples should be collected in three 40ml pre-cleaned certified containers containing sufficient 1:1 HCL to lower the pH to <2.

10.2 Solid samples should be collected in a 4-oz. clear wide mouth container or follow method 5035A.

10.3 Both liquid and solid samples should be refrigerated from the time of collection to analysis. A temperature of >0 to 6°C should be maintained.

10.3.1 Samples for method 5035 low level should be transported on dry ice and stored between –20 and -10°C until analysis. Low level 5035 soils are collected in a pre-weighed 40ml VOA vial, with stir-bar, and approximately 0.2ml of sodium bisulfate for every 1.0g of soil collected. Typically, due to a 5.0g sample amount 1.0ml of sodium bisulfate is sufficient.

10.3.2 Samples for method 5035 high level should be transported and stored at >0 to 6°C until analysis.

10.4 Analysis for both matrices, liquid and solid, must occur within 14 days of collection.

10.4.1 Liquid samples not preserved to pH<2 must be analyzed within 7 days for non halogenated compounds.

10.4.2 The laboratory attempts to analyze all liquid samples within 7 days to avoid potential preservation flags.

11.0 Quality control

11.1 All new analysts will demonstrate initial proficiency with the method by analyzing 4 LCS's for a precision and accuracy (P&A) evaluation prior to analyzing samples.

11.2 Each analyst must demonstrate continued proficiency as a work group annually by performing 4 LCS's. These LCS's do not have to be performed in the same batch they may be performed in one, two, three or four individual batches.

11.3 Quality control for this procedure is broken into two types: batch and instrument.

11.3.1 The batch must contain the following per 20 samples or fewer: Tune, CCV, MB, LCS and MS/MSD.

11.3.1.1 The batch QC and samples must be spiked with the surrogate.

11.3.1.1.1 The internals and surrogates are automatically spiked into each sample from the auto-sampler's standard vessel.

11.3.1.2 The LCS, MS and MSD are spiked manually with VCM1 and VCM2, when analyzing 8260C

11.3.1.2.1 The LCS is spiked 8µL into 100mL RO water. The MS and MSD are spiked 3.2µL into 40mL VOA vial.

11.3.1.3 When analyzing by method 624 the LCS is spiked with VCM1, VCM2, VCM3, VCMB, VCMD, VCMC, VCMG, VCMP, VCMX, and VCMA. The following is spiked per 100mL RO water.

8 µL of VCM1, VCM2, VCM3, VCMX, and VCM4

10 µL of VCMG and VCMD

20 µL of VCMA, VCMP and VCMC

11.3.1.3.1 The MS and MSD are spiked with VCM1 and VCM2. 3.2µL into 40mL VOA vial.

11.3.1.4 When analyzing by 8260 LL the LCS is spiked with VCM1, VCM2, VCM3, VCMB, VCMD, VCMC, VCMG, VCMP, VCMX, and VCMA. The following is spiked per 100mL RO water.

11.3.1.5 2µL of VCM1, VCM2, VCM3, VCMX, and VCM4

2.5µL of VCMG and VCMD

5µL of VCMA, VCMP and VCMC

11.3.1.5.1 The MS and MSD are spiked with VCM1 and VCM2. 0.8µl into 40mL VOA vial

i. The instrument must analyze the following QC at the stated interval:

1. A BFB tuning solution is run to verify the MSD is tuned correctly and must pass Table 4 Mass Intensity Criteria from method 8260C which has been previously programmed into Enviroquant.

2. An ICV must be analyzed immediately following calibration and pass the limits in the LIMS for the 624-W-CUSTOM test

code, or a CCV must be analyzed at the beginning of every 12-hour clock before samples can be analyzed.

3. A method blank will be run before any field samples to show there is no instrument contamination. Ideally an LCS will be run and pass both 8260C and 624 criteria before any samples, as to facilitate the flexibility of running both methods on the same analytical clock. However, for method 8260C the LCS can be run anytime during the analytical clock. If samples require 624 analysis, the LCS (QC check sample) must run and pass prior to sample analysis.

12.0 Calibration and standardization

12.1 Intermediate standards are valid for two months.

12.2 Gas standards are valid for one week from time of preparation.

12.3 Standards are prepared at eights levels: 250, 100, 50, 25, 10, 5, 2, and 1 µg/ml. LL standards are prepared at 50, 20, 10, 5, 4, 2, 1, and 0.5 µg/mL.

12.4 Before the initial calibration can be run a BFB tuning solution must be run and be evaluated.

12.4.1 Check BFB tuning solution prior to running the initial calibration. This is accomplished by choosing the tuner menu in enviroquant and selecting evaluate BFB. Choose “autofind to screen” option. This procedure automatically finds the apex of BFB and averages the three following scans: one scan to the left of apex, the apex, and one scan to the right, to obtain the spectra for BFB. It then applies the tuning criteria stated in Table 4 of method 8260**C** and Table 2 of method 624 to determine if a passing spectra has been obtained. If all criteria is met (indicated by a pass/fail list) then the MSD is assumed to be tuned correctly and can continue with section 12.4.2. If the tune fails then the analyst must rerun and reanalyze the tune. Upon a second failing tune corrective action must be taken. These actions may include cleaning the source and/or retuning the MSD. This is the only acceptable method to acquire and evaluate a BFB tuning solution.

12.4.2 Run and analyze the 8 different levels of standards listed in section 12.3. Evaluate each level before updating curve. Make sure the high level standard (250µg/L) did not saturate the detector. This is particularly important after the MSD source has been cleaned and/or a BFB tune of the MSD has occurred.

12.4.3 To update and evaluate the new calibration the following procedure is used. Save the current method as a new one. The naming convention usually stays the same and the next number is used. For example, a water calibration is named FULLW_XX, LL calibration is named 826025_XX, and a soil calibration is named FULLS_XX. Load the highest standard (50 for LL, 250 for 8260 and 624); then in enviroquant

choose the menu item InitCal, and update levels. A new screen will appear. Make sure the menu is set on recalibrate using level 250. In the responses box make sure replace is selected. Then choose, do update, and O.K. Repeat for all other initial calibration standard levels.

12.4.4 Once the calibration has been updated, choose InitCal in enviroquant and select, response factors to screen.

12.4.5 For any analyte with a %RSD of 20% or less, the calibration is considered linear and avg. response factors can be used. For any analyte >20% RSD either a linear regression or a quadratic curve fit must be used. To change what curve fit is being used for each individual analyte go to edit compounds, choose the analyte to change, and on page 1 you can amend the curve fit. If linear regression or quadratic is used an r squared value of >0.99 must be achieved. Choose “plot” and print the curve to PDF to be included in the calibration curve pdf package. A minimum of 5 standards must be used for each analyte. If quadratic fit is used, a minimum of 6 points are necessary. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then does not pass and maintenance should be done with a new curve following. To see if they meet method 8260C/624 criteria see Table 1.

13.0 Procedure

13.1 Preparation of aqueous samples

13.1.1 Remove sample from bag. Inspect sample for high level of sediment. Also inspect sample for oils or any other abnormal matrix, then place on autosampler.

13.1.2 Samples requiring dilutions are prepared in a 50 mL or 100 mL volumetric flask with RO water and transferred into a 40 mL VOA vial and placed on the instrument autosampler.

13.1.3 Section 13.6.3 describes loading the autosampler and the software that controls it.

13.2 Preparation of soil and waste samples by 5030C.

13.2.1 Weigh approximately 2 g or 5g (weight used depends on application of data) into a 40 mL pre-cleaned vial with magnetic stir-bar, and add 5ml RO water and cap.

13.2.2 If the sample is highly contaminated a methanol extraction is performed. A 10 g aliquot of the sample is weighed in to a 20ml VOA vial. 10ml of MeOH is added and the sample is hand shaken for 2 minutes. A 1.0ml aliquot of the extracted sample is then added to 50ml of RO water and place on the instrument autosampler. Historically some client samples are known pure product of a mixture of pure products. These samples

are extracted at a higher level (5 g of sample to 10ml of MeOH) and diluted greater than 50X.

13.2.3 Section 13.6.3 describes loading the autosampler and the software that controls it.

13.3 Preparation of soil by 5035A

13.3.1 Low level

13.3.1.1 A 40mL VOA vial with a magnetic stir bar and sodium bisulfate (preservative) is weighed and documented to the nearest 0.01g before shipment to client. The sodium bisulfate may be omitted if the sample reacts with the preservative.

13.3.1.2 Vials are returned to the laboratory by the client on dry ice.

13.3.1.3 Before analysis, the analysts must weigh the VOA vial with sample to the nearest 0.01g and documents the weight of the sample.

13.3.1.4 The vial is loaded into the automatic sampler.

13.3.1.5 Section 13.6.3 describes loading the autosampler and the software that controls it.

13.3.2 High level

13.3.2.1 A 40mL VOA vial with 10mL of methanol (with meniscus marked) is weighed and documented to the nearest 0.01g before shipment to the client.

13.3.2.2 Vials are packed to maintain a 4°C temperature and returned to the laboratory.

13.3.2.3 Before analysis, the analysts must weigh the VOA vial with sample to the nearest 0.01g and documents the weight of the sample.

13.3.2.4 An aliquot of the methanol is removed from the vial and used to make a dilution. 5mL of the dilution is placed in a new 40mL VOA vial with a stir bar and loaded into the automatic sampler. The lowest dilution factor that can be loaded is 1mL of methanol to 50mL of water. This is the highest concentration of methanol that can go through the instrument without causing damage.

13.3.2.5 Section 13.6.3 describes loading the autosampler and the software that controls it.

13.3 Daily routine startup

13.3.1 Check that there is adequate pressure in all the gas cylinders (helium). Less than 200-psi warrants changing the POD.

13.4.1.1 Turn POD valve off and remove regulator. Place cap on tank and move POD to the empty tank storage area. Choose a new POD of the same gas and replace regulator. Open the valve and check for leaks.

13.4.2 Check columns head pressure using the gauges on the GC control panel.

13.5 Routine maintenance

13.5.1 All maintenance is to be written in the maintenance logbook.

13.5.2 Always vent and cool the detector before replacing the column or performing maintenance where the MS would or could be subjected to the atmosphere.

13.5.3 Basic maintenance includes:

Cleaning and/or Sonnicating sample needle on Precept II/Solotek 72
Baking out trap on 3100 concentrator
Cooling the injection ports and oven to <80°C.
Replacing injection port liner.
Cutting <6'' of column.
Returning oven to normal operating temperatures.
Checking for leaks

13.5.4 Required maintenance

Changing 3100 concentrator trap
Cleaning the MSD
Flushing and baking out transfer lines.

13.6 Software setup and processing

13.6.1 Chemstation is used to collect, store, and analyze GC/MS data. The software is controlled through the main Chemstation software screen where there are various icons for building an instrument sequence, setting up the instrument, building methods, processing data, viewing real time analysis and details of the current analysis, reprocessing data and batch reprocessing as well as comparing chromatograms.

13.6.2 The sequence is the software's blueprint telling the system what to do next, with what method, and what adjustments are necessary to arrive at the final result. The sequence dictates

file names and must be set up prior to analysis. The software is now ready for data acquisition. Use the position and run command found in the sequence menu in the MS Top program.

13.6.3 The Teklink software controls the instrument autosampler and concentrator. Vials are loaded onto the autosampler when they are ready to be analyzed. In the Teklink software you can program the autosampler to run any or all positions in any order. It allows you to specify as "method" which contains stored parameters (purge time, dry purge time, etc..., transfer line temps, trap temps, etc...). It also allows you to choose internal standard/surrogate injection volumes. Once you have set up the sequence correctly, the option to upload it to the instrument is chosen. When all temperatures have met method parameters the Teklink software will allow you to start the sequence. It should be noted that the software also allows you to update or change the sequence in the middle if a need arises to do so.

13.6.4 Run Tune, CCV, Batch QC and samples. See section 11.3.2 for order in which Instrument and batch QC are to be run.

13.6.5 Process samples by going into Enviroquant. Check BFB tuning solution prior to running the CCV. This is accomplished by choosing the tuner menu and selecting "evaluate BFB". Choose "autofind to screen" option. This procedure automatically finds the apex of BFB and averages the three following scans: one scan to the left of the apex, the apex, and one scan to the right, to obtain the spectra for BFB. It then applies the tuning criteria stated in Table 4 of method 8260C and Table 2 of method 624 to determine if a passing spectra has been obtained. If all criteria is met (indicated by a pass/fail list) then the MSD is assumed to be tuned correctly and can continue with section 13.6.6. This method of acquiring BFB is the only acceptable procedure. If the tune fails then the analyst must rerun and reanalyze the tune. Upon a second failing tune corrective action must be taken. These actions may include cleaning the source and/or retuning the MSD.

13.6.6 Evaluate the CCV. Using enviroquant load the CCV data file. Select the ConCal menu and choose "edit continuing calibration criteria". A new screen will appear. Make sure the CCV level correlates to the concentration of the CCV run, usually this is 50ppb. Also make sure that the box labeled "report % difference" is using relative response factors. Click report and name it "R PAGE". Choose OK. Choose ConCal again, edit continuing calibration criteria, except this time choose, calculated concentration instead of relative response factors. Click report and name it "% DRIFT". Choose OK. Open "R PAGE" and "%DRIFT" in Adobe. Make sure that no

more than 20% of the compounds have and RSD of >20%. If the CCV fails the criteria then the analyst may choose to run the CCV again. If the second CCV run also fails the criteria maintenance and/or a new calibration must be performed. Method 624's CCV criterion is defaulted to 8260**C** because initial calibration is verified with the separate source LCS (ICV). See Table 2 for 624 and 8260**C** criteria. Print summary to crate "50 PPB" page by clicking on "Quant", "Generate report", Select "summary" to "Printer". Name the PDF "50 PPB". The macro uses criteria listed in Table 2 to generate a pass/fail column.

13.6.7 Evaluate Batch QC that is analyzed before any samples. The best foolproof way to check passing criteria is to transfer them into the LIMS, which is covered in section 13.9. Pay close attention to the evaluation of the method blank. Monitor, on a daily basis, the level of common solvent contaminants like MeCl2 and Acetone. Delete all hits less than the PQL in the MB.

13.6.8 Evaluate samples. The process of sample evaluation is dictated by the analyte list requested by the client. Despite the test code requested by the client, the analyst reviews the data for all analytes including all TPH regions. Load the data file that is to be processed. Using the Quant menu in enviroquant choose QEdit. This menu brings up a list of all the analytes and allows the analyst to delete false positives and hits below the PQL. It also allows the analyst to compare sample analyte spectra to the spectra of the daily CCV and the NIST spectra. Upon exiting QEdit the analyst is prompted to save or discard changes, choose save. Also inspect the chromatogram for unlabeled peaks by choosing "INT" then "draw chromatogram and label peaks". For any peaks that are not labeled and are considered high enough, double right click on the peak to obtain spectra. Choose "LSC", then "LSC for current scan". This process automatically performs a library search (using NIST) and produces a report with best three hits and an estimated concentration. Save this PDF file to be inserted into the raw data PDF.

13.6.8.1 TPH regions are defined by the five straight chain aliphatic hydrocarbons, pentane, hexane, octane, decane, and dodecane. A TPH region is defined by integrating mass 57 from the end of one hydrocarbon to the other. For instance, the C7 & C8 region is a manual integration of all hydrocarbons eluting after hexane to the end of the octane peak.

13.6.8.2 VOA TPH Fractionation Procedure. VOA fractionation is broken down into four fractions; C6,

C7-C8, C9-C10, and C11-C12 and uses ion 57 as the quantitating ion. The standard has C5, C6, C8, C10, and C12 in it. These hydrocarbons are used to set up the retention time windows for the entire range. For the C6 fraction, the retention time window begins just after C5 and ends just after C6. For the C7-C8 fraction, the retention time window begins just after C6 and ends just after C8. For the C9-C10 fraction, the retention time window begins just after C8 and ends just after C10. For the C11-C12 fraction, the retention time window begins just after C10 and ends just after C12. When quantifying these fractions, everything with a 57 ion in it within the retention time window is integrated. The calibration uses C6, C8, C10, and C12 to calculate the individual fractions. Since the entire range is integrated, there is not an upper limit as there is with every other analyte. A sample is only diluted when one or more peaks within the retention time window have saturated the instrument and have flat topped.

13.7 Adobe Acrobat

13.7.1 Processing data files is done mainly in Adobe as PDF files. After each BFB tuning solution, initial calibration standard, CCV, ICV, Batch QC, or sample data files are processed according to the above mentioned procedures their respective report is generated to the printer. With the default printer selected to Adobe Acrobat these printouts become PDF files. Each one is saved in a unique folder with a unique name.

13.7.2 Initial Calibrations are compiled as follows:

CURVE COVERSHEET
INITIAL CALIBRATION CRITERIA
BFB
REFC (including each analyte's curve plot if using linear regression or quadratic curve fit.)
250
100
50
25
10
5
2
1
LCS/SRM
MB

If an analytical clock was run immediately following the initial calibration then the following pages will be included as well.
QAQC
INJECTION LOG
MS
MSD

13.7.2.1 For LL, the initial calibration is compiled as follows:

CURVE COVERSHEET
INITIAL CALIBRATION CRITERIA
BFB
REFC (including each analyte's curve plot if using linear regression or quadratic curve fit.)
50
20
10
5
4
2
2
0.5
LCS/SRM
MB
If an analytical clock was run immediately following the initial calibration then the following pages will be included as well.
QAQC
INJECTION LOG
MS
MSD

13.7.3 Daily Instrument QC is compiled as follows:

DAILY COVERSHEET
DAILY STD CRITERIA
BFB
DAILY STD (%_RSD_DRIFT combination and std concentration pages)
50 PPB
R PAGE
% DRIFT
LCS
MB
PARENT SAMPLE
MS
MSD
QAQC
INJECTION LOG

13.7.3.1 For LL, daily instrument QC is compiled as follows:

DAILY COVERSHEET
DAILY STD CRITERIA
BFB
10 PPB
R PAGE
% DRIFT
LCS
MB
PARENT SAMPLE
MS
MSD
QAQC
INJECTION LOG

13.8 Creating PDF sets

13.8.1 Enter Adobe Acrobat.

13.8.2 Click on open file icon. Look in the C drive for file folder AA. This file contains a COVERSHEET to be used with every set. Typing CNTL+SHIFT+I will insert the desired page into the PDF folder. Typing CNTL+B will allow you to bookmark or name the page you are currently on. In this way you can create an entire file and save it under ADATA with a unique name.

13.8.3 Page layout should be as follows:

COVERSHEET
FIELD SAMPLES
DAILY PACKAGE
- BATCH QC (MB, LCS, MS, and MSD)
- INSTRUMENT QC (TUNE and DAILY)
- QAQC PAGE
- INJECTION LOG

CALIBRATION CURVE
- TUNE
- REFC
- RAW DATA

13.9 Omega LIMS

13.9.1 All field samples and batch QC are transferred into the AWAL database or Laboratory Information Management System (LIMS).

13.9.2 Click on OMEGA icon and enter name and password. Click on DATA ENTRY BY RUN. Click on ADD. Enter instrument ID as

5973-A, 5973-C or 5973-D according to the correct instrument, date and analyst. Click on DATA IMPORT. Find 5973B under specifications and enter test code. Click OK. Open and find desired file to import. Enter in percent moisture for all soil samples or check that one has imported with the soil sample. Check BATCH ID and Pfac values are correct if an extraction was performed. Go to view data, and calculate sequence. Check all values are correct. Check for flags and add qualifiers and comments to data as necessary.

13.9.3 Check that the MB is less than the PQL for all target compounds.

13.9.4 Check that the LCS, MS and MSD pass all current control limits.

13.9.5 Check the RPD is within current control limits on MSD.

13.9.6 Check that the surrogates pass method control limits.

13.9.7 Check that the Analysis and prep date are correct.

13.9.8 Check that the data is entered for the correct method as requested by the client.

13.9.9 Check the dilution factor is correct.

13.9.10 Check that the PQL's are adjusted for DF and % moisture.

13.9.11 Check that the units are correct.

13.9.12 At this point the analyst must decide if the data is acceptable or if it requires a re-run. Therefore, all this must be completed before the hold time expires.

14.0 Calculations

14.1 When preparing dilution of stock standards use the equation:

$C_1V_1 = C_2V_2$

Where,

C_1= concentration of stock
V_1 = volume of stock
C_2 = concentration of working standard
V_2 = volume of working standard

14.2 The instrument calculates results directly in ppb.

14.3 The technician is responsible for entering the correct extraction specifications into the PREP BATCH REPORT in the LIMS. A unique prep batch number is created for each analytical batch. The technician includes the initial volume used, the spike amount, and the final volume, which the LIMS uses to calculate

the extraction factor for each sample. When importing data, the LIMS automatically transfers this information and uses it to calculate the final result in ppb.

14.4 Calculate the raw spike target or MS targets to check if LIMS is correct:

Target = (amount spiked)(spike concentration) / (initial volume or weight)

14.5 The % moisture is calculated by the inorganic section and entered into the LIMS.

14.6 Manual integrations may **only** be performed when necessary.

14.6.1 The manual integration must take in the full peak (tails and all).

14.6.2 The manual integration when performed must be documented on the raw data (pdf'd) so that they can be reviewed and approved.

14.6.3 The entire batch (samples & QC) must be reviewed to assure manual integration is appropriate i.e. the double peak cut off in the sample is not being recorded in the standard.

15.0 Method performance

15.1 The laboratory tracks precision and accuracy through the plotting of quality control recoveries. The derived limits from these recoveries are updated annually as a minimum.

15.2 Surrogate and matrix spike limits for water and soil sample are updated semi annually by the Organic Supervisor. These limits can be found for each matrix in the LIMS.

16.0 Pollution prevention

16.1 All standards and samples are disposed of according to American West Analytical Laboratories Waste Management SOP.

16.2 Several solvents used in the laboratory are target analytes for this method. To prevent contamination the laboratory has developed the following rules:

16.2.1 Methylene Chloride and acetone may only be used and stored in the organic extraction lab;

16.2.2 The door to organic extraction must remain closed at all times;

16.2.3 The door to the GC/semi room must remain closed at all times and solvents must be kept in a hood.

16.2.4 The door to VOAs must remain closed at all times;

16.2.5 Personnel who have been the organic extraction room, the GC/SEMI room, or have handled solvents are not allowed in the VOA lab.

17.0 Data assessment and acceptance criteria for quality control measures

17.1 The method blank result must be below the laboratory PQL,

17.1.1 If reanalysis within hold time is not possible then the following options are available:

17.1.1.1 Method blank hit is less than 5% of the regulatory limit, or less than 5% of the sample results.

17.1.2 Blank subtraction is not allowed.

17.2 The LCS must recover within laboratory control limits.

17.2.1 must be analyzed every 20 samples or every tune

17.2.2 must be a separate source than the calibration standards

17.2.3 concentration should be low to mid range

17.2.4 The laboratory must generate in house acceptance limits for the LCS. These limits are listed in the LIMS.

17.2.5 When a calibration is run the second source routinely used as an LCS will be used for an ICV and must pass the criteria in 17.2.5.1.

17.2.5.1 The average percent recovery for all analytes including surrogates must be within the recovery limits set up in the LIMS.

17.3 The matrix spikes should recover within laboratory control limits.

17.3.1 must be analyzed every 20 samples

17.3.2 must be a separate source than the calibration standards

17.3.3 concentration should be low to mid range

17.3.4 Recoveries should be within limits listed in the LIMS. If there are outliers then careful inspection of the MS and MSD will determine if there is matrix effect occurring. If it is determined that there is matrix effect for the matrix spikes and the LCS passes criterion then the MS/MSD can be qualified in the LIMS. If a data qualifier is used for matrix effect on the MS/MSD then a DQ will also be place on the parent explaining that there were outliers on the MS/MSD

17.3.5 RPD's are also listed in the LIMS.

17.4 Surrogates

17.4.1 Recoveries limits are listed in the LIMS and updated semi annually.

18.0 Corrective actions for out of control data

18.1 If one of the blanks (ICB, CCB, or MB) fails, re-analyze. If the blank still fails, perform one of the following corrective actions:

18.1.1 If the ICB or CCB fails, contamination is suspect. The contamination could be coming from the instrument (column, detector) or the vials. Systematically eliminate the problem. If the problem is found to be, column or detector oriented recalibrate.

18.1.1.1 All instrument maintenance must be recorded in the instruments maintenance log with a calibration reference if applicable or next passing CCV.

18.2 If an ICV or a CCV fails, re-analyze a second time. If the standard fails a second time take appropriate corrective action.

18.2.1 Appropriate corrective action may include:

18.2.1.1 Remaking the calibration standards

18.2.1.2 Baking out trap

18.2.1.3 Running an instrument rinse to get rid of contamination

18.2.1.4 Recalibration

18.3 If the LCS fails, re-analyze a second time. If the standard still fails then corrective action must be taken.

18.4 If the MS or MSD fails and the instrument QC look good, sample matrix is suspected and the final results must be flagged matrix interference.

18.5 If the MSD RPD is out and re-prepping is not an option the results must be flagged non-homogenous.

19.0 Contingencies for handling out of control or unacceptable data

19.1 If reanalysis of samples cannot be performed within 14 days of collection, consult your supervisor immediately for appropriate action.

19.2 If a new sample cannot be obtained, the values reported must be flagged with the appropriate qualifiers.

19.3 If a matrix spike fails, due to matrix interference issues, flag the final report with the appropriate qualifier.

20.0 Waste management

20.1 All solvent waste generated during this procedure must be disposed in the waste solvent container in waste storage area.

20.1.1 Solvent waste must be free of water and non acidic before disposing in the waste container.

20.2 Samples that are pure (gas, paint thinners, oil, etc.) may be disposed in the solvent waste container.

20.3 Samples that are not pure but are heavily contaminated with a volatile or semi volatile should be left in their sample container and placed in the bin marked suspicious samples for disposal.

20.4 Standard vials are placed in the solvent vial collection barrel the waste storage area.

21.0 References

21.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

21.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Volatile Organic Compounds by Gas Chromatography Mass Spectrometry, Method 8260C, Revision 3, August 2006.

21.3 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), method 5035A, Closed System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002.

21.4 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003.

21.5 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. Method 624, Purgeables, 40 CFR, Appendix A, Part 136.

21.6 American West Analytical Laboratories Waste Management and Sample Disposal SOP, Revision 2, 2008.

22.0 Tables and diagrams

22.1 Table 1 Initial Calibration Criteria

8260C Calibration Criteria	**624 Calibration Criteria**
A BFB solution of 50ng must be run and meet the criteria in Table 4. (8260C 7.3.1). The mass spectra of BFB is obtained by three scans (the peak apex and the scans immediately preceding and following	A BFB solution of 50 ng must be run and meet the criteria in Table 2 (method 624). No directions are given in 624 as to how the spectra of BFB should be

the apex) and averaged.	obtained. By default 8260C recommendations will be used (624 10.3)
	All % RSD's must be less then 35% or a curve plot of response ratios may be used (624 7.3.3). Note: method 624 does not give specific criteria for coefficient of determination, but as default we will use method 8000B criteria (7.5.3) of greater then or equal to 0.99.
All % RSD's for each analyte must be less than or equal to 15% or avg. response factors may not be used for quantitation (8260C 7.3.8.1).	There is no minimum response criteria listed in method 624 so again we will default to method 8260C (7.3.5.4)
If the % RSD for any analyte exceeds 15% then a linear regression, or quadratic curve fit may be used with a min of 6 points for a quadratic as long as the coefficient of determination is greater then or equal to 0.99 (8000B 7.5.2/7.5.3).	

22.2 Table 2 Daily CCV

8260C Daily CCV Criteria	624 Daily CCV Criteria
A BFB solution of 50 ng must be run and meet the criteria in Table 4 (8260**C** 7.3.1). The mass spectra of the BFB is obtained by three scans (the peak apex and the scans immediately preceding and following the apex) and averaged (8260**C** 7.3.1.1)	A BFB solution of 50 ng must be run and meet the criteria in Table 2. No directions are given in 624 as to how the spectra of BFB should be obtained. By default 8260 **C** recommendations will be used (624 10.3).
	A passing LCS (QC check sample) containing all analytes of interest is required before sample analysis mat begin. All analytes must pass the QC limits generated in the LIMS which meet or exceed Table 5 limits in the method (624 7.4.3). The LCS is analyzed and evaluated after the CCV has met the criteria listed below.
☞ 90% of the analytes must have a %RSD or % Drift less than or equal to 20%. ☞ Use % RSD if avg. response factors are used to quantitate (8260**C** 7.4.5.1) ☞ Use % Drift only if a regression fit was used to quantitate (8260**C** 7.4.5.1/7.4.5.2)	Because a CCV is not specified for method 624, a CCV will be run and default to method 8260**C** for the CCC's as follows: ☞ 90% of the analytes must have a %RSD or % Drift less than or equal to 20%. ☞ Use % RSD if avg. response factors are used to quantitate (8260**C** 7.4.5.1) ☞ Use % Drift only if a regression fit was used to quantitate (8260**C** 7.4.5.1/7.4.5.2)

23.0 Clarification/Modifications of the method

23.1 Not Applicable

_____ Date_____
Organic Dept. Supervisor

_____ Date_____
Laboratory Director

_____ Date_____
QA/QC Officer

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Chlorinated Pesticides [Method No. 8081B]

Approvals (Signature/Date):

1-20-10	Adam W. Alban 21Jan10
Dennis Jonsrud GC Manager Date	Adam Alban Health & Safety Manager / Coordinator Date
1-21-10	Robert C Hanisch 1/22/10
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1.0 Scope and Application

1.1 This standard operating procedure (SOP) describes the determination of chlorinated pesticides using the methodology described in EPA SW-846 Method 8081B.

1.2 This SOP is applicable to the gas chromatographic (GC) analysis of extracts of soil and water samples. Table 1 lists the compounds that can be determined by this method and their associated routine reporting limits (RLs).

1.3 This SOP does not include the procedures for extracting soil and water samples. Refer to the following SOPs for sample extraction procedures:

DV-OP-0006	Extraction of Aqueous Samples by Separatory Funnel, SW846 3510C
DV-OP-0007	Concentration of Organic Extracts, SW846 3510C, 3520C, 3540C, and 3550C
DV-OP-0016	Ultrasonic Extraction of Solid Samples by SW846 3550C
DV-OP-0015	Microwave Extraction of Solid Samples by SW846 3546

1.4 Analytes, Matrix(s), and Reporting Limits

See Table 1 for analytes and reporting limits by matrix.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Chlorinated pesticides are extracted from a one-liter water sample with methylene chloride using a separatory funnel (Method 3510C). Detailed instructions are given in SOP DV-OP-0006. The methylene chloride extract is exchanged to hexane as described in SOP DV-OP-0007.

2.1.2 Chlorinated pesticides are extracted from a 30-gram soil subsample into a 50:50 acetone-methylene chloride solution by sonication (Method 3550C) or by microwave extraction (Method 3546). The extract is dried and exchanged to hexane. Detailed instructions are given in SOPs DV-OP-0016 and DV-OP-0015.

2.1.3 SOP DV-OP-0007 provides instructions for the concentration and cleanup of sample extracts. Florisil is used to clean extracts that show color. Sulfur is removed if observed. All extracts are in hexane and the final extract volume is 10 mL.

2.2 Analysis

2.2.1 Samples are analyzed using a gas chromatograph equipped with dual columns and dual electron capture detectors (ECDs).

2.2.2 The instrument is calibrated using external standards. Compounds are identified by their retention time on the columns.

2.2.3 Positive results from the primary column are confirmed with a second, dissimilar column. The laboratory maintains a total of four dissimilar columns for additional confirmation capability.

3.0 Definitions

3.1 Single-Component Pesticides: A pesticide formulation that consists of a single chemical compound. Most of the analytes determined by this procedure are single-compound pesticides.

3.2 Multi-Component Pesticides: A pesticide formulation that consists of more than one chemical compound. Toxaphene and Technical Chlordane are production mixtures of multiple compounds. Toxaphene is manufactured by the chlorination of camphenes, which produces a variety of compounds, not all of which are chromatographically resolved. Technical Chlordane is produced by the chlorination of a mixture of camphenes and pinenes.

3.3 Chlordane: As just described, Technical Chlordane (CAS# 12789-03-6) is a mixture of compounds. Method 8081B, Section 11.6.2 notes that it includes at least 11 major components and 30 minor components, and adds "the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch." The laboratory has found that manufacturing lots of Technical Chlordane produced at different times or at different production facilities have different ratios of the key components. For this reason, it is more common to analyze for the major components of technical Chlordane (α-Chlordane, γ-Chlordane, and heptachlor) instead of analyzing for the total mixture. For the purpose of reporting results under this SOP, the following compounds are reported. Alpha-chlordane (cis-chlordane) CAS # 5103-71-9 and gamma-chlordane (trans-chlordane) CAS # 5103-74-2. The laboratory may also report chlordane (not otherwise specified) or, n.o.s under CAS# 57-74-9.

3.4 The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Denver Quality Assurance Manual (QAM).

4.0 Interferences

4.1 Contamination by carryover can occur when a low concentration sample is analyzed immediately following a high concentration sample. It is the laboratory's policy to reanalyze any samples that follow an unusually concentrated sample and that show detectable levels of the same compounds that appeared in the preceding concentrated sample.

4.2 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3 Sulfur will interfere, and, when observed, is removed using cleanup procedures described in SOP DV-OP-0007.

4.4 Soil and water sample extracts are subject to Florisil cleanup when the extracts have noticeable color or whenever there is clear evidence of interferences in the initial sample chromatograms. Florisil removes low- to medium-molecular weight polar organic interferences from sample extracts. One limitation for this cleanup method is that recoveries for the most polar compounds, endosulfan sulfate and endrin aldehyde in particular, will be lower. Florisil has been observed to remove the compound kepone and is not used where the determination of kepone is required. Instructions for performing Florisil cleanups can be found in SOP DV-OP-0007.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.4 The ECD contains a ^{63}Ni radioactive source. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the facility's radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Radiation Safety Officer shall be immediately notified and a letter sent to the Colorado Department of Public Health and Environment.

5.1.5 As a safety precaution, all standards, samples, and extracts are handled in an approved fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the

method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects are exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
(1) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 An analytical system complete with a gas chromatograph and dual ECD (Ni-63) detectors is required. A data system capable of measuring peak area and/or height is required.

6.2 An analytical balance capable of weighing to 0.0100g.

6.3 Computer Software and Hardware

6.3.1 Please refer to the master list of documents and software located on G\QA\Read\Master List of Documents\Master List of Documents and Software.xls for the current software to be used for data processing.

6.4 **Columns**

6.4.1 Primary Column: CLPI, 30 m X 0.32 mm id

6.4.2 Secondary Column: CLPII, 30 m X 0.32 mm id

6.4.3 Additional columns that can be used for confirmation include 30 m X 0.32 mm id DB35-MS or DB-XLB.

6.5 Autosampler vials, crimp-top cap with PTFE-faced septa

6.6 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7.0 Reagents and Standards

Reagents

7.1 Hexane, pesticide grade; each lot tested for purity prior to use per SOP CA-Q-S-001 DV-1.

7.2 Carrier gas, ≥ 99.99999% pure hydrogen or helium

7.3 Make-up gas, ≥ 99.99980% pure nitrogen

Standards

7.4 Standards Verification

All standards are subject to verification using a second-source standard before they are used for sample analysis. This process is described in SOP DV-QA-0015.

7.5 Storage of Stock Standards

7.5.1 Commercial standards are received in flame-sealed ampoules or neat, 100% concentration, solutions. Stock standards are stored refrigerated at ≤ 6 °C. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.5.2 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem. Kepone in particular may demonstrate signs of degradation faster than the other compounds, and/or the expiration date. Endosulfan I and II appear to degrade in the presence of methanol. Gamma-BHC appears to degrade in the presence of acetone.

7.6 Calibration Stock Standards

All calibration stock standards are obtained from commercial sources.

NOTE: The availability of the specific commercial standard solutions upon which the following sections are based may change at any time. As a result, it may be necessary to alter the dilution scheme presented herein to accommodate changes in stock standard concentrations. All such changes are documented in the standards preparation records.

7.6.1 Routine Pesticide AB Mix Stock Standard, 1,000 µg/mL

The routine pesticide AB mix stock standard contains all of the "routine" single-component pesticides, as identified in Table 1 with the addition of Hexachlorobenzene at 100 µg/mL Accustandard APP-9-112 and Mirex at 100 µg/mL Accustandard P-066S.

7.6.2 Surrogate B Mix Stock Standard, 200 µg/mL

The surrogate B mix stock standard contains decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX).

7.6.3 Toxaphene Stock, 100 µg/mL

The Toxaphene stock standard contains a specific production mixture of Toxaphene. This mixture does not necessarily match all possible production mixtures that could be found in the environment. This can present problems for Toxaphene quantitation (see Section 12).

7.6.4 Chlordane Stock, 100 µg/mL

The Chlordane stock contains Technical Chlordane (CAS# 12789-03-6).

7.6.5 Appendix IX Calibration Stock

The Appendix IX stock calibration mixture contains the compounds at the concentrations listed in the following table.

Appendix IX Calibration Stock Standard

Compound	Concentration (µg/mL)
2,4-DDD	100
2,4-DDE	100
2,4-DDT	100
Chlorobenzilate	1,000
Chlorpyrifos	500
Diallate	10,000
Dicofol	1,000
Isodrin	500
Kepone	1,000
Mirex	500

7.6.6 Non-Routine Compounds

Other, non-routine compounds not listed in this section may be requested by a client and may be added to this procedure.

7.6.6.1 In these cases, all stock solutions will be obtained from commercial sources and will be verified with a second-source standard as described in Section 7.4 above.

7.6.6.2 Non-routine standards will be stored and treated as described in Section 7.5 above or as specified by the manufacturer.

7.6.6.3 Subsequent dilutions of specially requested compounds will be determined in a manner consistent with the client's recommendations for number of calibration points, inclusion of reporting limit, and concentration range adequate to represent the linearity of the instrument.

7.6.6.4 These specially requested, non-routine compounds either may be added to the dilution scheme used for routine compounds or may be prepared as a separate calibration.

7.6.6.5 All standards preparation for non-routine compounds shall be documented using the same method that is used for routine compounds.

7.7 Intermediate Level Calibration Standards

7.7.1 Routine Pesticide Mix C Intermediate Calibration Standard, 1.0 µg/mLThe intermediate level calibration standard for routine pesticide compounds

including Hexachlorobenzene and Mirex is prepared by diluting the AB (Section 7.6.1) and B (Section 7.6.2) mix stock standards in hexane as follows (all compounds are the same final concentration):

Mix C Intermediate Calibration Standard

Stock AB (mL)	Stock B (mL)	Hexane (mL)	Final Concentration of Each Pesticide (µg/mL)
0.1	0.5	99.4	1.0

7.7.2 Appendix IX Intermediate Calibration Standard

The Appendix IX intermediate level calibration standard is prepared by diluting 0.5 mL of the Appendix IX stock standard (Section 7.6.5) with hexane to a final volume of 50 mL, which results in the following concentrations:

Appendix IX Intermediate Calibration Standard

Compound	Concentration (µg/mL)
2,4-DDD	1.0
2,4-DDE	1.0
2,4-DDT	1.0
Chlorobenzilate	10.
Chlorpyrifos	5.0
Diallate	100.
Dicofol	10.
Isodrin	5.0
Kepone	10.

7.8 Working Level Calibration Standards

7.8.1 Routine Pesticide AB Mix Working Level Calibration Standards

The following volumes of the 1.0 µg/mL Mix C intermediate standard (Section 7.7.1) are diluted to 100 mL with hexane to produce calibration standards at 6 concentration levels, as summarized in the following table:

AB Mix Working Level Calibration Standards

Level	Volume of Mix C Intermediate Std (mL)	Final Concentration (µg/mL)
1	0.4	0.0040
2	1.0	0.010
3	2.5	0.025
4 *	5.0	0.050
5	7.5	0.075
6	10	0.10

* *This level is used as the Continuing Calibration Verification (CCV) standard. As a result, it may be convenient to make a larger volume of this calibration level, by diluting 12.5 mL of the intermediate standard with hexane to a final volume of 250 mL.*

7.8.2 Toxaphene Working Level Calibration Standards

The following volumes of the 100 µg/mL Toxaphene stock standard (Section 7.6.3) are diluted with hexane to the final volumes indicated in the following table:

Toxaphene Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Final Volume (mL)	Final Concentration (µg/mL)
1	0.010	5.0	0.20
2	0.025	5.0	0.50
3	0.05	5.0	1.0
4 *	0.2	10.0	2.0
5	0.25	5.0	5.0
6	0.5	5.0	10.0
* *This level is used as the CCV standard. To make additional volume of this standard, dilute 0.5 mL of the stock with hexane to a final volume of 250 mL.*			

7.8.3 Chlordane Working Level Calibration Standards

The following volumes of the 100 µg/mL Chlordane stock standard (Section 7.6.4) are diluted with hexane to the final volume indicated in the following table:

Chlordane Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Final Volume (mL)	Final Concentration (µg/mL)
1	0.005	10.0	0.05
2	0.02	10.0	0.20
3	0.05	10.0	0.50
4*	0.10	10.0	1.0
5	0.20	10.0	2.0
* *This level is used as the CCV standard. To make additional volume of this level, dilute 0.5 mL of the stock standard with hexane to a final volume of 250 mL.*			

7.8.4 Appendix IX Working Level Calibration Standards

The following volumes of the Appendix IX intermediate standard (Section 0) are diluted with hexane to a final volume of 1.0 mL. The following table summarizes the final compound concentration ranges for each calibration level. The concentration for each compound at each level is given in Table 3.

Appendix IX Working Level Calibration Standards

Level	Volume of Intermediate Std (mL)	Final Compound Concentration Range (µg/mL)
1	0.005	0.005 - 0.50
2	0.010	0.01 - 1.0
3	0.025	0.025 - 2.5
4 *	0.035	0.05 - 5.0
5	0.050	0.035 - 3.5
6	0.100	0.1 - 10

* *This level is used as the CCV. Because some compounds in this standard are not stable, it is not recommended to make extra volume of the level 4 standard.*

7.9 Second-Source Standards for Initial Calibration Verification (ICV)

The second-source stock standards are purchased from a vendor different from the one that supplied the stock calibration standards

7.9.1 Routine Pesticide AB Mix ICV Stock Standard, 1,000 µg/mL, (with Mirex at 100 µg/mL)

Commercial standards containing all single-component pesticide compounds are obtained from a vendor different from the one that supplied the calibration stock standard. Typically, the standards are obtained from Ultra Scientific (standard PPM-808C for the AB mix, standard EPA-1125 for Hexachlorobenzene, and standard PST-720S for Mirex).

7.9.2 Appendix IX ICV Stock Standard

Commercial standards are obtained at the same concentrations as shown for the calibration stock standards in Section 7.6.5, but from a different vendor (typically Ultra Scientific standard CUS-7007).

7.9.3 Surrogate ICV Stock Standards, 200 µg/mL

Commercial standards (typically Ultra Scientific standard ISM-320) are obtained containing decachlorobiphenyl (DCBP) and tetrachloro-m-xylene (TCMX).

7.9.4 ICV Intermediate Level Standards, 1.0 µg/mL

The intermediate level calibration standard for routine pesticide compounds is prepared by diluting the AB, Hexachlorobenzene, and Mirex, and surrogate stock standards (Sections 7.9.1 and 7.9.3) with hexane to a final volume of 25 mL as summarized in the table below. All compounds in the intermediate standard are at the same final concentration, i.e., 1.0 µg/mL.

Second-Source ICV Intermediate Standard

Vol of AB Stock (mL)	Vol of Mirex Stock (mL)	Vol of Surrogate Stock (mL)	Final Volume (mL)	Final Conc (µg/mL)
0.025	0.25	0.125	25.0	1.0

7.9.5 Routine Pesticide ICV Working Level Standard, 0.025 µg/mL

The working level ICV standard for the routine pesticide compounds is prepared by diluting the ICV intermediate standard (Section 7.9.4) in hexane follows:

Routine Pesticide Second-Source ICV Working Level Standard

Volume of Intermediate Standard (mL)	Final Volume (mL)	Final Concentration (µg/mL)
2.5	100	0.025

7.9.6 Appendix IX ICV Working Level Standard

The working level ICV standard for the Appendix IX compounds is prepared by diluting 0.025 mL of the second-source Appendix IX stock standard (Section 7.9.2) with hexane to a final volume of 100 mL. The following table lists the final concentration of each pesticide:

Appendix IX ICV Working Level Standard

Pesticide	Final Concentration (µg/mL)
2,4-DDD	0.025
2,4-DDE	0.025
2,4-DDT	0.025
Chlorobenzilate	0.25
Chlorpyrifos	0.125
Diallate	2.5
Dicofol	0.25
Isodrin	0.125
Kepone	0.125

7.10 Continuing Calibration Verification (CCV)Standards

The level 4 AB mix working calibration standard (Section 7.8.1) and the level 4 Appendix IX working calibration standard (Section 0) are used as the CCV standards.

7.11 RL Standard

The lowest concentration calibration standard (i.e., Level 1) is used as the RL standard.

7.12 Laboratory Control Standard (LCS) Spike Solution, 0.5 µg/mL

The working LCS spike solution is prepared by diluting 0.125 mL of the AB mix stock standard (Section 7.6.1) in acetone to a final volume of 250 mL in a volumetric flask, as summarized in the table below.

The LCS for batches of aqueous samples is prepared by adding 1.0 mL of the LCS spike solution to one liter of reagent water. The LCS for batches of soil samples is prepared by adding 1.0 mL of the LCS spiking solution to 30 g of Ottawa sand.

LCS Spiking Solution

Volume of AB Mix Stock (mL)	Conc of AB Mix Stock (µg/mL)	Final Volume (mL)	Final Concentration (µg/mL)
0.125	1000	250	0.5

7.13 Matrix Spike (MS) Spike Solution, 0.5 µg/mL

The working matrix spike solution is the same as the LCS spike solution (Section 7.12). Matrix spikes (MS and MSD) are prepared by adding 1.0 mL of the working spike solution to one liter of an aqueous sample or to a 30-gram soil subsample.

7.14 Toxaphene Spike Solution, 2.0 µg/mL

7.14.1 A Toxaphene stock standard solution at a concentration of 1,000 µg/mL is purchased from commercial sources.

7.14.2 The working Toxaphene spike solution is prepared in a 500 mL volumetric flask by adding 1.0 mL of the stock solution and diluting to volume with acetone.

7.14.3 Aqueous LCSs are prepared by adding 1.0 mL of the Toxaphene spike solution to 1.0 liter of reagent water. Soil LCSs are prepared by adding 1.0 mL of the Toxaphene spike solution to 30 grams of Ottawa sand.

7.14.4 Aqueous MS/MSDs are prepared by adding 1.0 mL of the Toxaphene spike solution to 1.0 liter of the selected aqueous sample. Soil sample MS/MSDs are prepared by adding 1.0 mL of the Toxaphene spike solution to 30 grams of the selected soil subsample.

7.15 Surrogate Spike Solution, 0.2 µg/mL

7.15.1 The surrogate stock solution, containing 200 µg/mL each of decachlorobiphenyl and tetrachloro-m-xylene (TCMX), is purchased form commercial sources.

7.15.2 The working surrogate spike solution is prepared in a 500 mL volumetric flask by adding 0.5 mL of the stock solution and diluting to volume with acetone.

7.15.3 For aqueous sample batches, 1.0 mL of the surrogate spike solution is added to each one-liter sample and QC sample. For soil sample batches, 1.0 mL of the surrogate spike solution is added to each 30-gram soil subsample and QC sample.

7.16 Column Degradation Mix (EVAL B)

7.16.1 The DDT/endrin breakdown stock standard solution is obtained from commercial sources, with endrin at a concentration of 1.0 µg/mL, and 4,4'-DDT at 2.0 µg/mL.

7.16.2 The working EVAL B solution is prepared in a 50 mL volumetric flask, by diluting 1.0 mL of the stock solution in hexane, as summarized in the following table:

Column Degradation Mix (Eval B Std) Spike Solution

Compound	Volume of Stock (mL)	Final Volume (mL)	Final Concentration (µg/mL)
Endrin	1.0	50	0.02
4,4'-DDT			0.04

7.17 Primer Mix

The concentration of the column primer mix is not critical. It generally consists of a mixture of CCV, old ICAL standards, and /or old soil LCS extracts. The primer mix is used to initialize the column and does not affect calibration or quantitation.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned, amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, pre-cleaned, wide-mouth jars with a Teflon-lined lid.

8.3 Samples are stored at 4 ± 2 °C.

8.4 Extracts are refrigerated at ≤ 6 °C.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	1 Liter	Cool 4 ± 2°C	7 Days	40 Days from extraction	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 4 ± 2°C	14 Days	40 Days from extraction	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Assurance Program.*

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, *Requirements for Federal Programs.*

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on an instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank for batches of aqueous samples consists of 1.0 liter of reagent water, and for batches of soil samples, consists of 30 grams of Ottawa sand, both of which are free of any of the analyte(s) of interest. The method blank is processed and analyzed just as if it were a field sample.

Acceptance Criteria: The result for the method blank must be less than the reporting

limit for the analyte(s) of interest or less than 10% of the analyte concentration found in the associated samples, whichever is higher. Note that some programs (e.g., AFCEE, Navy, and USACE) require that the maximum blank concentration must be less than one-half of the reporting limit or less than 10% of the lowest sample concentration.

Corrective Action: If target analytes in the blank exceed the acceptance limits, the source of the contamination must be investigated. All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If the analyte was not detected in the samples, then the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.5 Laboratory Control Sample (LCS)

At least one LCS must be processed with each preparation batch. For aqueous sample batches, the LCS consists of reagent water to which the analyte(s) of interest are added at a known concentration. For soil sample batches, the LCS consists of reagent sand to which the analyte(s) of interest are added at a known concentration. See Section 7.12 for the preparation of LCSs. The LCS is carried through the entire analytical procedure just as if it were a sample.

Acceptance Criteria: The recovery results for the LCS must fall within the established control limits. Control limits are set at ± 3 standard deviations around the historical mean. Where required, project-specific limits may be used in place of historical limits. Current control limits are maintained in the LIMS.

When there are more than 11 analytes in the LCS, then NELAC allows a specified number of results to fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

# of Analytes in LCS	# of Allowed MEs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must

be identified and corrective action taken.

Note: Some programs (e.g., South Carolina) do not allow marginal exceedances. Please see the QSAS's in the public folders for the current requirements.

Corrective Action: If LCS recoveries are outside of the established control limits, and the MS/MSD recoveries are also out of control limits then the system is out of control and corrective action must occur. If recoveries are above the upper control limit and the analyte(s) of interest is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Refer to Section 7.13 for preparation of matrix spikes. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

Acceptance Criteria: The recovery results for the MS and MSD must fall within the established control limits, which are set at ± 3 standard deviations around the historical mean. The relative percent difference (RPD) between the MS and MSD must be less than the established RPD limit, which is set at 3 standard deviations above the historical mean. Current control limits are maintained in the LIMS.

Corrective Action: If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of analytical problems, and qualified results may be reported. The situation must be described in an NCM and in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e., method blank, LCS, LCSD, MS, and MSD) is spiked with DCB and TCMX surrogate compounds. Refer to Section 7.15 for preparation of the surrogate spike solution.

Acceptance Criteria: The recovery of each surrogate must fall within established statistical limits, which are set at ± 3 standard deviations around the historical mean.

Corrective Action: If surrogate recoveries in the method blank are outside the established limits, verify calculations, standard solutions, and

acceptable instrument performance. High surrogate recoveries in the blank might be acceptable if the surrogate recoveries for the field samples and other QC samples in the batch are acceptable. Low surrogate recoveries in the blank require re-preparation and reanalysis of the associated samples, unless sample surrogate recoveries are acceptable and targeted compounds are not detected.

For field samples, surrogate recoveries are usually calculated and reported for DCB only. TCMX may also be added, however if two surrogate compounds are analyzed and recoveries calculated, and either surrogate fails to meet acceptance criteria, corrective actions are required. (This also applies to programs that require the use of only one surrogate.)

If surrogate recoveries fail, verify calculations, standard solutions, and acceptable instrument performance. High recoveries may be due to a co-eluting matrix interference, which can be confirmed by examining the sample chromatogram. Low recoveries may be due to adsorption by the sample matrix (i.e., clay particles, peat or organic material in the sample). Recalculate the data and/or reanalyze the extract if the checks reveal a problem.

If matrix interference is not obvious from the initial analysis, it is necessary to re-prepare / reanalyze a sample only once to demonstrate that poor surrogate recovery is due to a matrix effect, as long as it can be shown that the analytical system was in control.

10.0 Calibration and Standardization

10.1 TestAmerica Denver gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.1.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-S-005, *Calibration Curves (General).*

10.1.2 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 2 for typical operating conditions.

10.1.3 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.1.4 Unprocessed calibration data are transferred to the TARGET DB database for processing. After processing the calibration data, print the calibration report and review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration reports are scanned and stored as Adobe Acrobat files on the Public Drive.

10.2 Column Degradation Evaluation

10.2.1 Each day of before operation any calibration or calibration verification standards are analyzed, the column degradation evaluation mix (EVAL B) must be analyzed. In addition, some programs require injection of the degradation evaluation mix more frequently. The degradation check must be performed

whether or not DDT, endrin, or degradation compounds are designated as target analytes. The purpose of the evaluation is to determine whether instrument/column maintenance is needed. The preparation of this standard is described in Section 7.16.

10.2.2 The results of the analysis of the EVAL B standard solution are used to calculate column degradation in terms of DDT percent breakdown (%B) and Endrin %B as follows:

$$\text{DDT } \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100\% \qquad \textit{Equation 1}$$

Where A_{DDD}, A_{DDE}, and A_{DDT} are the peak responses for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT, respectively, in the EVAL B chromatogram.

$$\text{Endrin } \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100\% \qquad \textit{Equation 2}$$

Where A_{EK}, A_{EA}, and A_E are the peak responses for endrin ketone, endrin aldehyde, and endrin, respectively, in the EVAL B chromatogram.

10.2.3 Acceptance Criteria

The %B for each of these two compounds, DDT and endrin, must not be greater than 15%.

10.2.4 Corrective Action

If the breakdown of DDT and/or endrin exceeds the 15% limit, corrective action must be taken. This action may include any or all of the following:

- Replacing the injection port liner or the glass wool.
- Cutting off a portion of the injection end of the column or guard column.
- Replacing the GC column or guard column
- Replacing the y-splitter.

After taking the appropriate corrective action, the degradation evaluation standard must be reanalyzed and must pass acceptance criteria before conducting any calibration events.

10.3 The laboratory uses six calibration levels (as shown in Table 3) for the single-component pesticides. The lowest point on the calibration curve is at or below the reporting limit (RL). The highest standard defines the highest sample extract concentration that may be reported without dilution. The preparation of the calibration standards is described in Section 7.8.

10.4 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.5 Calibration for the multi-peak component analytes, Toxaphene and Technical Chlordane, begins with a single-point calibration at or near the RL. If any multi-peak components are found to be present in the samples, a calibration for the multi-component analyte(s) is conducted with a minimum of five calibration levels. The samples are then reanalyzed using the full calibration curve that brackets the quantitation range.

NOTE: Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems found must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious mis-injection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

- The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e., five levels for calibrations modeled with average calibration factors or linear regressions, or six levels for second-order curve fits.

NOTE: Second order curves are not allowed for South Carolina work.

10.6 External Standard Calibration

External standard calibration involves the comparison of instrument responses (e.g., peak area or peak height) from the target compounds in the sample to the responses of the target compounds in the calibration standards. The ratio of the detector response to the amount or concentration of target analyte in the calibration standard is defined as the calibration factor (CF), as follows:

$$CF = \frac{A_S}{C_S} \qquad \textit{Equation 3}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate in the calibration standard.

C_s = Concentration of the analyte or surrogate, in ng/mL, in the injected calibration standard.

10.7 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors or as calibration curves, using a systematic approach to selecting the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until the calibration acceptance criteria are met.

10.7.1 Linear Calibration Using Average Calibration Factor

Tabulate the peak area response for each target analyte in each calibration level against the concentration injected. For each analyte in each calibration

standard, calculate the calibration factor (CF) as shown in Equation 3 above. The calibration factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

For each target analyte, calculate the average calibration factor as follows:

$$AverageCalibrationFactor = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n} \qquad \textit{Equation 4}$$

Where:

CF_i = Calibration factor for the ith calibration level.

n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{CF}} \times 100\% \qquad \textit{Equation 5}$$

Where SD is the standard deviation of the average CF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)^2}{n-1}} \qquad \textit{Equation 6}$$

10.7.2 Evaluation of the Average Calibration Factor

The calibration relationship can be graphically represented as a line through the origin with a slope equal to the average calibration factor. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Note: The use of grand average (evaluation of the average response over all the compounds) is no longer allowed. Each compound must meet the RSD criteria.

Acceptance Criteria: The RSD must be ≤ 20%.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.7.3 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not necessarily pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). A weighted least squares regression may be used if at least three multi-point calibrations have been performed. The weighting used is the reciprocal of the square of the standard deviation. The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b \qquad \textit{Equation 7}$$

Where:

- y = Instrument response (peak area or height).
- x = Concentration of the target analyte in the calibration standard.
- a = Slope of the line.
- b = The y-intercept of the line.

For an external standard calibration, the above equation takes the following form:

$$A_s = aC_s + b \qquad \textit{Equation 8}$$

To calculate the concentration in an unknown sample extract, the regression equation (Equation 6) is solved for concentration, resulting in the following equation, where C_s is now C_e, the concentration of the target analyte in the unknown sample extract.

$$C_e = \frac{A_e - b}{a} \qquad \textit{Equation 9}$$

Where:

- A_s = Area of the chromatographic peak for the target analyte in the calibration standard.
- A_e = Area of the chromatographic peak for the target analyte in the sample extract.
- a = Slope of the line as determined by the least-squares regression.
- C_s = Concentration of the target analyte in the calibration standard.
- C_e = Concentration of the target analyte in the sample extract.
- b = Intercept of the line as determined by the least-squares regression.

10.7.4 Linear Regression Evaluation

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of a weighted regression over the use of an unweighted regression."

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than the reporting limit, and preferably less than the MDL.

Also examine the residuals, paying particular attention to the residuals at the low end of the curve. If the intercept or the residuals are large, a second-order regression should be considered.

The linear regression must have a correlation coefficient (r) ≥ 0.990. Some programs (e.g., AFCEE, DoD) require a correlation coefficient ≥ 0.995.

Corrective Action: If the correlation coefficient falls below the acceptance limit, linear regression cannot be used and a second-order regression should be attempted.

10.7.5 Non-Linear Calibration

When the instrument response does not follow a linear model over a sufficiently wide working range, or when the previously described calibration approaches fail acceptance criteria, a non-linear, second-order calibration model may be employed. The second-order calibration uses the following equation:

$$y = ax^2 + bx + c \qquad \textit{Equation 10}$$

Where a, b, and c are coefficients determined using a statistical regression technique; y is the instrument response; and x is the concentration of the target analyte in the calibration standard.

10.7.6 Non-Linear Calibration Evaluation

A minimum of six points must be used for a second-order regression fit.

Acceptance Criteria: The coefficient of determination must be ≥ 0.990.

Second-order regressions should be the last option. Note that some programs (e.g., South Carolina) do not allow the use of second-order regressions.

Before selecting a second-order regression calibration model, it is important to ensure the following:

- The absolute value of the intercept is not large relative to the lowest concentrations being reported.
- The response increases significantly with increasing standard concentration (i.e., the instrument response does not plateau at high concentrations).

- The distribution of concentrations is adequate to characterize the curvature.

Corrective Action: If the coefficient of determination falls below the acceptance limit and the other calibration models are unacceptable, the source of the problem must be investigated and the instrument recalibrated. Third-order regressions are not allowed at TestAmerica Denver.

10.8 Initial Calibration Verification (ICV), 0.025 µg/mL for most compounds

A mid-level standard that is obtained from a source different from that of the calibration standards (second-source standard) is used to verify the initial calibration (see Section 0). The ICV standard is analyzed immediately following the initial calibration (ICAL).

Acceptance Criteria: The result for the target analyte(s) in the ICV standard must be within ± 20% of the expected value(s).

Corrective Action: If this is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then repeat the ICAL.

10.9 Calibration Verification

10.9.1 12-Hour Calibration Verification

The 12-hour calibration verification sequence consists of, at a minimum, an instrument blank and the mid-level calibration standard. The 12-hour calibration verification sequence must be analyzed within 12 hours of the initial calibration and at least once every 12 hours thereafter when samples are being analyzed.

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.9.2 Continuing Calibration Verification (CCV), 0.05 µg/mL for most compounds

It may be appropriate to analyze a mid-level standard more frequently than every 12 hours. The mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard (see Section 7). At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCSs, and method blanks. Some programs, specifically drinking water programs, require a CCV after every 10 samples to minimize the number of samples requiring re-injection when QC limits are exceeded. If 12 hours elapse, analyze the 12-hour standard sequence instead.

10.9.3 RL Standard

It may also be appropriate to analyze a standard prepared at or very near the reporting limit (RL) for the method at the end of the analytical sequence, as a minimum (see Section 7.11). This standard can be used to rule out false negatives in client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The results for the RL standard are not evaluated unless the previous CCV fails acceptance criteria.

10.9.4 Acceptance Criteria for Continuing Calibration Verification (CCV)

10.9.4.1 Detected Analytes (≥/= RL)

For any analyte detected at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the preceding and following CCVs (i.e., bracketing CCVs) or 12-hour calibration, on the column used for quantitation, must be within ± 20% if an average curve fit is used. For other curve fits (i.e. linear or 2nd order) see DV-QA-027P ehich reduces the allowed %D to 15%.

In some cases, the nature of the samples being analyzed may be the cause of the failing %D. When the %D for an analyte falls outside of ± 20% in the CCV, and that analyte is detected in any or all of the associated samples, then those samples must be reanalyzed (at a dilution if column damage is eminent) to prove a matrix effect. If the drift is repeated in the reanalysis, the analyst must generate an NCM for this occurrence to explain that the drift was most likely attributable to the sample matrix and that the samples may be diluted and reanalyzed to minimize the effect if so desired by the client.

Refer to Section 12 for which result to report.

In cases where additional compounds are to be analyzed in conjunction with compounds defined by this method and that are not defined in the scope and application of method 8081B different CCV acceptance criteria may apply. Kepone is not recommended by method 8081B and the CCV acceptance criteria is defined as +/- 53%. Further these additional compounds will not be used in grand mean calculations as discussed in section 10.9.4.2.

The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100 \qquad \textit{Equation 11}$$

10.9.4.2 Analytes Not Detected (< RL)

For any analyte not detected in client samples, the %D for that analyte in the bracketing CCVs should also be within ± 20% an average curve fit or within 15% for other curve fits. Method 8081B references method 8000 for compounds with curve fits other than an average curve fit and the criteria in table 6 applies to those compounds. See also DV-QA-027P for further evaluation criteria. Any deviation for the calibration criteria outlined in this procedure must be documented in an NCM.

However, the analysis is acceptable if the average of the %D values for all the analytes is within ± 20% and the %D for any individual analyte is within ± 30%. The average %D is calculated by summing all the %D results in the calibration and dividing by the number of analytes. If an average %D is used and the %D for any individual analytes falls outside of ± 30%, then additional evaluation is needed as summarized in Table 6.

10.10 Retention Time Windows

Retention time (RT) windows must be determined for all analytes.

10.10.1 Determine new RT windows each time a new column is installed or annually, whichever is most frequent.

10.10.2 Make an injection of all analytes of interest each day over a 72-hour period.

10.10.3 Calculate the mean and standard deviation for the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \quad SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RT_i - \overline{RT}\right)^2}{n-1}}$$

Equations 12 & 13

Where:

RT_i = Retention time for the ith injection.

n = Number of injections (typically 3).

SD = Standard deviation.

NOTE: For the multi-component analytes, Toxaphene and Technical Chlordane, the mean and standard deviation must be calculated for each of the 3 to 6 major peaks used for sample calculations.

10.10.4 Set the width of the RT window for each analyte at ± 3 standard deviations of the mean RT for that analyte.

10.10.5 The center of the RT window for an analyte is the RT for that analyte from the last of the three standards measured for the 72-hour study.

10.10.6 The center of the window for each analyte is updated with the RT from the level 4 standard of the ICAL, or the CCV at the beginning of the analytical sequence. The width of each window remains the same until new windows are generated following the installation of a new column, or in response to an RT failure. The RT window width may be expanded if the RT drift observed in the ICAL is greater than the established window. The expanded window is noted on the ICAL checklist.

10.10.7 If the RT window as calculated above is less than ± 0.01 minute, use ± 0.01 minute as the RT window. This allows for slight variations in retention times caused by sample matrix.

11.0 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.3 Sample Preparation

11.3.1 Sample preparation for aqueous samples is described in SOP DV-OP-0006.

11.3.2 Sample preparation for solid samples is described in SOPs DV-OP-0016 and DV-OP-0015.

11.3.3 Cleanup and concentration of sample extracts are described in SOP DV-OP-0007.

11.3.4 The final extract volume in hexane is 10 mL.

11.3.5 Use hexane to dilute sample extracts, if necessary.

11.4 Gas Chromatography

Chromatographic conditions for this method are presented in Table 2. Use the ChemStation interface to establish instrument operating conditions for the GC. Raw data obtained by the ChemStation software is transferred to the TARGET DB database for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the TARGET DB software.

11.5 Sample Introduction

All extracts and standards are allowed to warm to room temperature before injection. An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract. Samples, standards, and QC samples must be introduced using the same procedure. Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

11.6 Analytical Sequence

An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification. Refer to Table 3 for the calibration levels used.

11.6.1 Prior to analyzing any calibration or calibration verification standards, the column degradation evaluation standard is injected and the results are evaluated as described in Section 10.2.

11.6.2 The daily calibration verification includes analysis of the 12-hour calibration sequence (Section 10.9.1) and updating the retention time windows (see Section 10.10).

11.6.3 If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration verification.

11.6.4 The following is a typical analytical sequence:

- Primer
- Hexane blank
- Eval B Std (column degradation evaluation)
- Daily initial CCVs

- LCS
- Method Blank
- 10 samples
- CCVs
- Followed by cycles of 10 samples and CCVs as needed
- Closing CCV

11.7 Daily Retention Time Windows

The center of the retention time (RT) windows determined in Section 10.10 are adjusted to the RT of each analyte as determined in the 12-hour calibration verification. The centers of the RT windows must be updated at the beginning of each analytical sequence and with each 12-hour calibration, but not for any other calibration verification standards.

11.8 Upon completion of the analytical sequence, transfer the raw chromatography data to the TARGET DB database for further processing.

11.8.1 Review chromatograms online and determine whether manual data manipulations are necessary.

11.8.2 All manual integrations must be justified and documented. See DV-QA-011P requirements for manual integration.

11.8.3 Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

11.8.4 Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

11.9 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD.

11.9.1 Perform a level 1 data review and document the review on the data review checklist (GC and HPLC Data Review Checklist).

11.9.2 Submit the data package and review checklist to the peer reviewer for the level 2 review. The data review process is explained in SOP DV-QA-0020.

12.0 Calculations / Data Reduction

12.1 Qualitative Identification

12.1.1 Tentative identification of an analyte occurs when a peak is found on the primary column within the RT window for that analyte, at a concentration above the reporting limit, or above the MDL if qualified data (J flags) are to be reported. Identification is confirmed if a peak is also present in the RT window for that analyte on the second (confirmatory) column and if the analyte concentration is greater than the MDL. When confirmation is made using a

second column, the analysis on the second column must meet all of the QC criteria for continuing calibration verification and RTs.

12.1.2 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2 Dual-Column Quantitation and Reporting

12.2.1 Each sample is analyzed on two different columns at the same time. The laboratory designates a primary column based on optimal separation of the compounds of interest and other desirable chromatographic characteristics. The result from the primary column is normally reported. The result from the secondary (confirmatory) column is reported if any of the following is true:

- There is obvious chromatographic interference on the primary column.
- The difference between the result for the primary column and the result for the secondary column is > 40% and chromatographic interference is evident.

12.2.2 Dual Column Results With > 40% RPD

12.2.2.1 If the relative percent difference (RPD) between the responses on the two columns is greater than 40%, the higher of the two results is reported unless there is obvious interference documented on the chromatogram.

12.2.2.2 If there is visible positive interference, e.g., co-eluting peaks, elevated baseline, etc., for one column and not the other, then report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.

12.2.2.3 If there is visible positive interference for both columns, then report the lower of the two results with the appropriate flag, footnote, and/or narrative comment in the final report.

12.2.2.4 The RPD between two results is calculated using the following equation:

$$\%RPD = \frac{|R_1 - R_2|}{\frac{1}{2}(R_1 + R_2)} \times 100\% \qquad \textit{Equation 14}$$

Where R_1 is the result for the first column and R_2 is the result for the second column.

12.3 Multi-Component Analytes (Toxaphene and Technical Chlordane)

12.3.1 Qualitative Identification

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the

compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3.2 Quantitation of Toxaphene

12.3.2.1 While Toxaphene contains a large number of compounds that produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. The unresolved complex mixture results in a "hump" in the chromatogram that is characteristic of the Toxaphene mixture of compounds. The resolved peaks are important for the identification of the mixture, and the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

12.3.2.2 To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the RTs of the first and last eluting Toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

12.3.2.3 Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. Using a subset of 4 to 6 peaks for quantitation provides results that agree well with the total peak approach and may avoid difficulties when interferences with Toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT.

12.3.2.4 When Toxaphene is determined using the 4 to 6 peaks approach, care must be taken to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms.

12.3.2.5 The chosen peaks must be within the established retention time. If there is an interference that affects the accuracy of results, the analyst may use as few as 4 major peaks. The same peaks that are used for sample quantitation must be used for calibration.

12.3.2.6 The heights or areas of the chosen peaks should be summed together to determine the Toxaphene concentration.

12.3.2.7 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: USACE projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.3.3 Quantitation of Technical Chlordane

12.3.3.1 Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. Cis-Chlordane (or α-Chlordane) and trans-Chlordane (or γ-

Chlordane) are the two most prevalent major components of Technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

12.3.3.2 When the GC pattern of the sample resembles that of Technical Chlordane, Chlordane may be quantitated by comparing the total area of the Chlordane chromatogram using 3 to 5 major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.

NOTE: Octachlor epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.

12.3.3.3 To measure the total area of the Chlordane chromatogram, construct the baseline of Technical Chlordane in each calibration chromatogram between the RTs of the first and last eluting Technical Chlordane components. Use this area and the mass or concentration of Technical Chlordane in each calibration standard to establish the calibration function (Section 10.7). Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration function to calculate the concentration in the sample extract.

12.3.3.4 When the GC pattern of Chlordane in a sample differs considerably from that of the Technical Chlordane standard, it may not be practical to relate a sample chromatogram back to the Technical Chlordane standard chromatogram. In these cases, all identifiable Chlordane components may be summed and reported as "Chlordane (not otherwise specified, CAS number 57-74-9)."

12.3.3.5 A third option for quantitating Technical Chlordane is to quantitate the peaks for α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

NOTE: CHD Flag section 12.6.2

12.3.3.6 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: USACE projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.4 Surrogate recovery results are calculated and reported for DCB. TCMX may also be added, however if the two surrogate compounds are analyzed, and recoveries are calculated, and either surrogate fails to meet control limits, corrective actions are required (this also applies to programs that require the use of only one surrogate). See section 9.7 for further details.

12.5 Calibration Range and Sample Dilutions

12.5.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover, unless other objective evidence indicates that the detection is not the result of carryover. Such evidence may include an observation where carryover was not observed when samples or blanks were analyzed after another sample with similar high compound recovery or when the detection in the sample with suspected carryover is much higher than the expected amount of carryover (i.e. the sample's concentration may be similar to or higher than the concentration found in the previous sample). It may also be necessary to dilute samples because of matrix interferences.

12.5.2 If the initial diluted run has no hits or hits below 20% if the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.5.3 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

12.5.4 Reporting Dilutions

Some programs (e.g., South Carolina and AFCEE) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

12.6 Interferences Observed in Samples

12.6.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

12.6.2 Suspected Negative Interferences

If peak detection is prevented by interferences, further cleanup should be attempted (see SOP DV-OP-0007). Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

If the individual isomers of chlordane are identified, but there is no pattern for the confirmation of "Technical Chlordane", and the project has ONLY technical chlordane requested, the results for technical chlordane should be qualified ("CLD") by the analyst to indicate the presence of the chlordane isomers.

12.6.3 Suspected Positive Interferences

If no further cleanup is reasonable and interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the project. Use of additional confirmation columns is another possible option, however caution is warranted in order to rule out false negatives. At a minimum, the Data Review Template prepared by the analyst should include the following comment for inclusion in the case narrative:

" *Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.*

Date _____ *Analyst* _____"

Sample dilution may be the only acceptable recourse to resolve detections when large amounts of non target matrix are observed.

12.7 Calculations

12.7.1 LCS and Surrogate Spike Recovery Calculation

LCS and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100\% \qquad \textit{Equation 15}$$

12.7.2 MS and MSD Recovery Calculation

Matrix spike recoveries are calculated as follows:

$$\text{MS or MSD } \%\text{Recovery} = \left(\frac{SSR - SR}{SA}\right) \times 100\% \qquad \textit{Equation 16}$$

Where:

SSR = Measured concentration in spiked sample.

SR = Measured concentration in unspiked sample.

SA = Concentration of spike added to sample.

12.7.3 MS/MSD RPD Calculation

The relative percent difference between the MS and MSD is calculated as follows:

$$\%RPD = \frac{|R_1 - R_2|}{\frac{1}{2}(R_1 + R_2)} \times 100\% \qquad \textit{Equation 17}$$

Where *R1* is the result for the MS and *R2* is the result for the MSD.

12.7.4 Concentration of Analyte in the Sample Extract

Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10.7 for details on establishing the calibration function):

Average Calibration Factor: $C_e = \frac{A_s}{CF}$ *Equation 18*

Linear Regression: $C_e = \frac{[A_s - b]}{a}$ *Equation 19*

Non-Linear Regression: $C_e = f(A_s)$ *Equation 20*

Where:

C_e = Concentration of the analyte in the sample extract (ng/mL).

A_s = Peak area for the analyte in the sample extract injection.

b = y-intercept of the calibration fit.

a = Slope of the calibration fit.

$f(A_s)$ = Mathematical function established by the non-linear regression.

12.7.5 Concentration of Analyte in Original Sample

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF$$ *Equation 21*

Where:

C_{sample} = Concentration of analyte in original sample (µg/L or µg/kg).

C_e = Concentration of analyte in sample extract injected in GC (ng/mL).

$1000\frac{ng}{\mu g}$ = Factor to convert ng/mL to µg/mL.

V_e = Volume of sample extract (mL).

V_s = Volume (or weight) of original sample (L or kg).

DF = Dilution Factor (post extraction dilutions)

12.8 All data are subject to two levels of review, which is documented on a checklist, as described in SOP DEN-QA-0020.

13.0 Method Performance

13.1 Initial Demonstration of Capability

An initial demonstration of capability for each method must be performed prior to analyzing samples.

13.1.1 For the standard analyte list, the initial demonstration consists of the preparation and analysis of a QC check sample (e.g., LCS) containing all of the standard analytes for the method, as well as a method detection limit (MDL) study (described in Section 13.2 below).

13.1.2 Four aliquots of the QC check sample are analyzed with the same procedures used to analyze samples, including sample preparation.

13.1.3 The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria (e.g., LCS control limits). All four results must meet acceptance criteria before the method can be used to analyze samples.

13.1.4 For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is successful analysis of an extracted standard at the reporting limit and a single point calibration.

13.2 Method Detection Limit (MDL)
An initial method detection limit study is performed for each analyte and each sample matrix type in accordance with Policy DV-QA-005P. An MDL verification is performed once a year to satisfy NELAC 2003 requirement. For DoD, AFCEE, and DOE projects, an MDL verification is performed quarterly. MDLs are stored in the LIMS.

13.3 Analyst Training and Qualification

13.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.3.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

14.0 Pollution Control

Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

15.2 The following waste streams are produced when this method is carried out:

15.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

15.2.2 Expired extract vial waste - Waste Stream A

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

16.0 References

16.1 Method 8081B, Organochlorine Pesticides by Gas Chromatography, Revision 2, February, 2007, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.2 Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

17.0 Method Modifications:

Item	Method xx	Modification
1	8081B	Method 8081B includes an internal standardization option. Because of the high probability of interferences affecting internal standards, this SOP allows only external standards.
2	8081B	Section 11.4.1.1, allows the use of a single-point calibration for the multi-component pesticides. In this SOP an initial single-point calibration is used, but a five-point calibration followed by reanalysis of associated samples is required when one of the multi-component pesticides is detected.
3	8081B	Method 8081B references 8000B, which allows the use of third-order calibration curves. TestAmerica Denver does not allow third-order curves.

18.0 Tables

Table 1: Analyte List and Standard Reporting Limits
Table 2: Typical Instrument Conditions

Table 3: Calibration Levels ((µg/mL)
Table 4: Column Degradation Evaluation Mix
Table 5: LCS/Matrix Spike and Surrogate Spike Levels
Table 6: Evaluation Criteria and Corrective Actions for Continuing Calibration Verification

19.0 Revision History

- Revision 0.1, dated 26 January 2010
  - Updated SOP references – DV-OP-0009 to DV-OP-0016, S-T-001 to CA-Q-S-001 DV-1, DV-QA-003 to DV-QA-003P, DV-QA-024 to DV-QA-024P, DV-QA-0033 to DV-QA-011P.
  - Removed DBPP references.
  - Changed 10.2.3 to read greater than instead of less than.
  - Changed section reference in 10.9.2 from section 0 to section 7.
  - Revised section 10.9.4.1 and 10.9.4.2
  - Removed section 12.4
  - Revised section 12.5.1

- Revision 0.1, dated 31 December 2009
  - Added criteria to section 9.5 stating that marginal exceedances are not allowed in all programs.
  - Added a not to Table 6 stating that average percent differences are not allowed in all programs when evaluating calibration verification standards.

- Revision 0, dated 01 November 2008
  - Initial Release

Table 1. Analyte List and Standard Reporting Limits

Compound	Water Reporting Limit (µg/L)	Soil Reporting Limit (µg/kg)
Aldrin	0.05	1.7
α-BHC	0.05	1.7
β-BHC	0.05	1.7
δ-BHC	0.05	1.7
γ-BHC (Lindane)	0.05	1.7
α-Chlordane	0.05	1.7
γ-Chlordane	0.05	1.7
Chlordane (technical)	0.5	17
Chlorobenzilate*	0.10	3.3
Chlorpyrifos*	0.05	1.7
2,4'-DDD*	0.05	0.33
4,4'-DDD	0.05	1.7
2,4'-DDE*	0.05	0.33
4,4'-DDE	0.05	1.7
2,4'-DDT*	0.05	0.33
4,4'-DDT	0.05	1.7
Diallate*	1.0	33.
Dicofol*	1.0	33.
Dieldrin	0.05	1.7
Endosulfan I	0.05	1.7
Endosulfan II	0.1	1.7
Endosulfan Sulfate	0.05	1.7
Endrin	0.05	1.7
Endrin Aldehyde	0.05	1.7
Endrin ketone	0.05	1.7
Heptachlor	0.05	1.7
Heptachlor Epoxide	0.05	6.7
Isodrin*	0.10	1.7
Kepone**	1.0	33.
Methoxychlor	0.10	3.3
Mirex	0.05	1.7
Toxaphene	5.0	10.

* These are non-routine compounds that require a separate calibration, and are analyzed only upon request.

** The laboratory has some clients with permits requiring kepone by method 8081A and 8081B. However, the method warns that kepone may change form during extraction and shift out of the expected retention time window. Kepone is <u>not</u> recommended by 8081A and 8081B.

Table 2. Typical Instrument Conditions

Parameter	Recommended Conditions*
Injection port temperature	200 °C
Dectector temperature	325 °C
Column 1 (HP6890 GC)	Rtx® CLPI: 30 m X 0.32 mm id, 0.5 µm
Column 2 (HP6890 GC)	Rtx®CLPII: 30 m X 0.32 mm id, 0.25 µm
HP6890 GC Temperature program and inlet pressure Columns 1 and 2	110 °C for 1 minute 35 °C/min to 180 °C 20 °C/min to 200 °C 35 °C/min to 235 °C and hold for 1 minute 25 °C/min to 300 °C and hold for 4 minutes 40 °C/min to 310 °C Pressure 20 psi, pulse to 40 psi for 1 minute
Column 3 (HP6890 GC)	DB-35MS: 30 m X 0.32 mm id, 0.5 µm
Column 4 (HP6890 GC)	DB-XLB: 30 m X 0.32 mm id, 0.5 µm
HP6890 GC Temperature program Columns 3 and 4	110 °C for 1 minute 35 °C/min to 245 °C and hold for 1.5 minutes 25 °C/min to 300 °C and hold for 4 minutes 40 °C/min to 310 °C
Injection	1 or 2 µL
Carrier gas	Hydrogen
Make up gas	Nitrogen, 60 mL/min
Y splitter	Restek or J&W or Supelco glass tee (Siltek)

* Variations in instrument conditions may exist in order to facilitate compound separation or to accommodate matrix effects from sample analysis.

NOTE: 4,4'-DDE and dieldrin are closely eluting pairs on the HP-5 column . Endosulfan II and 4,4'-DDD are closely eluting pairs on the 1701 column. For these reasons, these columns are no longer in use in the laboratory.

Table 3. Calibration Levels (μg/mL)

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Individual Mix AB						
Aldrin	0.004	0.01	0.025	0.05	0.075	0.10
α-BHC	0.004	0.01	0.025	0.05	0.075	0.10
β-BHC	0.004	0.01	0.025	0.05	0.075	0.10
δ-BHC	0.004	0.01	0.025	0.05	0.075	0.10
g-BHC (Lindane)	0.004	0.01	0.025	0.05	0.075	0.10
α-Chlordane	0.004	0.01	0.025	0.05	0.075	0.10
γ-Chlordane	0.004	0.01	0.025	0.05	0.075	0.10
4,4'-DDD	0.004	0.01	0.025	0.05	0.075	0.10
4,4'-DDE	0.004	0.01	0.025	0.05	0.075	0.10
4,4'-DDT	0.004	0.01	0.025	0.05	0.075	0.10
Dieldrin	0.004	0.01	0.025	0.05	0.075	0.10
Endosulfan I	0.004	0.01	0.025	0.05	0.075	0.10
Endosulfan II	0.004	0.01	0.025	0.05	0.075	0.10
Endrin	0.004	0.01	0.025	0.05	0.075	0.10
Endrin Aldehyde	0.004	0.01	0.025	0.05	0.075	0.10
Endrin ketone	0.004	0.01	0.025	0.05	0.075	0.10
Heptachlor	0.004	0.01	0.025	0.05	0.075	0.10
Heptachlor epoxide	0.004	0.01	0.025	0.05	0.075	0.10
Hexachlorobenzene	0.004	0.01	0.025	0.05	0.075	0.10
Methoxychlor	0.004	0.01	0.025	0.05	0.075	0.10
Endosulfan Sulfate	0.004	0.01	0.025	0.05	0.075	0.10
Mirex	0.004	0.01	0.025	0.05	0.075	0.10
Appendix IX Standards						
2,4'-DDD	0.005	0.010	0.025	0.05	0.035	0.10
2,4'-DDE	0.005	0.010	0.025	0.05	0.035	0.10
2,4'-DDT	0.005	0.010	0.025	0.05	0.035	0.10
Chlorobenzilate	0.050	0.10	0.25	0.50	0.35	1.0
Chlorpyrifos	0.025	0.050	0.125	0.25	0.175	0.5
Diallate	0.50	1.0	2.5	5.0	3.5	10.
Dicofol	0.050	0.10	0.25	0.50	0.35	1.0
Isodrin	0.025	0.050	0.125	0.25	0.175	0.5
Kepone	0.050	0.10	0.25	0.50	0.35	1.0
Multicomponent Standards						
Chlordane (Technical)	0.10	0.20	0.50	1.0	2.0	N/A
Toxaphene	0.20	0.50	1.0	2.0	5.0	10.0
Surrogates are included the AB Mix calibration mix at the following levels:						
Tetrachloro-m-xylene	0.005	0.10	0.025	0.05	0.075	0.10
Decachlorobiphenyl	0.005	0.10	0.025	0.05	0.075	0.10

Table 4. Column Degradation Evaluation Mix

Component	Concentration (μg/mL)
4,4'-DDT	0.040
Endrin	0.020

Table 5. LCS/Matrix Spike and Surrogate Spike Levels

Compound	(μg/L)	(μg/kg)
Aldrin	0.5	16.67
α-BHC	0.5	16.67
β-BHC	0.5	16.67
δ-BHC	0.5	16.67
γ-BHC (Lindane)	0.5	16.67
α-Chlordane	0.5	16.67
γ-Chlordane	0.5	16.67
4,4'-DDD	0.5	16.67
4,4'-DDE	0.5	16.67
4,4'-DDT	0.5	16.67
Dieldrin	0.5	16.67
Endosulfan I	0.5	16.67
Endosulfan II	0.5	16.67
Endosulfan Sulfate	0.5	16.67
Endrin	0.5	16.67
Endrin Aldehyde	0.5	16.67
Endrin Ketone	0.5	16.67
Heptachlor	0.5	16.67
Heptachlor Epoxide	0.5	16.67
Methoxychlor	0.5	16.67
Toxaphene (when required)		
Surrogates		
Decachlorobiphenyl	0.2	6.67
Tetrachlor-m-xylene (TCMX)	0.2	6.67

Table 6. Evaluation Criteria and Corrective Actions for Continuing Calibration Verification

Evaluation Criteria for a Specific Analyte				Evaluation / Corrective Actions
Average %D	Individual %D	RL Standard	Client Samples	
N/A	± 15%	N/A	≥ RL	Calibration is verified for the analyte(s) detected in the sample; no action required.
N/A	Outside of ± 15%	N/A	≥ RL	Calibration is not verified for the analyte(s) detected in the sample. The sample must be re-analyzed using a verified calibration.
± 15%	± 30%	N/A	ND	Calibration is acceptable because analytes were not detected in the sample. An NCM is required.
Outside of ± 15%	N/A	N/A	N/A	Calibration is not verified and corrective action must be taken. **NOTE:** The exception to this may be those cases where the client has requested a small subset of the analytes typically measured by the method and the %D for each of those analytes is within ± 15%. Corrective action may include clipping the column, changing the liner, or other minor instrument adjustments, followed by reanalyzing the standard twice. If both results pass acceptance criteria, the calibration may be used to process samples. If the overall average %D still varies by more than ±15%, a new calibration curve must be prepared. Reanalyze any samples that were either preceded by or followed by the failed CCV using a verified calibration.
± 15%	< -30% (low)	Detected	ND	Sample results are acceptable because the RL standard indicates that the analyte would have been detected if present in the sample. Explain in an NCM.
± 15%	< -30% (low)	ND	ND	Analyte was not detected in the RL standard, possibly as the result of a calibration drift in the negative direction, and therefore one cannot be sure that the analyte would have been detected in the sample if present. Reanalyze samples with verified calibration.
± 15%	> +30% (high)	N/A	ND	Sample results are acceptable because the CCV failed high and the analyte was detected in the RL standard, so if the analyte were present in the sample, it would definitely have been detected. Explain in an NCM.

Note: Some programs (e.g., South Carolina) do not allow the average percent difference to be used in evaluating calibration verification standards. Please see the QSAS's in the public folders for the current requirements.

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Polychlorinated Biphenyls (PCBs) by GC/ECD [SW846 Method 8082A]

Approvals (Signature/Date):

Teresa Williams 12/12/08	Adam W. Alban 18 Dec 08
Teresa Williams — Date	Adam Alban — Date
Technical Manager	Health & Safety Manager / Coordinator
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1.0 Scope and Application

This SOP describes the procedure for the determination of concentrations of polychlorinated biphenyls (PCB) as Aroclors using the methodology prescribed in EPA SW-846 Method 8082A.

This procedure is applicable to the analysis of extracts of aqueous, solid, and oil samples. When utilized for the analysis of oils, additional cleanup procedures may be required.

This SOP does not include the procedures for extracting environmental samples. Refer to TestAmerica SOPs DV-OP-0006, DV-OP-0007, and DV-OP-0009 for sample preparation procedures.

This SOP does not include the determination of the concentration of PCB congeners.

1.1 Analytes, Matrix(s), and Reporting Limits

Table 1 lists the specific Aroclors that are determined using this procedure and their associated reporting limits (RLs).

2.0 Summary of Method

2.1 Preparation

2.1.1 Aqueous Samples

PCBs are extracted from a one-liter aqueous sample with methylene chloride using a separatory funnel (SW-846 Method 3510). The extract is evaporated to dryness and exchanged to hexane. The final extract volume is 10 mL. The extraction procedure is detailed in SOP DV-OP-0006.

2.1.2 Solid Samples

PCBs are extracted from solid materials using a 50:50 acetone - methylene chloride mixture and ultrasonic agitation (Method 3550). The extract is evaporated to dryness and exchanged to hexane. The final extract volume is 10 mL. The extraction procedure is detailed in SOP DV-OP-0009.

2.1.3 Oil Samples

Oil samples are typically prepared by diluting 1 gram of sample to a final volume of 10 mL with hexane. The extraction procedure is detailed in SOP DV-OP-0012.

2.1.4 Wipe Samples

Wipes are typically collected using either filter paper or guaze. These samples can then be extracted using the procedure outlined in SOP DV-OP-0009.

2.1.5 Cleanup Procedures

Cleanup options are discussed in Section 4 below. Instructions for performing various cleanup procedures are detailed in SOP DV-OP-0007.

2.1 Analysis

Samples are analyzed using a gas chromatograph with dual electron capture detectors (ECDs). Specific Aroclor mixtures are identified by the pattern of peaks compared to chromatograms of reference standards. The concentrations of Aroclors in the sample extract are determined using an external standard calibration.

3.0 Definitions

3.1 Polychlorinated biphenyls (PCBs): PCBs are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl, with a general chemical formula of $C_{12}H_{10-x}Cl_x$. There are 209 possible congeners.

3.2 Aroclor: PCBs were produced as technical mixtures by the chlorination of biphenyl. Production processes were designed to produce mixtures with characteristic chlorine contents. In the United States, most of the PCBs in the environment are in the form of Aroclors, which were produced by Monsanto from the 1930s through 1977. Each Aroclor mixture is identified by a four-digit number, the first two digits of which indicate the number of carbons in the biphenyl ring, i.e., 12, and the second two of which indicate the weight percent of chlorine. For example, Aroclor 1254 has 12 carbons and 54% by weight chlorine. The exception is Aroclor 1016, which has 12 carbons and 42% by weight chlorine.

> **NOTE**: Each specific Aroclor produces a characteristic gas chromatographic pattern that represents the relative amounts of PCB congeners in the formulation. The formulation of the mixtures from batch to batch was fairly consistent, but never exactly the same. In almost all cases, the gas chromatogram can be used as a fingerprint to identify the specific Aroclor. Exceptions occurred for Aroclors 1254 and 1221. In each case, at least one batch was produced under different conditions, which resulted in an Aroclor mixture with the same approximate chlorine content , but with a significantly different distribution of congeners. These odd batches of 1254 and 1221 produce chromatographic patterns that are very different from the typical formulations. Standards for these odd batch Aroclors can be used to aid in the qualitative identification of Aroclors in environmental samples.

3.3 AR1660: Laboratory designation for the mixture of Aroclors 1016 and 1260.

3.4 AR2154: Laboratory designation for the mixture of Aroclors 1221 and 1254.

3.5 AR3262: Laboratory designation for the mixture of Aroclors 1232 and 1262.

3.6 AR4268: Laboratory designation for the mixture of Aroclors 1242 and 1268.

4.0 Interferences

4.1 Hydrocarbons can co-elute and thereby mask the Aroclor pattern. The laboratory uses acid cleanup with concentrated sulfuric acid to remove hydrocarbons from solid and oil sample extracts, and for water samples when extracts have noticeable color or whenever there is clear evidence of interferences in the initial sample chromatograms. Acid cleanup removes low-to-medium molecular weight polar organic interferences from sample extracts. Detailed instructions for performing acid cleanup are provided in SOP DV-OP-0007.

4.2 Sulfur will interfere and can be removed using procedures described in SOP DV-OP-0007.

4.3 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Any affected samples are re-analyzed.

4.4 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.5 Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD).

Note: A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.4 All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the TestAmerica Denver Radiation Safety Officer and the TestAmerica Corporate EH&S Director shall be immediately notified and a letter sent to the Colorado Department of Public Health and Environment.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating.

NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.

A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Materials with Serious or Significant Hazard Rating

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm (TWA) 125 ppm (STEL)	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hydrogen gas	Explosive	None	The main hazard is flammability. Exposure to moderate concentrations may cause dizziness, headache, nausea, and unconsciousness. Exposures to atmospheres less than 8 to 10% oxygen will bring about sudden unconsciousness, leaving individuals unable to protect themselves. Lack of sufficient oxygen may cause serious injury or death.

(1) Always add acid to water to prevent violent reactions.
(2) Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

6.2 A gas chromatographic system with dual columns and dual ECD (^{63}Ni) detectors, and a data system capable of measuring peak area and/or height.

6.3 Supplies

6.4 **Columns**

6.4.1 Primary Column: CLPI, 30 m x 0.32 mm id, 0.5 µm coating.

6.4.2 Secondary Column: CLPII, 30 m x 0.32 mm id, 0.25 µm coating.

6.4.3 Additional columns that can be used for confirmation include 30m x 0.32mm id HP5 or HP-1701.

6.5 Autosampler vials, crimp caps with PTFE-faced septa.

6.6 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7.0 Reagents and Standards

7.1 Reagents

- Acetone, 99.4% for organic residue analysis. Each lot is tested for purity prior to use per SOP S-T-001.
- Hexane, pesticide grade. Each lot is tested for purity prior to use per SOP S-T-001.
- Carrier Gas: ≥ 99.99999% pure hydrogen
- Make-up Gas: ≥ 99.99980% pure nitrogen

7.2 Standards

7.3 Stock Standards

7.3.1 All standards are subject to verification using a second-source standard before they are used for sample analysis. This process is described in SOP DV-QA-0015.

7.3.2 All standards must be refrigerated at 4 ± 2 °C. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using

7.3.3 Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually from the date of receipt or earlier if the vendor indicates an earlier date.

7.3.4 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. The standards must be replaced at least every six months, or sooner if comparison with check standards indicates a problem.

7.4 PCB and Surrogate Stock Calibration Standards

7.4.1 Stock A

For each of the Aroclors listed in Table 1, a commercially prepared stock standard solution is obtained. Each stock standard contains the specific Aroclor in pesticide-grade hexane (or in some cases, isooctane) at a concentration of 1,000 µg/mL.

7.4.2 Surrogate Stock B

A commercially prepared stock standard solution is obtained that contains the surrogate compounds tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) in acetone, each at a concentration of 200 µg/mL.

7.5 Intermediate and Working Level Calibration Standard Solutions

7.5.1 Stock C (Level 6 Calibration) Standard Solutions

A Stock C standard solution is prepared for the various Aroclors or combination of Aroclors as summarized in the following table. In each case, the Stock C standard solution is also the highest concentration (i.e., Level 6) calibration standard.

Stock C	Recipe	Conc (µg/mL)	Final Vol (mL)	Final Concentrations (µg/mL)	
AR1660	0.1 mL of Aroclor 1016 Stock A	1000	100	Aroclor 1016	1.0
	0.1 mL of Aroclor 1260 Stock A	1000		Aroclor 1260	1.0
	0.025 mL of surrogate Stock B	200		TCMX	0.05
				DCB	0.05
AR2154	0.1 mL of Aroclor 1221 Stock A	1000	100	Aroclor 1221	1.0
	0.1 mL of Aroclor 1254 Stock A	1000		Aroclor 1254	1.0
AR3262	0.1 mL of Aroclor 1232 Stock A	1000	100	Aroclor 1232	1.0
	0.1 mL of Aroclor 1262 Stock A	1000		Aroclor 1262	1.0
AR4268	0.1 mL of Aroclor 1242 Stock A	1000	100	Aroclor 1242	1.0
	0.1 mL of Aroclor 1268 Stock A	1000		Aroclor 1268	1.0
Aroclor 1248	0.1 mL of Aroclor 1248 Stock A	1000	100	Aroclor 1248	1.0

7.5.2 AR1660 Calibration Levels

A total of 6 calibration standards are prepared for AR1660 as summarized in the following table. As needed, the following table can be used to prepare calibration standards for any of the Aroclors, but only the AR1660 calibration standards include the surrogates. In all cases, measured volumes of the Stock C standard are diluted using pesticide-grade hexane to the final volume indicated in the following table.

Level	Vol of Stock C Used (mL)	Final Volume (mL)	Final PCB Conc (µg/mL)	Final Surrogate Conc (µg/mL)*
1	0.5	10	0.050	0.0025
2	1.0	10	0.10	0.005
3	2.5	10	0.25	0.0125
4 (CCV)	50.0	100	0.50	0.025
5	7.5	10	0.75	0.0375
6 (Stock C)			1.0	0.0500

* Surrogates are in the AR1660 calibration solutions only. None of the other Aroclor calibration solutions contain the surrogate compounds.

7.5.3 Working Single-Point PCB Calibration Standards

The Level 4 standard in the table above is used for single-point calibrations of the individual Aroclors. These standards are also used as pattern recognition standards.

7.6 Second-Source Standards for Initial Calibration Verification (ICV)

These standards are purchased from a vendor different from the one that supplied the stock calibration standards.

7.6.1 Second-Source Stock A' Aroclor Standard Solutions

Commercially prepared solutions in pesticide-grade hexane (or isooctane) are routinely obtained for Aroclors 1016 and 1260. The Aroclor concentration in each solution is 100 µg/mL. A second source may be obtained for the other Aroclors, if necessary.

7.6.2 Second-Source Surrogate Stock B' Standard Solution

A commercially prepared solution is obtained containing TCMX and DCB, each at a concentration of 200 µg/mL.

7.6.3 Second-Source Working Level Standards

The working level second-source ICV standard is prepared by combining 0.025 mL of Aroclor 1016 Stock A', 0.025 mL of Aroclor 1260 Stock A', and 0.00625 mL of surrogate Stock B', and diluting to a final volume of 10 mL with pesticide-grade hexane. This results in a concentration of 0.25 µg/mL for each of the Aroclors and 0.125 µg/mL for each of the surrogates. If a second source verification standard is prepared for any of the Aroclors other than the AR1660 mixture, the surrogates are not added.

7.7 Continuing Calibration Verification Standard (CCV), 0.5 µg/mL

The working CCV solution is the same as the Level 4 initial calibration standard, as shown in the table in Section 7.5.2.

7.8 RL Standard

The lowest concentration calibration standard (i.e., Level 1) is used as the RL Standard.

7.9 Laboratory Control Standard (LCS) Spiking Solution (AR1660)

NOTE: The LCS/MS spiking solution is prepared and used as part of the scope of the organic preparation SOPs DV-OP-0006 and DV-OP-0009. The following information is provided for reference only.

The working LCS spike solution is prepared in a 500 mL volumetric flask by combining 1 mL of the Aroclor 1016 Stock A standard and 1 mL of the Aroclor 1260 Stock A standard, and diluting to volume with acetone. The final concentration of each Aroclor is 2.0 µg/mL.

The LCS for a batch of aqueous samples is prepared by adding 1.0 mL of the 2.0 µg/mL LCS spiking solution to one liter of water. The LCS for a batch of soil samples is prepared by adding 1.0 mL of the 2.0 µg/mL LCS spiking solution to 30 grams of Ottawa sand.

7.10 Matrix Spike (MS) Spiking Solution:

The working matrix spike solution is the same as the LCS spike solution. Matrix spike samples are prepared by adding 1.0 mL of the working solution to a second one-liter aliquot of the selected aqueous sample, or to a 30-gram subsample of the selected soil sample. The MS duplicate (MSD) is prepared in the same way using a third aliquot of the selected sample.

7.11 Surrogate Spike Solution

7.11.1 Stock Surrogate Spike Solution:

A commercially prepared solution containing 200 µg/mL each of decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX) in acetone is purchased.

7.11.2 Working Surrogate Spike Solution

NOTE: Samples are spiked with the surrogate compounds during sample preparation, which is described in the organic preparation SOPs DV-OP-0006 and DV-OP-0009. The following information is provided for reference only.

The working surrogate spike solution is prepared in a 500 mL volumetric flask by adding 0.5 mL of the stock surrogate spike solution and diluting to volume with acetone. The surrogate compounds are added to all field and QC samples as follows:

Sample	Sample Volume (L) or Mass (grams)	Vol. of Surrogate Spike Solution Added (mL)
LCS (aqueous)	1 L reagent water	1.0
LCS (solid)	30 g Ottawa sand	1.0
MS/MSD (aqueous)	1 L sample aliquot	1.0
MS/MSD (solid)	30-gram subsample	1.0
Aqueous Sample	1 L sample aliquot	1.0
Solid Sample	30-gram subsample	1.0

7.12 Primer Mix

The primer mix typically consists of a mixture of CCV standards and/or old calibration standards. The concentrations of the components of the primer mix are not critical. The primer mix is injected one or more times prior to analyzing standards and samples to ensure that the chromatographic system is stable, i.e., that retention times are reproducible.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned amber glass bottles fitted with a Teflon-lined caps. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, wide-mouth jars with a Teflon-lined lid.

8.3 Samples are stored at 4 ± 2 °C.

8.4 Water samples must be extracted within 7 days of collection, and soil samples must be extracted within 14 days of collection.

8.5 Sample extracts are refrigerated in the dark at 4 ± 2 °C and analyzed within 40 days from extraction.

9.0 Quality Control

The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Control Program.

9.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.

9.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.3.1 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.4 **Sample QC**

9.5 **Initial Performance Studies**

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 12 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.6 **Batch Definition**

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument. See Policy DV-QA-003P for further details.

9.7 **Method blank**

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water (for aqueous sample batches) or Ottawa sand (for solid sample batches) to which the surrogate compounds are added. The method blank is subject to the entire extraction and analysis process.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above the reporting limit (RL) or above one-tenth of the concentration found in the associated samples. Note that some programs (e.g., AFCEE, Navy, and USACE) require that the maximum blank concentration must be less than one-half of the RL.

Corrective Action: If the method blank exceeds allowable levels, the source of the contamination should be investigated and all associated samples re-extracted and reanalyzed.

9.8 **Laboratory Control Sample (LCS)**

One LCS is prepared and analyzed with each batch of samples. The LCS is

prepared as described in Section 7.8. The LCS is subject to the entire extraction and analysis process.

Acceptance Criteria: The LCS recovery must be within the established control limits. The laboratory's standard control limits are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Current control limits are maintained in the LIMS.

Corrective Action: If recoveries are not within the established limits, the analytical system is out of control and corrective action must occur. All associated samples must be re-extracted and reanalyzed.

9.9 Matrix Spike (MS) and Matrix Spike Duplicate Samples (MSD)

One MS/MSD pair is required with each analytical batch. Note that some programs (e.g., North Carolina and South Carolina) require preparation and analysis of an MS/MSD pair at a 10% frequency. Preparation of the MS is described in Section 7.10. The MSD is another aliquot of the sample selected for the MS that is spiked in the same manner as the MS.

Acceptance Criteria: The MS and MSD recoveries must fall within the established control limits, which are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. The relative percent difference (RPD) between the MS and MSD must be less than the established limit, which is based on statistical analysis of past results, unless otherwise dictated by project requirements. Current control limits are maintained in the LIMS.

Corrective Actions: If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of analytical problems, and qualified results may be reported. The situation must be described in an NCM and in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

If the recovery for any component is outside control limits for both the MS and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.

The MS must be analyzed at the same dilution level as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.10 Surrogates

Each field sample, QC sample, and each calibration standard that is used for the AR1660 initial calibration, is spiked with surrogate compounds decachlorobiphenyl (DCB) and trichloro-m-xylene (TCMX). The surrogate spike solution is prepared as described in Section 7.11.

Acceptance Criteria: The surrogate recoveries must be within the established control limits, which are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise.

Corrective Action: If recoveries of the surrogates in blanks are outside of the control limits, check for calculation or instrument problems. High recoveries might be acceptable if the surrogate recoveries for the samples and other QC in the

batch are acceptable. Low surrogate recoveries in the blank require re-preparation and reanalysis of the associated samples.

For field samples, surrogate recovery is calculated and reported for DCB only. TCMX may also be added. However, if both surrogate compounds are added, and recoveries calculated, and either surrogate fails to fall within the control limits, corrective actions are required (this also applies to programs that require the use of only one surrogate).

If matrix interference is not obvious from the initial analysis, it is only necessary to re-prepare and reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effects, as long as the extraction/instrument system is proven to be working properly.

9.11 Instrument QC

9.12 TestAmerica Denver gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

9.12.1 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 2 for typical operating conditions.

9.12.2 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

9.12.3 Unprocessed calibration data are transferred to the TARGET DB database for processing. After processing the calibration data, print the calibration report and review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration reports are scanned and stored as Adobe Acrobat files on the Public Drive.

9.13 A new calibration curve must be generated initially, after major changes to the system, or when continuing calibration criteria cannot be met. Major changes include installation of new columns.

9.14 Initial Calibration (ICAL)

9.14.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-S-005, *Calibration Curves (General)*.

9.14.2 An external standard calibration using six concentration levels of the AR1660 mixture is routinely performed. (At least five calibration levels are required.) This provides concentration levels for Aroclor 1016, Aroclor 1260, and the surrogate compounds DCB and TCMX.

9.14.3 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

9.14.4 The calibration curves for Aroclors 1016 and 1260 and the surrogate compounds are modeled either as average calibration factors (CF) or as

calibration curves using a systematic approach to selecting the optimum calibration function.

9.14.5 The calibration for each of the other Aroclors (see Table 1) is initially determined using a single, mid-level calibration standard. As needed, the laboratory may generate a multi-point calibration for other commonly detected Aroclors, such as 1221, 1254, and 1248. When additional multi-point calibrations are developed for the other Aroclors, a second-source ICV standard is also analyzed.

NOTE: Samples from sites known to be contaminated with specific Aroclors should be analyzed using a multi-point calibration curve for the identified Aroclors. This information is provided to the analyst through special instructions in the LIMS.

NOTE: Generally, it is NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or the linear range is adjusted accordingly. The only exception is that a level may be removed from the calibration if the reason can be clearly documented, for example a broken vial. A minimum of five levels must remain in the calibration for a linear regression. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration.

9.14.6 The high and low standard for the initial calibration of the AR1660 mixture defines the acceptable quantitation range for all of the Aroclors. If a sample extract contains any Aroclor at a concentration that exceeds the upper range of the calibration, then the extract must be diluted and reanalyzed.

9.14.7 Select 5 major peaks in the analyte pattern (only 3 peaks are usable for Aroclor 1221). Calculate the response of each of the major peaks for each Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be co-eluting with contaminant peaks from the quantitation (i.e. peaks that are significantly larger than would be expected from the rest of the pattern).

NOTE: A minimum of three accurate peaks must be used to quantify an Aroclor.

9.15 External Standard Calibration

External standard calibration involves the comparison of instrument responses from the samples to the responses from the target compounds in the calibration standards. The area (or height) of a peak in a sample chromatogram is compared to the area (or height) of the peak in the standard chromatograms that appears at the same retention time. The ratio of the detector response to the concentration of the target analyte in the calibration standard is defined as the calibration factor (CF) and is calculated as follows:

$$CF = \frac{A_s}{C_s}$$ Equation 1

Where:

A_s = Peak area (or height) of the target analyte in the calibration standard.

C_s = Concentration of the target analyte in the calibration standard (µg/mL).

9.16 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors (CF) or as linear regression curves, using a systematic approach to select the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until calibration acceptance criteria are met.

9.16.1 Linear Calibration Using Average Calibration Factor (CF)

The calibration factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

The average calibration factor is calculated as follows:

$$\text{Average CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$ Equation 2

Where:

CF_i = The calibration factor for the ith calibration level.

n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{CF}} \times 100\%$$ Equation 3

Where SD is the standard deviation of the average RF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}\right)^2}{n-1}}$$ Equation 4

9.16.2 Evaluation of the Average Calibration Factor

Plot the calibration curve using the average CF as the slope of a line that passes through the origin. Examine the residuals, i.e., the difference

between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Acceptance Criteria: The RSD must be ≤ 20%. SW-846 Method 8000B allows evaluation of the grand average across all compounds, but some programs (e.g., AFCEE and South Carolina) require evaluation of each compound individually. Check project requirements.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

9.16.3 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated is the dependent variable (y) and the concentration as the independent variable (x). A weighted least squares regression may be used if at least three multi-point calibrations have been performed. The weighting used is the reciprocal of the square of the standard deviation. The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b \qquad \text{Equation 5}$$

Where:

y = Instrument response (peak area or height).

x = Concentration of the target analyte in the calibration standard.

a = Slope of the line.

b = The y-intercept of the line.

For an external standard calibration, the above equation takes the following form:

$$A_s = aC_s + b \qquad \text{Equation 6}$$

Where:

A_s = Peak area (or height) of the target analyte in the calibration standard.

C_s = Concentration of the target analyte in the calibration standard (µg/mL).

To calculate the concentration in an unknown sample extract, the regression equation 6 is solved for concentration, resulting in the following equation, where C_s is now C_e, the concentration of the target analyte in the unknown sample extract, and A_s is now A_e, the peak area (or height) of the target analyte in the sample extract.

$$C_e = \frac{A_e - b}{a} \qquad \text{Equation 7}$$

9.16.4 Evaluation of the Linear Least-Squares Regression Calibration Function

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of this for weighted regression over the use of an unweighted regression."

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than reporting limit (RL), and preferably less than the MDL.

Also examine the residuals, but with particular attention to the residuals at the bottom of the curve. If the intercept or the residuals are large, the calibration should be repeated since a higher order regression is not allowed for this method.

The linear regression must have a correlation coefficient (r) ≥ 0.99. Some programs (e.g., USACE and AFCEE) require a correlation coefficient ≥ 0.995.

Corrective Action: If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated since a higher order regression is not allowed for this method.

9.16.5 Second-order regressions and polynomial regression fits of third order or higher are not allowed for this method.

9.17 Second-Source Initial Calibration Verification (ICV)

The second-source ICV standard usually consists of Aroclors 1016 and 1260 only. The stock standards are obtained from a source different than that of the standards used for the calibration. The preparation of the ICV standard is described in Section 7.6. The concentration of each Aroclor in the ICV is 0.25 µg/mL; the concentration of each surrogate is 0.125 µg/mL. The ICV standard is analyzed immediately following the initial calibration.

If it is necessary to generate a multi-point calibration for any of the other Aroclors, then an ICV standard containing the specific Aroclor(s) is analyzed immediately following the calibration.

Acceptance Criteria: The result for the target analyte(s) in the ICV standard must be within ± 20% of the expected value.

Corrective Action: If this is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then repeat the ICAL.

9.18 Continuing Calibration Verification (CCV), 0.50 ug/mL.

12-Hour Calibration Verification

The 12-hour calibration verification sequence consists of, at a minimum, an instrument blank and the mid-level calibration standard. The 12-hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter when samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12-hour calibration sequence.

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

9.18.1 Continuing Calibration Verification (CCV), 0.5 µg/mL

It may be appropriate to analyze a mid-level standard more frequently than every 12 hours. The mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard. At a minimum, this is analyzed after every 10 samples, including matrix spikes, LCSs, and method blanks. If 12 hours elapse, analyze the 12-hour standard sequence instead.

9.18.2 RL Standard

9.18.3 It may also be appropriate to analyze a standard prepared at or very near the reporting limit (RL) for the method between every 10 sample injections (see Section 7.8). This standard can be used to rule out false negatives in client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The results for the RL standard are not evaluated <u>unless</u> the previous CCV fails acceptance criteria.

9.18.4 Acceptance Criteria for Continuing Calibration Verification (CCV)

Detected Analytes (≥ RL)

For any analyte <u>detected</u> at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the preceding and following CCVs (i.e., bracketing CCVs) or 12-hour calibration, on the column used for quantitation, must be within ± 20%.

In some cases, the nature of the samples being analyzed may be the cause of a failing %D. When the %D for an analyte falls outside of ± 20% in the CCV, and that analyte is detected in any or all of the associated samples, then those samples must be reanalyzed to prove a matrix effect. If the drift is repeated in the reanalysis, the analyst must generate an NCM for this occurrence to explain that the drift was most likely attributable to the sample matrix and that the samples may be diluted and reanalyzed to minimize the effect if so desired by the client.

Refer to Section 12 for which result to report.

The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100 \qquad \text{Equation 8}$$

Analytes Not Detected (< RL)

For any analyte not detected (ND) in client samples, the %D for that analyte in the bracketing CCVs should also be within ± 20%.

However, if the CCV %D exceeds +20% and the sample results are ND, it still may be possible to report sample results. In this case, the client should be consulted and an NCM written.

If the CCV % D falls below -20% and sample results are ND, but the target analytes are detected in the RL Standard, it may still be possible to report sample results, since the detection of the analyte(s) in the RL Standard indicate that there was sufficient sensitivity to detect the analyte(s) in the samples. In this case, the client should be consulted and an NCM written.

9.19 Retention Time (RT) Windows

Determine the retention time (RT) windows for the 5 major peaks selected for each Aroclor (3 peaks for Aroclor 1221). The AR1016 windows will be used to establish retention time windows for PCBs AR1221, AR1016, AR1232, AR1242, and AR1248. The AR1260 windows will be used to establish retention time windows for PCBs AR1254, AR1260, AR1262, and AR1268.

Determine new RT windows each time a new column is installed.

Inject a standard containing all analytes at least once each day over a 72-hour period.

Calculate the mean and standard deviation of the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RT_i - \overline{RT}\right)^2}{n-1}} \qquad \text{Equations 9 and 10}$$

Where:

RT_i = Retention time for the ith injection.
n = Number of injections (typically 3).
SD = Standard deviation.

The width of the RT window for each analyte is set at ± 3 times the standard deviation of the RTs determined for each analyte over the 72-hour period. For multi-response analytes, use the RT of major peaks.

The center of the RT window for each analyte is the RT from the last of the three analyses of the standard.

The center of the window for each analyte is updated with the RT from the level 4 standard of the ICAL, the CCV at the beginning of the analytical sequence, and with each subsequent 12-hour calibration verification. The width of each window remains the same until new windows are generated following the installation of a new column, or in response to an RT failure.

If the width of the RT window, as calculated above, is less than ±0.03 minute, use ± 0.03 minute as the RT window width. This allows for slight variations in RTs caused by sample matrix.

Acceptance Criteria for Retention Times

The RT for each compound in each CCV analysis must be within the RT windows established by the daily initial CCV.

Corrective Action for Retention Times

If a target analyte falls outside the established RT window in a CCV standard, either adjust the center of the window based on the CCV, or investigate the problem and calculate new RT windows. All samples analyzed after the last acceptable CCV must be reanalyzed.

9.19.1 Sample Retention Time Criteria

The surrogate must fall within the established RT window. Target analyte peaks must be within the established RT window to be reported as such. If the surrogate RT indicates an RT shift, it may be possible to accept a target analyte peak if it has not shifted relative to the surrogate peak.

9.19.2 Daily Retention Time Windows

The center of the retention time windows are adjusted to the retention time of each analyte as determined by the daily initial CCV. The centers of the retention time windows are adjusted at the beginning of each analytical sequence based on the daily initial CCV.

10.0 Procedure

10.1 Sample Preparation

Samples are extracted and prepared for analysis as described in SOPs DV-OP-0006 (aqueous samples) and DV-OP-0009 (solid samples).

10.2 Calibration

10.2.1 Chromatographic conditions for this method are presented in Table 2.

10.2.2 Use the ChemStation interface to establish instrument operating conditions for the GC.

10.2.3 Raw data obtained by the ChemStation software is transferred to the TARGET DB database for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the TARGET DB software.

10.2.4 The instrument is set up and calibrated as described in Section 10 above.

10.3 Sample Analysis

10.3.1 An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract. For dual-column instruments, 2 µL of sample extract are automatically injected onto two columns. For single-column instruments, 1 µL of sample extract is automatically injected onto one column.

10.3.2 Samples, standards, and QC samples must be introduced using the same procedure.

10.3.3 All extracts and standards are allowed to warm to room temperature before injection.

10.3.4 Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

10.4 Analytical Sequence

10.5 An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification. The daily run sequence is documented in a bound log book.

10.5.1 The daily calibration verification includes analysis of the 12-hour calibration sequence and updating the retention time windows.

10.5.2 If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration verification.

10.5.3 Following is the typical analytical sequence for routine sample analysis:

- Primer (Injection of any standard that contains all analytes to establish the stability of the chromatographic system.)
- Hexane instrument blank

- Daily initial CCV (Unless an ICAL is performed, which is immediately followed by the second-source initial calibration verification.)
- 10 sample injections (The first set of samples analyzed usually includes the method blank and the LCS, and may include matrix spikes.)
- CCV
- Followed by cycles of 10 sample injections and a CCV, as needed
- Closing CCV, instrument blank, and RL Standard

10.6 Retention Times

The centers of the retention time windows are updated with the mid point of the initial calibration and each 12 hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

Acceptance Criteria for Retention Times

The retention times of all compounds in each continuing calibration must be within the established retention time windows.

Corrective Action for Retention Times

If retention times doe not fall within the established RT windows, then all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

10.7 When a sample result exceeds the upper calibration range, then that sample extract is diluted to obtain a result in the upper half of the calibration range and reanalyzed. Any samples that were analyzed immediately following the high sample are evaluated for carryover. If the samples had target analyte detections at or above the RL, the samples must be reanalyzed to rule out carryover.

10.8 Upon completion of the analytical sequence, transfer the raw chromatography data to the TARGET DB database for further processing. Review chromatograms online and determine whether manual data manipulations are necessary. All manual integrations must be justified and documented. See DV-QA-0033 for requirements for manual integration. Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature. Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

10.9 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD. Perform a level 1 data review and document the review on the data review checklist (GC and HPLC Data Review Checklist). Submit the data package and review checklist to the Data Review Group for the level 2 review. The data review process is explained in SOP DV-QA-0020.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification of Aroclors

Retention time windows are used for identification of Aroclors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

11.2 Quantitation of Aroclors

Quantitation of Aroclors is accomplished using 5 major peaks (3 peaks for Aroclor 1221). The peaks must be within the established retention time windows. If there is an interference that affects the accuracy of results, the analyst may use as few as 3 major peaks (2 peaks for Aroclor 1221). The same peaks that are used for sample quantitation must be used for standards and QC quantitation.

11.3 Second column confirmation of Aroclors is performed only when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

> **NOTE:** USACE projects require the use of second-column confirmation of Aroclors unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

> **NOTE:** South Carolina requires second column confirmation.

11.4 **Dual Column Quantitation**

11.5 **NOTE:** Dual column quantitation is not routinely performed for PCB analysis. This section is included for those clients/projects that require dual column confirmation.

11.5.1 The result from a designated primary column is normally reported. The result from the secondary column is reported if any of the following is true:

- There is obvious chromatographic interference on the primary column.
- The difference between the result on the primary column and the result on the secondary column is > 40% and chromatographic interference is evident.

- A continuing or bracketing standard fails on the primary column, but is acceptable on the secondary column. However, if the difference between the primary column and secondary column results is > 40% and the primary column calibration verification fails, then the sample must be evaluated for reanalysis.

11.5.2 If the relative percent difference (RPD) between the results on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. The RPD is calculated as follows:

$$\%RPD = \frac{|R_1 - R_2|}{1/2(R_1 + R_2)} \times 100\% \qquad \text{Equation 11}$$

Where R_1 is the result for the primary column, and R_2 is the result for the secondary column.

11.6 Surrogate Recovery

11.6.1 Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB).

11.6.2 In cases where the addition of the surrogate tetrachloro-m-xylene (TCMX) is required, its recovery is calculated and reported. In cases where both surrogates are added, the recovery of each surrogate is evaluated and corrective action must be taken if either surrogate recovers outside of the established control limits and matrix interference is not evident. Depending on project requirements, corrective action may be necessary only if DCB and TCMX are both outside of acceptance limits.

11.7 Calibration Range and Sample Dilutions

11.8 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for any analyte, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

11.8.1 If the initial diluted run has no hits or hits below 20% if the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.8.2 Guidance for Dilutions Due to Matrix Interference

11.8.3 If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated

dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

11.8.4 Reporting Dilutions

11.8.5 Some programs (e.g., South Carolina and AFCEE) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported.

11.9 Interferences in Observed in Samples

11.9.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

11.9.2 Suspected Negative Interferences

11.9.3 If peak detection is prevented by interferences, further cleanup should be attempted. Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.9.4 Suspected Positive Interferences

11.9.5 If no further cleanup is reasonable and interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the project. Use of additional confirmation columns is another possible option. At a minimum, the Data Review Template prepared by the analyst should include the following comment for inclusion in the case narrative:

" Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.

Date _____ Analyst _____"

11.10 Calculations

11.10.1 Concentration of Analyte in Sample Extract

Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 9.16 for details on establishing the calibration function):

Average Calibration Factor: $$C_e = \frac{A_e}{CF}$$ Equation 12

Linear Regression: $$C_e = \frac{[A_e - b]}{a}$$ Equation 13

Where:

C_e	=	Concentration of the analyte in the sample extract (ng/mL).
A_e	=	Peak area for the analyte in the sample extract injection.
b	=	y-intercept of the calibration fit.
a	=	Slope of the calibration fit.

11.10.2 Concentration of Analyte in Original Sample

The concentration of the analyte in the original sample is calculated as follows:

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF \qquad \text{Equation 14}$$

Where:

C_{sample}	=	Concentration of analyte in original sample (µg/L or µg/kg).
C_e (ng/mL).	=	Concentration of analyte in sample extract injected in GC
$1000\frac{ng}{\mu g}$	=	Factor to convert ng/mL to µg/mL.
V_e	=	Volume of sample extract (mL).
V_s	=	Volume (or weight) of original sample (L or kg).
DF	=	Dilution Factor (post extraction dilutions)

11.10.3 Spike Recovery Calculation

LCS, MS, and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Measured Concentration}}{\text{Spiked Concentration}} \times 100\%$$

MS/MSD RPD Calculation

The percent difference between the analyte concentration in the MS and the MSD is calculated as follows:

$$RPD = \frac{|MS - MSD|}{1/2(MS + MSD)} \times 100\%$$

11.11 All data are subject to two levels of review, which is documented on a checklist, as described in SOP DV-QA-0020.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.2 An initial method detection limit study is performed for each analyte and each sample matrix type in accordance with Policy DV-QA-005P. An MDL verification is performed once a year to satisfy NELAC 2003 requirement. For DoD, AFCEE, and

DOE projects, an MDL verification is performed quarterly. MDLs are stored in the LIMS.

12.3 Demonstration of Capabilities

12.4 An initial demonstration of capability for each method must be performed prior to analyzing samples in accordance with DV-QA-0024.

12.4.1 For the standard analyte list, the initial demonstration consists of the preparation and analysis of a QC check sample containing all of the standard analytes for the method, as well as a method detection limit (MDL) study (described in Section 12.1).

12.4.2 Four aliquots of the QC check sample are analyzed with the same procedures used to analyze samples, including sample preparation.

12.4.3 The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples.

12.4.4 For non-standard analytes an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is successful analysis of an extracted standard at the reporting limit and a single point calibration.

12.5 Training Requirements

12.5.1 The Group/Team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.5.2 Each analyst performing the method must complete an initial demonstration of capability (IDOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the IDOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Safety Manual, and HS-001, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

- Waste hexane solvent: Flammable Solvent – Waste Stream C
- Vials containing extracts in hexane: Expired Extract Vials – Waste Stream A
- Concentrated sulfuric acid and hexane from sample cleanup: Concentrated Acids with Organics - Waste Stream V
- Expired reagents and standards – Contact Waste Coordinator

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

14.3 Samples containing polychlorinated biphenyls (PCB's) at concentrations $\geq$50 ppm are regulated under the Toxic Substance Control Act (TSCA) and must be segregated from all other waste streams. Analysts are responsible for contacting the Group Leader, Sample Control, and the Waste Coordinator immediately if a sample falls into the TSCA category.

15.0 References / Cross-References

15.1 Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatograph, Revision 1, February, 2007, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.2 Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.0 Method Modifications:

16.1.1 Method 8082A includes an internal standardization option. Because of the high probability of interferences affecting internal standards, this is strictly an external standard SOP.

16.1.2 Method 8082A references 8000B, which allows the use of third-order calibration curves. This SOP does not allow third-order calibration curves.

17.0 Attachments

Table 1. Analyte List and Standard Reporting Limits

Table 2. Typical Instrument Conditions

Table 3. Calibration Levels (µg/mL)

Table 4. LCS/Matrix Spike and Surrogate Spike Levels (µg/L)

18.0 Revision History

NA

Table 1. Analyte List and Standard Reporting Limits

Compound	Water Reporting Limit (µg/L)	Soil Reporting Limit (µg/kg)
Aroclor 1016	1.0	33
Aroclor 1221	1.0	33
Aroclor 1232	1.0	33
Aroclor 1242	1.0	33
Aroclor 1248	1.0	33
Aroclor 1254	1.0	33
Aroclor 1260	1.0	33
Aroclor 1262	1.0	33
Aroclor 1268	1.0	33

Table 2. Typical Instrument Conditions

Parameter	Recommended Conditions
Injection Port Temperature:	220 °C
Detector Temperature:	325 °C
Temperature Program:	100 °C for 1 minute 8 °C/min to 280 °C 25 °C/min to 300 °C
Column 1:	CLPI, 30 m x 0.32 mm id, 0.5 µm
Column 2:	CLPII, 30 m x 0.32 mm id, 0.25 µm
Injection:	1 or 2 µL
Carrier Gas:	Hydrogen
Make-up Gas:	Nitrogen
Y-splitter:	Restek or J&W or Supelco glass tee

Table 3. Calibration Levels (μg/mL)

Aroclors	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Aroclor 1016	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1221	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1232	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1242	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1248	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1254	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1260	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1262	0.05	0.1	0.25	0.5	0.75	1.0
Aroclor 1268	0.05	0.1	0.25	0.5	0.75	1.0
Surrogates are included in the AR1660 calibration mix at the following levels:						
Tetrachloro-m-xylene	0.002	0.004	0.010	0.025	0.0375	0.05
Decachlorobiphenyl	0.002	0.004	0.010	0.025	0.0375	0.05

Table 4. LCS/Matrix Spike and Surrogate Spike Levels (μg/L)

Compound(s)	Concentration (μg/L)
Aroclor 1016/Aroclor 1260 mix	2.0
Surrogates	
Decachlorobiphenyl (DCB)	0.2
Tetrachlor-m-xylene (TCMX)	0.2

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Determination of Volatile Organics by GC/MS [8260B, and 624]

Approvals (Signature/Date):

William Rhoades 12/1/09	Adam W. Alban 09Dec09
William Rhoades — Date	Adam Alban — Date
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1.0 Scope and Application

1.1 This method is applicable to the determination of volatile organic compounds (VOCs) in water, wastewater, soils, sludges, and other solid matrices. Standard analytes are listed in Tables 1 and 3.

1.2 This SOP is applicable to Method 8260B, which is appropriate for compliance testing under RCRA regulations. Appendices A and B present modifications to the procedures in the main SOP necessary for wastewater by Method 624 (CWA compliance testing). It is important that the differences among these methods are carefully observed.

1.3 This method can be used to quantify most volatile organic compounds that have boiling points below 200 °C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4 The method is based upon a purge-and-trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 0.5 to 60 µg/L for 8260B waters, 2.5 to 200 µg/kg for low-level soils, and 200 to 30,000 µg/kg for medium-level soils. The working range for Method 624 (5 mL purge) is 5-200 µg/L.

1.5 Reporting limits are listed in Tables 1, 3 and 5.

1.6 Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates (MS/MSD), and laboratory control spike samples (LCS).

2.0 Summary of Method

2.1 Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2 Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3 In the purge-and-trap process, an inert gas is bubbled through the solution at ambient temperature or at 40 °C (40 °C is required for low-level soils), and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components, which are detected with a mass spectrometer.

2.4 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 Definitions

3.1 Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each 4-bromofluorobenzene (BFB) analysis will normally start a new batch. Batches for high-level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

The Quality Control batch must contain a matrix spike/spike duplicate pair (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. If there is insufficient sample to perform the MS/MSD, then a duplicate LCS is used to establish batch precision. Refer to Policy DV-QA-003P for further details of the batch definition.

3.2 Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data. Reagent water is used as the blank medium for water batches and Ottawa Sand for soil batches.

3.3 Laboratory Control Sample (LCS)

A blank matrix (reagent water or Ottawa Sand) is spiked with the analytes of interest and is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.4 Surrogates

Surrogates are organic compounds that are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but that are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6 Calibration Check Compound (CCC)

CCCs are a representative group of compounds that are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial

calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7 System Performance Check Compounds (SPCC)

SPCCs are compounds that are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

3.8 Initial Calibration Verification (ICV)

The ICV is a second-source calibration verification standard. In this SOP, the LCS and the MS/MSD spikes are second-source standards.

3.9 Continuing Calibration Verification (CCV)

A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge-and-trap-grade methanol will greatly reduce introduction of contaminants. In extreme cases, the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3 Matrix interferences may be caused by non-target contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5 Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered, an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.3 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.

(1) Always add acid to water to prevent violent reactions.

(2) Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

- Sample Purger: The recommended purging chamber is designed to accept between 5 mL and 25 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

- Trap: A variety of traps may be used, depending on the target analytes required. The O.I. #10 (Tenax / Silica gel / Carbon Molecular Sieve) is recommended. Other traps such as the Vocarb 3000 or Vocarb 4000 may be used if the Quality Control criteria are met.

- Desorber: The desorber should be capable of rapidly heating the trap up to 270 °C depending on the trap packing material. Many such devices are commercially available.

- Sample Heater: A heater capable of maintaining the purge device at 40 °C is necessary for low level soil analysis.

- Purge-and-trap Autosampler: An autosampler capable of sampling from a sealed vial, Varian Archon, or equivalent.

- Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

- Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

  - Column 1: 60 m X 0.32 ID DB-624 with 1.8 µm film thickness.

  - Column 2: 75 m X 0.53 ID DB-624 wide bore with 3 µm film thickness.

  - Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 amu every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

- GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.

- Data System: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. In addition, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.2 Computer Software and Hardware

- Please refer to the master list of documents and software located on G\QA\Read\Master List of Documents\Master List of Documents and Software.xls for the current software to be used for data processing.

6.3 Supplies

- Microsyringes: 10 µL and larger, 0.006-inch ID needle.

- Syringe: 5 or 25 mL glass with Luerlok tip, if applicable to the purging device.

- Balance: Analytical balance capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

- Glassware:

- Vials: 20 mL with screw caps and Teflon liners.

- Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

- Spatula: Stainless steel.

- Disposable pipettes: Pasteur.

- pH paper: Wide range.

- Gases:

- Helium: Ultra high purity, gr. 5, 99.999%.

- Compressed air: Used for instrument pneumatics.

7.0 Reagents and Standards

7.1 Methanol: Purge and Trap Grade, High Purity

7.2 Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See Section 9.2.) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.3 If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.4 Calibration Stock Standard Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10 to -20 °C. Stock standards for gases must be replaced at least every week. Other stock standards must be replaced at least every 6 months.

7.5 Calibration Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20%, then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.6 Aqueous calibration standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.7 Internal standards (IS) are added to all samples, standards, and blank analyses. Refer to Table 9 for internal standard components.

7.8 Surrogate Standards: Refer to Table 10 for surrogate standard components and spiking levels.

7.9 Laboratory Control Sample Spiking Solutions: Refer to Table 11 for LCS components and spiking levels.

7.10 Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 11.

7.11 Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 50 ng/µL of BFB in methanol is prepared as described in Sections 7.3 and 7.4.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added. The holding time for acid-preserved samples is 14 days from sample collection. For compliance with Method 624 and 8260B, unpreserved samples must be tested within 7 days of collection.

8.2 Some compounds require special preservation. These are listed below:

8.2.1 Acrolein

- Both 40CFR and SW846 (chapter 4) have special preservation requirements to adjust the pH to between 4-5. For properly preserved samples (pH 4-5) the holding time is 14 days. There are no regulatory options for HCL preservation to pH < 2, however there are options for an unpreserved water sample.
  - 40 CFR 136 (Method 624): Unpreserved sample – if Acrolein is a target analyte the holding time is 3 days.
  - SW846 (Method 8260) Chapter 4: SW846 does not provide guidance for processing unpreserved samples. However, EPA MICE has interpreted the holding time on an unpreserved sample as 7 days.

8.2.2 Acrylonitrile

- Both 40 CFR 136 and SW846 (Chapter 4) have special preservation requirements to adjust the pH between 4-5. For properly preserved sample (pH 4-5) the holding time is 14 days. However, according to 40 CFR 136, the pH adjustment is not necessary for Acrylonitrile therefore the holding time for unpreserved samples is also 14 days.
  - 40 CFR (Method 624): Unpreserved sample – if only Acrylonitrile (no acrolein) is a target analyte the holding time is 14 days.
  - SW846 (Method 8260) Chapter 4: SW846 does not provide guidance on the processing of unpreserved samples. However, EPA MICE has interpreted the holding time on an unpreserved sample as 7 days.

8.2.3 2-Chloroethylvinyl ether (2-CEVE)

- According to 40 CFR 136 purgeable halocarbons (2-CEVE's category) do not require acid preservation. When aromatics are included as compounds if interest, acid preservation is required due to the rapid breakdown through bio degradation. The method 624 is designed to use unpreserved containers, but includes a caveat that refrigeration won't suffice for aromatics stored past 7 days. When aromatics are required, the method recommends collection of a separate acidified sample followed by refrigeration for 14 days. SW846 inlcudes specific information on the handling of this analyte.
  - 40 CFR 136 (Method 624): Unpreserved sample – Purgeable halocarbons (2-CEVE) do not require acid preservation and the holding time is 14 days.

- SW846 (Method 8260) Chapter 4: Unpreserved sample – If 2-chloroethylvinylether is an analyte of interest, collect a second set of samples without acid preservation and analyze as soon as possible – 7 days.

Preservation and Holding time for Volatiles (dechlorination as needed per method):

Analyte	Method	Preservation	Holding time
Acrolein	8260	<6°C (no HCL)	7 days
	8260	<6°C, pH 4-5	14 days
	624	<6°C (no HCL)	3 days
	624	<6°C, pH 4-5	14 days
Acrylonitrile	8260	<6°C (no HCL)	7 days
	8260	<6°C, pH 4-5	14 days
	624	<6°C (noHCL)	14 days
	624	<6°C, pH 4-5	14 days
2-CEVE	8260	<6°C (no HCL)	7 days
	624	<6°C (no HCL)	14 days

If aromatics are compounds of interest and biological activity is known or suspected, preserved aliquots must be collected.

8.2.4 The State of Colorado Attorney General's office issued a letter on July 1, 1998 requiring that all samples collected for analysis of volatile organic compounds in groundwater must be collected without acid preservation. The letter explains that this is done to avoid effervescence with alkaline samples and loss of volatiles. The letter also explains that the holding time for unpreserved ground waters is 14 days.

8.3 Preserved Soils

8.3.1 Solid samples are field preserved with sodium bisulfate solution for low-level analysis, or with methanol for high-level analysis. The holding time for sodium bisulfate or methanol preserved samples is 14 days.

8.3.2 Soil samples can also be taken using the EnCore™ sampler and preserved in the laboratory within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted. The holding time for EnCore™ samples varies based on client specifications and can be 48 hours, 7 days, or 14 days.

8.3.3 Soil samples can also be preserved with deionized water and then frozen. The holding time for frozen samples varies based on client specifications and can be 48 hours, 7 days, or 14 days.

8.4 There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the laboratory, the soil is preserved in methanol. This is the high-level procedure. If very low detection limits are needed (i.e., < 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore™ samplers or to use field preservation.

8.5 Sample Collection for High-Level Analysis using EnCore™ Samplers.

8.5.1 Ship one 5 g (or 25 g) EnCore™ sampler per field sample position.

8.5.2 An additional bottle must be shipped for percent moisture determination.

8.5.3 When the samples are returned to the laboratory, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL of methanol (25 mL of methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and record it on the label.

8.5.4 Add the correct amount of surrogate spiking mixture. (Add 20 µL of 2500 µg/mL solution for a nominal 25 g sample, 4 µL for a nominal 5 g sample.)

8.5.5 Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 200 µL of 250 µg/mL solution for a nominal 25 g sample, 40 µL for a nominal 5 g sample.) The addition of spike introduces a slight error (0.4%), which can be neglected, into the calculations.

8.5.6 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (200 µL of spike to 25 mL methanol or 40 µL spike to 5 mL methanol).

8.5.7 Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8 Allow to settle, then remove a portion of methanol and store in a clean Teflon-capped vial at <6 °C until analysis.

8.6 Sample Collection for High-Level Analysis using Field Methanol Preservation

8.6.1 Prepare a 2-ounce sample container by adding 25 mL of purge-and-trap grade methanol. (If a 5 g sample is to be used, add 5 mL of methanol to a 2-ounce container or VOA vial).

8.6.2 Seal the bottle and attach a label.

8.6.3 Weigh the bottle to the nearest 0.01g and record the weight on the label.

8.6.4 Ship with appropriate sampling instructions.

8.6.5 Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6 At client request, the methanol addition and weighing may also be performed in the field.

8.6.7 When the samples are returned to the laboratory, obtain the weight of the soil added to the vial and record it on the label.

8.6.8 Add the correct amount of surrogate spiking mixture. (Add 50 µL of 1250 µg/mL solution for a nominal 25 g sample, 10 µL for a nominal 5 g sample.)

8.6.9 Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 50 µL of 1250 µg/mL solution for a nominal 25 g sample, 10 µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.2%) which can be neglected, into the calculations.

8.6.10 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol: 50 µL of spike to 25 mL of methanol or 10 µL of spike to 5 mL of methanol.

8.6.11 Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12 Allow the soil to settle, then remove a portion of methanol and store in a clean, Teflon-capped vial at <6 °C until analysis.

8.7 Low-Level Procedure

8.7.1 If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the high-level (field methanol preserved or using the EnCore™ sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low-level procedure.

8.7.2 A purge-and-trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method.

8.7.3 The soil sample is taken using a 5g EnCore™ sampling device and returned to the laboratory. It is recommended that two EnCore™ samplers be used for each field sample position, to allow for any reruns that may be necessary. A separate sample for percent moisture determination is also necessary.

8.7.4 Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate, and 5 mL of reagent water.

8.7.5 Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6 Weigh the vial to the nearest 0.1 g and record the weight on the label.

8.7.7 Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and record it on the label.

8.7.8 Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and store at –10 °C until analysis.

8.7.9 Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the high-level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8 Unpreserved Soils

At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the laboratory. This is the old procedure based on Method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.

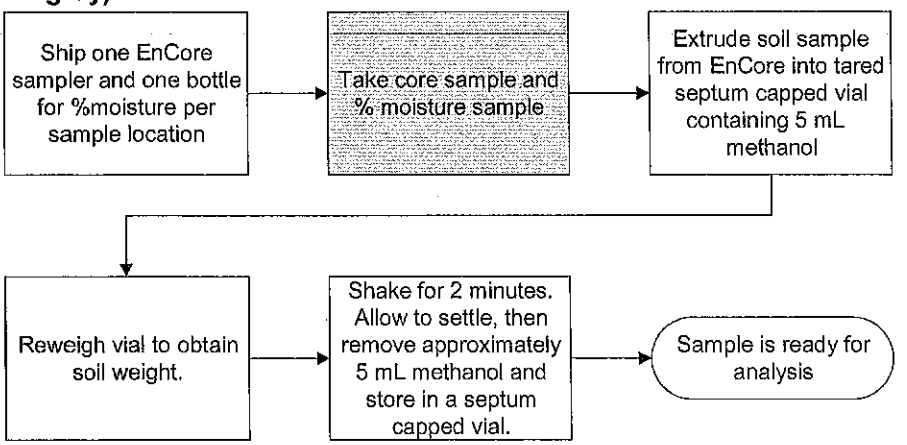
8.9 Aqueous samples are stored in glass containers with Teflon lined septa at <6 °C, with minimum headspace.

8.10 High-level solid extracts are aliquoted into two 1.5 mL glass vials with Teflon-lined caps and stored at <6 °C. The extracts are stored with minimum headspace.

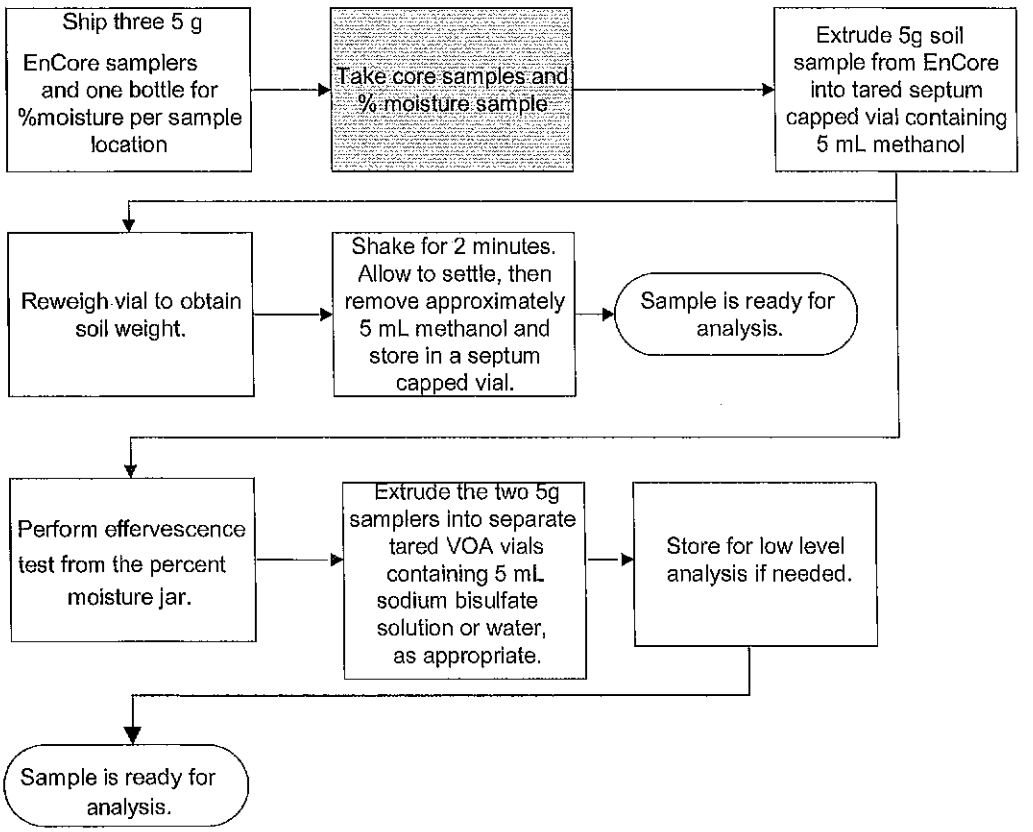
8.11 The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.12 A holding blank is stored in each refrigerator with the samples. This is analyzed every 7 – 14 days (see SOP DV-QA-0013).

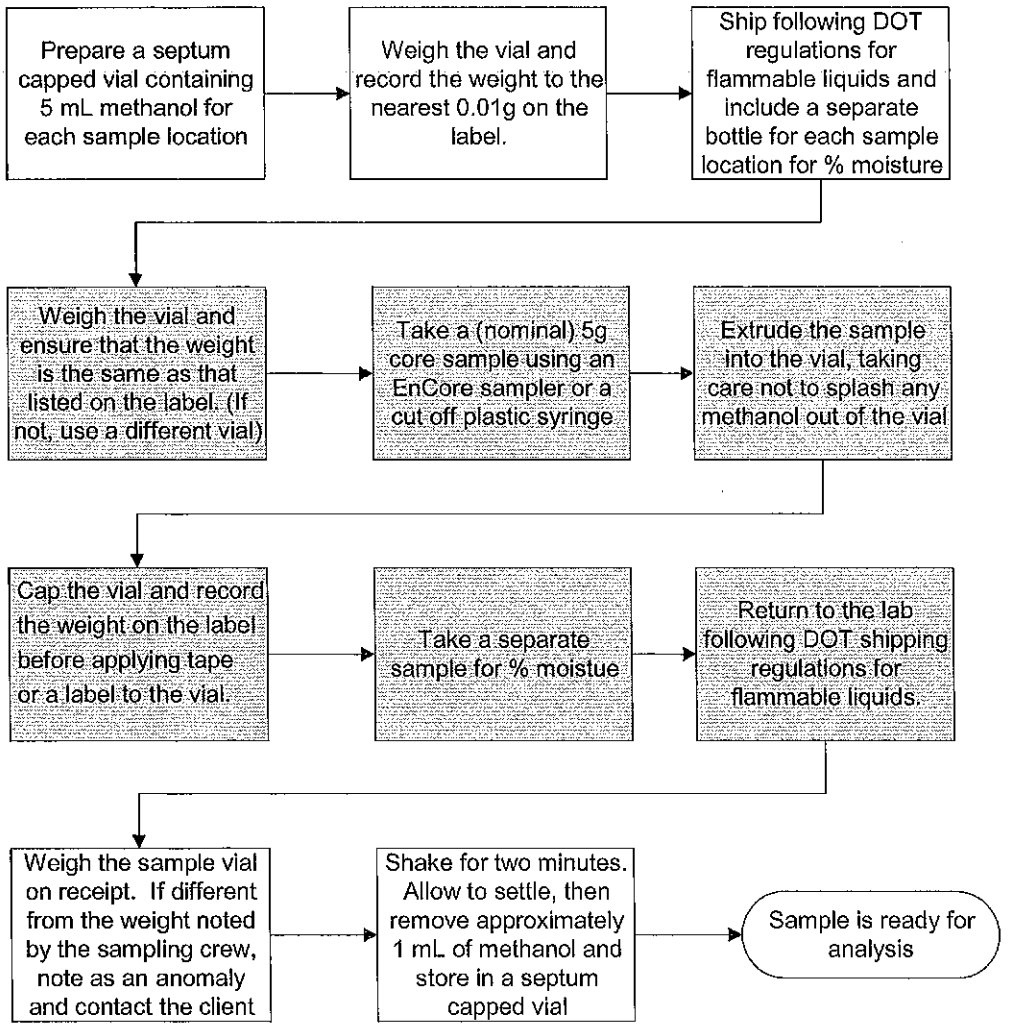
EnCore procedure when low level is not required (field steps in gray)



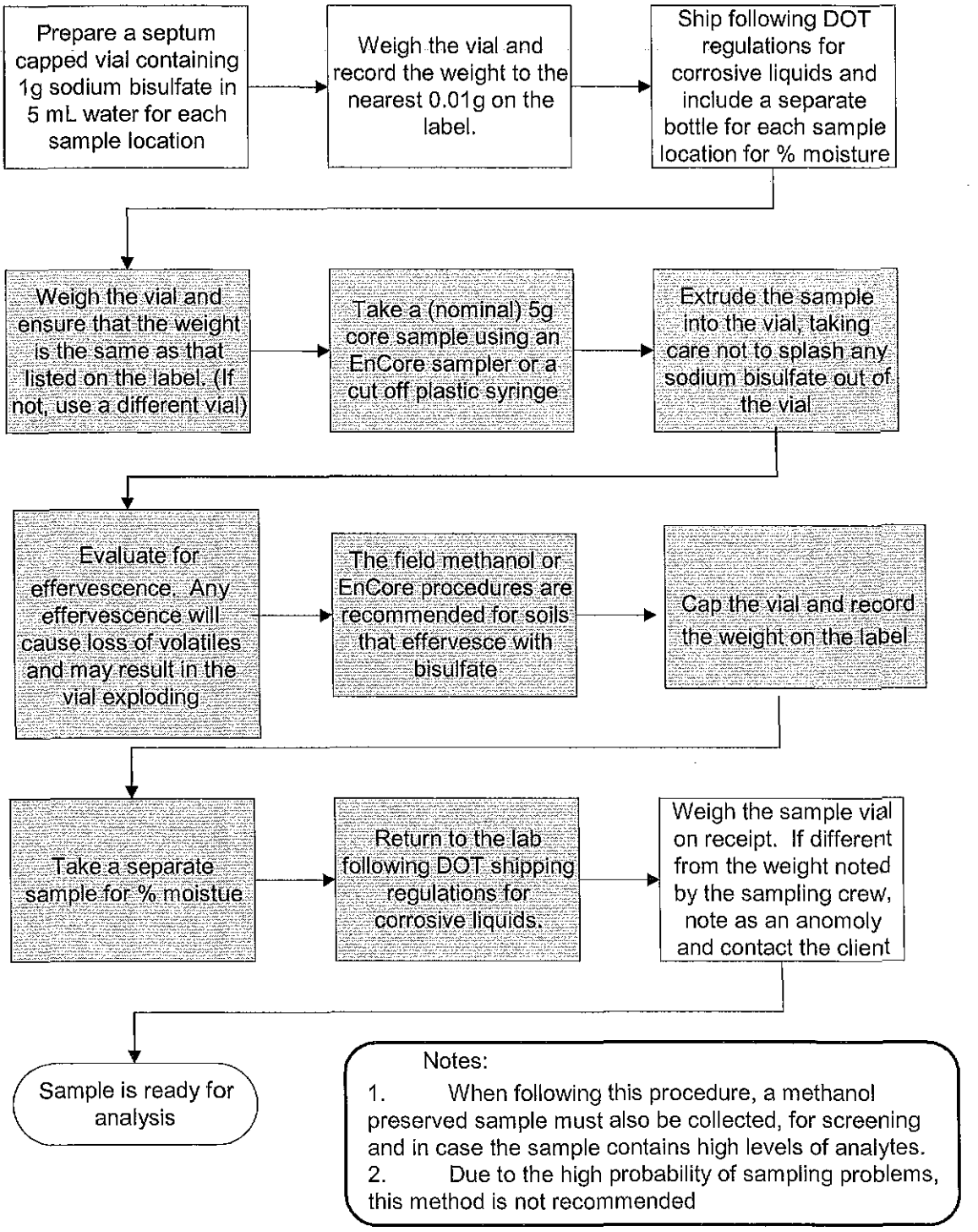
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



Notes:

1. When following this procedure, a methanol preserved sample must also be collected, for screening and in case the sample contains high levels of analytes.
2. Due to the high probability of sampling problems, this method is not recommended

9.0 Quality Control

The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

- The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Control Program.
- Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.
- Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.
- Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

Sample QC- The following quality control samples are prepared with each batch of samples.

9.1 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument. See Policy DV-QA-003P for further details.

9.2 Method Blanks

For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles in water, the method blank consists of reagent water. For low-level volatiles in soil, the blank medium is Ottawa sand. For medium-level volatiles, the method blank consists of 5.0 mL of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure.

Acceptance Criteria: The method blank must not contain any analyte of interest at or above one-half the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

The method blank must have acceptable surrogate recoveries.

Corrective Actions: If the analyte is a common laboratory contaminant (i.e., methylene chloride, acetone, 2-butanone), the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the associated samples.

If there is no target analyte greater than one-half the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

If surrogate recoveries in the blank are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.3 Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Tables 8 and 16.

Acceptance Criteria: Acceptance limits for surrogate recoveries are set at ± 3 standard deviations around the historical mean. Surrogate recovery limits are updated semi-annually and stored in the LIMS

Corrective Actions: If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Re-prepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is necessary to re-prepare/reanalyze a sample only once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and re-preparation/reanalysis is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.4 Laboratory Control Samples (LCS)

An LCS is analyzed for each batch. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS is prepared from a different source than are the calibration standards. The LCS contains a representative subset of the analytes of interest (See Table 11), and must contain the same analytes as the matrix spike.

Acceptance Criteria: The LCS recovery for the control analytes must be within established control limits. Unless otherwise specified in a reference method or project requirements, the control limits are set at ± 3 standard deviations around the mean of the historical data. An LCS that is determined to be within acceptance criteria effectively demonstrates that the analytical system is in control and validates system performance for the samples in the associated batch. Recovery limits are updated semi-annually and stored in the LIMS

If there are a large number of analytes in the LCS, then a specified number of results may fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. Marginal exceedances are recognized and allowed by NELAC, the DoD, AFCEE, and the DOE. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

# of Analytes in LCS	# of Allowed Marginal Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must be identified and corrective action taken.

Note: Additional criteria are stated in the North Carolina QAS.

Note: Some programs (e.g., South Carolina) do not allow marginal exceedances. Please see the QSAS's in the public folders for the current requirements.

Corrective Actions: If any analyte or surrogate is outside established control limits as described above, the system is out of control and corrective action must occur. Corrective action will normally be re-preparation and reanalysis of the batch.

If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS. This type of justification should be reviewed and documented with the client before reporting.

If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 11. The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

Acceptance Criteria: The MS/MSD recovery for the control analytes must be within established control limits. Unless otherwise specified in a reference method or project requirements, the control limits are set at ± 3 standard deviations around the mean of the historical data. The relative percent difference (RPD) between the MS and the MSD must be less than the established RPD limit, which is based on statistical analysis of historical data. MS/MSD recovery and RPD limits are updated semi-annually and stored in the LIMS.

Corrective Actions: If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

If an MS/MSD is not possible due to limited sample, then an LCS duplicate should be analyzed. The RPD between the LCS and LCSD is compared to the established acceptance limit.

9.6 Acid Preservation or pH adjustment

The stability of 2-chloroethylvinylether, acrolein, and according to the regulations, acrylonitrile is reduced when subjected to low pH. It is therefore not recommended that these compounds be analyzed routinely from preserved VOA vials and since there is no reasonable way to achieve pH between 4 and 5, it is recommended that unpreserved vials be used for the analysis of these compounds.

Acceptance Criteria:	To ensure detection of these compounds, samples must be processed correctly. Where method 624 is being used for compliance purposes, the regulatory hold times take precedence.
Corrective Actions:	If 624 data are not being generated for compliance purposes, the technical stability of the compounds may be considered. Where method 8260 is the base method, it is allowable to qualify the results estimated. To deviate from the regulatory hold times, the following documentation must be maintained: A NCM must be generated by the lab that the samples are for non-compliance. A NCM must be generated that results are not method compliant.

9.7 Quality Assurance Summaries (QAS)

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements. Quality Assurance Summaries are posted in the Public folders under Public Folders\All Public Folders\Arvada\Denver QASs.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.1 Sample Preparation

10.1.1 Preliminary Evaluation

10.1.1.1 Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

10.1.1.2 Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to

the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 5 µL of sample, then serial dilutions must be made in volumetric flasks.

The diluted concentration is to be estimated to be in the upper half of the calibration range.

10.1.2 Sample Analysis Procedure

10.1.2.1 All analysis conditions for samples must be the same as for the continuing calibration standards (including purge volume, time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

10.1.2.2 All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, an LCS, and a method blank.

10.1.2.2.1 If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. The 12-hour tuning requirements in Section 10.1.11.3 and 12-hour continuing calibration requirements in 10.1.13 must still be met. However, if any re-tuning or recalibration of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For high-level soils the batch is defined at the sample preparation stage.

10.1.2.2.2 Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

10.1.2.2.3 It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

10.1.3 Water Samples

10.1.3.1 All samples and standard solutions must be at ambient temperature before analysis.

10.1.3.2 Fill a syringe with the sample. If a dilution is necessary, it may be made in the syringe if the sample aliquot is ≥ 5 µL. Check and document the pH of the remaining sample.

10.1.3.3 Add 200 ng of each internal and surrogate standard (10 µL of a 20 µg/mL solution, refer to Tables 9 and 10). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 10 µg/L solution for a 20 mL sample). Inject the sample into the

purging chamber.

10.1.3.4 For TCLP samples, use 2.0 mL of TCLP leachate and spike it with 5 µL of the 40 µg/mL TCLP spiking solution.

10.1.3.5 Purge the sample for eleven minutes (the trap should be below 50 °C).

10.1.3.6 After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

10.1.3.7 Desorb time, bake time, and temperature are optimized for the type of trap in use. **The same conditions must be used for samples and standards.**

10.1.4 Methanol Extract of Soils

10.1.4.1 Rinse a gas-tight syringe with organic-free water. Fill the syringe with the same volume of organic-free water as used in the calibrations.

10.1.4.2 Add no more than 100 µL of methanolic extract (from Section 8.5 or 8.5.8) to the syringe. Add internal standard.

10.1.4.3 Load the sample onto the purge and trap device and analyze as for aqueous samples.

10.1.4.4 If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

10.1.5 Liquid Wastes that are Soluble in Methanol and Insoluble in Water

10.1.5.1 Pipette 2 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

10.1.5.2 Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For an MS/MSD pair or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution are used.

10.1.5.3 Rinse a gas-tight syringe with organic-free water. Fill the syringe with the same volume of organic-free water as used in the calibrations.

10.1.5.4 Add no more than 100 µL of methanolic extract (from Section 8.5 or 8.5.8) to the syringe. Add internal standard (if used).

10.1.5.5 Load the sample onto the purge and trap device and analyze as for aqueous samples.

10.1.5.6 If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

10.1.6 Aqueous and Low -Level Soil Sample Analysis (purge-and-trap units that sample directly from the VOA vial)

10.1.6.1 Purge-and-trap units that sample from the VOA vial should be equipped with a module that automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

10.1.6.2 If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise, the internal and surrogate standards must be added to the vial.

NOTE: Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to be analyzed as soils.

10.1.6.3 Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

10.1.6.4 For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

10.1.7 Low-Level Solids Analysis using Discrete Autosamplers

NOTE: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

10.1.7.1 This method is based on purging a heated sediment/soil sample mixed with sodium bisulfate solution containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40 °C.

10.1.7.2 Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

10.1.7.3 Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the high-level method described in Section 10.1.4.

10.1.7.4 Connect the purge vessel to the purge and trap device.

10.1.7.5 Rinse a 5 mL gas-tight syringe with organic-free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Inject the spiked water into the purge chamber that contains the soil sample.

10.1.7.6 The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

10.1.7.7 Add the heater jacket or other heating device and start the purge-and-trap unit.

10.1.7.8 Soil samples that have low internal standard recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

10.1.8 Initial Review and Corrective Actions

10.1.8.1 If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minute from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.1.8.2 If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

Sample internal standard areas are compared to the continuing calibration internal standard areas. Responses from 50% to 200% are acceptable. If a sample fails to meet these internal standard criteria, further investigation is necessary. If the change in sensitivity is a matrix effect confined to an individual sample, reanalysis is not necessary. If the change in sensitivity is due to instrumental problems, all affected samples must be reanalyzed after the problem is corrected.

10.1.8.3 The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect, but reanalysis at a dilution should be considered.

10.1.9 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be

reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

10.1.9.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

10.1.9.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will be reported only at client request.

10.1.10 Summary

Prior to the analysis of samples and blanks, the GC/MS system must be tuned and calibrated. Tuning is accomplished by analyzing 4-bromofluorobenzene (BFB) to establish that the GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations to determine the linearity of the response utilizing target calibration standards. The calibration must be verified each twelve-hour time period for each GC/MS system. The use of separate calibrations is required for water and low soil matrices.

10.1.11 Recommended Instrument Conditions

10.1.11.1 General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 amu
Scan Time:	to give at least 5 scans/peak, ≤ 2 second/scan
Injector Temperature:	200 – 250 °C
Source Temperature:	According to manufacturer's specifications
Transfer Line:	Temperature: 250 – 300 °C
Purge Flow:	40 mL/minute
Carrier Gas Flow:	1-15 mL/minute, dependent upon column specifications

10.1.11.2 Gas Chromatograph Suggested Temperature Program

The following temperature programs vary with the column type used.

<u>BFB Analysis</u>

Isothermal: 170 – 200 °C

Sample Analysis

Initial Temperature: 40 °C
Initial Hold Time: 4 minutes
Temperature Program: 8 °C/minute
Final Temperature: 184 °C
Second Temperature Program: 40 °C/minute
Final Temperature: 240 °C
Final Hold Time: 2.6 minutes

10.1.11.3 Instrument Tuning

Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 12 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.1.12 Initial Calibration

10.1.12.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-S-005, *Calibration Curves (General)*.

10.1.12.2 A series of five or more initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Calibration levels for a 20 mL purge are 1, 2, 5, 10, 30, and 60 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Tables 2, 4, and 6 list the calibration levels for each analyte. The purge volume for Method 624 is 5 mL (see calibration levels in Table B-3). Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument or program requirements. Calibration levels below the reporting limit may be removed provided that there is a minimum of five calibration points, and the lowest standard is at or below the TestAmerica reporting limit.

10.1.12.3 The same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.1.12.4 It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for some tests.

10.1.12.5 Internal standard calibration is used. The internal standards are listed in Tables 9. Target compounds should reference the nearest internal standard. Each calibration standard is

analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.1.12.6 Evaluation of retention times – The relative retention time of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

10.1.12.7 The % RSD of the calibration check compounds (CCC) must be less than or equal to 30%. Refer to Table 14. See Table A-3 for method 624 criteria.

10.1.12.8 The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 13 for the SPCC compounds and required minimum response factors.

10.1.12.9 If the software in use is capable of routinely reporting curve coefficients for data validation purposes and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. The correlation coefficient (coefficient of determination for non-linear curves) must be ≥ 0.990.

Note: Additional criteria are stated in the North Carolina QAS.

10.1.12.10 If the software in use is capable of routinely reporting curve coefficients for data, and if the average of all the %RSDs in the calibration is > 15%, then calibration on a curve must be used for all analytes with %RSD > 15%. The analyst should consider instrument maintenance to improve the linearity of response. Otherwise, the correlation coefficient, r (coefficient of determination, r2 for non-linear curves) must be ≥ 0.990.

Note: Some states (like Arizona) and federal programs do not allow the use of grand mean. Refer to the Arizona QAS and SOP DV-QA-024P.

10.1.12.11 Once the initial calibration has been evaluated and determined to be valid, the calibration must be verified with an Initial Calibration Verification (ICV) using a standard prepared from an alternate source. All compounds in the ICV must be <35 % drift when compared to the initial calibration, except poor performers (see Table 17) which must be <55% drift. The ICV is generally run at the same concentration as the level 5 standard. See Table A-2 for method 624 criteria.

10.1.12.12 If time remains in the 12-hour period initiated by the BFB

injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration, Section 10.1.13.

10.1.12.13 A separate five point calibration must be prepared for analysis of low-level soils. Low-level soils analysis requires the use of a closed vial autosampler. Each standard is prepared by spiking the methanol standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Methanol soil extracts should be analyzed using the water calibration curve.

10.1.12.14 Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the

10.1.12.15 reporting limit with each continuing calibration rather than a five point initial calibration. The primary ion for the single standard must generate a peak clearly visible over background noise (greater than three standard deviations at a minimum) and be free of spectral interferences. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary. A footnote or narrative comment should describe the basis of the reported result.

10.1.13 Continuing Calibration

10.1.13.1 The initial calibration must be verified every twelve hours.

10.1.13.2 Continuing calibration begins with analysis of BFB as described in Section 10.1.11.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 4 calibration standard is used as the continuing calibration standard. See Table A-2 for method 624 criteria.

10.1.13.3 The RF data from the standards are compared with the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 11.3.4.

10.1.13.4 The % drift of the CCCs must be ≤ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 13. In addition, the % drift for most non-CCC analytes must be ≤ 35 %, and for poor performers ≤ 50 % (See Table 17), with allowance for up to six target analytes to have a % drift greater than the applicable limit. For agencies that require specific control limits for non-CCC compounds (i.e., State of Arizona) see Table 16. See Table A-2 for method 624 criteria.

Note: Additional criteria are stated in the North Carolina QAS.

10.1.13.4.1 If none of the CCCs are required analytes, project specific calibration specifications (which may include the use of the CCCs listed in Table 14) must be agreed with the client.

10.1.13.4.2 Cyclohexanone, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane. No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal

Treatment Standard and FO-39 regulatory lists.

10.1.13.5 The retention time of the internal standards in the continuing calibration standard cannot change by more than 30 seconds when compared to the most recent five-point calibration. The internal standard areas must not change by more than a factor of 2 (50 - 200 %) from the mid point standard of the most recent five-point calibration.

10.1.13.6 If the CCCs and/or the SPCCs do not meet the criteria in Sections 10.1.13.3 and 10.1.13.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action, such as a different type of column, will require a new initial calibration.

10.1.13.7 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample desorbed less than or equal to 12 hours after the BFB is acceptable.)

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

11.1.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library (same library as used for routine sample analysis). Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

NOTE: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.

11.1.1.1 The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

11.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

11.1.1.3 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra,

the corresponding sample abundance must be between 20 and 80 %.)

11.1.2 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

11.1.3 All data are subject to two levels of technical review, as described in SOP DV-QA-0020.

11.2 Tentatively Identified Compounds (TICs)

11.2.1 If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. The following guidelines apply:

11.2.1.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

11.2.1.2 The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

11.2.1.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.2.1.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

11.2.1.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or co-eluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

11.2.1.6 Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst *assign a tentative identification.*

11.3 Calculations.

11.3.1 Response factor (RF):

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Equation 1

Where:

A_x = *Area of the characteristic ion for the compound to be measured.*

A_{is} = *Area of the characteristic ion for the specific internal standard.*

C_{is} = *Concentration of the specific internal standard, ng.*

C_x = *Concentration of the compound being measured, ng.*

11.3.2 Standard deviation (SD):

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2}{n-1}}$$

Equation 2

Where:

X_i = *Value of X at i through n.*
n = *Number of points.*
$\overline{X}$ = *Average value of X_i.*

11.3.3 Percent relative standard deviation (%RSD):

$$\%RSD = \frac{SD}{\overline{RF}} \times 100\%$$

Equation 3

Where $\overline{RF}$ is the mean of RF values for the calibration.

11.3.4 Percent drift between the initial calibration and the continuing calibration:

$$\%Drift = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100\%$$

Equation 4

Where:

$C_{expected}$ = *Known concentration in standard.*
C_{found} = *Measured concentration using selected quantitation method.*

11.3.5 See SOP CA-Q-S-005 for more detailed calibration equations.

11.3.6 Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is ≤ 15%.

11.3.6.1 Calculation of concentration using Average Response Factors:

$$\text{Concentration } (\mu g/L) = \frac{x}{\overline{RF}}$$

Equation 5

11.3.6.2 Calculation of concentration using Linear fit:

$$\text{Concentration } (\mu g/L) = A + Bx$$

Equation 6

11.3.6.3 Calculation of concentration using Quadratic fit:

$$Concentration(\mu g / L) = A + Bx + Cx^2$$

Equation 7

Where:

x = *see equations 8, 9, and 10.*

A = *intercept of the calibration function.*
B = *slope of calibration function.*
C = *curvature of a second-order calibration function.*

11.3.6.4 Calculation of x for Water and water-miscible waste:

$$x = \frac{A_x I_s D_f}{A_{is} V_0}$$ *Equation 8*

Where:

A_x = *Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion).*
A_{is} = *Area of the characteristic ion for the internal standard.*
I_s = *Amount of internal standard added in ng.*

$$D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

V_o = *Volume of water purged, mL.*

11.3.6.5 Calculation of x for High-level soils:

$$x = \frac{(A_x)(I_s)(V_t)(1000)D_f}{(A_{is})(V_a)(W_s)(D)}$$ *Equation 9*

Where:

A_x, I_s, D_f, A_{is}, = *same as used in equation 8 above.*
V_t = *Volume of total extract, mL (typically 25 mL).*
V_a = *Volume of extract added for purging, µL.*
W_s = *Weight of sample extracted, g.*
D = $\frac{100 - \%moisture}{100}$

11.3.6.6 Calculation of x for Low level soils:

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$ *Equation 10*

Where:

A_x, I_s, D_f, A_{is}, = *same as used in equation 8 above.*
D = *same as in equation 9 above.*
W_s = *Weight of sample added to the purge vessel, g.*

11.3.6.7 Calculation of TICs

The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area in the total ion chromatogram for the compound being measured.
A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference.
RF = 1

In other words, the concentration is equal to x as defined in equations 8, 9, and 10.

11.3.7 MS/MSD Recovery

$$\%\text{Recovery} = \frac{SSR - SR}{SA} \times 100\% \qquad \textit{Equation 11}$$

Where:
SSR = Spike sample result.
SR = Sample result.
SA = Spike added.

11.3.8 Relative % Difference calculation for the MS/MSD:

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100\% \qquad \textit{Equation 12}$$

Where:
RPD = Relative percent difference.
MSR = Matrix spike result.
MSDR = Matrix spike duplicate result.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 Method Detection Limit Study an initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Prepare and analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy # DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 Demonstration of Capabilities

12.2.1 All personnel are required to perform an initial demonstration of proficiency

(IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

- Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.
- Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

12.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.3.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.1 The following waste streams are produced when this method is carried out:

14.1.1 Methanol Waste - Vial Waste and Flammable – Waste Streams A and C

14.1.2 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

14.1.3 Acidified Water – Waste Stream W

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 Method 8260B, Volatile Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.2 40CFR, Part 136, Appendix A (Method 624).

15.3 Method 5030B, Purge-and-Trap for Aqueous Samples, Revision 2, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.4 Method 5035, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Revision 0, December, 1996, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.0 Method Modifications:

Item	Method	Modification
1	SW846 8260B	Ion 119 is used as the quantitation ion for chlorobenzene-d_5.
2	SW846 8260B	The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.
3	SW846 8260B	This SOP has been written to allow for a 20 mL purge volume for waters. An additional 5 mL of DI water is added to all samples, QC and calibration standards. The final purge volume is 25 mL.

4	SW846 8260B	Method 8260B recommends that the purge vessel is run through an additional purge cycle after 25 mL sample analysis to remove carryover. Instead, purge vessels are oven baked between analyses or disposable vessels are used one time only.
5	SW846 8260B	SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In addition, most software available does not allow weighting of the curve. Unweighted curves may exhibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, if the overall average is ≤ 15% then the ICAL is considered acceptable and any compounds that are not ≤15% will use linear regression.
6	EPA 624	Method 624 is required for demonstration of compliance with CWA permits, e.g., NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table A-1. If compounds are added to the analysis, all of the method criteria must be satisfied for the additional compounds.
7	EPA 624	The tune period for this method is defined as 24 hours, which is the maximum elapsed time before the tune check is performed. Calibration verifications are done at the same 24 hour frequency.
8	EPA 624	The initial calibration curve for this method requires at least three points, as shown in Table A-3.

9	EPA 624	Sample concentrations are calculated using the average RRF from the initial calibration curve.
10	EPA 624	CCC evaluation is the same as shown in 10.4.5.
11	EPA 624	Each target analyte is assigned to the closest eluting internal standard.
12	EPA 624	Initial demonstration of Proficiency • The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table A-2
12	EPA 624	Initial calibration curve requirements: • Target compounds must have RSD ≤ 35%. • If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.
13	EPA 624	Continuing calibration verification requirements: • The continuing calibration standard is from a different source than the initial calibration standard. The daily CCAL concentration is 20 ug/L. The acceptance criteria are listed in Table A-2. Matrix Spike and LCS Requirements • The matrix spike and LCS are spiked at 20 µg/L, prepared from the same source containing all analytes of interest. A matrix spike duplicate is not necessary for this method. The recovery limits for matrix spike and LCS recovery are listed in Table A-2.
15	EPA 624	Consistent with the other volatile methods, corrections for recovery are not allowed.

16	EPA 624	Qualitative Identification - The relative intensities of ions should agree to within ±20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)
17	EPA 624	Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. TestAmerica routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.
18	EPA 624	Section 5.3.2 of the source method describes a packed analytical column. TestAmerica routinely employs capillary columns when performing this method.
19	EPA 624	The source method provides a suggested list of compounds for internal and surrogate standards. Others are permitted by the method. TestAmerica uses three internal standards, including chlorobenzene-d5 and 1,4-dichlorobenzene-d4, which are not listed in Table 3 of the source method. Toluene-d8 is used as a surrogate compound, which is also not listed in the source method.
20	EPA 624	The lab is preparing internal standards at 10 ug/L and applying the same criteria designed for 30 ug/L in the Method. The lower the concentration is consistent with the greater sensitivity provided by capillary columns as compared to the older packed columns described in the method. It could only be more challenging for the lab to meet the acceptance criteria at 10 ug/L; it provides a higher level of data quality.
21	EPA 624	Method 624 describes a mass scan range of 25 to 260 amu. Table 13 lists all of the ions used for analysis. None of the ions are below 35 amu. Therefore, we scan from 35 to 300 and include all ions needed for analysis.

22	EPA 624	Method 624 describes dilutions "if response of any m/z" exceeds the response for the highest m/z in the ICAL. As the m/z ratio is always directly proportional to the concentration, evaluation based on dilution (per 11.10) is equivalent.
23	EPA 624	Method 624 has criteria for unresolved isomers. The problems of isomeric resolution for the routine analytes listed in this SOP were worked through when the laboratory developed its implementation of the method. For example, we know through experience that meta and para xylenes will not be resolved and it was not necessary to include an evaluation for the xylenes in each analysis. Any development work to add compounds would take this into account.

17.0 Attachments

Table 1. TestAmerica Primary List Reporting Limits for 8260B
Table 2. Soil Calibration Levels, 5-gram Purge
Table 3. TestAmerica Appendix IX List Reporting Limits
Table 4. TestAmerica Appendix IX List Calibration Levels, 5-gram Purge, µg/kg
Table 5. TestAmerica 8260 List Reporting Limits
Table 6. Water 8260 List Calibration Levels (µg/L)
Table 7. Low-Level Soil 8260 List Calibration Levels, 5-gram Purge, µg/kg[1]
Table 8. Low-Level Soil AFCEE 8260 List Calibration Levels (µg/kg)
Table 8A. Water AFCEE 8260 List Calibration Levels (µg/L)
Table 9. Internal Standards
Table 10. Surrogate Standards
Table 11. Matrix Spike and LCS Standard
Table 12. BFB Key Ion Abundance Criteria
Table 13. SPCC Compounds and Minimum Response Factors
Table 14. CCC Compounds
Table 15. Characteristic Ions
Table 16. State of Arizona CCV Limits (% Recovery)
Table 17. List 1 Poorly performing Compounds
Table A-1. Method 624 Analytes and Reporting Limits, 5-mL Purge
Table A-2. Method 624 QC Acceptance Criteria
Table A-3. Calibration Levels for 624, 5 mL Purge

18.0 Changes from Previous Revision

- Revision 3.1, dated 11 December 2009
  - Added Trichloroethene to Table 11.
  - Updated section 16 to describe the process of adding and additional 5 ml of DI water to all samples and QC.
  - Added a note to section 9.4 that marginal exceedances are not allowed for some programs.
  - Updated the language in section 16 item 5 to describe the current practice.
- Revision 3.0, dated 21 January 2009
  - Added clarification of sample preservation requirements to section 8.
  - Adjusted Table 16 for South Carolina requirements to utilize default limits.
  - Added Table 8A for AFCEE water calibration levels.
- Revision 2.1, dated 16 July 2007
  - Add reference to North Carolina QAS for additional requirements to sections 9.6, 10.4.8, and 10.5.4.
  - Remove Nitrogen as an allowable substitution for Helium in section 6.8.
  - Added the current list of spike compounds to Table 11.
  - Updated references to include 5030B and 5035.
  - Removed EPA 524.2 references.

- Revision 2.0
  - The method blank acceptance criteria and corrective actions were updated in Section 9.4.

Table 1. TestAmerica Primary List Reporting Limits for 8260B (cont.)

Compound	CAS Number	Reporting Limits[1]		
		20 mL Water(µg/L)	Low Soil (µg/kg)	Med Soil (µg/kg)
Dichlorodifluoromethane	75-71-8	2	10	400
Chloromethane	74-87-3	2	10	400
Bromomethane	74-83-9	2	10	400
Vinyl chloride	75-01-4	2	10	400
Chloroethane	75-00-3	2	10	400
Trichlorofluoromethane	75-69-4	2	10	400
Acrolein	107-02-8	20	100	4000
Acetone	67-64-1	10	20	800
Trichlorotrifluoroethane	76-13-1	1	5	200
Ethanol	64-17-5	200	500	20,000
Iodomethane	74-88-4	1	5	200
Carbon disulfide	75-15-0	1	5	200
Methylene chloride	75-09-2	1	5	200
Tert-Butyl alcohol	75-65-0	50	200	8,000
1,1-Dichloroethene	75-35-4	1	5	200
1,1-Dichloroethane	75-34-3	1	5	200
Trans-1,2-Dichloroethene	156-60-5	1	5	200
Acrylonitrile	107-13-1	20	100	4000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	5	20	800
Hexane	110-54-3	1	5	200
Cis-1,2-Dichloroethene	156-59-2	1	5	200
1,2-Dichloroethene (Total)	540-59-0	2	10	400
Tetrahydrofuran	109-99-9	5	20	800
Chloroform	67-66-3	1	5	200
1,2-Dichloroethane	107-06-2	1	5	200
Dibromomethane	74-95-3	1	5	200
2-Butanone	78-93-3	5	20	800
1,4-Dioxane	123-91-1	200	500	20,000
1,1,1-Trichloroethane	71-55-6	1	5	200
Carbon tetrachloride	56-23-5	1	5	200
Bromodichloromethane	75-27-4	1	5	200
1,2-Dichloropropane	78-87-5	1	5	200

Table 1. TestAmerica Primary List Reporting Limits for 8260B (cont.)

Compound	CAS Number	Reporting Limits[1]		
		20 mL Water(µg/L)	Low Soil (µg/kg)	Med Soil (µg/kg)
Cis-1,3-Dichloropropene	10061-01-5	1	5	200
Trichloroethene	79-01-6	1	5	200
Dibromochloromethane	124-48-1	1	5	200
1,2-Dibromoethane	106-93-4	1	5	200
1,2,3-Trichloropropane	96-18-4	1	5	200
1,1,2-Trichloroethane	79-00-5	1	5	200
Benzene	71-43-2	1	5	200
Ethylmethacrylate	97-63-2	1	5	200
Trans-1,3-Dichloropropene	10061-02-6	1	5	200
Bromoform	75-25-2	1	5	200
4-Methyl-2-pentanone	108-10-1	5	20	800
2-Hexanone	591-78-6	5	20	800
Tetrachloroethene	127-18-4	1	5	200
Toluene	108-88-3	1	5	200
1,1,2,2-Tetrachloroethane	79-34-5	1	5	200
2-Chloroethyl vinyl ether[2]	110-75-8	N/A[2]	50	800
Vinyl acetate	108-05-4	2	10	400
Chlorobenzene	108-90-7	1	5	200
Ethylbenzene	100-41-4	1	5	200
Styrene	100-42-5	1	5	200
t-1,4-Dichloro-2-butene	110-57-6	1	5	200
m and p Xylenes		1	5	200
o-xylene	95-47-6	1	5	200
Total xylenes	1330-20-7	2	10	400
1,3-Dichlorobenzene	541-73-1	1	5	200
1,4-Dichlorobenzene	106-46-7	1	5	200
1,2-Dichlorobenzene	95-50-1	1	5	200

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

[2] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 2. Soil Calibration Levels, 5-gram Purge

Compound	Calibration Level, µg/kg						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Dichlorodifluoromethane	2.5	5	10	20	50	100	200
Chloromethane	2.5	5	10	20	25	100	200
Bromomethane	2.5	5	10	20	50	100	200
Vinyl chloride	2.5	5	10	20	50	100	200
Chloroethane	2.5	5	10	20	50	100	200
Trichlorofluoromethane	2.5	5	10	20	50	100	200
Acrolein	25	50	100	200	500	1,000	2,000
Acetone	10	20	40	80	200	400	800
Trichlorotrifluoroethane	2.5	5	10	20	50	100	200
Ethanol	125	250	500	1,000	2,500	5,000	10,000
Iodomethane	2.5	5	10	20	50	100	200
Carbon disulfide	2.5	5	10	20	50	100	200
Methylene chloride	2.5	5	10	20	50	100	200
tert-Butyl alcohol	50	100	200	400	1,000	2,000	4,000
1,1-Dichloroethene	2.5	5	10	20	50	100	200
1,1-Dichloroethane	2.5	5	10	20	50	100	200
trans-1,2-Dichloroethene	2.5	5	10	20	50	100	200
Acrylonitrile	25	50	100	200	500	1,000	2,000
Methyl *tert*-butyl ether (MTBE)	2.5	5	10	20	50	100	200
Hexane	2.5	5	10	20	50	100	200
cis-1,2-Dichloroethene	2.5	5	10	20	50	100	200
Tetrahydrofuran	5	10	20	40	100	200	400
Chloroform	2.5	5	10	20	50	100	200
1,2-Dichloroethane	2.5	5	10	20	50	100	200
Dibromomethane	2.5	5	10	20	50	100	200
2-Butanone	10	20	40	80	200	400	800
1,4-Dioxane	125	250	500	1,000	2,500	5,000	10,000
1,1,1-Trichloroethane	2.5	5	10	20	50	100	200

Table 2. Soil Calibration Levels, 5-gram Purge (cont.)

Compound	Calibration Level, µg/kg						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Carbon tetrachloride	2.5	5	10	20	50	100	200
Bromodichloromethane	2.5	5	10	20	50	100	200
1,2-Dichloropropane	2.5	5	10	20	50	100	200
cis-1,3-Dichloropropene	2.5	5	10	20	50	100	200
Trichloroethene	2.5	5	10	20	50	100	200
Dibromochloromethane	2.5	5	10	20	50	100	200
1,2-Dibromoethane	2.5	5	10	20	50	100	200
1,2,3-Trichloropropane	2.5	5	10	20	50	100	200
1,1,2-Trichloroethane	2.5	5	10	20	50	100	200
Benzene	2.5	5	10	20	50	100	200
Ethylmethacrylate	5	10	20	40	100	200	400
trans-1,3-Dichloropropene	2.5	5	10	20	50	100	200
Bromoform	2.5	5	10	20	50	100	200
4-Methyl-2-pentanone	10	20	40	80	200	400	800
2-Hexanone	10	20	40	80	200	400	800
Tetrachloroethene	2.5	5	10	20	50	100	200
Toluene	2.5	5	10	20	50	100	200
1,1,2,2-Tetrachloroethane	2.5	5	10	20	50	100	200
2-Chloroethyl vinyl ether	2.5	5	10	20	50	100	200
Vinyl acetate	5	10	20	40	100	200	400
Chlorobenzene	2.5	5	10	20	50	100	200
Ethylbenzene	2.5	5	10	20	50	100	200
Styrene	2.5	5	10	20	50	100	200
t-1,4-Dichloro-2-butene	2.5	5	10	20	50	100	200
m and p Xylenes	5	10	20	40	100	200	400
o-xylene	2.5	5	10	20	50	100	200
1,3-Dichlorobenzene	2.5	5	10	20	50	100	200
1,4-Dichlorobenzene	2.5	5	10	20	50	100	200
1,2-Dichlorobenzene	2.5	5	10	20	50	100	200

Table 3. TestAmerica Appendix IX List Reporting Limits

Compound	CAS Number	Reporting Limits[1]		
		20 mL Water µg/L	Low Soil µg/kg	Medium Soil µg/kg
Allyl Chloride	107-05-1	2	10	400
Acetonitrile	75-05-8	20	100	4000
Dichlorofluoromethane		2	10	400
Isopropyl ether	108-20-3	2	10	400
Chloroprene	126-99-8	1	5	200
n-Butanol	71-36-3	50	200	8,000
Propionitrile	107-12-0	4	20	800
Methacrylonitrile	126-98-7	1	5	200
Isobutanol	78-83-1	50	200	8,000
Methyl methacrylate	80-62-6	1	5	200
1,1,1,2-Tetrachloroethane	630-20-6	1	5	200
1,2-Dibromo-3-chloropropane	96-12-8	2	10	400
Ethyl ether	60-29-7	2	10	400
Ethyl Acetate	141-78-6	4	20	800
2-Nitropropane	79-46-9	2	10	400
Cyclohexanone[2]	108-94-1	N/A[2]	N/A[2]	N/A[2]
Isopropylbenzene	98-82-8	1	5	200

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

[2] Cyclohexanone decomposes to 1,1-dimethoxycyclohexane in methanolic solution. Reporting limits cannot be accurately determined.

Table 4. TestAmerica Appendix IX List Calibration Levels, 5-gram Purge, µg/kg

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Allyl Chloride	5	10	20	50	100	200
Acetonitrile	50	100	200	500	1,000	2,000
Dichlorofluoromethane	5	10	20	50	100	200
Isopropyl ether	25	50	100	250	500	1,000
Chloroprene	5	10	20	50	100	200
n-Butanol	100	200	400	1,000	2,000	4,000
Propionitrile	50	100	200	500	1,000	2,000
Methacrylonitrile	50	100	200	500	1,000	2,000
Isobutanol	100	200	400	1,000	2,000	4,000
Methyl methacrylate	10	20	40	100	200	400
1,1,1,2-Tetrachloroethane	5	10	20	50	100	200
1,2-Dibromo-3-chloropropane	5	10	20	50	100	200
Ethyl ether	5	10	20	50	100	200
Ethyl Acetate	10	20	40	100	200	400
2-Nitropropane	5	10	20	50	100	200
Cyclohexanone	200	400	800	2,000	4,000	8,000
Isopropylbenzene	5	10	20	50	100	200

Table 5. TestAmerica 8260 List Reporting Limits

Compound	CAS Number	Reporting Limits[1]		
		20 mL Water µg/L	Low Soil µg/kg	Medium Soil µg/kg
2,2-Dichloropropane	590-20-7	1	5	200
Bromochloromethane	74-97-5	1	5	200
1,1-Dichloropropene	563-58-6	1	5	200
1,3-Dichloropropane	142-28-9	1	5	200
1-Chlorohexane	544-10-5	1	5	200
1,1,1,2-Tetrachloroethane	630-20-6	1	5	200
Isopropylbenzene	98-82-8	1	5	200
Bromobenzene	108-86-1	1	5	200
n-Propylbenzene	103-65-1	1	5	200
2-Chlorotoluene	95-49-8	1	5	200
4-Chlorotoluene	106-43-4	1	5	200
1,3,5-Trimethylbenzene	108-67-8	1	5	200
tert-Butylbenzene	98-06-6	1	5	200
1,2,4-Trimethylbenzene	95-63-6	1	5	200
sec-butylbenzene	135-98-8	1	5	200
4-Isopropyltoluene	99-87-6	1	5	200
n-Butylbenzene	104-51-8	1	5	200
1,2-Dibromo-3-chloropropane	96-12-8	1	5	200
1,2,4-Trichlorobenzene	120-82-1	1	5	200
Napthalene	91-20-3	1	5	200
Hexachlorobutadiene	87-68-3	1	5	200
1,2,3-Trichlorobenzene	87-61-6	1	5	200

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

Table 6. Water 8260 List Calibration Levels (µg/L)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Acetone	Not used	Not used	8.0	20	40	120	240
Acetonitrile	Not used	Not used	20	50	100	300	600
Acrolein	5.0	10	20	50	100	300	600
Acrylonitrile	Not used	Not used	20	50	100	300	600
Allyl chloride	Not used	Not used	2.0	5.0	10	30	60
Benzene	0.5	1.0	2.0	5.0	10	30	60
Bromobenzene	0.5	1.0	2.0	5.0	10	30	60
Bromochloromethane	0.5	1.0	2.0	5.0	10	30	60
Bromodichloromethane	0.5	1.0	2.0	5.0	10	30	60
Bromoform	0.5	1.0	2.0	5.0	10	30	60
Bromomethane	Not used	Not used	2.0	5.0	10	30	60
n-Butanol	Not used	Not used	40	100	200	600	1200
2-Butanone (MEK)	Not used	4.0	8.0	20	40	120	240
tert-Butyl alcohol	10	20	40	100	200	600	1200
n-Butylbenzene	0.5	1.0	2.0	5.0	10	30	60
sec-butylbenzene	0.5	1.0	2.0	5.0	10	30	60
tert-Butylbenzene	0.5	1.0	2.0	5.0	10	30	60
Carbon disulfide	0.5	1.0	2.0	5.0	10	30	60
Carbon tetrachloride	0.5	1.0	2.0	5.0	10	30	60
Chlorobenzene	0.5	1.0	2.0	5.0	10	30	60
Chloroprene	0.5	1.0	2.0	5.0	10	30	60
2-Chloro-1,3-butadiene	0.5	1.0	2.0	5.0	10	30	60
Chlorodibromomethane	0.5	1.0	2.0	5.0	10	30	60
Chloroethane	Not used	Not used	2.0	5.0	10	30	60
2-Chloroethy vinyl ether	Not used	Not used	2.0	5.0	10	30	60
Chloroform	0.5	1.0	2.0	5.0	10	30	60
1-Chlorohexane	0.5	1.0	2.0	5.0	10	30	60
Chloromethane	Not used	Not used	2.0	5.0	10	30	60
2-Chlorotoluene	0.5	1.0	2.0	5.0	10	30	60

Table 6. Water 8260 List Calibration Levels (µg/L) (cont.)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
4-Chlorotoluene	0.5	1.0	2.0	5.0	10	30	60
Cyclohexane	0.5	1.0	2.0	5.0	10	30	60
Cyclohexanone	20	40	80	200	400	1200	2400
1,2-Dibromo-3-chloropropane	0.5	1.0	2.0	5.0	10	30	60
1,2-Dibromoethane (EDB)	0.5	1.0	2.0	5.0	10	30	60
Dibromomethane	0.5	1.0	2.0	5.0	10	30	60
1,2-Dichlorobenzene	0.5	1.0	2.0	5.0	10	30	60
1,3-Dichlorobenzene	0.5	1.0	2.0	5.0	10	30	60
1,4-Dichlorobenzene	0.5	1.0	2.0	5.0	10	30	60
Cis-1,4-dichloro-2-butene	0.5	1.0	2.0	5.0	10	30	60
Trans-1,4-dichloro-2-butene	0.5	1.0	2.0	5.0	10	30	60
Dichlorodifluoromethane	Not used	Not used	2.0	5.0	10	30	60
1,1-Dichloroethane	0.5	1.0	2.0	5.0	10	30	60
1,2-Dichloroethane	0.5	1.0	2.0	5.0	10	30	60
cis-1,2-Dichloroethene	0.5	1.0	2.0	5.0	10	30	60
trans-1,2-Dichloroethene	0.5	1.0	2.0	5.0	10	30	60
1,1-Dichloroethene	0.5	1.0	2.0	5.0	10	30	60
Dichlorofluoromethane	0.5	1.0	2.0	5.0	10	30	60
1,2-Dichloropropane	0.5	1.0	2.0	5.0	10	30	60
1,3-Dichloropropane	0.5	1.0	2.0	5.0	10	30	60
2,2-Dichloropropane	0.5	1.0	2.0	5.0	10	30	60
cis-1,3-Dichloropropene	0.5	1.0	2.0	5.0	10	30	60
trans-1,3-Dichloropropene	0.5	1.0	2.0	5.0	10	30	60
1,1-Dichloropropene	0.5	1.0	2.0	5.0	10	30	60
1,2-Dichloro-1,1,2-trichloroethane	0.5	1.0	2.0	5.0	10	30	60
1,2-Dichloro-1,1,1trichloroethane	0.5	1.0	2.0	5.0	10	30	60
1,4-Dioxane	25	50	100	250	500	1500	3000
Ethanol	Not used	Not used	100	250	500	1500	3000
Ethyl acetate	1.0	2.0	4.0	10	20	60	120
Ethylbenzene	0.5	1.0	2.0	5.0	10	30	60

Table 6. Water 8260 List Calibration Levels (µg/L) (cont.)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Ethylene oxide	62.5	125	250	625	1250	3750	7500
Ethyl ether	0.5	1.0	2.0	5.0	10	30	60
Ethyl methacrylate	1.0	2.0	4.0	10	20	60	120
Hexachlorobutadiene	0.5	1.0	2.0	5.0	10	30	60
Hexane	0.5	1.0	2.0	5.0	10	30	60
2-Hexanone	Not used	4.0	8.0	20	40	120	240
Iodomethane	0.5	1.0	2.0	5.0	10	30	60
Isobutyl alcohol	Not used	Not used	40	100	200	600	1200
Isopropylbenzene	0.5	1.0	2.0	5.0	10	30	60
Isopropyl ether	2.5	5.0	10	25	50	150	300
4-Isopropyltoluene	0.5	1.0	2.0	5.0	10	30	60
Methacrylonitrile	5.0	10	20	50	100	300	600
Methylene chloride	0.5	1.0	2.0	5.0	10	30	60
Methyl methacrylate	1.0	2.0	4.0	8.0	20	60	120
4-Methyl-2-pentanone	Not used	4.0	8.0	20	40	120	240
Methyl *tert*-butyl ether (MTBE)	Not used	Not used	2.0	5.0	10	30	60
Napthalene	0.5	1.0	2.0	5.0	10	30	60
2-Nitropropane	Not used	Not used	2.0	5.0	10	30	60
2-Pentanone	Not Used	4.0	8.0	20	40	120	240
Propionitrile	5.0	10	20	50	100	300	600
n-Propylbenzene	0.5	1.0	2.0	5.0	10	30	60
Styrene	0.5	1.0	2.0	5.0	10	30	60
1,1,1,2-Tetrachloroethane	0.5	1.0	2.0	5.0	10	30	60
1,1,2,2-Tetrachloroethane	0.5	1.0	2.0	5.0	10	30	60
Tetrachloroethene	0.5	1.0	2.0	5.0	10	30	60
Tetrahydrofuran	Not used	Not used	4.0	10	20	60	120
Toluene	0.5	1.0	2.0	5.0	10	30	60
1,2,3-Trichlorobenzene	0.5	1.0	2.0	5.0	10	30	60
1,2,4-Trichlorobenzene	0.5	1.0	2.0	5.0	10	30	60
1,1,1-Trichloroethane	0.5	1.0	2.0	5.0	10	30	60
1,1,2-Trichloroethane	0.5	1.0	2.0	5.0	10	30	60

Table 6. Water 8260 List Calibration Levels (µg/L) (cont.)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Trichloroethene	0.5	1.0	2.0	5.0	10	30	60
Trichlorofluoromethane	Not used	Not used	2.0	5.0	10	30	60
1,2,3-Trichloropropane	0.5	1.0	2.0	5.0	10	30	60
1,1,1-Trichloro-2,2-dichloroethane	0.5	1.0	2.0	5.0	10	30	60
1,1,2-Trichloro-2,2-dichloroethane	0.5	1.0	2.0	5.0	10	30	60
Trichlorotrifluoroethane	0.5	1.0	2.0	5.0	10	30	60
2,2-Dichloro-1,1,1-trifluoroethane	0.5	1.0	2.0	5.0	10	30	60
1,2,4-Trimethylbenzene	0.5	1.0	2.0	5.0	10	30	60
1,3,5-Trimethylbenzene	0.5	1.0	2.0	5.0	10	30	60
Vinyl acetate	1.0	2.0	4.0	10	20	60	120
Vinyl chloride	Not used	1.0	2.0	5.0	10	30	60
m and p Xylenes	1.0	2.0	4.0	10	20	60	120
o-xylene	0.5	1.0	2.0	5.0	10	30	60

Table 7. Low-Level Soil 8260 List Calibration Levels, 5-gram Purge, µg/kg[1]

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
2,2-Dichloropropane	5	10	20	50	100	200
Bromochloromethane	5	10	20	50	100	200
1,1-Dichloropropene	5	10	20	50	100	200
1,3-Dichloropropane	5	10	20	50	100	200
1-Chlorohexane	5	10	20	50	100	200
1,1,1,2-Tetrachloroethane	5	10	20	50	100	200
Isopropylbenzene	5	10	20	50	100	200
Bromobenzene	5	10	20	50	100	200
n-Propylbenzene	5	10	20	50	100	200
2-Chlorotoluene	5	10	20	50	100	200
4-Chlorotoluene	5	10	20	50	100	200
1,3,5-Trimethylbenzene	5	10	20	50	100	200
tert-Butylbenzene	5	10	20	50	100	200
1,2,4-Trimethylbenzene	5	10	20	50	100	200
sec-butylbenzene	5	10	20	50	100	200
4-Isopropyltoluene	5	10	20	50	100	200
n-Butylbenzene	5	10	20	50	100	200
1,2-Dibromo-3-chloropropane	5	10	20	50	100	200
1,2,4-Trichlorobenzene	5	10	20	50	100	200
Napthalene	5	10	20	50	100	200
Hexachlorobutadiene	5	10	20	50	100	200
1,2,3-Trichlorobenzene	5	10	20	50	100	200

Table 8. Low-Level Soil AFCEE 8260 List Calibration Levels (µg/kg)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Acetone	4	20	40	100	200	400
Benzene	2	10	20	50	100	200
Bromobenzene	2	10	20	50	100	200
Bromochloromethane	2	10	20	50	100	200
Bromodichloromethane	2	10	20	50	100	200
Bromoform	2	10	20	50	100	200
Bromomethane	2	10	20	50	100	200
2-Butanone (MEK)	4	20	40	100	200	400
n-Butylbenzene	2	10	20	50	100	200
sec-Butylbenzene	2	10	20	50	100	200
tert-Butylbenzene	2	10	20	50	100	200
Carbon disulfide	2	10	20	50	100	200
Carbon tetrachloride	2	10	20	50	100	200
Chlorobenzene	2	10	20	50	100	200
Chlorodibromomethane	2	10	20	50	100	200
Chloroethane	2	10	20	50	100	200
2-Chloroethyl vinyl ether	2	10	20	50	100	200
Chloroform	2	10	20	50	100	200
1-Chlorohexane	2	10	20	50	100	200
Chloromethane	2	10	20	50	100	200
2-Chlorotoluene	2	10	20	50	100	200
4-Chlorotoluene	2	10	20	50	100	200
1,2-Dibromo-3-chloropropane (DBCP)	2	10	20	50	100	200
1,2-Dibromoethane (EDB)	2	10	20	50	100	200
Dibromomethane	2	10	20	50	100	200
1,2-Dichlorobenzene	2	10	20	50	100	200
1,3-Dichlorobenzene	2	10	20	50	100	200
1,4-Dichlorobenzene	2	10	20	50	100	200
Dichlorodifluoromethane	2	10	20	50	100	200

Table 8. Low-Level Soil AFCEE 8260 List Calibration Levels (µg/kg)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
1,1-Dichloroethane	2	10	20	50	100	200
1,2-Dichloroethane	2	10	20	50	100	200
cis-1,2-Dichloroethene	2	10	20	50	100	200
trans-1,2-Dichloroethene	2	10	20	50	100	200
1,1-Dichloroethene	2	10	20	50	100	200
1,2-Dichloropropane	2	10	20	50	100	200
1,3-Dichloropropane	2	10	20	50	100	200
2,2-Dichloropropane	2	10	20	50	100	200
cis-1,3-Dichloropropene	2	10	20	50	100	200
trans-1,3-Dichloropropene	2	10	20	50	100	200
1,1-Dichloropropene	2	10	20	50	100	200
Ethylbenzene	2	10	20	50	100	200
Hexachlorobutadiene	2	10	20	50	100	200
2-Hexanone	4	20	40	100	200	400
Isopropylbenzene	2	10	20	50	100	200
4-Isopropyltoluene	2	10	20	50	100	200
Methylene chloride	2	10	20	50	100	200
4-Methyl-2-pentanone	4	20	40	100	200	400
Methyl *tert*-butyl ether (MTBE)	4	20	40	100	200	400
Napthalene	2	10	20	50	100	200
n-Propylbenzene	2	10	20	50	100	200
Styrene	2	10	20	50	100	200
1,1,1,2-Tetrachloroethane	2	10	20	50	100	200
1,1,2,2-Tetrachloroethane	2	10	20	50	100	200
Tetrachloroethene	2	10	20	50	100	200
Toluene	2	10	20	50	100	200
1,2,3-Trichlorobenzene	2	10	20	50	100	200
1,2,4-Trichlorobenzene	2	10	20	50	100	200
1,1,1-Trichloroethane	2	10	20	50	100	200
1,1,2-Trichloroethane	2	10	20	50	100	200
Trichloroethene	2	10	20	50	100	200

Table 8. Low-Level Soil AFCEE 8260 List Calibration Levels (µg/kg)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Trichlorofluoromethane	2	10	20	50	100	200
1,2,3-Trichloropropane	2	10	20	50	100	200
1,2,4-Trimethylbenzene	2	10	20	50	100	200
1,3,5-Trimethylbenzene	2	10	20	50	100	200
Vinyl acetate	2	10	20	50	100	200
Vinyl chloride	2	10	20	50	100	200
m and p Xylenes	4	20	40	100	200	400
o-xylene	2	10	20	50	100	200

Table 8A. Water AFCEE 8260 List Calibration Levels (µg/L)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Acetone	0.6	2.0	4.0	10.0	20	60	120
Benzene	0.3	1.0	2.0	5.0	10	30	60
Bromobenzene	0.3	1.0	2.0	5.0	10	30	60
Bromochloromethane	0.3	1.0	2.0	5.0	10	30	60
Bromodichloromethane	0.3	1.0	2.0	5.0	10	30	60
Bromoform	0.3	1.0	2.0	5.0	10	30	60
Bromomethane	0.3	1.0	2.0	5.0	10	30	60
2-Butanone (MEK)	0.6	2.0	4.0	10.0	20	60	120
n-Butylbenzene	0.3	1.0	2.0	5.0	10	30	60
sec-Butylbenzene	0.3	1.0	2.0	5.0	10	30	60
tert-Butylbenzene	0.3	1.0	2.0	5.0	10	30	60
Carbon disulfide	0.3	1.0	2.0	5.0	10	30	60
Carbon tetrachloride	0.3	1.0	2.0	5.0	10	30	60
Chlorobenzene	0.3	1.0	2.0	5.0	10	30	60
Chlorodibromomethane	0.3	1.0	2.0	5.0	10	30	60
Chloroethane	0.3	1.0	2.0	5.0	10	30	60
2-Chloroethyl vinyl ether	0.3	1.0	2.0	5.0	10	30	60
Chloroform	0.3	1.0	2.0	5.0	10	30	60
1-Chlorohexane	0.3	1.0	2.0	5.0	10	30	60
Chloromethane	0.3	1.0	2.0	5.0	10	30	60
2-Chlorotoluene	0.3	1.0	2.0	5.0	10	30	60
4-Chlorotoluene	0.3	1.0	2.0	5.0	10	30	60
1,2-Dibromo-3-chloropropane (DBCP)	0.3	1.0	2.0	5.0	10	30	60
1,2-Dibromoethane (EDB)	0.3	1.0	2.0	5.0	10	30	60
Dibromomethane	0.3	1.0	2.0	5.0	10	30	60
1,2-Dichlorobenzene	0.3	1.0	2.0	5.0	10	30	60
1,3-Dichlorobenzene	0.3	1.0	2.0	5.0	10	30	60
1,4-Dichlorobenzene	0.3	1.0	2.0	5.0	10	30	60
Dichlorodifluoromethane	0.3	1.0	2.0	5.0	10	30	60

Table 8A. Water AFCEE 8260 List Calibration Levels (µg/L) (cont.)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
1,1-Dichloroethane	0.3	1.0	2.0	5.0	10	30	60
1,2-Dichloroethane	0.3	1.0	2.0	5.0	10	30	60
cis-1,2-Dichloroethene	0.3	1.0	2.0	5.0	10	30	60
trans-1,2-Dichloroethene	0.3	1.0	2.0	5.0	10	30	60
1,1-Dichloroethene	0.3	1.0	2.0	5.0	10	30	60
1,2-Dichloropropane	0.3	1.0	2.0	5.0	10	30	60
1,3-Dichloropropane	0.3	1.0	2.0	5.0	10	30	60
2,2-Dichloropropane	0.3	1.0	2.0	5.0	10	30	60
cis-1,3-Dichloropropene	0.3	1.0	2.0	5.0	10	30	60
trans-1,3-Dichloropropene	0.3	1.0	2.0	5.0	10	30	60
1,1-Dichloropropene	0.3	1.0	2.0	5.0	10	30	60
Ethylbenzene	0.3	1.0	2.0	5.0	10	30	60
Hexachlorobutadiene	0.3	1.0	2.0	5.0	10	30	60
2-Hexanone	0.6	2.0	4.0	10.0	20	60	120
Isopropylbenzene	0.3	1.0	2.0	5.0	10	30	60
4-Isopropyltoluene	0.3	1.0	2.0	5.0	10	30	60
Methylene chloride	0.3	1.0	2.0	5.0	10	30	60
4-Methyl-2-pentanone	0.6	2.0	4.0	10.0	20	60	120
Methyl *tert*-butyl ether (MTBE)	0.6	2.0	4.0	10.0	20	60	120
Naphthalene	0.3	1.0	2.0	5.0	10	30	60
n-Propylbenzene	0.3	1.0	2.0	5.0	10	30	60
Styrene	0.3	1.0	2.0	5.0	10	30	60
1,1,1,2-Tetrachloroethane	0.3	1.0	2.0	5.0	10	30	60
1,1,2,2-Tetrachloroethane	0.3	1.0	2.0	5.0	10	30	60
Tetrachloroethene	0.3	1.0	2.0	5.0	10	30	60
Toluene	0.3	1.0	2.0	5.0	10	30	60
1,2,3-Trichlorobenzene	0.3	1.0	2.0	5.0	10	30	60
1,2,4-Trichlorobenzene	0.3	1.0	2.0	5.0	10	30	60
1,1,1-Trichloroethane	0.3	1.0	2.0	5.0	10	30	60
1,1,2-Trichloroethane	0.3	1.0	2.0	5.0	10	30	60
Trichloroethene	0.3	1.0	2.0	5.0	10	30	60

Table 8A. Water AFCEE 8260 List Calibration Levels (µg/L) (cont.)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Trichlorofluoromethane	0.3	1.0	2.0	5.0	10	30	60
1,2,3-Trichloropropane	0.3	1.0	2.0	5.0	10	30	60
1,2,4-Trimethylbenzene	0.3	1.0	2.0	5.0	10	30	60
1,3,5-Trimethylbenzene	0.3	1.0	2.0	5.0	10	30	60
Vinyl acetate	0.3	1.0	2.0	5.0	10	30	60
Vinyl chloride	0.3	1.0	2.0	5.0	10	30	60
m and p Xylenes	0.6	2.0	4.0	10.0	20	60	120
o-xylene	0.3	1.0	2.0	5.0	10	30	60

Table 9. Internal Standards

Internal Standard	Standard Concentration (µg/mL)	Quantitation Ion
Fluorobenzene	20	96
Chlorobenzene-d_5	20	119
1,4-Dichlorobenzene-d_4	20	152

NOTES:

1) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal standard in the sample at 10 µg/L for a 20 mL purge.

2) Except for high-level soils, the surrogate and internal standards may be combined in one solution.

Table 10. Surrogate Standards

Surrogate Compounds	Standard Concentration (µg/mL)
1,2-Dichloroethane-d_4	20
Dibromofluoromethane	20
Toluene-d_8	20
4-Bromofluorobenzene	20

NOTES:

1) 10 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample at 10 µg/L for a 20 mL purge.

2) Except for high-level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 11. Matrix Spike and LCS Standard

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	20
Methylene Chloride	20
Trans-1,2-Dichloroethene	20
1,1-Dichloroethane	20
1111-Trichloroethane	20
Carbon Tetrachloride	20
Benzene	20
Trichloroethene	20
1,2-Dichloropropane	20
Bromodichloromethane	20
2-Chloroethyl Vinyl Ether	20
Toluene	20
Tetrachloroethene	20
Chlorobenzene	20
Ethylbenzene	20
1,3-Dichlorobenzene	20

NOTES:

1) 10 µL of the standard is added to the LCS or matrix spike sample. This results in a concentration of each spike analyte in the sample of 10 µg/L for a 20 mL purge.
2) Recovery and precision limits for the LCS, MS, and MSD are generated from historical data and are maintained by the QA department.
3) Full analyte spikes or different compounds may also be used at the laboratory's option or at client request.

Table 12. BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40 % of Mass 95
75	30 to 60 % of Mass 95
95	Base Peak, 100 % Relative Abundance
96	5 to 9 % of Mass 95
173	Less than 2 % of Mass 174
174	Greater than 50 % of Mass 95
175	5 to 9 % of Mass 174
176	Greater than 95 %, but less than 101 % of Mass 174
177	5 to 9 % of Mass 176

Table 13. SPCC Compounds and Minimum Response Factors

Compound	8260B Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	> 0.100
1,1,2,2-Tetrachloroethane	0.300
Chlorobenzene	0.300

Table 14. CCC Compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	≤ 30.0	≤ 20.0
1,1-Dichloroethene	≤ 30.0	≤ 20.0
Chloroform	≤ 30.0	≤ 20.0
1,2-Dichloropropane	≤ 30.0	≤ 20.0
Toluene	≤ 30.0	≤ 20.0
Ethylbenzene	≤ 30.0	≤ 20.0

Table 15. Characteristic Ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Dibromofluoromethane	111	113	
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
Acetone	43	58	
Methylene chloride	84	49	51, 86
Tert-Butyl alcohol	59	74	
Trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
Cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121

Table 15. Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Benzene	78	52	77
Trichloroethene	130	95***	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
Cis-1,3-Dichloropropene	75	77	39
Trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
Trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	41	76	78
Acetonitrile	41	40	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74

Table 15. Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	
2,2-Dichloropropane	77	97	
Bromochloromethane	128	49	130
1,1-Dichloropropene	75	39	110
1,3-Dichloropropane	76	41	78
1-Chlorohexane	91	55	41
1,1,1,2-Tetrachloroethane	131	133	
Bromobenzene	156	158	77
n-Propylbenzene	120	91	65
2-Chlorotoluene	126	91	65
1,3,5-Trimethylbenzene	105	120	77
4-Chlorobenzene	126	91	89
t-Butylbenzene	119	134	91
sec-Butylbenzene	134	105	
4-Isopropyltoluene	119	134	91
n-Butylbenzene	91	92	134
1,2,4-Trichlorobenzene	180	182	
Hexachlorobutadiene	225	227	223
Naphthalene	128	127	
1,2,3-Trichlorobenzene	180	182	

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-butanone, but m/z 72 must be present for positive identification.

*** Used as quantitation ion for AFCEE waters.

Table 16. State of Arizona ICV/CCV Quality Control Limits

QC Limits not specified in method	Default QC (method specified or laboratory historical if not specified)
CCV Non-CCC compounds	CCC limits (≤30%)
ICV	Same as CCV (≤30%)
Reporting Limit	Must be supported by low level initial calibration standard
LCS/LCSD	Lab historical
MS/MSD	Lab historical

NOTES:

1) Based on ADHS Rule A.A.C.R9-14-615.C.8. Director approved on June 29, 2005 for the labs to use default limits as an alternative to developing statistically derived limits.

Table 17. List 1 Poorly Performing Compounds

Acetone	Ethanol
Acetonitrile	Ethyl acetate
Acrolein	Ethylene oxide
Acrylonitrile	2-Hexanone
n-Butanol	Isobutyl alcohol
2-Butanone (MEK)	Isopropanol
tert-Butyl alcohol	Methacrylonitrile
Carbon disulfide	Methyl acetate
2-Chloroethyl vinyl ether	4-Methyl-2-pentanone
cis-1,4-Dichloro-2-butene	2-Nitropropane
trans-1,4-Dichloro-2-butene	2-Pentanone
Dichlorodifluoromethane	2-Propanol
Dichlorofluoromethane	Propionitrile
1,2-Dibromo-3-chloropropane (DBCP)	Tetrahydrofuran
1,2-Dichlorotetrafluoroethane	Tetrahydrothiophene
1,2-Dichloro-1,1,2-trifluoroethane (Freon 123a)	1,1,2-Trichloro-1,2,2-trifluoroethane

2,2-Dichloro-1,1,1-trifluoroethane	Trichlorofluoromethane
1,4-Dioxane	Vinyl acetate

The laboratory's GC/MS group identified this list of compounds based on current and historical performance. The recovery performance was reviewed against full spike recovery data and method performance data, where available , to validate each compound as a "poor performer."

Table A-1. Method 624 Analytes and Reporting Limits, 5-mL Purge

Analytes	µg/L
Benzene	5
Bromodichloromethane	5
Bromoform	5
Bromomethane	5
Carbon tetrachloride	5
Chlorobenzene	5
Chloroethane	5
2-Chloroethyl vinyl ether	5
Chloroform	5
Chloromethane	5
Dibromochloromethane	5
1,2-Dichlorobenzene	5
1,3-Dichlorobenzene	5
1,4-Dichlorobenzene	5
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
Ethylbenzene	5
Methylene chloride	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
Vinyl chloride	5

Table A-2. Method 624 QC Acceptance Criteria

Analytes	Daily QC Check (CCV) Acceptance Criteria (20 µg/L spike)	Mean Recovery, Initial Demonstration Acceptance Criteria (IDOC) (20 µg/L spike)	Std Dev, Initial Demonstration Acceptance Criteria (IDOC) (20 µg/L spike)	Matrix Spike and LCS Acceptance Criteria (% Recovery)
Benzene	12.8 - 27.2	15.2 - 26.0	6.9	37 - 151
Bromodichloromethane	13.1 - 26.9	10.1 - 28.0	6.4	35 - 155
Bromoform	14.2 - 25.8	11.4 - 31.1	5.4	45 - 169
Bromomethane	2.8 - 37.2	D - 41.2	17.9	D - 242
Carbon tetrachloride	14.6 - 25.4	17.2 - 23.5	5.2	70 - 140
Chlorobenzene	13.2 - 26.8	16.4 - 27.4	6.3	37 - 160
Chloroethane	7.6 - 32.4	8.4 - 40.4	11.4	14 - 230
2-Chloroethyl vinyl ether	D - 44.8	D - 50.4	25.9	D - 305
Chloroform	13.5 - 26.5	13.7 - 24.2	6.1	51 - 138
Chloromethane	D - 40.8	D - 45.9	19.8	D - 273
Dibromochloromethane	13.5 - 26.5	13.8 - 26.6	6.1	53 - 149
1,2-Dichlorobenzene	12.6 - 27.4	11.8 - 34.7	7.1	18 - 190
1,3-Dichlorobenzene	14.6 - 25.4	17.0 - 28.8	5.5	59 - 156
1,4-Dichlorobenzene	12.6 - 27.4	11.8 - 34.7	7.1	18 - 190
1,1-Dichloroethane	14.5 - 25.5	14.2 - 28.5	5.1	59 - 155
1,2-Dichloroethane	13.6 - 26.4	14.3 - 27.4	6.0	49 - 155
1,1-Dichloroethene	10.1 - 29.9	3.7 - 42.3	9.1	D - 234
trans-1,2-Dichloroethene	13.9 - 26.1	13.6 - 28.5	5.7	54 - 156
1,2-Dichloropropane	6.8 - 33.2	3.8 - 36.2	13.8	D - 210
cis-1,3-Dichloropropene	4.8 - 35.2	1.0 - 39.0	15.8	D- 227
trans-1,3-Dichloropropene	10.0 - 30.0	7.6 - 32.4	10.4	17- 183
Ethylbenzene	11.8 - 28.2	17.4 - 26.7	7.5	37 - 162
Methylene chloride	12.1 - 27.9	D - 41.0	7.4	D - 221
1,1,2,2-Tetrachloroethane	12.1 - 27.9	13.5 - 27.2	7.4	46 - 157
Tetrachloroethene	14.7 - 25.3	17.0 - 26.6	5.0	64 - 148
Toluene	14.9 - 25.1	16.6 - 26.7	4.8	47 - 150
1,1,1-Trichloroethane	15.0 - 25.0	13.7 - 30.1	4.6	52 - 162
1,1,2-Trichloroethane	14.2 - 25.8	14.3 - 27.1	5.5	52 - 150
Trichloroethene	13.3 - 26.7	18.6 - 27.6	6.6	71 - 157
Trichlorofluoromethane	9.6 – 30.4	8.9- 31.5	10.0	17 - 181
Vinyl chloride	0.8 – 39.2	D - 43.5	20.0	D - 251

Analytes not listed on the table must meet a CCV drift criteria of ± 30%. Method 624 does not specify second source (ICV) criteria. The laboratory has adopted criteria of ± 30% difference for the ICV.

Table A-3. Calibration Levels for 624, 5 mL Purge

Compound	Level 1	Level 2	Level 3	Level 4
Acetone	10	40	100	400
Acrolein	5.0	20	50	200
Acrylonitrile	5.0	20	50	200
Benzene	5.0	20	50	200
Bromodichloromethane	5.0	20	50	200
Bromoform	5.0	20	50	200
Bromomethane	5.0	20	50	200
2-Butanone	10	40	100	400
Dichlorodifluoromethane	5.0	20	50	200
Carbon disulfide	5.0	20	50	200
Carbon tetrachloride	5.0	20	50	200
Chlorobenzene	5.0	20	50	200
Dibromochloromethane	5.0	20	50	200
Chloroethane	5.0	20	50	200
2-Chloroethyl vinyl ether	5.0	20	50	200
Chloroform	5.0	20	50	200
Chloromethane	5.0	20	50	200
1,2-Dibromo-3-chloropropane	5.0	20	50	200
1,2-Dibromoethane (EDB)	5.0	20	50	200
Dibromomethane	5.0	20	50	200
1,2-Dichlorobenzene	5.0	20	50	200
1,3-Dichlorobenzene	5.0	20	50	200
1,4-Dichlorobenzene	5.0	20	50	200
Dichlorodifluoromethane	5.0	20	50	200
1,1-Dichloroethane	5.0	20	50	200
1,2-Dichloroethane	5.0	20	50	200
cis-1,2-Dichloroethene	5.0	20	50	200
trans-1,2-Dichloroethene	5.0	20	50	200
1,1-Dichloroethene	5.0	20	50	200
Dichlorofluoromethane	5.0	20	50	200
1,2-Dichloropropane	5.0	20	50	200
cis-1,3-Dichloropropene	5.0	20	50	200
trans-1,3-Dichloropropene	5.0	20	50	200

Table A-3. Calibration Levels for 624, 5 mL Purge (continued)

Compound	Level 1	Level 2	Level 3	Level 4
Ethylbenzene	5.0	20	50	200
Freon-113	10	40	100	400
2-Hexanone	10	40	100	400
Methylene chloride	5.0	20	50	200
4-Methyl-2-pentanone	10	40	100	400
Methyl *tert*-butyl ether (MTBE)	10	40	100	400
Styrene	5.0	20	50	200
1,1,1,2-Tetrachloroethane	5.0	20	50	200
1,1,2,2-Tetrachloroethane	5.0	20	50	200
Tetrachloroethene	5.0	20	50	200
Tetrahydrofuran	5.0	20	50	200
Toluene	5.0	20	50	200
1,1,1-Trichloroethane	5.0	20	50	200
1,1,2-Trichloroethane	5.0	20	50	200
Trichloroethene	5.0	20	50	200
Trichlorofluoromethane	5.0	20	50	200
1,2,3-Trichloropropane	5.0	20	50	200
Vinyl acetate	5.0	20	50	200
Vinyl chloride	5.0	20	50	200
4-Methyl-2-pentanone	10	40	100	400
m and p Xylenes	10	40	100	400
o-xylene	5.0	20	50	200

If the response factor (RF) is constant over the working range (<35% RSD), the average RF may used for calculations. Alternatively, a calibration curve may be used if the correlation coefficient is ≥ 0.99.

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Title: GC/MS Analysis Based On Methods 8270D

Approvals (Signature/Date):

William Rhoades 12/1/09 William Rhoades — Date Technical Manager	Adam W. Alban 07 Dec 09 Adam Alban — Date Health & Safety Manager / Coordinator
Karen Kuoppala 12-4-09 Karen Kuoppala — Date Quality Assurance Manager	Robert C Hanisch 12/7/09 Robert C. Hanisch — Date Laboratory Director

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1.0 Scope and Application

1.1 This method is based upon standard method SW846 8270D, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices.

1.1.1 The modifications presented in Appendix A may be followed for analysis of samples following method 8270 (best practices).

1.1.2 Direct injection of a sample may be used in limited applications.

1.1.3 Refer to Tables 1 and 2 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. This method may be amenable to additional compounds. If non-standard analytes are required, they must be validated by the procedures described in section 13 before sample analysis.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method. They are reported as ¾-methylphenol.
- Hexachlorophene and famphur analysis are not quantitatively reliable by this method.
- Kepone should be analyzed by GC/ECD.
- Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

1.3 The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

2.0 Summary of Method

2.1 Aqueous samples are extracted with methylene chloride using a continuous extractor or a separatory funnel.

2.2 Solid samples are extracted with methylene chloride / acetone using sonication. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS.

2.3 Waste dilution is used for samples that are miscible with the solvent.

2.4 Extraction procedures are detailed in the following SOPs:

DV-OP-0006	Extraction of Aqueous Samples by Separatory Funnel, SW846 3510C and EPA 600 Series
DV-OP-0007	Concentration of Organic Extracts, SW846 3510C, 3520C, 3540C, 3550B, 3550C, 3660B, 3665A and EPA 600 Series
DV-OP-0008	Extraction of Aqueous Samples by Continuous Liquid/Liquid Extraction (CLLE) by Method SW-846 3520C and Methods 625 and 607
DV-OP-0016	Ultrasonic Extraction of Solid Samples, SW846 3550C

2.5 Qualitative identification of the analytes in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3.0 Definitions

3.1 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / matrix spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). If it is not possible to prepare both an MS and MSD due to limitations of sample amount, then a duplicate LCS should be prepared and analyzed. The RPD between the LCS and LCSD must be less than or equal to the RPD limit established for the MS/MSD.

3.2 Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the TAL QC Program document (DV-QA-003P) for further details of the batch definition.

3.3 Method Blank (MB) - An analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.4 Laboratory Control Sample (LCS) - A blank matrix (reagent water or Ottawa Sand) spiked with the analytes of interest that is carried through the entire analytical procedure. Analysis

of this sample with acceptable recoveries of the spiked analytes demonstrates that the laboratory techniques for this method are acceptable.

3.5 Matrix Spike (MS) – An aliquot of a matrix (water or soil) fortified (spiked) with known amounts of specific analytes and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.6 Matrix Spike Duplicate (MSD) - A second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method by measuring the relative percent difference (RPD) between the MS and MSD results.

3.7 Surrogates - Organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, MS, and MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

4.0 Interferences

4.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample. Cleanup procedures may help to eliminate select interferences, as follows:

- Method 3640A, Gel-Permeation Chromatography (GPC) - Removes higher molecular weight hydrocarbons by size exclusion chromatography, which is most frequently used for biological samples (TestAmerica Denver does not have a GPC unit).
- Method 3660B, Sulfur Cleanup – If a sulfur peak is detected, copper or mercury can be used to treat the extract and remove the sulfur
- Other, more aggressive cleanup procedures listed in SW-846 may be used for select compounds listed in this procedure, but may cause degradation of some of the more reactive compounds. Consult with a technical expert in the laboratory for more difficult interference problems.

Details concerning cleanup steps are described in the organic extraction SOP DV-OP-0007.

4.2 Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section (Section 9.3). Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.3 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

NOTE: Latex and vinyl gloves provide no protection against the organic solvents used in this method. Nitrile or similar gloves must be used.

5.1.2 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.4 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power before performing any maintenance.

5.1.5 The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and must be done either in a hood with the

sash down to chest level or while wearing a face shield over safety glasses.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating.

NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.

A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Materials with Significant or Serious Hazard Rating

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Sodium Hydroxide	Corrosive	2 mg/m3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Gas chromatograph/mass spectrometer system: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2 Column: 30 m x 0.25 mm I.D., 0.5-µm film thickness fused-silica capillary column coated with 5% diphenyl/95% dimethyl polysiloxane(Restek Rtx®-5MS or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer: Capable of scanning from 35 to 500 u (previously "amu") every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) that meets all of the criteria in Table 4 when 25 ng of the GC/MS tuning standard is injected through the GC.

6.4 Autosampler: LEAP Technologies CTC A200S, HP7683 Autosampler or equivalent.

6.5 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.6 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.7 Syringe: 10 µL or 5µL Hamilton Laboratory grade syringes or equivalent. The 5 µL syringe is used for the Agilent ALS to be able to inject 0.5 µL.

6.8 Carrier gas: Ultra high-purity helium.

7.0 Reagents and Standards

7.1 A minimum five-point calibration curve is prepared when average response factors or linear regression curve fitting is used. Six calibration points are required for second-order curve fits. The low point should be at or below the reporting limit. Refer to tables 11 and 12 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An internal standard (IS) solution is prepared. Compounds in the IS Mix are acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1 Internal standards are added to all standards and extracts to result in a final concentration of 40 µg/mL. For example, if the volume of an extract aliquot used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added to the aliquot. See Appendix B for the levels used for the 8270 best practice method.

7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the extraction SOPs (refer to Section 2.4 for extraction SOPs numbers). Surrogate compounds and levels are listed in Table 9.

Acid Surrogates	Base Surrogates
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-tribromophenol	Terphenyl-d4
Phenol-d5	Nitrobenzene-d5
2-chlorophenol-d4	1,2,-Dichlorobenzene-d4

7.4 GC/MS Tuning Standard: A methylene chloride solution containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 50 µg/mL.

7.5 Laboratory Control Spiking Solution: Prepare as indicated in the extraction SOPs (refer to

Section 2.4 for extraction SOPs numbers). LCS compounds and levels are listed in Table 7.

7.6 Matrix Spike Solution: Prepare as indicated in the extraction SOPs (refer to Section 2.4 for extraction SOPs numbers). The matrix spike compounds and levels are the same as the LCS compounds.

7.7 The standards are stored away from any light source at 6 °C (-10 °C recommended). The standard stock solutions expire after one year from preparation date or at the earliest expiration date assigned by the vendor to any parent standard, whichever is earlier. The continuing calibration standard should be replaced every week, when there are visible signs of degradation, or when the standard fails to meet QC criteria.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	1 liter amber	1 Liter	Cool 4 ± 2°C	7 Days	40 Days from extraction	40 CFR Part 136.3 And SW846 Chapter 4
Soils	4oz Jar	30 grams	Cool 4 ± 2°C	14 Days	40 Days from extraction	SW846 Chapter 4

9.0 Quality Control

9.1 Initial Performance Studies

9.1.1 Before analyzing samples, the laboratory must establish a method detection limit (MDL). See Section 13 for a discussion of detection limit studies.

9.1.2 In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument they will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13 for more details.

9.2 Control Limits

9.2.1 In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits are determined every 6 months. The recovery limits are the mean recovery ±3 standard deviations for surrogates, MS, and LCS. Precision limits for the MS/MSD pair results is the absolute value of the mean relative percent difference (RPD) +3 standard deviations.

9.2.2 These limits do not apply to dilutions, but surrogate and matrix spike recoveries will be reported unless the dilution is 4x or more.

9.2.3 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into the LIMS or other database so that accurate historical control limits can be generated. For multiple dilutions reported from the same extract, surrogates will be reported for all dilutions of less than 4x. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.4 Refer to the QC program document, DV-QA-003P, for further details of control limits.

9.3 Method Blank (MB)

For aqueous sample batches, the method blank is reagent water; for solid sample batches, the method blank is clean sand. In either case, the method blank is free of the analytes of interest and is spiked with the surrogates. At least one method blank must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than ½ of the reporting limit or less than 10% of the analyte concentration found in the associated samples, whichever is higher. When a compound is above ½ the reporting limit a NCM needs to be completed.

NOTE: All programs require that the maximum blank concentration must be less than one-half of the reporting limit or less than 10% of the lowest sample concentration.

Corrective Action: Re-preparation and reanalysis of all samples associated with an unacceptable method blank. If the analyte was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.4 Instrument Blank

Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample (LCS)

The LCS is prepared using reagent water for aqueous methods and Ottawa sand for solid sample methods. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency. The compounds must be spiked at a concentration equivalent to 100 or 150 µg/L, depending on the analyte, unless a special QAS states a specific level. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

Acceptance Criteria: All analytes must be within established control limits. See QC Policy DV-QA-003P for details on establishing control limits.

Corrective Action: If any analyte in the LCS is outside the laboratory-established historical control limits or project-specific control limits, as applicable, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS. This type of justification should be reviewed and documented with the client before reporting.
- If re-extraction and reanalysis of the batch are not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The matrix spike is a second aliquot of one of the samples in the batch. The matrix spike duplicate is a third aliquot of the same sample. The MS and MSD are spiked with the same analytes as the LCS (See Tables 9 and 10). An MS/MSD pair is prepared and analyzed with every batch of samples.

Acceptance Criteria: The percent recovery (%R) must fall within either historical limits or project-specific limits, as applicable. The relative percent difference (RPD) between the MS and MSD results must be less than or equal to the established historical or project-specific limit. See QC Policy DV-QA-003P for details on establishing control limits

Corrective Action: If any individual recovery or RPD fails the acceptance criteria, then corrective action must occur. Initially check the recovery of the analyte in question in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is considered to be in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any analyte fails acceptance criteria for the MS, MSD, and the LCS, the laboratory operation is considered to be out of out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.
- If it is not possible to prepare both an MS and MSD due to limitations of sample amount, then a duplicate LCS should

be prepared and analyzed. The RPD between the LCS and LCSD must be less than or equal to the RPD limit established for the MS/MSD.

- The MS/MSD pair must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted to concentrations below the calibration range.

9.7 Surrogates

9.7.1 Each sample, blank, and QC sample is spiked with the surrogate standards. Surrogate compounds must be spiked at either 100 or 150 ug/L, depending on the surrogate. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 9. For the Best Practice method, see table B-4 in Appendix B.

Acceptance Criteria: Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

Corrective Action: If any surrogates are outside of the limits, then the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.
- Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

NOTE: The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

9.7.2 If the sample with failed surrogate recoveries was a sample used for an MS/MSD pair and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample and the MS and the MSD do not require reanalysis. This phenomenon indicates a possible matrix problem.

9.7.3 If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate).

9.7.4 If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effects.

9.8 Nonconformance and Corrective Action

9.8.1 Procedural variations are allowed only if deemed necessary in the

professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The nonconformance shall be addressed in the case narrative, and the NCM shall be filed in the project file. The NCM process is described in more detail in SOP DV-QA-0031.

9.8.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents and approved by a supervisor and QA Manager.

9.8.3 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

9.9 Quality Assurance Summaries (QAS) or Program Distillations

Certain clients may require specific project or program QC that may supersede the requirements presented in this section. Quality Assurance Summaries (also known as Program Distillations) should be developed to address these requirements.

9.10 TestAmerica QC Program

Details of the Denver Quality Control Program, including corrective action guidelines, are presented in SOP DV-QA-003P, *Quality Control Program*. Refer to this document if in doubt regarding corrective actions.

10.0 Procedure

10.1 Sample Preparation

Samples are prepared according to the following organic preparation SOPs, as applicable:

DV-OP-0006	Extraction of Aqueous Samples by Separatory Funnel, SW846 3510C and EPA 600 Series
DV-OP-0007	Concentration of Organic Extracts, SW846 3510C, 3520C, 3540C, 3550B, 3550C, 3660B, 3665A and EPA 600 Series
DV-OP-0008	Extraction of Aqueous Samples by Continuous Liquid/Liquid Extraction (CLLE) by Method SW-846 3520C and Methods 625 and 607
DV-OP-0016	Ultrasonic Extraction of Solid Samples, SW846 3550C

10.2 Sample Analysis Procedure

10.2.1 Calibrate the instrument as described in Section 10. Depending on the target compounds required by the client, it may be necessary to use more than one set of calibration standards.

10.2.2 All samples must be analyzed using the same instrument conditions as the preceding continuing calibration verification (CCV) standard.

10.2.3 Add internal standard to an aliquot of the extract to result in a 40-ng/µL concentration (for example, 20 µL of internal standard solution at, 400 µg/mL in 200 µL of extract). Mix thoroughly before injection into the instrument.

10.2.4 Inject the aliquot into the GC/MS system using the same injection technique as used for the standards.

10.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration verification.

10.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst (see DV-QA-0033, Acceptable Manual Integration Practices) or automatically by the data system. The minimum documentation required includes a hard copy of original data system peak integration and a similarly scaled hard copy showing the manual integration with analyst initials and date.

10.2.7 Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.

10.2.8 Library searches of peaks present in the chromatogram that are not target compounds, i.e., Tentatively Identified Compounds (TIC), may be performed if required by the client. They are evaluated using the criteria in Section 12.2.

10.2.9 The internal standard response in the sample must be within 50 - 200% of the response in the CCV.

10.2.10 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights.

10.3 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

10.3.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are significantly less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment. For example,

samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

10.3.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will be reported only at client request.

10.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, freeze them at 6°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

10.5 Retention Time Criteria for Samples

10.5.1 If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.5.2 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

10.6 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP DV-WC-0023 for determination of percent moisture.

10.7 Procedural Variations

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described

10.8 Troubleshooting Guide

10.8.1 Daily Instrument Maintenance

In addition to the checks listed in Appendix D, the following daily maintenance should be performed.

- Clip Column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Install new or cleaned gold seal and washer as necessary.
- Perform mass calibration as necessary.

10.8.2 Major Maintenance

A new initial calibration is necessary following certain maintenance procedures. These maintenance procedures include changing the column, cleaning the repeller, cleaning the source, replacing the multiplier, and replacing the "top board" or RF-related electronics. Refer to the manufacturer's manual for specific guidance.

11.0 Calibration

11.1 Summary

The instrument is tuned for DFTPP, calibrated initially with a minimum of a five levels, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 3.

11.2 All standards and extracts are allowed to warm to room temperature before injecting.

11.3 Instrument Tuning

At the beginning of every twelve-hour shift when analyses are to be performed, the GC/MS system must be checked to see if the acceptance criteria are achieved for DFTPP (decafluorotriphenylphosphine), see Table 4. The mass spectrum is acquired with three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. The background subtraction should be designated only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or any other discrete peak that does not co-elute with DFTPP.

11.3.1 Inject 25 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 4 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

11.3.2 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. The acceptance criteria for the peak tailing factor for benzidine is < 2.0 and pentachlorophenol is < 2.0. DDT breakdown must be <20%. Refer to section 12 for the appropriate calculations.

11.3.3 Degradation of DDE and DDD must not exceed 20%.

11.4 Initial Calibration

11.4.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-S-005, Calibration *Curves (General)*.

11.4.2 Internal Standard (IS) Calibration Procedure: Internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

11.4.3 Compounds are typically assigned to the IS with the closest retention time. The laboratory tries to maintain consistent internal standard references

across instruments. As a result, there may be a few cases where compounds are very close to two different internal standards that this is not true.

11.4.4 Evaluation of retention times – The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units.

11.4.5 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest when average response factors or linear regression curve fits are used. Six standards must be used for a quadratic least-squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response.

11.4.6 For AFCEE projects, the five calibration levels will be those shown in Table 10. The table also lists a sixth calibration level that is used if a second-order regression fit is needed. The only exceptions would be for the AFCEE projects requiring special reporting limits, i.e., reporting limits different than those in the AFCEE program QAPP. Additional calibration points may be required for special projects.

11.4.7 Rejection of Calibration Points

11.4.7.1 Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

11.4.7.2 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious misinjection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

- The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e. five levels for calibrations modeled with average response factors or linear regressions, or six levels for second-order curve fits.

11.4.8 Add the internal standard mixture to result in a 40-ng/µL final concentration. (For example, if the volume of the calibration standard used is 0.5 mL, add 50 µL of the 400 µg/mL internal standard). The concentrations of all analytes are listed in Tables 11 and 12. For the Best Practice method, see Table B-5 in Appendix B.

11.4.9 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against the concentration for each compound and internal standard. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12. No sample analysis may be performed unless the following criteria are met.

11.4.10 The RSD must be < 20% for each compound of interest.

11.4.10.1 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with RSD > 20% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve fit, then the appropriate curve should be used for quantitation.

11.4.10.2 If the RSD in the initial calibration is > 20%, then calibration using a curve fit, must be used for those analytes with RSD > 20%. Linear or quadratic curve fits may be used. Use of a weighted regression is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response.

11.4.10.3 If a linear regression equation is used, the correlation coefficient r must be greater than 0.99. Use of second-order regression equations may be used on rare occasions. In these cases, the intercept and degree of curvature should be examined to be sure that results will be reliable throughout the working range, and the coefficient of determination must be greater than 0.990. When linear regression is used the first point of the calibration is recalculated under the new calibration with the values agreeing within 30% of the true values.

Note: South Carolina can only be analyzed using linear calibration.

11.4.10.4 An initial calibration verification containing all components from a second source (an alternate vendor, or, a unique lot from the same vendor) must be analyzed after the initial calibration. Acceptance criteria for ICV percent recovery (%R) are 75-125% for DoD projects (e.g., AFCEE) and 70-130% for non-DoD projects (e.g., 8270C HSL components).

Note: Several states (Arizona) and/or federal programs have special requirements. Be sure to review state QAS summaries and SOP DV-QA-024P for special requirements.

11.4.11 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or column, then repeat the calibration procedure.

11.4.12 The minimum response factor for the most common target analytes from Table 16 must be met.

11.4.13 Weighting of Calibration Data Points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. 1/Concentration2 weighting (often called 1/X2 weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability. Because the data system does not indicate the type of weighting used, the analyst must make a notation on the initial calibration form as to the weighting used (e.g. 1/x or $1/x^2$).

11.4.14 If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration, Section 11.5.

NOTE: Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration. For additional information on calibrations see SOP CA-Q-S-005.

11.5 Continuing Calibration Verification (CCV)

11.5.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 25-ng injection of DFTPP must result in a mass spectrum for DFTPP, which meets the criteria given in Table 4.

11.5.2 Following a successful DFTPP analysis, the continuing calibration verification (CCV) standard(s) are analyzed. The standard(s) must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the CCV.

11.5.3 The following criteria must be met for the CCV to be acceptable:

- The percent difference or drift (%D) of each compound must be ≤ 20%. (See Section 12 for calculations.)

Note: Some states (Wisconsin) have special continuing calibration requirements when initial calibration is performed using a quadratic curve. Please refer to state specific QAS.

- Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If the criterion is not met for more than 20% of the compounds include in the calibration, then corrective action must take place prior to the analysis for samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit.
- The internal standard response of the CCV must be within 50 - 200% of the response in the same level of the corresponding calibration.
- If any internal standard retention time in the CCV changes by more than 30 seconds from that of the same level of the corresponding initial calibration, the chromatographic system must be inspected for malfunctions and corrections made, as required.

11.5.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample injected less than or equal to 12 hours after the DFTPP is acceptable.)

11.5.5 Each of the most common target analytes in the CCV must meet the minimum response factors listed in table 16. If they are not met, the system is evaluated, and corrective action takes place before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

12.0 Calculations / Data Reduction

12.1 Qualitative Identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

NOTE: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.

12.1.1 The sample component relative retention time must compare to within ± 0.06 RRT units of the relative retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

12.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

12.1.3 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

12.1.4 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.5 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Following are guidelines for making tentative identification:

12.2.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

12.2.2 The relative intensities of the major ions should agree to within ±30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 20%and 80%.)

12.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or the presence of co-eluting compounds.

12.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.2.6 Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.3 Isomers with identical mass spectra and close elution times pose problems for definitive identification. The following compounds fall into this category:

Aniline and bis(2-chloroethyl) ether

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Identification of these compounds requires both experience and extra precautions on the part of the analyst. Specifically, the analyst must more closely scrutinize the comparison of retention times between the unknown and the calibration standard. The analyst must also check that all isomers have distinct retention times.

12.4 A second category of problem compounds consist of the poor responders or compounds that chromatograph poorly. The integrations for these types of compounds should be checked manually. The following compounds are included in this category:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol
Ariazine
Famphur
Benzidine

12.5 Calculating the Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{RF} \times 100\%$$

Where:

RF = Mean of RFs from the initial calibration for a compound

SD = Standard deviation for the mean RF from the initial calibration for a compound

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}}$$

RFi = RF for each of the calibration levels

n = Number of RF values

12.6 Calculating the Continuing Calibration Percent Drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

Where:

Cactual = Known concentration in standard
Cfound = Measured concentration using selected quantitation method

12.7 Calculating the Concentration in the Extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.7.1 Average Response Factor Calibration

If the RSD of the response factors for each compound of interest in the initial calibration is ≤20%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

Where:

Cex = Concentration in the extract, µg/mL
Rx = Response for the analyte
Ris = Response for the internal standard
Cis = Concentration of the internal standard
$\overline{RF}$ = Average response factor

12.7.2 Linear Fit Calibration

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

Where:

Cex = Concentration in the extract, µg/mL
Rx = Response for the analyte
Ris = Response for the internal standard
Cis = Concentration of the internal standard
A = Intercept of linear calibration line
B = Slope of linear calibration line

12.7.3 Quadratic Fit Calibration

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

Where:

Cex	=	Concentration in the extract, µg/mL
Rx	=	Response for the analyte
Ris	=	Response for the internal standard
Cis	=	Concentration of the internal standard
A	=	Intercept
B	=	Factor for the linear term of the quadratic calibration function
C	=	Factor for the curvature term of the quadratic calibration function

12.8 Calculating the Concentration in the Sample

12.8.1 Calculation for Aqueous Samples

$$\text{Concentration, } \mu\text{g / L} = \frac{C_{ex} V_t}{V_o}$$

Where:

Cex	=	Concentration in the extract
Vt	=	Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that Vt = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then Vt = 2,000.)
Vo	=	Volume of the sample that was extracted (mL)

12.8.2 Calculation for Sediment, Soil, Sludge, and Waste Samples

Results for sediments, sludges, and soils are usually calculated on a dry-weight basis, and for waste, on a wet-weight basis.

$$\text{Concentration, } \mu\text{g / kg} = \frac{C_{ex} V_t}{W_s D}$$

Where:

Cex	=	Concentration in the extract
Vt	=	Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that Vt = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then Vt = 2,000.)
Ws	=	Weight of sample extracted or diluted in grams
D	=	(100 - % moisture in sample)/100, for a dry-weight basis or 1 for a wet-weight basis

12.9 MS/MSD Percent Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where:

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.10 Calculating the Relative Percent Difference (RPD) MS/MSD Pair

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

Where:

RPD = Relative percent difference
MSR = Matrix spike result
MSDR = Matrix spike duplicate result

12.11 Relative Response Factor Calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

Ax = Area of the characteristic ion for the compound being measured
Ais = Area of the characteristic ion for the specific internal standard
Cx = Concentration of the compound being measured (µg/L)
Cis = Concentration of the specific internal standard (µg/L)

12.12 Calculation of TICs

The calculation of TICs (tentatively identified compounds) is identical to the above calculation (12.11) with the following exceptions:

Ax = Area of the total ion chromatogram for the compound being measured
Ais = Area of the total ion chromatogram for the nearest internal standard without interference
RF = 1

12.13 Calculating Percent DDT Breakdown

$$\%\,\text{DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDDarea}}$$

The areas for the 235 ion are used for this calculation.

12.14 Calculating the Peak Tailing Factor

$$TailingFactor = \frac{BC}{AB}$$

Where:

Peak width (AC) is measured at 10% peak height, and divided into two line segments at the peak centroid, so that .

AC = AB + BC, with
AB = left-hand segment
BC = right-hand segment

13.0 Method Performance

13.1 Method Detection Limit Study (MDL)

An initial MDL study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows

13.1.1 Prepare seven replicates at three to five times the estimated MDL concentration.

13.1.2 Extract and analyze the MDL standards as described in Section 10.

13.1.3 Calculate the mean concentration found (X) in µg/L, and the standard deviation of the mean concentration in µg/L, for each analyte. Then calculate the MDL (single-tailed, 99% confidence level, as described in Policy DV-QA-005P) for each analyte.

13.1.4 MDL studies are repeated annually, or verified quarterly, and MDL results are stored in the laboratory LIMS system. See Policy DV-QA-005P for further details concerning MDL studies.

13.1.5 The current MDL value is maintained in the TestAmerica Denver LIMS.

13.2 MDL Verification (MDLV)

Calculated MDLs from the annual studies are subject to quarterly verification by analyzing an MDLV standard prepared at 1-2 times the calculated MDL concentration. An MDLV standard is analyzed immediately after each MDL study and quarterly thereafter. This standard is subject to the entire preparation and analysis process.

Acceptance Criteria:	The calculated MDL is verified if the MDLV standard is detected, nominally signal to noise ratio ≥ 3, under routine instrument conditions.
Corrective Actions:	If the first MDLV is not detected, the MDLV standard will be reprepared and analyzed at twice the original concentration. The lowest concentration that produces a detectable signal will then be reported as the MDL.

13.3 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows:

13.3.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.3.2 Calculate the mean recovery and standard deviation for each analyte of interest.

13.3.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

13.4 Training Requirements

13.4.1 Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP DV-QA-0024.

13.4.2 Non-standard Analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration should include the analysis of an extracted standard at the reporting limit and a single point calibration.

14.0 Pollution Control

14.1 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Safety Manual, and HS-001, "Waste Management Program."

15.2 The following waste streams are produced when this method is carried out

15.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

15.2.2 Methylene Chloride- B

15.2.3 Flammable Solvent- Waste Stream C

15.2.4 Used vials- Waste Stream A

NOTE: Radioactive, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

16.0 References / Cross-References

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Revision 3, February 2007, Method 8270D.

17.0 Method Modifications:

17.1 Modifications from Reference Method

17.1.1 A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.3 This procedure includes the option for weighted linear regression curves using 1/concentration^2 weighting factors. Section 7.5.2 of Method 8000B discusses the use of weighted least square regression based on 1/standard deviation^2 weighting factors, which would require multiple analyses of each standard to determine the standard deviation. IAETL has presented information to the EPA Office of Solid Waste demonstrating that the variance (standard deviation^2) is proportional to the standard concentration. EPA accepted this argument and issued a letter in July 1998, which authorizes the use of 1/concentration^2 weighting factors.

18.0 Attachments

Table 1. TAL Primary Standard and Standard Reporting Limits
Table 2. TAL Appendix IX Standard Reporting Limits
Table 3. Suggested Instrument Conditions

Table 4. DFTPP Key Ions and Ion Abundance Criteria
Table 5. Characteristic Ions, Primary Standard (in approximate retention time order)
Table 6. Characteristic Ions, Appendix IX Standard (in approximate retention time order)
Table 7. 8270C LCS Compounds
Table 8. TCLP LCS Compounds
Table 9. 8270C Surrogate Compounds
Table 10. Calibration Levels for AFCEE Projects, µg/mL
Table 11. Calibration Levels, Primary Standard, µg/mL
Table 12. Calibration Levels, Appendix IX Standard, µg/mL
Table 13. Initial Demonstration Recovery and Precision Limits
Table 14. List 1 Reliably Performing Compounds
Table 15. List 2 Poorly Performing Compounds
Table 16 Minimum Response Factor Criteria for Initial and Continuing Calibration Verification
APPENDIX A. Modifications Required for Analysis of Wastewater Following Method 8270 Best Practice (8270BP)
Table A-1. TAL Method 8270BP Standard Reporting Limits
Table A-2. Method 8270BP Calibration Levels
Table A-3. Method 8270BP LCS Spike Concentrations
Table A-4. 8270BP Surrogate Compounds
Table A-5. Suggested Instrument Conditions for 8270BP
APPENDIX B. Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

19.0 Revision History

- Revision 0.1, dated 11 December 2009
  - Added requirements for degradation criteria for DDD and DDE in the tune to section 11.3.3.
  - Removed statement allowing a ICV standard from the same vendor and lot as long as it is prepared by a separate analyst from section 11.4.10.4.

Table 1.

TAL Primary Standard and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous (µg/L)	Low Soil/Sediment (µg/kg)
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	4	330
1,4-Dichlorobenzene	106-46-7	4	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	4	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)2	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	4	330
2-Nitroaniline	88-74-4	10	1600
Dimethyl phthalate	131-11-3	4	330
Acenaphthylene	208-96-8	4	330
3-Nitroaniline	99-09-2	10	1600
Acenaphthene	83-32-9	4	330
2,4-Dinitrophenol	51-28-5	30	1600
4-Nitrophenol	100-02-7	10	1600
Dibenzofuran	132-64-9	4	330
2,4-Dinitrotoluene	121-14-2	10	330

Table 1.

TAL Primary Standard and Standard Reporting Limits (cont.)

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous (µg/L)	Low Soil/Sediment (µg/kg)
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	4	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	4	330
4-Nitroaniline	100-01-6	10	1600
4,6-Dinitro-2-methylphenol	534-52-1	20	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	4	330
Anthracene	120-12-7	4	330
Carbazole	86-74-8	4	330
Di-n-butyl phthalate	84-74-2	4	330
Fluoranthene	206-44-0	4	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	4	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	4	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
4,4-Methylenebis(2-chloroaniline)	101-14-4	100	330
Chrysene	218-01-9	4	330
Di-n-octylphthalate	117-84-0	4	330
Benzo(b)fluoranthene	205-99-2	4	330
Benzo(k)fluoranthene	207-08-9	4	330
Benzo(a)pyrene	50-32-8	4	330
Indeno(1,2,3-cd)pyrene	193-39-5	4	330
Diethyl phthalate	84-66-2	4	660
Dibenz(a,h)anthracene	53-70-3	4	330
Benzo(g,h,i)perylene	191-24-2	4	330
Acetophenone	98-86-2	10	330
3/4-Methylphenol	108-39-4	10	330
1,4-Dioxane	54841-74-6	20	660

1. The TAL primary standard is the standard normally used at TAL. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.
2. 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

Table 2.

TAL Appendix IX Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous (µg/L)	Low Soil/Sediment (µg/kg)
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	10	660
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	1600
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	50	1600
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin	297-97-2	10	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp	3689-24-5	50	1000
Phorate	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate	2303-16-4	20	660
Dimethoate	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	10	660
Methyl Parathion	298-00-0	50	1600
1-chloronaphthalene	90-13-1	10	330
Biphenyl	92-51-3	10	330

Table 2.

TAL Appendix IX Standard Reporting Limits (cont.)

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous (µg/L)	Low Soil/Sediment (µg/kg)
4-Nitroquinoline-1-oxide	56-57-5	100	3300
Parathion	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
Isodrin	465-73-6	10	330
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	20	660
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	10	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660
Diphenylamine	122-39-4	10	330

1. The Appendix IX standard contains additional analytes required for the Appendix IX list. The TAL primary standard must also be analyzed to include all of the Appendix IX list.
2. May also be analyzed by method 8141, which can achieve lower reporting limits.
3. May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits.

Table 3.

Suggested Instrument Conditions

Mass Range:	35 - 500 amu
Scan Time:	≤ 1 second/scan
Initial Column Temperature/Hold Time:	40 °C for 1 minute
Column Temperature Program:	40 - 325 °C at 25 °C/min.
Final Column Temperature/Hold Time:	325 °C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature:	250 °C
Transfer Line Temperature:	290 °C
Source Temperature:	According to manufacturer's specifications
Injector:	Grob-type, split / splitless
Sample Volume:	0.5 µl
Carrier Gas:	Helium at 3.4 mL/min.

Table 4.

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	40 - 100% of mass 198
443	17 - 23% of mass 442

Table 5.

Characteristic Ions, Primary Standard (in approximate retention time order)

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
1,4-Dioxane	88	58	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	77
2,2'-oxybis(1-chloropropane)[1]	45	77	79
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	271
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153

Table 5.

Characteristic Ions, Primary Standard (in approximate retention time order) (cont.)

Analyte	Primary	Secondary	Tertiary
2,6-Dinitrotoluene	165	63	89
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	105	51
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Famphur	218	93	125
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
4,4-Methylenebis(2-Chloroanaline)	231	266	-
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 6.

Characteristic Ions, Appendix IX Standard (in approximate retention time order)

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	77
3/4-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	54
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	50	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169	168	115
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160

Table 6.

Characteristic Ions, Appendix IX Standard (in approximate retention time order) (cont.)

Analyte	Primary	Secondary	Tertiary
Parathion	109	97	291
Isodrin	193	66	195
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 7.

8270C LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract
1,2,4-Trichlorobenzene	100
Acenaphthene	100
2,4-Dinitrotoluene	100
Pyrene	100
N-Nitroso-di-n-propylamine	100
1,4-Dichlorobenzene	100
Pentachlorophenol	150
Phenol	150
2-Chlorophenol	150
4-Chloro-3-methylphenol	150
4-Nitrophenol	150

Table 8.

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract
1,4-Dichlorobenzene	50
2,4-Dinitrotoluene	50
Hexachlorobenzene	50
Hexachlorobutadiene	50
Hexachloroethane	50
2-Methylphenol	50
3/4-Methylphenol	100
Nitrobenzene	50
Pentachlorophenol	100
Pyridine	50
2,4,5-Trichlorophenol	50
2,4,6-Trichlorophenol	50

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA group.

Table 9.

8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
1,2-Dichlorobenzene-d4[1]	100
Phenol-d5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d4[1]	150

1. Included in standard mix, but not routinely evaluated for method 8270C

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 10.

Calibration Levels for AFCEE Projects, µg/mL

Analyte	Std Conc 1	Std Conc 2	Std Conc 3	Std Conc 4	Std Conc 5	Std Conc 6	Addnl Conc for 2nd Order ICALs
Pyridine	20	50	80	120	200	---	160
N-nitrosodimethylamine	10	20	50	80	120	200	---
Aniline	10	20	50	80	120	200	---
Phenol	10	20	50	80	120	200	---
Bis(2-chloroethyl)ether	10	20	50	80	120	200	---
2-Chlorophenol	10	20	50	80	120	200	---
1,3-Dichlorobenzene	10	20	50	80	120	200	---
1,4-Dichlorobenzene	10	20	50	80	120	200	---
Benzyl alcohol	10	20	50	80	120	200	---
1,2-Dichlorobenzene	10	20	50	80	120	200	---
2-Methylphenol	10	20	50	80	120	200	---
2,2'-oxybis(1-chloropropane)[1]	10	20	50	80	120	200	---
4-Methylphenol	10	20	50	80	120	200	---
N-Nitroso-di-n-propylamine	10	20	50	80	120	200	---
Hexachloroethane	10	20	50	80	120	200	---
Nitrobenzene	10	20	50	80	120	200	---
Isophorone	10	20	50	80	120	200	---
2-Nitrophenol	10	20	50	80	120	200	---
2,4-Dimethylphenol	10	20	50	80	120	200	---
Benzoic acid	50	50	80	120	200	---	160
Bis(2-chloroethoxy)methane	10	20	50	80	120	200	---
2,4-Dichlorophenol	10	20	50	80	120	200	---
1,2,4-Trichlorobenzene	10	20	50	80	120	200	---
Naphthalene	10	20	50	80	120	200	---
4-Chloroaniline	10	20	50	80	120	200	---
Hexachlorobutadiene	20	20	50	80	120	200	---
4-Chloro-3-methylphenol	10	20	50	80	120	200	---
2-Methylnaphthalene	10	20	50	80	120	200	---
Hexachlorocyclopentadiene	20	50	80	120	200	---	160
2,4,6-Trichlorophenol	10	20	50	80	120	200	---
2,4,5-Trichlorophenol	10	20	50	80	120	200	---
2-Chloronaphthalene	10	20	50	80	120	200	---
2-Nitroaniline	20	50	80	120	200	---	160
Dimethyl phthalate	10	20	50	80	120	200	---
Acenaphthylene	10	20	50	80	120	200	---
3-Nitroaniline	20	50	80	120	200	---	160
Acenaphthene	10	20	50	80	120	200	---
2,4-Dinitrophenol	20	50	80	120	200	---	160
4-Nitrophenol	20	50	80	120	200	---	160
Dibenzofuran	10	20	50	80	120	200	---
2,4-Dinitrotoluene	10	20	50	80	120	200	---
2,6-Dinitrotoluene	10	20	50	80	120	200	---
Diethylphthalate	10	20	50	80	120	200	---

Table 10.

Calibration Levels for AFCEE Projects, µg/mL (cont.)

Analyte	Std Conc 1	Std Conc 2	Std Conc 3	Std Conc 4	Std Conc 5	Std Conc 6	Addnl Conc for 2nd Order ICALs
4-Chlorophenyl phenyl ether	10	20	50	80	120	200	---
Fluorene	10	20	50	80	200	200	---
4-Nitroaniline	20	50	80	120	200	200	---
4,6-Dinitro-2-methylphenol	20	50	80	120	200	200	---
N-Nitrosodiphenylamine	10	20	50	80	200	200	---
Azobenzene[2]	10	20	50	80	200	200	---
4-Bromophenyl phenyl ether	10	20	50	80	200	200	---
Hexachlorobenzene	10	20	50	80	200	200	---
Pentachlorophenol	20	50	80	120	200	200	---
Phenanthrene	10	20	50	80	200	200	---
Anthracene	10	20	50	80	200	200	---
Carbazole	10	20	50	80	200	200	---
Di-n-butyl phthalate	10	20	50	80	200	200	---
Fluoranthene	10	20	50	80	200	200	---
Benzidine	50	50	80	120	200	200	---
Pyrene	10	20	50	80	200	200	---
Butyl benzyl phthalate	10	20	50	80	200	200	---
3,3'-Dichlorobenzidine	10	50	80	120	200	200	---
Benzo(a)anthracene	10	20	50	80	200	200	---
Bis(2-ethylhexyl)phthalate	10	20	50	80	200	200	---
Chrysene	10	20	50	80	200	200	---
Di-n-octylphthalate	10	20	50	80	200	200	---
Benzo(b)fluoranthene	10	20	50	80	200	200	---
Benzo(k)fluoranthene	10	20	50	80	200	200	---
Benzo(a)pyrene	10	20	50	80	200	200	---
Indeno(1,2,3-cd)pyrene	10	20	50	80	200	200	---
Dibenz(a,h)anthracene	10	20	50	80	200	200	---
Diethyl phthalate	10	20	50	80	200	200	---
Benzo(g,h,i)perylene	10	20	50	80	200	200	---

1. 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.
2. Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 11.

Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Pyridine	--	20	50	80	120	160	200
N-nitrosodimethylamine	10	20	50	80	120	160	200
Aniline	10	20	50	80	120	160	200
Phenol	10	20	50	80	120	160	200
Bis(2-chloroethyl)ether	10	20	50	80	120	160	200
2-Chlorophenol	10	20	50	80	120	160	200
1,3-Dichlorobenzene	10	20	50	80	120	160	200
1,4-Dichlorobenzene	10	20	50	80	120	160	200
Benzyl alcohol	10	20	50	80	120	160	200
1,2-Dichlorobenzene	10	20	50	80	120	160	200
2-Methylphenol	10	20	50	80	120	160	200
2,2'-oxybis(1-chloropropane)[1]	10	20	50	80	120	160	200
4-Methylphenol	10	20	50	80	120	160	200
N-Nitroso-di-n-propylamine	10	20	50	80	120	160	200
Hexachloroethane	10	20	50	80	120	160	200
Nitrobenzene	10	20	50	80	120	160	200
Isophorone	10	20	50	80	120	160	200
2-Nitrophenol	10	20	50	80	120	160	200
2,4-Dimethylphenol	10	20	50	80	120	160	200
Benzoic acid	--	20	50	80	120	160	200
Bis(2-chloroethoxy)methane	10	20	50	80	120	160	200
2,4-Dichlorophenol	10	20	50	80	120	160	200
1,2,4-Trichlorobenzene	10	20	50	80	120	160	200
Naphthalene	10	20	50	80	120	160	200
4-Chloroaniline	10	20	50	80	120	160	200
Hexachlorobutadiene	10	20	50	80	120	160	200
4-Chloro-3-methylphenol	10	20	50	80	120	160	200
2-Methylnaphthalene	10	20	50	80	120	160	200
Hexachlorocyclopentadiene	--	20	50	80	120	160	200
2,4,6-Trichlorophenol	10	20	50	80	120	160	200
2,4,5-Trichlorophenol	10	20	50	80	120	160	200
2-Chloronaphthalene	10	20	50	80	120	160	200
2-Nitroaniline	--	20	50	80	120	160	200
Dimethyl phthalate	10	20	50	80	120	160	200
Acenaphthylene	10	20	50	80	120	160	200
3-Nitroaniline	--	20	50	80	120	160	200
Acenaphthene	10	20	50	80	120	160	200
2,4-Dinitrophenol	--	20	50	80	120	160	200
4-Nitrophenol	--	20	50	80	120	160	200
Dibenzofuran	10	20	50	80	120	160	200
2,4-Dinitrotoluene	10	20	50	80	120	160	200
2,6-Dinitrotoluene	10	20	50	80	120	160	200
Diethylphthalate	10	20	50	80	120	160	200
4-Chlorophenyl phenyl ether	10	20	50	80	120	160	200

Table 11.

Calibration Levels, Primary Standard, µg/mL (cont.)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Fluorene	10	20	50	80	120	160	200
4-Nitroaniline	--	20	50	80	120	160	200
4,6-Dinitro-2-methylphenol	--	20	50	80	120	160	200
N-Nitrosodiphenylamine	10	20	50	80	120	160	200
Azobenzene[2]	10	20	50	80	120	160	200
4-Bromophenyl phenyl ether	10	20	50	80	120	160	200
Hexachlorobenzene	10	20	50	80	120	160	200
Pentachlorophenol	--	20	50	80	120	160	200
Phenanthrene	10	20	50	80	120	160	200
Anthracene	10	20	50	80	120	160	200
Carbazole	10	20	50	80	120	160	200
Di-n-butyl phthalate	10	20	50	80	120	160	200
Fluoranthene	10	20	50	80	120	160	200
Benzidine	--	20	50	80	120	160	200
Pyrene	10	20	50	80	120	160	200
Butyl benzyl phthalate	10	20	50	80	120	160	200
3,3'-Dichlorobenzidine	--	20	50	80	120	160	200
Benzo(a)anthracene	10	20	50	80	120	160	200
Bis(2-ethylhexyl)phthalate	10	20	50	80	120	160	200
4,4-Methylenebis(2-chloroaniline)	10	20	50	80	120	160	200
Chrysene	10	20	50	80	120	160	200
Di-n-octylphthalate	10	20	50	80	120	160	200
Benzo(b)fluoranthene	10	20	50	80	120	160	200
Benzo(k)fluoranthene	10	20	50	80	120	160	200
Benzo(a)pyrene	10	20	50	80	120	160	200
Indeno(1,2,3-cd)pyrene	10	20	50	80	120	160	200
Dibenz(a,h)anthracene	10	20	50	80	120	160	200
Diethyl phthalate	10	20	50	80	120	160	200
Benzo(g,h,i)perylene	10	20	50	80	120	160	200

1. 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether
2. Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 12.
Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
2-Picoline	10	20	50	80	120	160	200
N-Nitrosomethylethylamine	10	20	50	80	120	160	200
Methyl methanesulfonate	10	20	50	80	120	160	200
N-Nitrosodiethylamine	10	20	50	80	120	160	200
Ethyl methanesulfonate	10	20	50	80	120	160	200
Pentachloroethane	--	20	50	80	120	160	200
Acetophenone	10	20	50	80	120	160	200
N-Nitrosopyrrolidine	10	20	50	80	120	160	200
N-Nitrosomorpholine	10	20	50	80	120	160	200
o-Toluidine	10	20	50	80	120	160	200
3-Methylphenol	10	20	50	80	120	160	200
N-Nitrosopiperidine	10	20	50	80	120	160	200
o,o,o-Triethyl-Phosphorothioate	--	20	50	80	120	160	200
a,a-Dimethyl-phenethylamine	--	20	50	80	120	160	200
2,6-Dichlorophenol	10	20	50	80	120	160	200
Hexachloropropene	--	20	50	80	120	160	200
p-Phenylenediamine	--	20	50	80	120	160	200
n-Nitrosodi-n-butylamine	10	20	50	80	120	160	200
Safrole	--	20	50	80	120	160	200
1,2,4,5-Tetrachlorobenzene	10	20	50	80	120	160	200
Isosafrole 1 + 2	10	20	50	80	120	160	200
1,4-Dinitrobenzene	10	20	50	80	120	160	200
1,4-Naphthoquinone	--	20	50	80	120	160	200
1,3-Dinitrobenzene	10	20	50	80	120	160	200
Pentachlorobenzene	10	20	50	80	120	160	200
1-Naphthylamine	10	20	50	80	120	160	200
2-Naphthylamine	10	20	50	80	120	160	200
2,3,4,6-Tetrachlorophenol	--	20	50	80	120	160	200
5-Nitro-o-toluidine	10	20	50	80	120	160	200
Thionazin	10	20	50	80	120	160	200
1,3,5-Trinitrobenzene	--	20	50	80	120	160	200
Sulfotepp	--	20	50	80	120	160	200
Phorate	--	20	50	80	120	160	200
Phenacetin	10	20	50	80	120	160	200
Diallate 1 + 2	10	20	50	80	120	160	200
Dimethoate	10	20	50	80	120	160	200
4-Aminobiphenyl	--	20	50	80	120	160	200
Pentachloronitrobenzene	--	20	50	80	120	160	200
Pronamide	10	20	50	80	120	160	200
Disulfoton	--	20	50	80	120	160	200
2-secbutyl-4,6-dinitrophenol (Dinoseb)	10	20	50	80	120	160	200
Methyl parathion	--	20	50	80	120	160	200
4-Nitroquinoline-1-oxide	--	20	50	80	120	160	200
Parathion	--	20	50	80	120	160	200

Table 12.

Calibration Levels, Appendix IX Standard, µg/mL (cont.)

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Isodrin	10	20	50	80	120	160	200
Methapyrilene	--	20	50	80	120	160	200
Aramite 1 and 2	10	20	50	80	120	160	200
p-(Dimethylamino) azobenzene	10	20	50	80	120	160	200
p-Chlorobenzilate	10	20	50	80	120	160	200
3,3'-Dimethylbenzidine	10	20	50	80	120	160	200
2-Acetylaminofluorene	--	20	50	80	120	160	200
Dibenz (a,j)acridine	10	20	50	80	120	160	200
7,12-Dimethylbenz(a) anthracene	10	20	50	80	120	160	200
3-Methylcholanthrene	10	20	50	80	120	160	200

Table 13.

Initial Demonstration Recovery and Precision Limits

Compound	Spiking Concentration, µg/L	Limit for Relative Standard Deviation	Limit for Average Recovery, %
Acenaphthene	60	27.6	60.1-132.3
Acenaphthylene	60	40.2	53.5-126.0
Aldrin[1]	60	39.0	7.2-152.2
Anthracene	60	32.0	43.4-118.0
Benz(a)anthracene	60	27.6	41.8-133.0
Benzo(b)fluoranthene	60	38.8	42.0-140.4
Benzo(k)fluoranthene	60	32.3	25.2-145.7
Benzo(a)pyrene	60	39.0	31.7-148.0
Benzo(ghi)perylene	60	58.9	D-195.0
Benzylbutyl phthalate	60	23.4	D-139.9
B-BHC[1]	60	31.5	41.5-130.6
d-BHC[1]	60	21.6	D-100.0
Bis(2-chloroethyl) ether	60	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	60	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	60	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	60	41.1	28.9-136.8
4-Bromophenyl phenyl ether	60	23.0	64.9-114.4
2-Chloronaphthalene	60	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	60	33.4	38.4-144.7
Chrysene	60	48.3	44.1-139.9
4,4'-DDD[1]	60	31.0	D-134.5
4,4'-DDE[1]	60	32.0	19.2-119.7
4,4'-DDT[1]	60	61.6	D-170.6
Dibenzo(a,h)anthracene	60	70.0	D-199.7

Table 13.

Initial Demonstration Recovery and Precision Limits (cont.)

Compound	Spiking Concentration, µg/L	Limit for Relative Standard Deviation	Limit for Average Recovery, %
Di-n-butyl phthalate	60	16.7	8.4-111.0
1,2-Dichlorobenzene	60	30.9	48.6-112.0
1,3-Dichlorobenzene	60	41.7	16.7-153.9
1,4-Dichlorobenzene	60	32.1	37.3-105.7
3,3'-Dichlorobenzidine	60	71.4	8.2-212.5
Dieldrin[1]	60	30.7	44.3-119.3
Diethyl phthalate	60	26.5	D-100.0
Dimethyl phthalate	60	23.2	D-100.0
2,4-Dinitrotoluene	60	21.8	47.5-126.9
2,6-Dinitrotoluene	60	29.6	68.1-136.7
Di-n-octylphthalate	60	31.4	18.6-131.8
Endosulfan sulfate[1]	60	16.7	D-103.5
Endrin aldehyde	60	32.5	D-188.8
Fluoranthene	60	32.8	42.9-121.3
Fluorene	60	20.7	71.6-108.4
Heptachlor[1]	60	37.2	D-172.2
Heptachlor epoxide[1]	60	54.7	70.9-109.4
Hexachlorobenzene	60	24.9	7.8-141.5
Hexachlorobutadiene	60	26.3	37.8-102.2
Hexachloroethane	60	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	60	44.6	D-150.9
Isophorone	60	63.3	46.6-180.2
Naphthalene	60	30.1	35.6-119.6
Nitrobenzene	60	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	60	55.4	13.6-197.9
PCB-1260[1]	60	54.2	19.3-121.0
Phenanthrene	60	20.6	65.2-108.7
Pyrene	60	25.2	69.6-100.0
1,2,4-Trichlorobenzene	60	28.1	57.3-129.2
4-Chloro-3-methylphenol	60	37.2	40.8-127.9
2-Chlorophenol	60	28.7	36.2-120.4
2,4-Chlorophenol	60	26.4	52.5-121.7
2,4-Dimethylphenol	60	26.1	41.8-109.0
2,4-Dinitrophenol	60	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	60	93.2	53.0-100.0
2-Nitrophenol	60	35.2	45.0-166.7
4-Nitrophenol	60	47.2	13.0-106.5
Pentachlorophenol	60	48.9	38.1-151.8
Phenol	60	22.6	16.6-100.0
2,4,6-Trichlorophenol	60	31.7	52.4-129.2

1. Organochlorine pesticides and PCBs project DQOs generally require better sensitivity than is provided by 8270C, so methods 8081 and 8082 are used instead. These compounds will not be included in the initial demonstration of capability for method 8270C.

Table 14.

List 1 Reliably Performing Compounds

Acenaphthene	Dibenzofuran	1H-Indene
Acenaphthylene	1,4-Dioxane	Indeno(1,2,3-cd)pyrene
Acetophenone	n-Dodecane	Isophorone
Alachlor	n-Docosane	1-Methylnaphthalene
Aniline	1,2-Dichlorobenzene	2-Methylnaphthalene
Anthracene	1,3-Dichlorobenzene	2-Methylphenol
Atrazine	1,4-Dichlorobenzene	4-Methylphenol
Benzo(a)anthracene	2,3-Dichlorobenzeneamine	Methylstyrene
Benzo(a)pyrene	3,3'-Dichlorobenzidine	Naphthalene
Benzo(b)fluoranthene	2,4-Dichlorophenol	2-Nitroaniline
Benzo(k)fluoranthene	Diethyl phthalate	3-Nitroaniline
Benzo(g,h,i)perylene	2,4-Dimethylphenol	4-Nitroaniline
Benzoic acid	Dimethyl phthalate	Nitrobenzene
Benzyl alcohol	Di-n-butyl phthalate	2-Nitrophenol
Bis(2-chloroethoxy)methane	4,6-Dinitro-2-methylphenol	4-Nitrophenol
Bis(2-chloroethyl)ether	2,4-Dinitrophenol	N-Nitrosodimethylamine
Bis(2-ethylhexyl)phthalate	2,4-Dinitrotoluene	N-Nitroso-di-n-propylamine
4-Bromophenyl phenyl ether	2,6-Dinitrotoluene	N-Nitrosodiphenylamine
Butyl benzyl phthalate	1,2-Diphenylhydrazine (as Azobenzene)	2,2'-Oxybis(1-chloropropane) aka "bis(2-chloroisopropyl) ether"
Caprolactam	Di-n-octyl phthalate	n-Octadecane
Carbazole	n-Eicosane	Pentachlorophenol
4-Chloroaniline	Famphur	Phenanthrene
4-Chloro-3-methylphenol	Fluoranthene	Phenol
2-Chloronaphthalene	Fluorene	Pyrene
2-Chlorophenol	Hexachlorobenzene	Pyridine
4-Chlorophenyl phenyl ether	Hexachlorocyclopentadiene	n-Tetradecane
Chrysene	Hexachlorobutadiene	1,2,4-Trichlorobenzene
n-Decane	Hexachloroethane	2,4,5-Trichlorophenol
Dibenz(a,h)anthracene	n-Hexadecane	2,4,6-Trichlorophenol

Table 15.

List 2 Poorly Performing Compounds

2-Acetylaminofluorene	Diphenylamine	N-Nitrosopyrrolidine
Acrylamide	Disulfoton	Parathion
4-Aminobiphenyl	2-Ethoxyethanol	Pentachlorobenzene
Aramite (#1)	Ethyl methanesulfonate	Pentachloroethane
Aramite (#2)	Hexachlorophene	Pentachloronitrobenzene
Benzenethiol	Hexachloropropene	Perylene
Benzidine	Isosafrole (#1)	Phenacetin
Benzyl chloride	Isosafrole (#2)	p-Phenylenediamine
Biphenyl	Isodrin	Phorate
Carbofuran phenol	Methapyrilene	Phthalic anhydride
Chlorobenzilate	Methomyl	2-Picoline
Diallate (#1)	3-Methylcholanthrene	Pronamide
Diallate (#2)	6-Methylchrysene	Quinoline
Dibenz(a,h)acridine	4,4"-Methylenebis(2-chloroaniline)	Safrole
Dibenz(a,j)acridine	Methyl methanesulfonate	2-secbutyl-4,6-dinitrophenol (Dinoseb)
Dibenzo(a,e)pyrene	Methyl Parathion	Sulfotepp
Tris(2,3-Dibromopropyl) phosphate	1-Naphthylamine	1,2,4,5-Tetrachlorobenzene
2,6-Dichlorophenol	2-Naphthylamine	2,3,4,6-Tetrachlorophenol
Dimethoate	1,4-Naphthoquinone	Thionazin
p-(Dimethylamino)azobenzene	5-Nitro-o-toluidine	o-Toluidine
7,12-Dimethylbenz(a)anthracene	4-Nitroquinoline-1-oxide	2,4- and 2,6-Toluenediamine
3,3'-Dimethylbenzidine	N-Nitrosodiethylamine	Triethylamine
N,N-Dimtheylformamide	n-Nitrosodi-n-butylamine	Triethylphosphate
a,a-Dimethyl-phenethylamine	N-Nitrosomethylethylamine	o,o,o-Triethylphosphorothioate
1,3-Dinitrobenzene	N-Nitrosomorpholine	1,3,5-Trinitrobenzene
1,4-Dinitrobenzene	N-Nitrosopiperidine	

Table 16
Minimum Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-oxybis(1-chloropropane)[1]	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethylphthalate	0.010
Acenaphthylene	0.900
2,6-Dinitrotoluene	0.200
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
Dibenzofuran	0.800
4-Nitrophenol	0.010
2,4-Dinitrotoluene	0.200
Diethylphthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
Fluorene	0.900
4-Chlorophenylphenylether	0.400
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
N-Nitrosodiphenylamine	0.010
4-Bromophenylphenylether	0.100

Table 16
Minimum Response Factor Criteria for Initial and Continuing Calibration Verification(cont.)

Analyte	Minimum Response Factor (RF)
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butylphthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butylbenzylphthalate	0.010
Benzo(a)Anthracene	0.800
3,3'-Dichlorobenzidine	0.010
Chrysene	0.700
Bis(2-ethylhexyl)phthalate	0.010
Di-n-octylphthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

APPENDIX A

Modifications Required for Analysis of Samples Following Method 8270 Best Practice (8270BP)

REQUIREMENTS FOR METHOD 8270 BEST PRACTICE (8270BP)

- Method Best Practice is utilized to obtain lower reporting limits while still providing full scan data. The standard analyte list and reporting limits are listed in Table B-1.
- This method is only applicable to the analysis of low level samples. The appropriate range for aqueous samples is 1 to 100 ug/L and 30 to 1650 ug/Kg. Attempts to analyze samples with concentrations much higher than this for target compounds, or high concentrations of non-target compounds will likely result in a decline in the quality control parameters for the method. Once the instrument has been adversely impacted by high level samples, it may not be possible to bring it back into control in a reasonable time frame.
- The extraction is the same with one exception. The final volume of the extract is 2 mL.
- The tune period for this method is defined as 12 hours.
- Initial calibration curve requirements are as follows:
  - Same as for 8270 detailed in Section 11.4 of this SOP.
  - The calibrations levels are shown in Table B-2.
- Continuing calibration verification requirements are as follows:
  - Same as for 8270 detailed in Section 11.5 of this SOP, except the level 7 calibration point is used.
- Matrix Spike and LCS requirements are as follows:
  - The spike levels are listed in Table B-3.
- Internal Standards: The internal standard concentrations are listed in Table B-4.
- Surrogates: The surrogate concentrations are listed in Table B-5.
- Instrument Conditions are shown in Table B-6.

Table A-1.

TAL Method 8270BP Standard Reporting Limits

Analytes	CAS Number	Aqueous, µg/L
Pyridine	110-86-1	20
N-nitrosodimethylamine	62-75-9	5
Aniline	62-53-3	5
Phenol	108-95-2	10
Bis(2-chloroethyl)ether	111-44-4	1
2-Chlorophenol	95-57-8	5
Benzyl alcohol	100-51-6	5
2-Methylphenol	95-48-7	5
2,2'-oxybis(1-chloropropane)[2]	108-60-1	5
4-Methylphenol	106-44-5	5
N-Nitroso-di-n-propylamine	621-64-7	5
Hexachloroethane	67-72-1	5
Nitrobenzene	98-95-3	5
Isophorone	78-59-1	5
2-Nitrophenol	88-75-5	5
Benzoic acid	65-85-0	10
Bis(2-chloroethoxy)methane	111-91-1	5
2,4-Dichlorophenol	120-83-2	5
1,2,4-Trichlorobenzene	120-82-1	5
Naphthalene	91-20-3	5
4-Chloroaniline	106-47-8	5
Hexachlorobutadiene	87-68-3	5
4-Chloro-3-methylphenol	59-50-7	5
2-Methylnaphthalene	91-57-6	5
Hexachlorocyclopentadiene	77-47-4	5
2,4,6-Trichlorophenol	88-06-2	5
2,4,5-Trichlorophenol	95-95-4	5
2-Chloronaphthalene	91-58-7	5
2-Nitroaniline	88-74-4	5
Dimethyl phthalate	131-11-3	5
Acenaphthylene	208-96-8	5
3-Nitroaniline	99-09-2	5
Acenaphthene	83-32-9	5
2,4-Dinitrophenol	51-28-5	5
4-Nitrophenol	100-02-7	5
Dibenzofuran	132-64-9	5
2,4-Dinitrotoluene	121-14-2	5
2,6-Dinitrotoluene	606-20-2	5
4-Chlorophenyl phenyl ether	7005-72-3	5
Fluorene	86-73-7	5
4-Nitroaniline	100-01-6	5
4,6-Dinitro-2-methylphenol	534-52-1	10
N-Nitrosodiphenylamine	86-30-6	5
Azobenzene	103-33-3	5
4-Bromophenyl phenyl ether	101-55-3	5

Table A-1.

TAL Method 8270BP Standard Reporting Limits (cont.)

Analytes	CAS Number	Aqueous, µg/L
Hexachlorobenzene	118-74-1	1
Pentachlorophenol	87-86-5	10
Phenanthrene	85-01-8	1
Anthracene	120-12-7	5
Carbazole	86-74-8	5
Di-n-butyl phthalate	84-74-2	5
Fluoranthene	206-44-0	1
Benzidine	92-87-5	1
Pyrene	129-00-0	5
Butyl benzyl phthalate	85-68-7	5
3,3'-Dichlorobenzidine	91-94-1	5
Benzo(a)anthracene	56-55-3	1
Bis(2-ethylhexyl)phthalate	117-81-7	5
Chrysene	218-01-9	1
Di-n-octylphthalate	117-84-0	5
Benzo(b)fluoranthene	205-99-2	5
Benzo(k)fluoranthene	207-08-9	5
Benzo(a)pyrene	50-32-8	5
Indeno(1,2,3-cd)pyrene	193-39-5	5
Diethyl phthalate	84-66-2	5
Dibenz(a,h)anthracene	53-70-3	5
Benzo(g,h,i)perylene	191-24-2	5
1,4-Dioxane	123-91-2	1

Table A-2.

Method 8270BP Calibration Levels

Calibration Level	Calibration Concentration, µg/mL
1	0.25
2	0.40
3	1.00
4	2.50
5	5.00
6	7.50
7	10.
8	12.5
9	20.0
10	40.0
SSV	5.0

Table A-3.

Method 8270BP LCS Spike Concentrations

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	10
Bis(2-chloroethyl)ether	10
2-Chlorophenol	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
1,2-Dichlorobenzene	10
2,2'-oxybis(1-chloropropane)	10
N-Nitroso-di-n-propylamine	10
Hexachloroethane	10
Nitrobenzene	10
Isophorone	10
2-Nitrophenol	10
2,4-Dimethylphenol	10
Bis(2-chloroethoxy)methane	10
2,4-Dichlorophenol	10
1,2,4-Trichlorobenzene	10
Naphthalene	10
Hexachlorobutadiene	10
4-Chloro-3-methylphenol	10
Hexachlorocyclopentadiene	10
2,4,6-Trichlorophenol	10
2-Chloronaphthalene	10
Dimethyl phthalate	10
Acenaphthylene	10
Acenaphthene	10
2,4-Dinitrophenol	10
4-Nitrophenol	10
2,4-Dinitrotoluene	10
2,6-Dinitrotoluene	10
Diethylphthalate	10
4-Chlorophenyl phenyl ether	10
Fluorene	10
4,6-Dinitro-2-methylphenol	10
N-Nitrosodiphenylamine	10
4-Bromophenyl phenyl ether	10
Hexachlorobenzene	10
Pentachlorophenol	10
Phenanthrene	10
Anthracene	10
Di-n-butyl phthalate	10
Fluoranthene	10
Benzidine	10
Pyrene	10
Butyl benzyl phthalate	10
3,3'-Dichlorobenzidine	10
Benzo(a)anthracene	10

Table A-3.

Method 8270BP LCS Spike Concentrations (cont.)

LCS Compounds	Spiking Level, ng/µL in extract[1]
Bis(2-ethylhexyl)phthalate	10
Chrysene	10
Di-n-octylphthalate	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(a)pyrene	10
Indeno(1,2,3-cd)pyrene	10
Dibenz(a,h)anthracene	10
Benzo(g,h,i)perylene	10
N-Nitrosodimethylamine	10
1,4-Dioxane	10

Table A-4.

8270BP Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract
Nitrobenzene-d5	5
2-Fluorobiphenyl	5
Terphenyl-d14	5
1,2-Dichlorobenzene-d4[1]	5
Phenol-d5	7.5
2-Fluorophenol	7.5
2,4,6-Tribromophenol	7.5
2-Chlorophenol-d4[1]	7.5

Table A-5.

Suggested Instrument Conditions for 8270BP

Mass Range:	35 - 500 amu
Scan Time:	≤1 second/scan
Initial Column Temperature/Hold Time:	50 °C for 1 minutes
Column Temperature Program:	50 - 320 °C at 35°C/min.
Final Column Temperature/Hold Time:	325 °C/4 min hold
Injector Temperature:	275 °C
Transfer Line Temperature:	290 °C
Source Temperature:	230 °C
Injector:	Single Taper Direct Connect Liner /splitless
Sample Volume:	0.5 µl
Carrier Gas:	Helium at 1.0mL/min.
Column:	DB-5 Capillary 20m x 0.18mm x 0.36 um film thickness

APPENDIX B

Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

MASS SPECTROMETER Instrument Maintenance Schedule				
Daily	Weekly	As Needed	Quarterly	Annually
Check for sufficient gas supply. Check for correct column flow and/or inlet pressure	**Check mass calibration (PFTBA or FC-43).**	**Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add oil if needed between service contract maintenance.**	**Check vacuum, relays, gas pressures, and flows.**	**Replace the exhaust filters on the mechanical rough pump every 1 to 2 years.**
Check temperatures of injector, detector. Verify temperature programs.		**Replace electron multiplier when the tuning voltage approaches the maximum and/or when sensitivity falls below required levels.**		**Change the oil in the mechanical rough pump.**
Check inlets, septa.		**Clean source, including all ceramics and lenses. Source cleaning is indicated by a variety of symptoms, including inability of the analyst to tune the instrument to specifications, poor response, and high background contamination.**		**Relubricate the turbomolecular pump-bearing wick.**
Check baseline level.		**Repair/replace jet separator.**		
Check values of lens voltages, electron multiplier, and relative abundance and mass assignments of the calibration compounds.		**Replace filaments when both filaments burn out or performance indicates the need for replacement.**		

APPENDIX B

Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph (cont.)

GAS CHROMATOGRAPH Instrument Maintenance Schedule (For GC/MS only.)	
Daily	*As Needed*
Check for sufficient supply of carrier and detector gases. Check for correct column flow and/or inlet pressures.	***Replace front portion of column packing or guard column or break off front portion of capillary columns. Replace column if this fails to restore column performance or when column performance indicates it is required (e.g., peak tailing, poor resolution, high backgrounds, etc.).***
Check temperatures of injectors and detectors. Verify temperature programs.	***Change glass wool plug in injection port and/or replace injection port liner when front portion of column packing is changed or front portion of capillary column is removed.***
Check inlets, septa. ***Clean injector port.***	***Replace septa.***
Check baseline level.	***Perform gas purity check (if high baseline indicates that impure carrier gas may be in use).***
Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks.	***Repair or replace flow controller if constant gas flow cannot be maintained.***
	Reactivate flow controller filter dryers when the presence of moisture is suspected.
	Autosampler: Replace syringe, fill wash bottle, dispose of waste bottle contents.

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Mercury in Water by Cold Vapor Atomic Asorption (CVAA) [SW 7470A]

Approvals (Signature/Date):

8/5/09	Adam W. Alban 05 Aug 09
Richard Clinkscales — Date	Adam Alban — Date
Inorganic Operations Manager	Health & Safety Manager / Coordinator
08-07-09	8/7/09
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Quality Assurance Manager	Laboratory Director

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1.0 Scope and Application

1.1 This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A.

1.2 Method 7470 is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts.

1.3 All matrices require sample preparation prior to analysis.

1.4 The reporting limit is 0.0002 mg/L (0.2 µg/L), except for TCLP leachates that have a 0.002 mg/L (2 ug/L) reporting limit.

2.0 Summary of Method

This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3.0 Definitions

3.1 Dissolved Metals: Those elements that pass through a 0.45-µm membrane. (Sample is acidified after filtration).

3.2 Total Metals: The concentration determined on an unfiltered sample following digestion.

4.0 Interferences

4.1 Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2 Potassium permanganate, which is used to breakdown organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3 Copper also has been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.4 Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides will require dilution. During the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

4.5 Interference from certain volatile organic materials that absorb at the wavelength used for the method may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.6 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.7 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.1.2 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.3 Potassium permanganate is a strong oxidizing agent. It is incompatible and must be stored separately from hydroxylamine hydrochloride and stannous chloride, the reducing agents used in this procedure, and from acids.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- Temperature controlled, mechanically re-circulating water bath capable of maintaining a temperature of 90-95°C.
- Mercury Auto-analyzers; either of the following can be used, or equivalent:
  - CETAC Mercury Analyzer with Autosampler and Auto-Diluter
  - Perkin-Elmer FIMS Mercury Analyzer with Autosampler

6.2 Supplies

- Digestion Tubes – disposable glass, 18mm x 150mm, plastic cap
- Argon, 99.999% purity
- Calibrated automatic pipettes or Class A glass volumetric pipettes (see SOP DV-QA-0008 for details on calibrating mechanical pipettes).
- Class A volumetric flasks.
- Thermometer, non-mercury column, accurate to ±1°C at 95 °C (see SOP DV-QA-0001 for calibration details).
- Disposable cups or tubes.
- 0.45 µm syringe filters

7.0 Reagents and Standards

NOTE: The preparation of reagents and standards is recorded in Standards Log, a computerized database. The reagents and standards are listed on the bench sheet and the pipettes and/or balances used in the preparations are also listed on the bench sheet. A printout from Standards Log accompanies the bench sheet to provide preparation details for each prepared reagent and standard.

7.1 **Reagent water:** Must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2 **Nitric acid (HNO3):** concentrated, trace metal grade or better.

7.3 **Hydrochloric acid (HCl):** concentrated, trace metal grade or better.

7.4 **Hydrochloric Acid, 3%, carrier solution for the FIMS Analyzer:**
Add about one liter of reagent water to a two-liter plastic bottle. Add 60 mL of concentrated hydrochloric acid and dilute to the mark with reagent water.

7.5 **Sulfuric acid (H2SO4):** concentrated, trace metal grade or better.

7.6 **Calibration Blank, Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Method Blank (MB), 1% HNO3:**
Add 0.5 L of concentrated HNO3 to a 50-liter carboy partially filled with reagent water. Dilute to 50 L with reagent water.

7.7 Stannous Chloride ($SnCl_2$) Solution, reagent grade, 1.3% (w/v) per manufacturer's instructions. (PE FIMS Only)

7.7.1 Place approximately 100 mL of deionized water in a 2-L volumetric flask.

7.7.2 Slowly add 60 mL of concentrated HCl to the flask and swirl to mix.

7.7.3 Add 26.4 grams of $SnCl_2$ to the flask.

7.7.4 Place a large stir bar in the flask and put the flask on a stir plate.

7.7.5 Stir the contents of the flask until the reagent is completely dissolved.

7.7.6 Remove the stir bar and bring to volume with deionized water.

7.8 Stannous Chloride Solution, reagent grade, 10% (w/v) per manufacturer's (CETAC) instructions

7.8.1 Place approximately 100 mL of deionized water in a 2-L volumetric flask

7.8.2 Slowly add 200 mL of concentrated HCl to the flask and swirl to mix.

7.8.3 Add 200 grams of $SnCl_2$ to the flask.

7.8.4 Place a large stir bar in the flask and put the flask on a stir plate.

7.8.5 Stir the contents of the flask until the reagent is completely dissolved.

7.8.6 Remove the stir bar and bring to volume with deionized water.

7.9 Sodium chloride-hydroxylamine hydrochloride solution:
Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride (reagent grade) to every 100 mL of reagent water.

NOTE: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.10 Potassium permanganate ($KMnO_4$), 5% solution (w/v):
Dissolve 5 g of potassium permanganate (reagent grade, "suitable for mercury determination") for every 100 mL of reagent water.

7.11 Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v):
Dissolve 5 g of potassium persulfate, reagent grade, for every 100 mL of reagent water.

7.12 Purchased Mercury Stock Solutions

7.12.1 Primary Mercury Calibration Standard Solution, 1,000 mg/L

7.12.2 Second-source Mercury Standard (different vendor than primary calibration standard), 100 mg/L.

7.13 Calibration Working Standard Solution, 10 mg/L.

7.13.1 Add approximately 90 mL of 1% HNO_3 to a 100 mL Class A volumetric flask.

7.13.2 Pipet 1.00 mL of the 1000 mg/L primary mercury calibration standard solution (see Section 7.12.1) into the flask.

7.13.3 Dilute to the mark on the flask with 1% HNO_3.

7.13.4 Stopper the flask and shake to mix.

7.13.5 Transfer the solution to a 125 mL Nalgene bottle.

7.13.6 Document the preparation of the solution in the Standards Log database.

7.13.7 Prepare this solution fresh monthly or more often if necessary.

7.14 Daily Calibration Working Solution, 100 µg/L

7.14.1 Add approximately 90 mL of 1% HNO3 to a 100 mL Class A volumetric flask.

7.14.2 Pipet 1.00 mL of the 10 mg/L Calibration Working Standard solution (see Section 7.13) into the flask.

7.14.3 Dilute to the mark on the flask with 1% HNO3 (final volume of 100.0 mL).

7.14.4 Stopper the flask and shake to mix.

7.14.5 Transfer the solution to a 125 mL Nalgene bottle.

7.14.6 Document the preparation of the solution in the Standards Log database.

7.15 Daily Initial Calibration (ICAL)Standards.

7.15.1 To each of six volumetric flasks, add approximately 80 mL of 1% HNO3.

7.15.2 For each calibration level, add the amount of Daily Calibration Working Solution to the flask as indicated in the following table and bring the solution to a final volume of 100.0 mL. The final concentration for each calibration level is listed in the following table:

Daily ICAL Standards

Calibration Level	Volume of Daily Calibration Working Solution (100 µg/L)	Final Hg Concentration (µg/L)
1	0.20	0.2
2	0.50	0.5
3	1.0	1.0
4	2.0	2.0
5	5.0	5.0
6	10.0	10.0

7.15.3 Stopper each flask and mix thoroughly.

7.15.4 Document the preparation of the solution in the Standards Log database.

7.15.5 Prepare the calibration solutions each day prior to calibration.

7.16 Continuing Calibration Verification Standard, 5.0 µg/L.

7.16.1 The CCV is prepared exactly as the 5.0 µg/L calibration standard, and from the same source. Refer to Section 7.15.

7.16.2 Prepare sufficient volume of the standard for analysis of a CCV after every 10 samples.

7.17 Second-Source Initial Calibration Verification (ICV) Intermediate Standard, 700 µg/L.
Add 0.7 mL of the 100 mg/L ICV stock standard (see Section 17.12) to a 100 mL volumetric flask partially filled with 1%HNO3 and dilute to the mark. Record this information in the Standards Log database.

7.18 Second-Source Initial Calibration Verification (ICV) Working Standard, 7.00 µg /L.
Add 1.0 mL of the 700 µg/L ICV intermediate standard (see Section 7.17) to a 100 mL volumetric flask partially filled with 1%HNO3 and dilute to the mark. Record this information in the Standards Log database.

7.19 Laboratory Control Sample (LCS), 5 µg/L
The LCS is prepared by adding 0.5 mL of the 100 µg/L Daily Calibration Working Standard to 10 mL of reagent blank in a digestion tube.

7.20 Matrix Spike and Matrix Spike Duplicate (MS/MSD), 5 µg/L

7.20.1 The MS is prepared by adding 0.5 mL of the 100 µg/L Daily Calibration Working Solution to a digestion tube containing a second10-mL aliquot of the selected sample.

7.20.2 The MSD is prepared in the same manner as the MS using a third aliquot of the selected sample.

7.21 Reporting Limit (RL) Check Standard, 0.2 µg/L
The 0.2 µg/L calibration standard is analyzed as a sample to verify the reporting limit. Denoted as RL or RLSTD in the run sequence.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE	50 mLs	HNO_3, pH < 2	28 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

- The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

- Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.
- Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.
- Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.1 **Sample QC** - The following quality control samples are prepared with each batch of samples.

9.1.1 Preparation Batch

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.1.2 Method Blank (MB)

The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. At least one method blank must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than the reporting limit or less than 10% of the mercury concentration found in the associated samples, whichever is higher. Note that some programs (e.g., AFCEE, Navy, and USACE) require that the maximum blank concentration must be less than one-half of the reporting limit or less than 10% of the lowest sample concentration.

Corrective Action: All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If mercury was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.1.3 Laboratory Control Sample (LCS)

The LCS is a blank to which a known concentration of the target analyte has been added. At least one aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure.

Acceptance Criteria: Maximum control limits for LCS recoveries for Method 7470A are 80-120%. In-house control limits based on three standard deviations of the mean of past results are used as long as they are at least as tight as the limits in the methods (see TestAmerica Denver Policy DV-QA-003P for further details on establishing control limits).

Corrective Action: If LCS recoveries are outside established control limits, the system is out of control and corrective action must occur. If recoveries are above the upper control limit and mercury is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.1.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a second aliquot of a selected field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a third aliquot of the same sample (spiked exactly as the MS) prepared and analyzed along with the sample and matrix spike. One MS/MSD pair must be processed for each preparation batch. Some programs may require the use of sample duplicates in place of or in addition to MS/MSDs. In addition, some programs will allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Attachment 1).

Acceptance Criteria: Control limits are statistically determined based on three standard deviations of the mean of the laboratory's historical data. The recoveries for the MS and MSD must fall within 75-125%. The relative percent difference between the MS and MSD cannot exceed 20%.

Corrective Action: If analyte recoveries or the RPD between duplicates fall outside the acceptance range, then LCS recovery must be in control for the data to be reported. If there is no evidence of analytical problems and all other QC criteria are met, then qualified results may be reported and the situation must be described in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that

analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC, then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

9.1.5 Serial Dilution

Some programs (e.g., DoD programs) require that a fivefold (1+4) dilution must be included in each analytical batch for each sample matrix.

Acceptance Criteria: The results must be within 10% of the expected value, assuming that the sample concentration is at least 25x the MDL concentration.

Corrective Action: If the control limit is not met, all associated sample results must be qualified.

9.1.6 Post-Digestion Spikes

Some programs (e.g., Dupont, DOE) require the inclusion of a post-digestion spike in each analytical batch. The post-digestion spike is prepared by adding 0.25 mL of the 100 µg/L Daily Calibration Working Solution to 6.6 mL of filtered sample digestate. Post-digestion spikes are performed as an additional check for matrix interference.

Acceptance Criteria: The percent recovery limits for the post-digestion spike are 85 to 115%.

Corrective Action: If the acceptance criteria are not met, all associated sample results must be qualified.

9.1.7 Method of Standard Addition (MSA)

The method of standard additions is an option for the analysis of samples shown to have significant matrix effects, e.g., unacceptably low MS/MSD recoveries or under certain conditions for TCLP analysis (see Attachment 5)

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

9.2.1.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-S-005, *Calibration Curves (General)*.

9.2.1.2 Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

9.2.1.3 Calibrate using six standards and a blank. The concentration levels are listed in Attachment 1.

NOTE: It is generally not acceptable to reject calibration points for this method.

9.2.1.4 The calibration curve must have a correlation coefficient of ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

9.2.2 Initial and Continuing Calibration Blanks

9.2.2.1 An initial calibration blank is tested immediately after the daily ICAL standards.

Acceptance Criteria: The absolute value of the blank result must be less than the reporting limit. Some programs require that blanks be less than 2x the MDL (refer to special project requirements).

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.2.2.2 Continuing calibration blanks are run after every 10 samples and at the end of the run.

Acceptance Criteria: The absolute value of the blank result must be less than the reporting limit. Some programs require that blanks be less than 2x the MDL (refer to special project requirements).

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.2.3 Initial Calibration Verification (ICV), 7 μg/L

The accuracy of the calibration standards is verified by testing a second source standard (ICV).

Acceptance Criteria: The ICV result must be within 10% of the true value.

Corrective Action: If the ICV acceptance limit is exceeded, the analysis should be terminated, the accuracy of the calibration standards checked, and the instrument recalibrated.

9.2.4 Reporting Limit Check Standard (RL), 0.2 μg/L

The accuracy of results at the reporting limit is verified by testing a standard in every analytical run that is prepared at the reporting limit concentration.

Acceptance Criteria: The results for this standard must be within 50% of the expected value (20% for USACE and DoD projects).

Corrective Action: If the RL check acceptance limit is exceeded, the analysis should be terminated, the instrument operation checked, and the instrument recalibrated.

9.2.5 Continuing Calibration Verification (CCV), 5.0 µg/L

Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the run. The CCV must be a mid-range standard at a concentration other than that of the ICV.

Acceptance Criteria: The CCV result must fall within 20% of the true value.

Correction Action: Sample results may be reported only when bracketed by valid CCV pairs. If a mid-run CCV fails, the CCV may be re-analyzed once without modification to the instrument's operating conditions. If the re-analyzed CCV is found to be in control, the CCV analysis must be repeated with successful results or the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV failure was not directly instrument related, the associated samples must be re-prepared and reanalyzed.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM shall be filed in the project file.

10.1 Sample Preparation

10.1.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB), as well as the field samples, are processed through the digestion procedure.

10.1.2 Transfer 10.0 mL of well mixed sample and 20.0 mL of each calibration and calibration verification standard to a clean sample digestion tube. The additional volume of calibration and calibration verification standards is necessary to ensure sufficient volume to complete the analytical sequence. Be sure to add twice the amount of reagents to the calibration and calibration standards. Additional CCV and CCB solution may have to be prepared for larger sample runs.

10.1.3 Prepare an MB, LCS, MS, and MSD for each batch.

10.1.3.1 The MB consists of 10.0 mL of 1% HNO3.

10.1.3.2 The LCS is prepared by adding 0.5 mL of the 100 µg/L Daily Calibration Working Solution to 10 mL of 1% HNO3 in a digestion tube.

10.1.3.3 The MS is prepared by adding 0.5 mL of the 100 µg/L Daily Calibration Working Solution to a digestion tube containing a second 10-mL aliquot of the selected sample.

10.1.3.4 The MSD is prepared in the same manner as the MS using a third aliquot of the selected sample.

10.1.4 Add 0.5 mL of concentrated H2SO4 and 0.25 mL of concentrated HNO3 to the samples in the digestion tubes, mixing after each addition.

10.1.5 Add 1.5 mL of 5% potassium permanganate solution to each sample. For samples high in organic materials or chlorides, dilute the sample until the purple color persists for at least 15 minutes.

10.1.6 Add 0.8 mL of potassium persulfate solution, cap the vial, and heat for two hours in a water bath at 90 - 95°C. Record the start and stop times and the temperature on the bench sheet. Verify that a purple color persists or a black precipitate is present after the two hours of heating. If this is not true, repeat the digestion using a smaller aliquot of sample.

10.1.7 Allow the samples and standards to cool at room temperature.

10.2 Calibration

10.2.1 All calibration standards are digested together with samples, as described in Section 10.1, prior to analysis.

10.2.2 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.3 Sample Analysis

NOTE: Because of differences between various makes and models of CVAA instrumentation, detailed push-button operating instructions are not provided here. Refer to the specific instrument-operating manual for detailed autosampler setup and operation protocols.

NOTE: The injection of samples and the addition of stannous chloride are done automatically by the instrument. Refer to the specific instrument manual for details.

10.3.1 When ready to begin analysis, add 0.6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains.

10.3.2 All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

10.3.3 If the sample results are negative and the absolute value is greater than the reporting limit, the sample must be diluted and reanalyzed.

10.3.4 The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

10.3.5 If any samples have a visible precipitate, then filter those samples plus the method blank and LCS through 0.45 µm syringe filters.

NOTE: The method blank and LCS must be subject to all preparation and analysis steps in order to accurately represent the batch.

10.3.6 Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB. Re-sloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

10.3.7 The following analytical sequence must be used for Method 7470A. Refer to Quality Control Section 9.0 and Attachment 2 for quality control criteria to apply to Method 7470A.

Instrument Calibration
ICB
ICV
RL
Maximum of 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete the run.
CCV
CCB

NOTE: Samples included in the count between CCVs include the method blank, LCS, MS, MSD, and field samples.

10.3.8 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

- Recovery of the analyte in the matrix spike is not at least 50%;
- The concentration of the analyte does not exceed the regulatory level; and
- The concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Attachment 1. Attachment 5 provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

10.3.9 To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

10.3.10 See Attachment 7 for guidelines for minimizing contamination of samples and standards. See Attachment 8 for guidance on troubleshooting and preventive maintenance.

11.0 Calculations / Data Reduction

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 **Concentration** = Hg concentration *(µg/L)* = $C \times D$

Where:

C = Concentration (µg/L) from instrument readout
D = Instrument dilution factor

11.4 Appropriate factors must be applied to sample values if dilutions are performed.

11.5 Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy (DV-QA-004P).

11.6 **Documentation and Record Management**
The following documentation comprises a complete CVAA raw data package:

- Sample preparation bench sheet(s), to include the batch number, list of samples, preparation analyst and date, instrument analysis analyst and date, identification of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes). See Attachment 3.
- Raw data (direct instrument printout).
- Run log printout from instrument software where this option is available or manually-generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Attachment 4.

- Standards Documentation to include source, lot, preparation date, and expiration date. A printout from Standards Log provides all required information except identification of measuring equipment used.
- Nonconformance summary (if applicable).

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Prepare and analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

- Four LCSs are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.
- If the recoveries do not meet the historical acceptance criteria, the test must be repeated. Repeated failures indicate the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

12.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.3.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or

other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually. Initial Demonstration of Capability

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produce when this method is carried out:

- Aqueous Acidic (Metals) - Corrosive - Waste Stream J
- Expired reagents and standards – Contact the Waste Coordinator.

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, March 2005.

15.3 U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 7470A	Chapter 1 of SW846 specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.
2	EPA 7470A	This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."
3	EPA 7470A	Methods 7470A and 7471A state that working mercury standards "should be prepared fresh daily." The laboratory frequently prepares up to three batches of mercury samples, including digested calibration standards, each day. The third batch is typically prepared and digested late in the day, and then is analyzed the morning of the next day. The laboratory has developed the following information demonstrating that analysis within 24 hours, but on the second calendar day from preparation produces reliable results and is acceptable to the EPA: • Successful proficiency testing PT results for samples that were prepared and analyzed within 24 hours, but on successive days (e.g., ERA WP-66); • Successful analysis of true NIST mercury standards within every analytical batch; and • A written comment from the EPA MICE Hotline stating that, with the supporting lab data, their opinion was that the laboratory's practice is "within the letter of the method as written."
4	EPA 7470A	Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.0 Attachments

Figure 1: Aqueous Sample Preparation Flow Chart
Figure 2: CVAA Mercury Analysis Flow Chart
Attachment 1: Mercury Reporting Limits, Calibration Levels, QC Standard and Spiking Levels
Attachment 2: Summary of Quality Control Requirements
Attachment 3a: Example Metals Preparation Benchsheet - FIMS
Attachment 3b: Example Metals Preparation Benchsheet -CETAC
Attachment 4: Example Raw Data Checklist
Attachment 5: MSA Guidance
Attachment 6: Troubleshooting Guide
Attachment 7: Contamination Control Guidelines
Attachment 8: Preventative Maintenance

18.0 Revision History

- Revision 0.2 dated 07 August 2009
  - Sections 7.17 and 7.18 were updated to use 1% HNO3 from reagent blank.
  - Sections 10.1.3.1 and 10.1.3.2 were updated to use 1% HNO3 from reagent blank.
  - Changed SOP name DV-QA-003P from QC Policy to Quality Assurance Program.

- Revision 0.1, dated 16 February 2008
  - Section 9.1.2: Changed control limit to 10% to match soil SOP
  - Section 9.2.2: Changed the stated control limits for special projects from ½ the RL to 2x the MDL
  - Deleted section 12.2 for IDL requirements
  - Section 12.3: Noted that LCSs will be used for verification

Figure 1.

Aqueous Sample Preparation Flow Chart

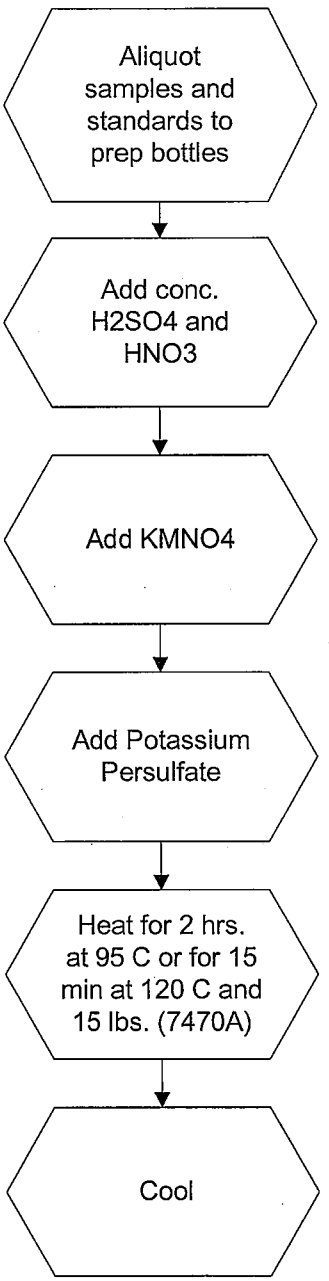
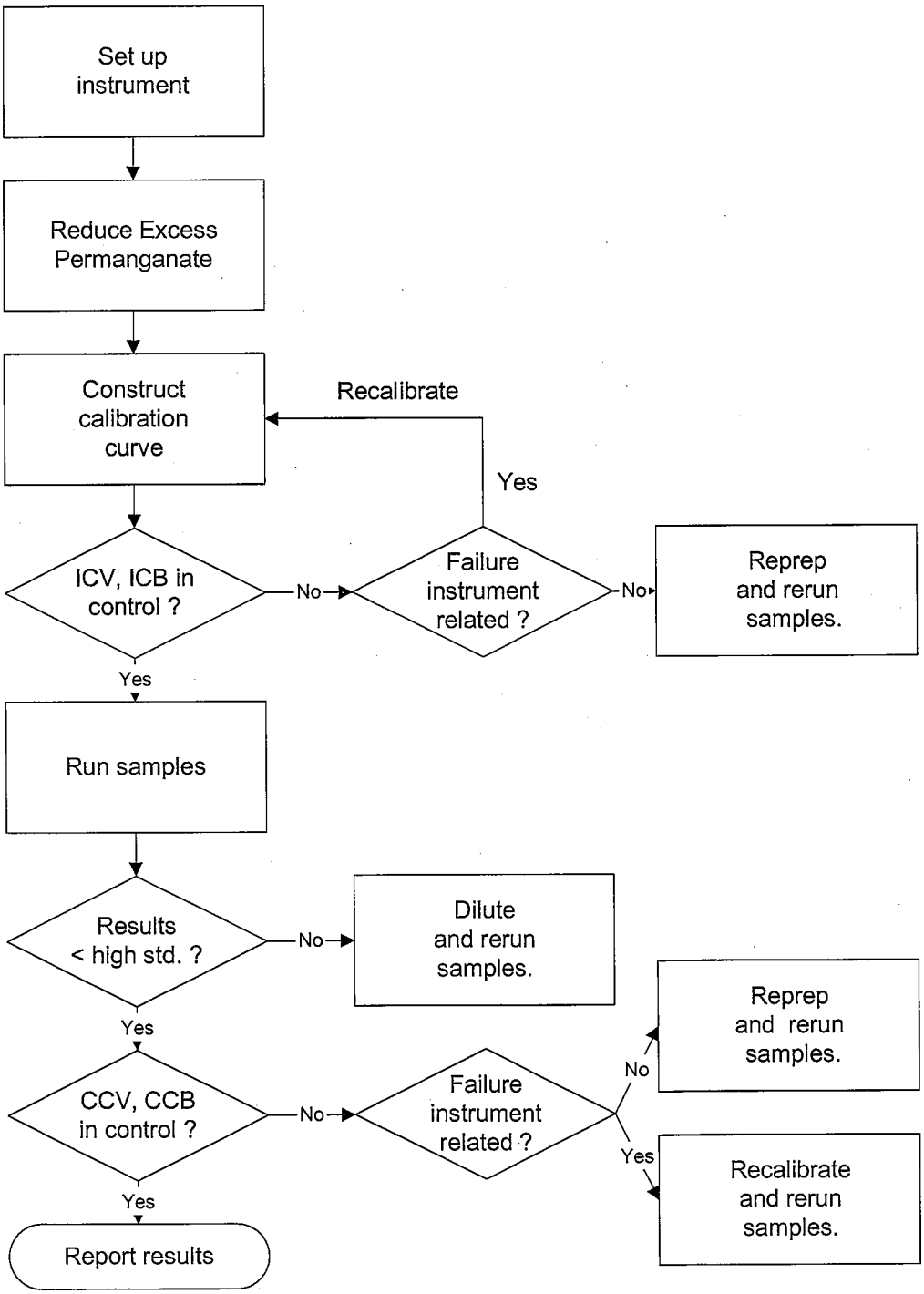


Figure 2.

CVAA Mercury Analysis Flow Chart



Attachment 1.

Mercury Reporting Limits, Calibration Levels, QC Standard and Spiking Levels (µg/L)

Standard Aqueous RL	0.2
TCLP RL	0.2
Std 0	0
Std 1	0.2
Std 2	0.5
Std 3	1.0
Std 4	2.0
Std 5	5.0
Std 6	10.0
ICV	7.0
LCS/CCV	5.0
Aqueous MS	5.0
TCLP MS	5.0

Attachment 2.

Summary of Quality Control Requirements

QC Parameter	Frequency *	Acceptance Criteria	Corrective Action
ICV	Beginning of every analytical run.	90 - 110% recovery	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.2.3).
ICB	Beginning of every analytical run, immediately following the ICAL.	Absolute value must be < RL, 2x the MDL for DoD	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.2.2).
CCV	Every 10 samples and at the end of the run.	80 - 120% recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.2.5).
CCB	Immediately following each CCV.	Absolute value must be < RL, 2x the MDL for DoD	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.2.2).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than the RL (< ½ RL for DoD) Sample results greater than 10x the blank concentration are acceptable.	Re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.1.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	In-house 3 standard deviation control limits, not to exceed 80-120% recovery.	Terminate analysis; Correct the problem; Re-digest and reanalyze all samples associated with the LCS (see Section 9.1.3).
Matrix Spike	One per 10 samples preparation batch of up to 20 samples.	In-house 3 standard deviation control limits, not to exceed 75-125% recovery	In the absence of client-specific requirements, flag the data (see Section 9.1.4).
Matrix Spike Duplicate	See Matrix Spike	In-house 3 standard deviation control limits, not to exceed 20% RPD	See Corrective Action for Matrix Spike.

Attachment 3a.

Example Metals Preparation Benchsheet – FIMS

SUPPLEMENTAL METALS PREP SHEET
(Used in conjunction with METALS PREP LOG/BATCH SUMMARY)

Hg PREP & ANALYSIS - WATERS

SOP: DEN-MT-0015 QC Batch #: _____

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING
TestAmerica Denver

Prep Date: 1/14/08	Prep By: DAW	Analysis Date: 1/14/08	Analyst: DAW
Balance ID: H53865		***Thermometer ID:*** MT 4025	

Digestion Cycles	Start Time	Temp °C	End Time	Temp °C
	12:10	93	14:10	93

Purple color persists or black ppt present: [X] Yes [ ] No If "No", explain in Comments below.

Digestion Tube Lot # :

For dissolved mercury only, were samples filtered in the lab? [ ] Yes [ ] No
One or more samples were filtered prior to analysis at the instrument. [ ] Yes [ ] No
If "yes", then the method blank and the LCS were also filtered in the same manner using the same type of filter.
Analyst(s) Initials: [ ]

Reagents Used

Reagent	Manufacturer	Lot #	Standards Log #	Vol (mL)
HNO_3	JT Baker	E27027		0.25
H_2SO_4	Fisher	E43040		0.5
HCl	JT Baker	E40030		used by instrument
1.3% $SnCl_2$	Fisher	E20625	STD-1033-08	added by instrument
NaCl / NH_2OH	Fisher	E13654	STD-1032-08	0.6
	Fisher	E20644		
$KMnO_4$	Fisher	C30018	STD-1020-08	1.5
$K_2S_2O_8$	Fisher	0626[illegible]	STD-6304-07	0.8

Parent Calibration Stock Standards

	Lot #	Verification #	Exp. Date
Second Source	A2-HG02019	STD-2102-07	06/01/08
Primary Calibration	F004[illegible]4	STD-1008-08	04/03/08

Standards Preparation **Final digestate volume = 10 mls**

Standards	Final Conc	Parent Standard	Standards Log #	Vol (mL)	Pipette
Cal Working	10 mg/L	Primary Cal	See Attached Standards Log Printouts	1.00	20
Daily Cal Working	100 ug/L	Cal Working		1.00	20
ICAL 0.2	0.2 ug/L	Daily Cal Working		0.2	20
ICAL 0.5	0.5 ug/L	Daily Cal Working		0.5	20
ICAL 1	1.0 ug/L	Daily Cal Working		1.0	20
ICAL 2	2.0 ug/L	Daily Cal Working		2.0	20
ICAL 5	5.0 ug/L	Daily Cal Working		5.0	19
ICAL 10	10 ug/L	Daily Cal Working		10.0	19
CCV	5 ug/L	Daily Cal Working		5.0	20
ICV Intermed	700 ug/L	ICV Stock		0.70	20
ICV Daily Working	7.0 ug/L	ICV Intermed		1.00	20
LCS	5 ug/L	Daily Cal Working		0.5	20
MS/MSD	5 ug/L	Daily Cal Working		0.5	20
RL	0.2 ug/L	Daily Cal Working		0.2	20

Second Source ICV Intermediate Stock Standard Prep **Standards Log #:** STD-1017-08

NOTE: Details for each reagent & standard prep are documented in the attached Standards Preparation Logbook Record.

Comments

I certify that all information above is correct and complete.

Signature: ***Date:***

REVIEWED BY: _____ Date: _____

SAMPLE

Attachment 3b.

Example Metals Preparation Benchsheet – CETAC

SUPPLEMENTAL METALS PREP SHEET
(Used in conjunction with METALS PREP LOG/BATCH SUMMARY)

Hg PREP & ANALYSIS - WATERS

SOP: DEN-MT-0015 QC Batch #: _____

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING
TestAmerica Denver

Prep Date: 1/15/08	Prep By: DAW	Analysis Date: 1/16/08	Analyst: DAW
Balance ID: H53865		***Thermometer ID:*** MT 4025	

Digestion Cycles	Start Time	Temp °C	End Time	Temp °C
	15:30	93	17:30	93

Purple color persists or black ppt present: [X] Yes [ ] No If "No", explain in Comments below.

Digestion Tube Lot # :

For dissolved mercury only, were samples filtered in the lab? [ ] Yes [ ] No
One or more samples were filtered prior to analysis at the instrument. [ ] Yes [ ] No
If "yes", then the method blank and the LCS were also filtered in the same manner using the same type of filter.
Analyst(s) Initials: [ ]

Reagents Used

Reagent	Manufacturer	Lot #	Standards Log #	Vol (mL)
HNO_3	JT Baker	E27027		0.25
H_2SO_4	Fisher	E43040		0.5
HCl	JT Baker	E40030		used by instrument
10% $SnCl_2$	Fisher	E20623	STD-1019-08	added by instrument
NaCl / NH_2OH	Fisher	E13654	STD-1032-08	0.6
	Fisher	E09641		
$KMnO_4$	Fisher	C30618	STD-1020-08	1.5
$K_2S_2O_8$	Fisher	062601	STD-6084-07	0.8

Parent Calibration Stock Standards

	Lot #	Verification #	Exp. Date
Second Source	AB-HG-2049	STD-2102-07	06/01/08
Primary Calibration	500424	STD-1008-08	04/03/08

Standards Preparation — Final digestate volume = 10 mls

Standards	Final Conc	Parent Standard	Standards Log #	Vol (mL)	Pipette
Cal Working	10 mg/L	Primary Cal	See Attached Standards Log Printouts	1.00	20
Daily Cal Working	100 ug/L	Cal Working		1.00	20
ICAL 0.2	0.2 ug/L	Daily Cal Working		0.2	20
ICAL 0.5	0.5 ug/L	Daily Cal Working		0.5	20
ICAL 1	1.0 ug/L	Daily Cal Working		1.0	20
ICAL 2	2.0 ug/L	Daily Cal Working		2.0	20
ICAL 5	5.0 ug/L	Daily Cal Working		5.0	19
ICAL 10	10 ug/L	Daily Cal Working		10.0	19
CCV	5 ug/L	Daily Cal Working		5.0	20
ICV Intermed	700 ug/L	ICV Stock		0.70	20
ICV Daily Working	7.0 ug/L	ICV Intermed		1.00	20
LCS	5 ug/L	Daily Cal Working		0.5	20
MS/MSD	5 ug/L	Daily Cal Working		0.5	20
RL	0.2 ug/L	Daily Cal Working		0.2	20

Second Source ICV Intermediate Stock Standard Prep **Standards Log #:** STD-1017-08

NOTE: Details for each reagent & standard prep are documented in the attached Standards Preparation Logbook Record.

Comments

I certify that all information above is correct and complete.

Signature: ***Date:***

REVIEWED BY: _____ **Date:** _____

SAMPLE

Attachment 4.

Example Raw Data Checklist

TESTAMERICA-DENVER

Applicable QC Batches:_____

_____

_____

Industrial Mercury Analysis Raw Data Checklist

Revision 2 -March 5, 2008

Analyst's Checklist

	yes	no	n/a
1. Were the special instructions for prep and/or analysis followed?	☐	☐	☐
2. Is the correlation coefficient ≥ 0.995?	☐	☐	☐
3. Is the blank less than the reporting limit or properly anomalized?	☐	☐	☐
4. Is the LCSs within limits or properly anomalized?	☐	☐	☐
5. Is the ICV and all CCVs within limits?	☐	☐	☐
6. Are all CCBs within ± one reporting limit from zero?	☐	☐	☐
7. Were the CCVs and CCBs run with up to 10 samples between each set?	☐	☐	☐
8. Are the reporting limits correct and reflect any dilutions?	☐	☐	☐
9. Are the number of significant figures correctly reported?	☐	☐	☐
10. Are the benchsheets complete (including calibration and standard verification #'s)?	☐	☐	☐
11. Are all comments, footnotes, and anomalies properly documented?	☐	☐	☐
12. Are holding time violation forms completed and attached?	☐	☐	☐
13. Has all sample data been entered into LIMS?	☐	☐	☐
14. Has all QC data been entered into LIMS?	☐	☐	☐
15. Has the data entered into LIMS been checked for errors?	☐	☐	☐
16. For TCLP results, is the sample data within 20% of Regulatory Level (0.2 mg/L)?	☐	☐	☐

Analyst's Name:_____ Date:_____

Data Review's Checklist

	yes	no	n/a
1. Have the calculations been checked?	☐	☐	☐
2. Is the correlation coefficient ≥ 0.995?	☐	☐	☐
3. Is all the QC data within the control limits and/or properly anomalized?	☐	☐	☐
4. Are all the significant figures and reporting limits correct?	☐	☐	☐
5. Have any comments, footnotes, and anomalies been properly documented?	☐	☐	☐
6. Have any data errors been documented and entered into LIMS?	☐	☐	☐
7. Is prep date correct in LIMS?	☐	☐	☐
8. Has the data package been copied and filed?	☐	☐	☐
9. If TCLP result within 20% of Reg. Level (0.2 mg/l) and MS < 50%, was MSA performed?	☐	☐	☐

Reviewed by:_____ Date:_____

Comments:_____

_____

_____

Anomalies:_____

_____

_____

EXAMPLE

Attachment 5.

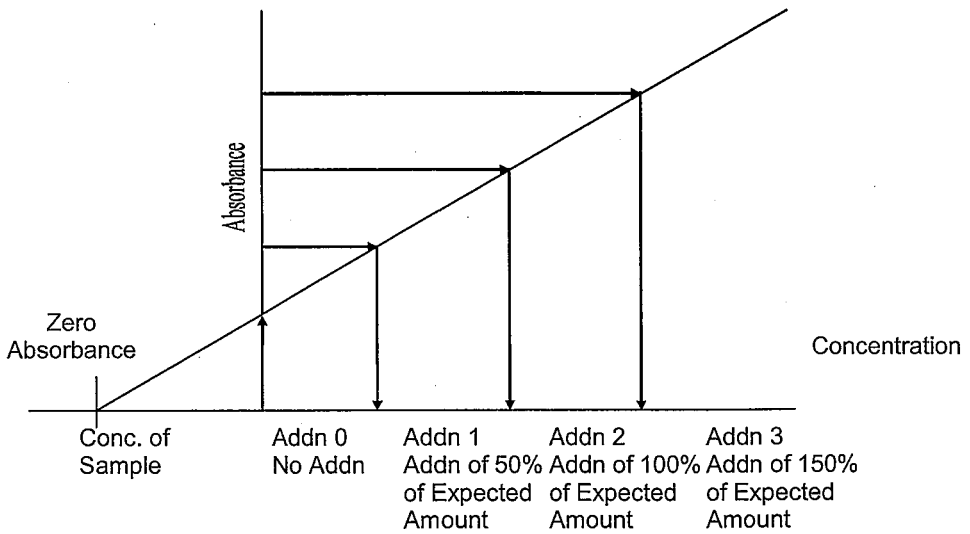
MSA Guidance

Method of Standard Addition (MSA)

Four equal volume aliquots of sample are measured and known amounts of standards are added to three of the aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration, and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of an analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. The absorbance (or response) is plotted on the vertical axis versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. The correlation coefficient (r) and the x-intercept (where y=0) of the curve are calculated. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 6.

Troubleshooting Guide

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak
Erratic Readings	Source lamp not aligned properly Lamp not pre-warmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

Attachment 7.

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered gloves should not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- If an unusually high sample is analyzed, segregate the glassware and soak with sulfuric acid prior to routine cleaning.

Attachment 8.

Preventative Maintenance

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs, record the date, time, and instrument number; describe the problem; and explain the corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational:

Cold Vapor Atomic Absorption (Leeman PS 200 and CETAC Analyzer)

Daily	Monthly	Annually
Change rinse solution.	Check Hg lamp intensity.	Change Hg lamp.
Optimize light path.		Check liquid/gas separator.
Check nitrogen flow.		
Check tubing. Replace as needed.		
Check drain.		
Check condition of dryer		

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THE LEADER IN ENVIRONMENTAL TESTING

ICP Analysis for Trace Elements by SW-846 Method 6010C

Approvals (Signature/Date):

Doug Gomer 6/19/09
Doug Gomer — Date
Metals Supervisor

Adam W. Alban 19 June 09
Adam Alban — Date
Health & Safety Manager / Coordinator

Karen Kuoppala 6.19.09
Karen Kuoppala — Date
Quality Assurance Manager

Robert C. Hanisch 6/19/09
Robert C. Hanisch — Date
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1.0 Scope and Application

1.1 This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICPAES). This procedure references Method 6010C for hazardous waste (RCRA) testing.

1.2 The elements that can be determined by this procedure are listed in Attachment 1, together with the routine reporting limits. Additional elements may be analyzed under Method 6010C provided that the method performance criteria presented in Section 12.0 are met.

1.3 The laboratory digests water samples according to SOP DV-IP-0010. The methods require digestion of waters, with the following exceptions, i.e.:

- The sample is visibly transparent with a turbidity measurement of 1 NTU or less.
- The sample consists of one liquid phase and is free of particulate or suspended matter following acidification.

1.4 Silver concentrations must be below 1.0 mg/L in aqueous sample digestates and 100 mg/kg in solid matrix sample digestates. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data. Samples with silver concentrations exceeding these levels must be re-prepared and reanalyzed using a smaller sample amount.

1.5 The digestion procedure for soil samples is described in SOP DV-IP-0015.

1.6 State-specific requirements may take precedence over this SOP for drinking water sample analyses. Review special instructions for each project before starting work.

2.0 Summary of Method

2.1 The laboratory uses simultaneous ICPAES instruments, with both axial and radial viewing configurations. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs.

2.2 Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photo-multiplier tubes or a charge injection device (CID). The photo-currents from the photo-multiplier tubes or a charge injection device (CID) are processed and controlled by a computer system.

2.3 A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.4 Refer to the appropriate SOPs for details on sample preparation methods: DV-IP-0010 for aqueous samples, and DV-IP-0015 for soil samples.

3.0 Definitions

3.1 **Trace ICP** – in this SOP, an ICP with the viewing angle along the long axis of the torch (axial ICP) is referred to as a Trace ICP.

3.2 **Dual View ICP** – an ICP equipped with both radial and axial viewing capabilities.

3.3 **Dissolved Metals** - Those elements which pass through a 0.45-µm membrane. (The sample is acidified after filtration).

3.4 **Potentially Dissolved Metals** - Potentially dissolved metals is the concentration of metals in solution after acidifying the sample with nitric acid to pH <2, holding at room temperature for 8 to 96 hours, and then filtering through a 0.45-µm membrane filter. This definition is based on the Colorado surface water regulations.

3.5 **Suspended Metals** - Those elements which are retained by a 0.45-µm membrane.

3.6 **Total Metals** - The concentration determined on an unfiltered sample following vigorous digestion.

3.7 **Total Recoverable Metals** - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.8 **Reporting Limit (RL) -** The lowest concentration to which results are reported without qualification. Details concerning RLs are presented in Policy QA-009.

4.0 Interferences

4.1 Spectral, physical, and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by the following:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.2 A background correction technique is used to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.3 Spectral Interferences

4.3.1 Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte signal. If such conditions exist,

the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections must be applied to the analyte to compensate for the effects of these unwanted emissions.

4.4 Physical Interferences

4.4.1 An internal standard (IS), yttrium or other suitable element, is added to all solutions to correct and monitor physical interferences. Use of a peristaltic pump and the mass flow controller also help to overcome physical interferences. Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If internal standard recoveries are not acceptable (see Section 0), then dilution of the sample may be necessary to overcome the interferences. Where the use of an internal standard might actually degrade the accuracy of the analytical result, sample results may be reported without IS correction.

4.5 Chemical Interferences

4.5.1 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not significant with the ICP technique, but if observed, can be minimized by buffering the sample, matrix matching, or standard addition procedures.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with

pacemakers should not go near the instrument while in operation.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

(1) Always add acid to water to prevent violent reactions.
(2) Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Thermo Jarrell Ash ICP 61E Trace Analyzer and Thermo Fischer ICP 6500E Trace Analyzer are currently used. Instruments with demonstrated equivalent performance can also be used

6.1.2 Radio Frequency Generator.

6.1.3 Argon gas supply, welding grade or equivalent.

6.1.4 Coolflow or appropriate water-cooling device.

6.1.5 Peristaltic Pump.

6.1.6 Autosampler.

6.2 Supplies

6.2.1 Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.2.2 Class A volumetric flasks.

6.2.3 Autosampler tubes.

7.0 Reagents and Standards

7.1 Shelf-Life

7.1.1 Stock standards, standards as received from the vendor, expire on the date assigned by the vendor. If no date is assigned by the vendor, a one-year expiration will be assigned by the laboratory.

7.1.2 The expiration date of intermediate concentration standards or working standards cannot be later than the date assigned to any of the stock standards used to prepare the intermediate solution.

7.1.3 If visible deterioration is noted for any standard, it must be re-verified against a second-source. Any standard that does not verify must be replaced immediately.

7.2 Standards

7.2.1 Standards used for calibration and quality control purposes must be NIST traceable, where available. Multi-component custom blend standards must be verified against a second-source standard before they are put into use (the only exception is standards purchased directly from NIST), as described in SOP DV-QA-0015.

7.2.2 Intermediate standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon,

polyethylene, or polypropylene bottles. Silver standards must be protected from light. The preparation frequency is governed by the parent standard with the earliest expiration date unless specified otherwise in this SOP. Detailed instructions regarding the preparation of standards and reagents are given in this section. Alternate procedures are allowed as necessary to accommodate volume requirements as long as final concentrations are maintained and an accurate description of the standard or reagent used is entered into the Standards Log database.

7.2.3 Calibration and QC standards are prepared in water with hydrochloric and nitric acids in order to approximate the acidic matrix of the various digests analyzed. This is an important point. Even with the use of yttrium as an internal standard, deviations from these concentrations can cause physical effects, as discussed in Section 4.4 of this procedure.

7.3 Reagent Blank / Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

7.3.1 Fill a 20-liter carboy with about 18 liters of reagent water. Slowly add the appropriate amount of concentrated HNO_3 and concentrated HCl. Mix carefully.

7.4 Stock ICSA and ICSAB Standards

The following standards are purchased from commercial sources:

Stock ICSA & ICSAB Standard	Elements	Concentration (mg/L)
ICSA Std	Fe Al, Ca, Mg	2,000 5,000
ICSAB Std	Ba, Be, Co, Cr, Cu, Mn, V Ag, Cd, Ni, Pb, Zn	50 100
ICSAB 1	Li, Mo, Sb, Sr As, B, P Se K, Na	100 200 500 5000
ICSAB 1B	Tl	1,000
ICSAB 2	Ti Sn	100 1,000
10,000 Si	Si	10,000
Th	Th	1,000
U	U	1,000
Zr	Zr	1,000
S	S	1,000
Bi	Bi	1,000

7.5 ICSA Working Standard

A combined working ICSA standard is made in a 250-mL volumetric flask using the following volumes of the Stock ICSA and ICSAB Standards:

Stock Standard	Volume of Stock Added (mL)
ICSA Std	25
1,000 mg/L U Standard	0.5

Adjust to volume (250 mL) using the reagent blank solution. This produces the final ICSA standard concentrations shown in Attachment 5.

7.6 ICSAB Working Standard

A combined working ICSAB standard is made in a 250-mL volumetric flask using the following volumes of the Stock ICSAB Standards:

Combined Working ICSAB Standard

Stock Standard	Volume of Stock Added (mL)
ICSA Std	25
ICSAB Std	2.5
ICSAB 1	2.5
ICSAB 1B	2.5
ICSAB 2	2.5
10,000 mg/L Si	0.25
1,000 mg/L S	0.25
1,000 mg/L Th	0.5
1,000 mg/L U	0.5
1,000 mg/L Zr	0.25
1,000 mg/l Bi	0.25

Adjust to volume (250 mL) using the reagent blank solution. This produces the final ICSAB standard concentrations shown in Attachment 5.

7.7 High Calibration Check Standard

The high concentration check standard is the same as the Working ICAL Standards.

7.8 Laboratory Control Sample (LCS) Stock Standards

The LCS stock standards are purchased from commercial sources. The stocks are custom-made standards purchased at ready-to-use concentrations as follows:

LCS STOCK STANDARD	ELEMENTS	CONCENTRATION (MG/L)
ICP Prep Spike #1	Ca, K, Mg, Na P Al, As, Ba, Se, Th, Tl, U,Bi Fe, Sr Co, Mn, Ni, Pb, V, Zn Cu Cr Ag, Be, Cd	5,000 1,000 200 100 50 25 20 5
ICP Prep Spike #2	Sb, Zr B, Mo, Ti Sn Si (SiO_2)	50 100 200 1000 (2140)
Sulfur	S	200

Soil Batches – LCS spikes for soil batches are prepared by adding 1.0 mL of the LCS to a digestion tube containing 5 mL of reagent water. The AFCEE program requires the addition of 1 g of glass beads to the digestion tube.

Water Batches – LCS spikes for water batches are prepared by adding 0.5 mL of LCS Stock Standard to a digestion tube containing 50 mL of reagent water.

Note: The LCS are spiked with each analyte of interest of interest at the project-specific action levels or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range.

7.9 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

The same LCS stock standards described in the previous section, 7.8, are also used to prepare matrix spikes. The same media and spike concentrations are used as well.

7.10 Post Digestion Spike (PDS) Standards (Analyte Addition Spike Standards)

The custom standards tabulated below are purchased from a commercial source. Add 0.1 mL of each to 10 mL (100X) of digestate or dilution of digestate.

PDS Stock	Elements	Conc. (mg/L)
PDS 1	Ag, Be, Cd, Co, Cr, Cu, Mn, Ni, Sr, V Ba, Pb, Li As, Se, Tl, Zn, Th U Al, Fe P Ca, Mg, Na, K	5.0 10 20 50 100 200 2,000
PDS 2	Mo, Ti, Zr B, Sb, Sn Si	5.0 10 500

7.11 Initial Calibration (ICAL) Standards for the Dual View ICP

7.11.1 Stock Calibration Standards

The following stock solutions are purchased from commercial sources.

Stock Standard	Elements	Conc. (mg/L)
STLDEN-STD-2	Mo, Ti, Zr Sn Si	100 200 1,000
STLDEN-STD-3B	Ag, Al, B, Ba, Cd, Co, Cr, Cu, Be, Mn, Ni, Sr, V, Zn Li, P Ca, Na Mg K Fe	100 200 1,000 4,000 10,000 500

Stock Standard	Elements	Conc. (mg/L)
Al, Ca, Fe, Na, S Stocks	Al, Ca, Fe, Na, S	10,000
As, Bi, Pb, Sb, Se, Tl, Th, U, Stocks	As, Bi, Pb, Sb, Se, Tl, Th, U	1,000

7.11.2 Working Initial Calibration Standard (ICAL1) for Dual View ICP

Add 5.0 mL each of STLDEN-STD-2 and STLDEN-STD-3B to a 500-mL volumetric flask partially filled with reagent blank solution. Add 1 mL of the As, Pb, Sb, Se, Tl, stock. Dilute to the mark with reagent blank.

7.14.3 Working Initial Calibration Standard (ICAL2a) for Dual View ICP

Add 10 mL of each of the Al, Fe, and 50 mL Na 10,000 mg/L stock solutions; 10 mL each of the Th and 20 mL of the U 1,000 mg/L stock solution; 2ml of 1000mg/l Bi and1 mL of 10,000 mg/L Sulfur to a 1,000-mL volumetric flask partially filled with reagent blank and dilute to the mark with reagent blank.

7.12 Initial Calibration Verification (ICV) for Dual View ICP

7.12.1 ICV Stock Standards

The following stock solutions are purchased from commercial sources:

Stock Standard	Elements	Conc. (mg/L)
ICVL SOL A	Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, V, Zn Se, Tl Ca, Na Mg K	25 25 50 200 1,000 2,000

Stock Standard	Elements	Conc. (mg/L)
ICVL SOL B	Ag, Mo, Sb, Ti, Zr Sn Si P	25 50 200 200
ICVH Stock	Al, Ca, Fe,Na U, Th	4,000 500
Sulfur	S	1000
Bismuth	Bi	1000

7.12.2 Working High Initial Calibration Verification (ICVH)

Add 2.0 mL of the ICVH Stock, 0.1ml of 1000mg/l Bi and 0.8 mL of the Sulfur 1000 mg/L to a 200 mL volumetric flask partially filled with reagent blank solution and dilute to the mark.

7.12.3 Working Low Initial Calibration Verification (ICVL)

Add 2.0 mL of each of the ICVL SOL A and ICVL SOL B stock solutions to a 200-mL volumetric flask partially filled with reagent blank solution and dilute to the mark.

7.13 Reporting Limit Standard (RLSTD)

7.13.1 RL Stock Standard

The following stock solutions are purchased from commercial sources:

Standard	Elements	Conc. (mg/L)
STLDEN-RL-1A	As, Sb, Se, Tl Pb	10 3.0
STLDEN-RL-2	Si Sn Mo, Ti, Zr	500 20 10
STLDEN-RL-3	Ag, Cr, Cu, Ni, Th, V, Zn, Li Al, B Ba, Cd, Co, Sr Be Ca, Mg Fe K, Na, P Mn U	10 100 5.0 1.0 200 30 1,000 3.0 60
Sulfur	S	100
Bismuth	Bi	100

7.13.2 Daily Working Reporting Limit Standard (RLSTD2 or RLSTD3)

Add 100 µL of each of STLDEN-RL-1A (optional for RLSTD2), STLDEN-RL-2, STLDEN-RL-3, Bismuth 100 mg/l and Sulfur 100 mg/L to a 100-mL volumetric flask partially filled with reagent blank and dilute to the mark. Working RL standards must be prepared fresh each day.

7.14 Working High Continuing Calibration Verification (CCVH1) for Dual View ICP

Dilute 500 mL of the working ICAL2 solution (Section 7.14.3) to 1,000 mL with reagent blank solution.

7.15 Working Low Continuing Calibration Verification (CCVL1) for Dual View ICP

Dilute 500 mL of the working ICAL1 solution (Section 7.14.2) to 1,000 mL with reagent blank solution.

7.16 Low Level ICV/Low Level CCV for Dual View ICP

The low level ICV/CCV verification stock standards are custom-made commercial standards as follows:

LLICV/LLCCV Stock Standard	Elements	Conc. (mg/L)
LLICV/LLCCV-1	K	300
	Na	100
	Ca, Mg	20
	Al, Bi, Fe	10
	U	6
	Ni	4
	Zn	2
	As, Cu, Se,Tl,Th	1.5
	Ba, Cr, Co, Li, Mn, Ag, Sr, V	1
	Pb	0.9
	Cd	0.5
	Be	0.1

LLICV/LLCCV Stock Standard	Elements	Conc. (mg/L)
LLICV/LLCCV-2	P	300
	Si	50
	B	10
	Sn	10
	Mo	2
	Zr	1.5
	Sb	1
	Ti	1

7.16.1 Low Level ICV\ Low Level CCV, Working Standards

RL Standard	Vol. of Stock Added (mL)
ICP-LLCCV1	5
ICP-LLCCV-2	5

Adjust to volume (500 mL) using the reagent blank solution.

7.17 Reagents

7.17.1 Concentrated nitric acid (HNO_3), trace metals grade or better.

7.17.2 Concentrated hydrochloric acid (HCl), trace metals grade or better.

7.17.3 Reagent water must be produced by a Millipore DI system or equivalent, with a minimum resistivity of 1.0 Mohm/cm at 25˚C.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE	50 mLs	HNO_3, pH < 2; Cool 4 ± 2°C	180 Days	40 CFR Part 136.3
Soils	Glass	3 grams	Cool 4 ± 2°C	180 Days	N/A

[1] Inclusive of digestion and analysis.

The exception is the analysis of dissolved silica by Method 200.7, which must be analyzed within 28 days from the date of collection.

Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. Initial and periodic performance studies (IDOCs, detection limits, linear range studies, IECs, background correction points, and rinse time determinations) are described in Section 12. The process of establishing control limits, and the use of control charts are described more completely in QA-003, Quality Control Program. Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.2 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See Policy DV-QA-003P for further details.

9.4 Method Blank

The blank is de-ionized water taken through the procedure as if it were a sample. A method blank is required with every batch of 20 or less samples.

Acceptance Criteria: The method blank must not contain any analytes of interest above the project specific reporting limit. In the absence of project specific reporting limits the blanks needs to be less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given batch, whichever is greater. Note that the DoD QSM and AFCEE 4.0 QAPP require that the blank be less than one half of the RL.

Corrective Action: If the method blank exceeds allowable levels, all associated samples must be redigested and reanalyzed. A possible exception is the situation in which the analyte is not detected

in any of the associated samples, but this can only be done with client approval and it must be addressed in the final report case narrative.

9.5 Laboratory Control Sample (LCS)

The LCS is prepared as described in Section 7.8. One LCS is required with each analytical batch.

Acceptance Criteria: The recovery of the LCS must be within historical control limits. Historical control limits are based on three standard deviations of past results, and must be 80-120% or tighter. In the instance where the LCS recovery is greater than 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the report narrative. The process of establishing control limits is described in more detail in the Policy DV-QA-003P. The control limits are stored in the lab's LIMS system.

Corrective Action: If the LCS recovery falls outside of the established limits, all associated samples must be redigested and reanalyzed

9.6 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

MS/MSDs are prepared as described in Section 7.8. One MS/MSD pair is required with each analytical batch. Note that some programs (e.g., North Carolina and South Carolina) require the MS/MSDs to be run at a 10% frequency. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing on only the specific sample spiked.

Samples identified as field blanks cannot be used for MS/MSD analysis. Note that if client instructions on the chain of custody form tell the lab to use a field blank for the MS/MSD, this should be double-checked with the laboratory PM.

Acceptance Criteria: The recoveries for the MS and MSD must be within the historical control limits or the project-required control limits, whichever are appropriate. Historical control limits are based on three standard deviations of past results, and should be within the established project-specific method control limits, if they exist. The process of establishing control limits is described in more detail in Policy QA-003. The control limits are stored in the laboratory's LIMS system. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is flagged MSB. Acceptance limits derived from historical data should be no wider than +/-25%.

Corrective Action: If MS/MSD recoveries fall outside of the established limits and the LCS is in control, the data will be flagged as outside of control limits. Document the results, which are then used by

the lab PM to prepare the case narrative to warn the client that the sample result is suspect.

Acceptance Criteria: The relative percent difference (RPD) between the MS and MSD must be less than or equal to the historical RPD control limit. Historical control limits are based on three standard deviations of past results, and must be no greater than 20%.

Corrective Action: If the RPD fails to meet precision limit and the recoveries pass, the control limits should be checked as this would be a very rare occurrence if the limits are set properly. If the LCS is in control, it indicates long-term precision, and precision failures within the batch may be due to sample non-homogeneity. MS/MSD results which fall established control limits must be addressed in the narrative. Document the result, which is then used by the lab PM to prepare the case narrative.

9.7 Serial Dilution Test

A dilution test is performed for each batch of samples. The purpose of this test is to ensure that neither positive or negative interferences are biasing the analytical results. The serial dilution test should be performed on the same sample used to perform the MS/MSD.

Acceptance Criteria: If the analyte concentration is sufficiently high (minimally, a factor of 10 times the lower limit of quantitation), an analysis of a 1:5 dilution (e.g., 1 mL of sample diluted to 5 mL with reagent blank solution) must agree within ± 10% of the original determination.

Corrective Action: If the two results do not agree within ± 10%, then a chemical or physical interference is suspected. A qualifier flag is assigned to the data and an NCM prepared, which is then used by the lab PM to prepare the case narrative to warn the client the sample result is suspect.

9.8 Post Digestion Spike (PDS)

Whenever the MS/MSD recoveries are unacceptable, a PDS spike must be performed. The PDS spike is prepared as described in Section 7.10. Some programs, e.g., AFCEE, require a PDS analysis whenever the serial dilution test fails. Other programs, e.g., DoDQSM, require a PDS to be included in every batch. Check project requirements. For these programs, the same sample that was used for the serial dilution test should be used for the PDS.

Acceptance Criteria: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80-120% for Method 6010C. The spike addition should produce a minimum level of 10 times to a maximum of 100 times the lower limit of quantitation.

Corrective Action: If the spike is not recovered within the specified limits, a matrix effect is confirmed. The series of tests (MS/MSD, serial

dilution, and PDS) should be described in NCMs so that they can be included in the report case narrative.

9.9 Method of Standard Additions (MSA)

This technique involves constructing a calibration curve in the sample matrix itself to compensate for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift.

Attachment 11 provides more guidance on performing MSA analyses.

9.10 Interference Check Analysis (ICSA / ICSAB)

The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Sections 7.4, 7.5, and 7.6 for the preparation of the ICSA and ICSAB solutions. Attachment 4 lists the final concentrations. All analytes are spiked into the ICSAB solution. The ICSA and ICSAB solutions are analyzed at the beginning of the run.

Acceptance Criteria: The ICSAB results for the all analytes must fall within 80-120% of the true value. If any ICSAB analyte result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the samples rerun.

The absolute value of ICSA results for the non-interfering elements with reporting limits ≤ 10 µg/L must be ≤ 2 x RL. The absolute value of ICSA results for the non-interfering elements with RLs > 10 µg/L must be ≤ RL.

Corrective action: If the ICSA results for the non-interfering elements do not meet these limits, the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required, then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in an absolute value > 2 x RL, then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal > 2x RL, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data do not meet the above conditions, then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to

the raw results. If the results are recalculated manually, the calculations must be clearly documented on the raw data.

9.11 Monitoring Internal Standard Results

Yttrium is automatically added as an internal standard (IS) to every solution tested through use of a third pump channel and mixing coil. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

Acceptance Criteria: If the internal standard counts fall within ±30% of the counts observed in the ICAL blank (STD1-Blank), then the data are acceptable.

Corrective Action: If the internal standard counts in the field samples are outside of the control limits, the following apply:

- The field samples must be diluted and reanalyzed;
- The IS concentrations must be raised; or
- A different internal standard must be used.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.

10.3 Sample Preparation

Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-*IP-0010 and DV-IP-0015*).

10.4 Calibration

10.4.1 Instrument Start Up

Set up the instrument with the operating parameters recommended by the manufacturer. Complete any required preventative maintenance as indicated on the ICPAES Preventative Maintenance Log (see example in Attachment 14).

Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.4.2 Initial Calibration (ICAL)

The calibration curve is established on each day of operation using a blank and one standard. The preparation of the ICAL standards is described in Section 7. The final concentrations of the ICAL standards are presented in Attachments 3 and 4.

The validity of the calibration curve is confirmed by analysis of the ICV, CCV, ICB, RL Check standard and Low Level ICV/CCV) which are run immediately after the ICAL. Some programs require a high-level verification check as well.

10.4.2 Initial Calibration Verification (ICV)

Calibration accuracy is verified using a second-source standard (ICV) that is at or below a concentration near the mid-point of the working range. The ICV is analyzed immediately after the ICAL. The preparation of this standard is described in Section 7. The concentrations of the ICV standard are presented in Attachments 3 and 4.

Acceptance Criteria: For Method 6010, the ICV result must fall within 10% of the true value for that solution. The standard deviation must be <5% (the laboratory is using at least two exposures for all ICP analyses).

Corrective Action: If the ICV fails to meet acceptance limits, the standard may be reanalyzed without modification to the instrument operating conditions. *Two consecutive, acceptable analyses are required before the analytical run may continue.* Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.3 Mid Level Continuing Calibration Verification (CCV)

The preparation of the CCV solutions are described in Section 7. The final concentrations of the CCVs are presented in Attachments 3 and 4. Note that the CCV is made at a different concentration than the ICV to meet NELAC requirements. CCVs are analyzed after the ICV, after every ten samples, and at the end of the analytical run.

Acceptance Criteria: The CCV must be within 10% of the expected value to meet Method 6010 requirements. The relative standard deviation must be <5%.

Corrective Action: If the CCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions. *Two consecutive, acceptable analyses are required before the analytical run may continue.* Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed.

10.4.4 Low Level Initial Calibration (LLICV) and Continuing Calibration Verification (LLCCV)

The preparation of the LLCCV solution is described in Section 7. The low-level CCV needs to be analyzed at the beginning and end of every run sequence. If low level samples are expected then the low-level CCV should also be run every ten samples.

Acceptance Criteria: The LLCCV must be within +/-30% of the expected value to meet Method 6010C requirements.

Corrective Action: If the CCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions.

Two consecutive, acceptable analyses are required before the analytical run may continue. If the calibration cannot be verified within theses specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed. TestAmerica will not hold samples with concentrations greater than 10x the reporting limit to the 30% acceptance criteria.

10.4.5 Initial Calibration Blank (ICB)

System cleanliness is verified by analyzing an ICB after the first CCV. The preparation of the ICB is described in Section 7.

Acceptance Criteria: The absolute value of the ICB result must be < RL. Note that some programs (e.g., DoDQSM, v3.0) require the blank to be $\leq$ 2 x MDL.

Corrective Action: If the ICB fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.6 Calibration Check Standard (RLSTD)

Calibration accuracy at the RL is verified by analyzing a standard prepared at a concentration at or below the laboratory's standard reporting limit. The preparation of this standard is described in Section 7. Alternate RLSTD concentrations may be used as necessary to meet client requirements as long as an accurate description of the standard used is entered into the Standards Log database.

Acceptance Criteria: For routine work and for programs that allow the RL to be as low as 2 x MDL (e.g., AFCEE), the acceptance limits are $\pm$ 50% of the expected value. For some

programs (e.g., DoDQSM), the RLSTD needs to be 5 x MDL, and the acceptance limit is then ± 20%.

Corrective Action: If the RL Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.7 Lower Limit of Quantitation Check (LLQC)

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. The difference between the LLQC and the LLICV/CCV is that this standard is carried through the entire preparation and analytical procedure.

Acceptance Criteria: LLQC is verified when all analytes are detected within ± 30% of their true value.

Corrective Action: If the LLQC fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.8 High-Level Calibration Check Standard

The method 6010 defines the linear working range used for daily analysis based on the LDR studies performed every six months, in which case this standard is not required. However, some programs require verification of the high end of the linear range at different frequencies. For example, the AFCEE QAPP, version 4.0, requires evaluation of a high check standard every three months.

Acceptance Criteria: The result for this standard must be within 10% of the expected value.

Corrective Action: If the High-Level Calibration Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified. Alternately, results that do not exceed the level of the highest calibration standard may be accepted and reported.

10.4.9 Continuing Calibration Blank (CCB)

CCBs, prepared as in Section 7.3, are analyzed after each CCV.

Acceptance Criteria: The absolute value of the CCB must be less than the RL or less than 1/10 the concentration found in associated samples. Note that some programs (e.g., DoDQSM, v3.0) require the blank to be ≤ 2 times the MDL.

Corrective Action: If the CCB is greater than these limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, instrument maintenance should be considered, the calibration re-verified, and all samples analyzed since the last successful CCB must be reanalyzed.

10.5 Sample Analysis

10.5.1 Replicate Readings

The laboratory averages the results from two exposures for Axial and Dual View ICP for each standard, field sample, and QC sample due to sample volume limitations of the autosampler tube. For Axial ICP analyses, the results of the sum channels for Se, Sb and Pb must be used for reporting.

10.5.2 Rinse Time Between Samples

Prior to calibration and between each sample/standard, the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 12.7 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

10.5.3 The following analytical sequence is used:

Instrument Calibration
High Standard Verification
ICV
LLICV
CCV
ICB
RL Verification Standard
LLQC (as needed)
ICSA
ICSAB
CCV
CCB
LLCCV
10 samples
CCV
CCB
LLCCV
10 samples
CCV
CCB

LLCCV
Repeat sequence with 10 samples between CCV/CCB pairs
CCV
CCB
LLCCV

10.5.4 Full method-required QC must be available for each wavelength used in determining reported analyte results. Guidelines are provided in the appendices for minimizing contamination of samples and standards (Attachment 11), performing preventive maintenance (Attachment 12), and troubleshooting (Attachment 10).

10.5.5 Dilutions for High Levels of Elements of Interest

For 6010, results must fall within the linear range. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. Dilutions must be prepared using the reagent blank solution to maintain the correct acid strength.

10.5.6 Dilutions for High Levels of Interfering Elements

Dilutions are also required for an element that is included in an IEC calculation if it exceeds the linear range. If a dilution is not performed, the IEC may be inaccurately applied. Therefore, even if an over-range analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted to a level at or below the working range.

11.0 Calculations / Data Reduction

ICV percent recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{ICV Found Value}}{\text{ICV True Value}}\right) \times 100\%$$

CCV percent recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{CCV Found Value}}{\text{CCV True Value}}\right) \times 100\%$$

Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{SSR - SR}{SA}\right) \times 100\%$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equation:

$$RPD = \left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2} \right)} \right] \times 100$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

The final concentration for a digested aqueous sample is calculated as follows:

$$\text{Final Concentration (mg/L)} = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$\text{Final Concentration (mg/kg), dry weight} = \frac{C \times V \times D}{W \times S}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

NOTE: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

The LCS percent recovery is calculated according to the following equation:

$$\%R = \left(\frac{\text{LCS Found Value}}{\text{LCS True Value}} \right) \times 100\%$$

The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading × 5)

Appropriate factors must be applied to sample values if dilutions are performed.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial MDL study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

Prepare seven standards at three to five times the estimated MDL concentration.

The MDL standards are processed through the entire analytical process, including the digestion.

Calculate the mean concentration found (X) in µg/L, and the standard deviation of the mean concentration in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy QA-005) for each analyte.

MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy QA-005 for further details concerning MDL studies.

12.2 MDL Verification (MDLV)

Calculated MDLs from the annual studies are subject to quarterly verification by analyzing an MDLV standard prepared at 1-2 times the calculated MDL concentration. An MDLV standard is analyzed immediately after each MDL study and quarterly thereafter. This standard is subject to the entire preparation and analysis process.

Acceptance Criteria: The calculated MDL is verified if the MDLV standard is detected and the result is significantly different than the blank.

Corrective Actions: If the first MDLV is not detected, the MDLV standard will be re-prepared and analyzed at twice the original concentration. The lowest concentration that produces a detectable signal will then be reported as the MDL.

12.3 Instrument Detection Limit Study

Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each wavelength used for analysis.

Prepare seven digested reagent blank solutions.

The IDL standards are run on three non-consecutive days.

IDL results for each day are calculated as three times the standard deviations for the mean of the seven measured concentrations. The final IDL concentration is the average of the three daily IDL values.

See Policy QA-014 for a discussion of IDL studies and evaluation of IDL results.

12.4 Linear Dynamic Range (LDR)

The LDR must be determined initially (i.e., at initial setup) and then every three months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample.

The LDR must be determined from a linear calibration prepared in the normal manner using the normal operating procedures described in Sections 10 and 11.

The LDR is determined by analyzing successively higher standard concentrations of the analyte. A minimum of three standards is required for the initial and on-going studies, and one of the levels must be close to the upper end of the range. The highest concentration must be within 10% of the stated concentration.

The highest standard that meets this criterion defines the maximum concentration that can be reported for sample analysis without dilutions.

If the instrument is adjusted in any way that may affect the LDRs, new dynamic ranges must be determined. The LDR data must be documented and kept on file.

12.5 Background Correction Points

To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength of interest and record the apparent emission intensity from all other method analytes. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations.

Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.

12.6 Interelement Corrections (IECs)

ICP interelement correction (IEC) factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be re-determined.

When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC, then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs.

Refer to the facility-specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which produces a false analytical result with an absolute value greater than the RLs shown in Attachment 1. Note that the USACE program requires a control limit of 2|MDL|, which is feasible when verified MDLs are used.

To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace and CID detector instruments as reflected by the ICSA response.

12.7 Rinse Time Determination

Rinse times must be determined annually.

To determine the appropriate rinse time for a particular ICP system, a standard containing the highest concentration level that would be reported for samples is aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system.

For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level).

Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

12.8 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows:

Four aliquots of the ICV are analyzed using the same instrumental conditions and procedures used to analyze samples. The analyst must employ ICV's from four distinct analytical sequences. Using these four ICV's demonstrates the analyst's ability to optimize and calibrate the instrument and to prepare analytical silutions. Calculate the mean recovery and standard deviation of the mean recovery for each analyte of interest.

If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP DV-QA-0024.

12.9 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP DV-QA-0024.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Safety Manual, and HS-001, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

Acid solutions from ICP drain - Waste Stream J

Metals waste potentially contaminated with Cat 1 radioactive materials – Waste Stream RJ

Note: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Update IV, February 2007, Method 6010C.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 6010C	This procedure uses mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.
2	EPA 6010C	The alternate run sequence presented in Section 10.5.3 is consistent with method requirements. Additional QC (i.e., ICSA) analyses were added to accommodate the CLP

		protocol requirements.
3	EPA 6010C	Method 6010 states that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific "concentration range around the calibration blank." Because of the lack of definition for "concentration range around the calibration blank," the laboratory has adopted the procedure in EPA CLP ILMO4.0 for determining IECs,
4	EPA 6010C	Section 9.9 of Method 6010C states: "If less than acceptable accuracy and precision data are generated, additional quality control tests are recommended prior to reporting concentration data for the elements in this method." The dilution test helps determine if a chemical or physical interference exists. Because the laboratory sometimes does not have prior knowledge if the MS/MSD will be within criteria, the analyst may select to perform a dilution test on one sample in each preparation batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. In this procedure, matrix interference is determined by evaluating data for the LCS, MS/MSD, and serial dilutions. The laboratory must request documented, clear guidance when a unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.0 Attachments

Attachment 1 Metals Analyzed by ICP and Reporting Limits
Attachment 2 Matrix Spike and Aqueous Laboratory Control Sample Levels
Attachment 3 Low Level ICV and CCV Spiking Levels
Attachment 4 Interference Check Sample Concentrations
Attachment 5 TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels
Attachment 6 6500 Initial Calibration &Continuing Calibration Verification Standards
Attachment 7 Summary of Quality Control Requirements
Attachment 8 ICP Data Review Checklist
Attachment 9 MSA Guidance
Attachment 10 Troubleshooting Guide
Attachment 11 Contamination Controls
Attachment 12 Preventative Maintenance

18.0 Revision History

NA

Attachment 1

Metals Analyzed by ICP and Reporting Limits

ELEMENT	Symbol	CAS #	6010 Analyte	Reporting Limit (µg/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	100	10
Antimony[trace]	Sb	7440-36-0	X	10	1
Arsenic[trace]	As	7440-38-2	X	15	1
Barium	Ba	7440-39-3	X	10	1
Beryllium	Be	7440-41-7	X	1	0.1
Bismuth	Bi	7440-69-9		100	10
Boron	B	7440-42-8	X	100	10
Cadmium[trace]	Cd	7440-43-9	X	5	0.5
Calcium	Ca	7440-70-2	X	200	20
Chromium	Cr	7440-47-3	X	10	1
Cobalt	Co	7440-48-4	X	10	1
Copper	Cu	7440-50-8	X	15	2
Iron	Fe	7439-89-6	X	100	10
Lead[trace]	Pb	7439-92-1	X	9	0.8
Lithium	Li	7439-93-2	X	10	5
Magnesium	Mg	7439-95-4	X	200	20
Manganese	Mn	7439-96-5	X	10	1
Molybdenum	Mo	7439-98-7	X	20	2
Nickel	Ni	7440-02-0	X	40	4
Phosphorus	P	7723-14-0	X	3,000	300
Potassium	K	7440-09-7	X	3,000	300
Selenium[trace]	Se	7782-49-2	X	15	1.3
Silicon	Si	7631-86-9		500	50
Silver[trace]	Ag	7440-22-4	X	10	1
Sodium	Na	7440-23-5	X	1	100
Strontium	Sr	7440-24-6	X	10	1
Sulfur	S	7704-34-9	X	200	2
Thallium[trace]	Tl	7440-28-0	X	15	1.2
Thorium	Th	7440-29-1		15	15
Tin	Sn	7440-31-5	X	100	10
Titanium	Ti	7440-32-6	X	10	1
Uranium	U	7440-61-1		60	20
Vanadium	V	7440-62-2	X	10	2
Zinc	Zn	7440-66-6	X	20	2
Zirconium	Zr	7440-67-7		15	1

Attachment 2

Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (µg/L)	Matrix Spike Level (µg/L)
Aluminum	2,000	2,000
Antimony	500	500
Arsenic	2,000	2,000
Barium	2,000	2,000
Beryllium	50	50
Bismuth	2,000	2,000
Boron	1,000	1,000
Cadmium	50	50
Calcium	50,000	50,000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1,000	1,000
Lead	500	500
Lithium	1,000	1,000
Magnesium	50,000	50,000
Manganese	500	500
Molybdenum	1,000	1,000
Nickel	500	500
Phosphorous	10,000	10,000
Potassium	50,000	50,000
Selenium	2,000	2,000
Silicon	10,000	10,000
Si (as SiO_2)	21,400	21,400
Silver	50	50
Sodium	50,000	50,000
Strontium	1,000	1,000
Sulfur	2,000	2,000
Thallium	2,000	2,000
Thorium	2,000	2,000
Tin	2,000	2,000
Titanium	1,000	1,000
Uranium	2,000	2,000
Vanadium	500	500
Zinc	500	500
Zirconium	500	500

Attachment 3

Low Level ICV/CCV

ELEMENT	LCS Level (µg/L)
Aluminum	100
Antimony	10
Arsenic	15
Barium	10
Beryllium	1
Bismuth	100
Boron	100
Cadmium	5
Calcium	200
Chromium	10
Cobalt	10
Copper	15
Iron	100
Lead	9
Lithium	10
Magnesium	200
Manganese	10
Molybdenum	20
Nickel	40
Phosphorous	3,000
Potassium	3,000
Selenium	15
Silicon	500
Si (as SiO_2)	1070
Silver	10
Sodium	1,000
Strontium	10
Thallium	15
Thorium	15
Tin	10
Titanium	10
Uranium	60
Vanadium	10
Zinc	20
Zirconium	15

Attachment 4

Interference Check Sample Concentrations

Element	ICSA (µg/L)	ICSAB (µg/L)
Aluminum	500,000	500,000
Antimony	-	1,000
Arsenic	-	2,000
Barium	-	500
Beryllium	-	500
Bismuth	-	1,000
Boron	-	2,000
Cadmium	-	1,000
Calcium	500,000	500,000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200,000	200,000
Lead	-	1,000
Lithium	-	1,000
Magnesium	500,000	500,000
Manganese	-	500
Molybdenum	-	1,000
Nickel	-	1,000
Phosphorous	-	2,000
Potassium	-	50,000
Selenium	-	5,000
Silicon	-	10,000
Silica	-	21,400
Silver	-	1,000
Sodium	-	50,000
Strontium	-	1,000
Sulfur	-	1,000
Thallium	-	10,000
Titanium	-	1,000
Vanadium	-	500

Attachment 4

Interference Check Sample Concentrations cont'd

Element	ICSA (µg/L)	ICSAB (µg/L)
Zinc	-	1,000
Tin	-	10,000
Thorium	-	10,000
Uranium	2,000	2,000
Zirconium	-	1,000

Attachment 5

TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (µg/L)	Regulatory Limit (µg/L)	Spike Level (µg/L)
Arsenic	500	5000	4000
Barium	10000	100000	12000
Cadmium	100	1000	1100
Chromium	500	5000	5200
Lead	500	5000	5500
Selenium	250	1000	3000
Silver	500	5000	1050
Copper	100	N/A	2250
Zinc	200	N/A	2500

Attachment 6

6000 Dual View Calibration, ICV & CCV Standards

Element	Calibration Level	ICV (µg/L)	CCV (µg/L)
Aluminum Lo	1,000	250	500
Aluminum Hi	100,000	40,000	50,000
Antimony	2,000	250	1,000
Arsenic	2,000	250	1,000
Barium	1,000	250	500
Beryllium	1,000	250	500
Bismuth	2,000	500	1000
Cadmium	1,000	250	500
Calcium	10,000	2,000	5,000
Chromium	1,000	250	500
Cobalt	1,000	250	500
Copper	1,000	250	500
Iron Lo	5,000	250	2,500
Iron Hi	100,000	80,000	50,000
Lead	2,000	250	1000
Magnesium	40,000	10,000	20,000
Manganese	1,000	250	500
Molybdenum	1,000	250	500
Nickel	1,000	250	500
Phosphorous	2,000	2,000	1,000
Potassium	100,000	20,000	50,000
Selenium	2,000	500	1,000
Silver	1,000	250	500
Sodium Lo	10,000	2000	5,000
Sodium Hi	500,000	40,000	250,000
Strontium	1,000	250	500
Sulfur	10,000	4,000	5,000
Thallium	2,000	500	1,000
Thorium	10,000	3,000	5,000
Tin	2,000	500	1,000
Vanadium	1,000	250	500
Uranium	20,000	5,000	10,000
Zinc	1,000	250	500
Zirconium	1,000	250	500

Attachment 7
Summary Of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between multiple exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
CCV	After the ICV, after every 10 samples and at the end of the run.	90-110% recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
RL Standard	At the beginning of the run	Results must within 50%	Terminate analysis; Correct the problem; Recalibrate.
LLICV/CCV	At the beginning of the run and after every 10 samples	Recovery must be within 30%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable LLCCV.
ICB	Beginning of every analytical run, immediately following the initial CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCB	Immediately following each CCV (except for the CCV following the ICV).	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run	See Section 9.10	See Section 9.10
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.10
Dilution Test	One per prep batch.	For samples > 50x MDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.

See Section 10.5.6 for run sequence to be followed.

Attachment 7

Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.4)	Re-run once in a clean tube. If >RL, re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	LCS must be within 80 - 120% recovery or in-house control limits. Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.5)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples.	75 – 125% recovery or tighter in-house control limits.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate (MSD)	One per sample preparation batch of up to 20 samples. 10% frequency for some programs (see 0)	75 – 125 % recovery; RPD ≤ 20% or tighter in-house control limits.	See Corrective Action for Matrix Spike.

Attachment 8

ICP Data Review Checklist

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

ICP Data Review Checklist

Run/Project Information:		
Run Date:	**Analyst:**	**Instrument:**
Prep Batches Run:		
Methods Used: 6010B / 200.7		

Review Items	**Yes**	**No**	**N/A**	**2nd Level**
A. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits?				
2. Method blank done per prep batch and < RL or CRDL (CLP)?				
3. MS run at required frequency and within limits?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
5. Serial dilution done per prep batch (or per SDG for CLP)?				
6. Post digest spike analyzed if required (CLP & AFCEE only)?				
B. Calibration/Instrument Run QC				
1. ICV/CCV analyzed at appropriate frequency and within control limits? (**6010B:** CLP = 90 - 110%; **200.7:** ICV = 95 - 105%, CCV = 95 - 105% for 40 CFR 136B, 90 - 110% for RCRA/ SDWA) If not in control, was the CCV reanalyzed twice to show return to control as per NELAP?				
2. ICB/CCB analyzed at appropriate frequency and < RL or < CRDL (CLP) or < 2X MDL (AFCEE 4.0)?				
3. High Standard (HICH) reanalyzed before samples and recovered within QC limits? (6010B/200.7: 95 - 105%)				
4. RL STD run and recovered within QC limits? (± 30% for non-CLP, ± 20% for DoD / AFCEE 4.0 / USACE)				
5. ICSA/ICSAB run at required frequency and within SOP limits? (ICSA < 2X MDL AFCEE 4.0)				
C. Sample Results				
1. For 6010B, were samples with concentrations > the linear range for any parameter diluted and reanalyzed? For 200.7, were samples with concentrations within 90% of the linear range diluted and reanalyzed?				
2. Are all reported results bracketed by in control QC?				
D. Other				
1. Are all nonconformances documented appropriately?				
2. Calculations checked for errors?				
3. Transcriptions checked for errors? (Example: Are dilution factors that are entered into the sequence log correct?)				
4. All client/project specific requirements met?				
5. Date/time of analysis verified as correct?				

Analyst: _____ **Date:** _____

Comments: _____

2nd Level Reviewer: _____ **Date:** _____

Comments: _____

SAMPLE

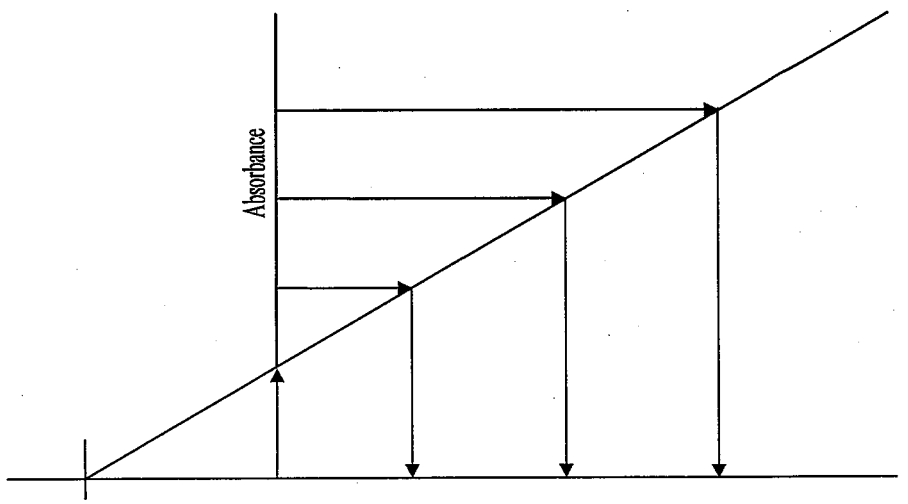
Attachment 9

MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the absolute value of the point of interception of the horizontal axis is the concentration of the unknown.



Zero
Absorbance

Conc. of
Sample

For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear (r=0.995 or greater) over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 10

Troubleshooting Guide

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Replace RF generator
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

Attachment 11

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves should not be used in the metals laboratory because the powder contains silica and zinc as well as other metallic analytes.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

Attachment 12
Preventive Maintenance

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

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ICP PREVENTIVE MAINTENANCE LOG

MAINTENANCE	MONTH:			YEAR:			
Daily > Fill rinse solution / IS solution. > Make RL check standard solution. > Check torch tip for residue. > Check nebulizer flow. > Check waste container & empty as needed. > Check expiration dates of all standards. **Weekly** > Replace pump tubing. **As Needed** > Clean nebulizer & drain chamber. > Replace torch; realign and optimize. > Replace rinse / standard bottles. > Replace capillary tubing / sipper probe. **Monthly** > Clean air filters on instrument. > Check internal fluid reservoir. **Yearly** > Change internal cooling fluid.	1	2	3	4	5	6	7
	8	9	10	11	12	13	14
	15	16	17	18	19	20	21
	22	23	24	25	26	27	28
	29	30	31				

EXAMPLE

L:\QA\Edit\Logbooks\Metals\ICP Preventive Mtce Log

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THE LEADER IN ENVIRONMENTAL TESTING

Inductively Coupled Plasma Mass Spectrometry for Trace Element Analysis by SW-846 Method 6020A

Approvals (Signature/Date):

Doug Gomer 6/19/09 Doug Gomer — Date Metals Group Supervisor	Adam W. Alban 19 June 09 Adam Alban — Date Health & Safety Manager / Coordinator
Karen Kuoppala 6.19.09 Karen Kuoppala — Date Quality Assurance Manager	Robert C Hanisch 6/19/09 Robert C. Hanisch — Date Laboratory Director

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1.0 Scope and Application

1.1 This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP/MS) based on EPA Method 6020A.

1.2 Method 6020 lists twenty-three elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Tl, V, and Zn). This procedure has been developed for thirty-five elements (see Attachment 8), and additional elements may be included provided that the method performance criteria presented in Sections 9 and 13 are met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the promulgated methods.

1.3 The procedure is applicable to the analysis of acid digested waters, soils, and wastes. The preliminary acid digestion for aqueous samples is described in SOP DV-IP-0014, and the digestion procedure for soils is given in SOP DV-IP-0015.

2.0 Summary of Method

2.1 Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into an R.F. plasma. There the sample is decomposed and desolvated.

2.2 The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution better than or equal to 0.9 amu (see Section 3) peak width at 10% of the peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier.

2.3 Interference must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and the constituents of the sample matrix. Recommended elemental equations, which correct for many of these interferences, are listed in Attachment 1. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3.0 Definitions

3.1 **Atomic Mass Unit (amu)** – Obsolete term replaced by "unified atomic mass unit (u)" or "dalton (Da)", which denotes a small unit of mass that is used to express atomic and molecular masses. It is defined to be 1/12 of the mass of one atom of carbon-12, or 1.66053886 X 10-27 kg.

3.2 **Dissolved Metals** - Those elements which pass through a 0.45-µm membrane filter (sample is acidified after filtration).

3.3 **Total Metals** - The concentration determined on an unfiltered sample following vigorous acid digestion.

3.4 **Total Recoverable Metals** - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.

3.5 **Instrument Detection Limit (IDL)** - See Section 12.2.

3.6 **Sensitivity** - The slope of the analytical curve (i.e., the functional relationship between raw instrument signal and the concentration).

3.7 **Tuning Solution** - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.8 **Initial Calibration Verification / Quality Control Standard (ICV)** - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.9 **Continuing Calibration Verification (CCV).** - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.10 **Interference Check Standard (ICS)** - A solution containing both interfering and analyte elements of know concentration that is used to verify background and interelement correction factors.

3.11 **Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB)** - A multi-element standard of known concentrations that is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

3.12 **Reagent Blank** - High purity (> 18 megohm-cm) water containing the same acid matrix as the calibration standards that is carried through the entire digestion process.

3.13 **Calibration Blank** - High purity (> 18 megohm- cm) water acidified with the same acid concentrations present in the standards and samples. Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.14 **Method Reporting Limit (MDL)** - The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

3.15 **Low Level ICV (LLICV) / Continuing Calibration Verification (LLCCV)** - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

4.0 Interferences

4.1 Isobaric Interferences

Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2 Isobaric Molecular and Doubly Charged Ion Interferences

- Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Attachment 3 lists isobaric interferences which might possibly affect required analytes. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance,

corrections must be applied and the data flagged to indicate the presence of interferences.

- Chloride in samples can produce low recoveries for antimony and silver. If chloride interference is a concern, 1% HCl can be added during digestion, but calibration standards must be adjusted to include 1% HCl also.

4.3 Physical Interferences

- Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.
- Internal standards should be added at a level to give approximately 50,000 - 800,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 50 amu of the mass of the measured analyte.
- Matrix effects are monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020, the internal standard recoveries in samples can not fall below 70% of the intensity of the calibration standard. If they fall outside this window, a five-fold dilution (1:4) is performed on the sample to correct for matrix effects and the sample is reanalyzed.
- Memory effects are dependent on the relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.4 The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded.

People with pacemakers should not go near the instrument while in operation.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Inductively Coupled Plasma Mass Spectrometer (ICP/MS) capable of providing resolution, less than or equal to 0.9 amu at 10% peak height from 6-253 amu and 1.0 amu at 5% peak height from 6-253 amu with a data system that allows corrections for isobaric interferences and the application of the internal standard technique.
- A four-channel peristaltic pump.
- Autosampler with autosampler tubes.

6.2 Supplies

- Argon gas: High purity grade (99.99%).
- Appropriate water cooling device.
- Calibrated automatic pipettes or Class A glass volumetric pipettes.

7.0 Reagents and Standards

7.1 Storage and Shelf-Life

7.1.1 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Standards stored at concentrations as received from the vendor and mid-level dilutions must be replaced prior to the expiration date assigned by the vendor. If no expiration date is provided, the stocks and mid-level standards may be stored for up to one year. They must be replaced sooner if verification from an independent source indicates a problem.

7.1.2 Working standards, i.e., all standards at concentrations ready to analyze on the ICP/MS (all except tuning mixes, ICSA and ICSAB mixes, which are received at ready-to-use concentrations), are prepared fresh daily.

7.2 Standards

7.2.1 Tuning Solution

The tuning solution is purchased as a custom multi-element mix. The elements and concentrations of the constituents are shown in Attachment 9.

Prepare the Tuning Solution as detailed below.

- Obtain a clean 1 L volumetric flask
- Place 500 mL of reagent water and 10 mL of conc. HNO_3 in the flask
- Pipet 1mL of the Tuning Solution Stock into the flask
- Dilute to volume with reagent water. Stopper and mix.

7.2.2 Dual Detector Solution

The dual detector solution is purchased as a custom multi-element mix or as single element solutions.

Prepare the Dual Detector Solution as detailed below.

- Add approximately 50 mL of 3% HNO_3 to a 100 mL volumetric flask
- Pipet 1.0 mL each of 2008Cal-1 and 2008Cal-2 into the flask
- Pipet 2.0 mL of the 10 mg/L Sn standard into the flask
- Pipet 0.2 mL of the 1,000 mg/L Se standard into the flask
- Pipet 0.1 mL of the 1,000 mg/L Be standard into the flask
- Pipet 0.1 mL of the 1,000 mg/L Ba standard into the flask
- Dilute to volume with 3% HNO_3

7.2.3 Calibration Standards

Stock calibration standards are purchased as custom multi-element mixes or as single element solutions. Each day of analysis, the standards are diluted to working levels using 3% nitric acid. The concentrations are given in Attachment 12.

Prepare the Working Calibration Standard as detailed below.

- Add approximately 50 mL of 3% HNO_3 to a 100 mL volumetric flask
- Pipet 0.5 mL each of 2008Cal-1 and 2008Cal-2 into the flask
- Pipet 1.0 mL of the 10 mg/L Sn standard into the flask
- Pipet 0.5 mL of the 1,000 mg/L Fe standard into the flask
- Dilute to volume with 3% HNO_3

7.2.4 Initial Calibration Verification (ICV) Standard

7.2.4.1 Initial Calibration Standard

The ICV stock is from a source different than the source for the calibration standards. Each day of analysis, the ICV standards are prepared in 3% nitric acid to the concentrations shown in Attachment 12.

Prepare the Working ICV as detailed below.

- Add approximately 30 mL of 3% HNO_3 to a 50 mL volumetric flask
- Pipet 0.2 mL each of ICP-MS ICV Sol. A and Sol. B into the flask
- Dilute to volume with 3% HNO_3

7.2.5 Continuing Calibration Verification (CCV) Standard

7.2.5.1 Calibration Verification

The CCV is prepared from the same source as the calibration standards. The CCV standards are prepared fresh each day of analysis in 3% nitric acid. The concentration is shown in Attachment 12.

Prepare the Working CCV as detailed below.

- Dilute by 2X a known volume of the Working Calibration Standard in 3% HNO_3

7.2.6 Reporting Limit (RL) Standards

The reporting limit standards are prepared fresh daily from the same stock as the calibration standards using 3% nitric acid. The concentrations must be less than or equal to the reporting limits.

Prepare the standard Reporting Limit Standard as detailed below.

- Add approximately 5 mL of 3% HNO_3 to a 10 mL volumetric flask
- Pipet 0.1 mL of Calibration standard into the flask
- Pipet 0.09 mL of the 1 mg/L Sn standard into the flask
- Pipet 0.09 mL of the 1 mg/L Zn standard into the flask
- Dilute to volume with 3% HNO_3

Prepare the AFCEE Reporting Limit Standard as detailed below.

- Dilute the Reporting Limit Standard 5X in 3% HNO_3

7.2.7 Daily Linear Range Standard

The Linear Range standard is prepared from the same stock as the calibration standards using 3% nitric acid. The daily linear range check standards are run at 1,000 µg/L.

Prepare the Daily Linear Range Standard as detailed below.

- Add approximately 5 mL of 3% HNO_3 to a 10 mL volumetric flask
- Pipet 0.5 mL of the 2008Cal-1 standard into the flask
- Pipet 0.5 mL of the 2008Cal-2 standard into the flask
- Pipet 1.0 mL of the 10 mg/L Sn standard into the flask
- Dilute to volume with 3% HNO_3

7.2.8 Spiking Stock Solution

The spike stock solution is prepared from the same stock as the calibration standards using 3% nitric acid. Spike concentrations are listed in Attachment 12.

Prepare the Spiking Stock as detailed below.

- Obtain a clean vial
- Pipet 2.0 mL of the 10 mg/L Sn standard into the vial
- Pipet 1.0 mL of the 2008Cal-1 standard into the vial
- Pipet 1.0 mL of the 2008Cal-2 standard into the vial

7.2.9 Interference Check Standard Solutions (ICSA / ICSAB)

The interference solutions are purchased as a custom multi-element mix.

Prepare the ICSA Solution as detailed below.

- Add approximately 25 mL of 3% HNO_3 to a 50 mL volumetric flask
- Pipet 5.0 mL of the 6020ICS-0A standard into the flask.
- Dilute to volume with 3% HNO_3
- Stopper and shake to mix.

Prepare the ICSAB Solution as detailed below. The ICSAB is prepared fresh weekly.

- Add approximately 5 mL of 3% HNO_3 to a 10 mL volumetric flask
- Pipet 1.0 mL of the 6020 ICS standard into the flask
- Pipet 0.2 mL of the Spike Stock into the flask
- Dilute to volume with 3% HNO_3

7.3 Low Level Initial Calibration Verification / Continuing Verification

Add approximately 5ml of 3% HNO3 to a 100ml volumetric flask

Pipet 1.0 ml of ICPMS-LLCCV-1

Pipet 1.0 ml of ICPMS-LLCCV-2

Dilute to volume with 3%HNO3

7.4 Reagents

7.4.1 Reagent Water - ASTM Type I or equivalent for the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.4.2 **Nitric Acid Diluent, 3% HNO_3 -** Carefully dilute 60 mL of concentrated HNO_3 to 2.0 L with reagent water. This solution is used to dilute samples, and it is used for calibration blanks.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	HDPE	50 mLs	HNO_3, pH < 2	180 Days	40 CFR Part 136.3
Soils	Glass	4 oz	Cool 4 ± 2°C	180 Days	N/A

9.0 Quality Control

9.1 Quality control requirements are also summarized in Attachment 11.

9.2 Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Control limits are maintained in the laboratory LIMS system. See QC Policy DV-QA-003P for definition of QC terms, details about establishing control limits, elements of a preparation batch, and guidelines for evaluating batch QC.

9.3 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate and the NCM can be included in the report narrative. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031.

9.4 **Method Blank (MB)**
For aqueous and soil samples, the method blank consists of reagent water that has been processed in the same manner as the samples. For soil samples analyzed under the AFCEE QAP, the method blank consists of <1 mm glass beads that have been processed in the same manner as the samples. One method blank must be processed with each preparation batch.

Acceptance Criteria: Method blank results are acceptable if the concentration for each analyte of interest is less than the project specific reporting limit (RL). In the absence of project specific reporting limits, if the blank is less than 10% of the lower limit of quanititation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable.

NOTE: Some programs (e.g., USACE) require control of method blanks to a concentration equal to one-half of the RL.

Corrective Action: If the method blank does not meet the acceptance criteria, the source of contamination should be investigated to determine if the problem can be minimized or eliminated. Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following circumstances, may be reported as qualified (qualifier flags or narrative comments):

- The same analyte was not detected in the associated samples;
- The method blank concentration is less than 1/10 of the measured concentration of any sample in the batch;
- The method blank concentration is less than 1/10 the specified regulatory limit; or
- The analyte is a common laboratory contaminant (copper, iron, lead, calcium, magnesium, potassium, sodium, or zinc) less than 2 times the RL. Note that some programs do not recognize common lab contaminants.

If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.5 Laboratory Control Sample (LCS)

The LCS consists of reagent water that is spiked with the analytes of interest at the project specific action level or, when lacking specific action levels, at approximately mid-point of the linear dynamic range (summarized in Attachment 12). For soil samples analyzed under the AFCEE QAP, the LCS consists of <1 mm glass beads that have been spiked with the analytes of interest and processed in the same manner as the samples. One LCS must be processed for each preparation batch.

Acceptance Criteria: LCS control limits are based on three standard deviations of past laboratory results. These limits must not exceed 80-120% for Method 6020. The control limits are maintained in the LIMS system.

Corrective Action: If the LCS % recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reprocessed for analysis. One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples.

9.6 Matrix Spike / Matrix Spike Duplicate (MS / MSD)

The MS is prepared by taking a second aliquot of a selected sample and spiking it with the analytes of interest at same level as the LCS (summarized in Attachment 12). An MSD is prepared by taking a third aliquot of a selected sample and spiking it with the analytes of interest at same level as the LCS (summarized in Attachment

12). The MS and MSD are processed in the same manner as the samples. One MS/MSD pair must be processed for each preparation batch. However, some programs (e.g., AFCEE) require that matrix spikes can be performed only on project samples, and that the samples to be used are identified on the chain of custody form. The spike concentration should be the same level as the LCS.

Acceptance Criteria: Control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 75-125% recovery, and 20% relative percent difference (RPD). The control limits are maintained in the LIMS system.

Corrective Action: If MS/MSD results do not meet the acceptance criteria and all other quality control criteria have been met, then a matrix interference is suspected. Failed matrix spikes are flagged automatically, and are discussed in the final report case narrative.

9.7 Interference Check Solutions (ICSA/ICSAB)

The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Attachment 6. The interference check solutions must be analyzed at the beginning of every analytical run or once every 12 hours, whichever is more frequent. The results of solution "A" and solution "AB" should be monitored for possible interferences. See Attachment 6 for analyte concentrations.

NOTE: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (e.g., ICPAES), acceptance criteria will be applied at that level and the data accepted.

Acceptance Criteria: The results for the trace elements (B portion) must be +/- 20% of the expected value.

Corrective Action: If the ICSAB results exceed the 20% limit, then the analysis sequence must be terminated. The problem must be investigated and fixed. The ICS and all affected samples must be re-analyzed.

9.8 Internal Standards Evaluation for Samples

The IS recovery in samples can not fall below 70% of the intensity of the calibration blank. If sample IS recoveries fall outside of these criteria, a five-fold (1:4) dilution must be performed, the dilution analyzed, and the same acceptance criteria applied.

9.9 Serial Dilution

One serial five-fold dilution should be analyzed per batch for each matrix. If the analyte concentration is within the linear range of the instrument and sufficiently high (minimally, a factor of 10 above the reporting limit after dilution), the serial dilution must agree to within 10% of the original analysis. If not, an interference effect is suspected, which must be described in an anomaly report and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

9.10 Post-Digestion Spike Addition (PDS)

A PDS is performed for each batch. An analytical spike (minimum level of 10 times and a maximum of 100 times the lower limit of quantitation) added to a portion of a prepared sample, or its dilution, should be recovered to within 80-120% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.3 Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-IP-0014 and DV-IP-0015).

10.4 Sample Preparation
Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-IP-0014 and DV-IP-0015).

10.5 Calibration

10.5.1 Instrument Start Up
Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.5.2 Instrument Tuning / Mass Calibration
Tune the instrument with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 4 times.

Mass calibration and resolution checks using the tuning solution must be completed at the beginning of every day.

Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

Mass Resolution Check - The resolution must be verified to be less than 0.9 amu full width at 10% peak height.

10.5.3 Initial Calibration
The ICP/MS is calibrated each day of operation using a blank and a single standard (see Section 7.2.3). At least three integrations are employed.

The validity of the calibration is determined by the subsequent calibration verifications, which are performed at concentrations as described in the next sections.

10.5.4 Low-Level Initial Calibration Verification (LLICV)

A low-level ICV standard at or below the reporting limit (see Section 7.3) is analyzed immediately after the initial calibration. This is a standard obtained from the same vendor used for calibration.

Acceptance Criteria: The ICV recovery must be within 70-130%. The ICV can be reanalyzed, but two consecutive successful results must be obtained or corrective action is taken.

Corrective Action: If the ICV results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.5.5 Mid-Level Second-Source Initial Calibration Verification (ICV)

A 40 µg/L ICV standard (see Section 7.2.4) is analyzed immediately after the initial calibration. This is a standard obtained from a different vendor than the standard used for calibration.

Acceptance Criteria: The ICV recovery must be within 90-110%. The ICV can be reanalyzed, but two consecutive successful results must be obtained or corrective action is taken.

Corrective Action: If the ICV results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.5.6 Calibration Blank

An initial calibration blank (ICB) is analyzed after the ICV. Continuing calibration blanks (CCBs) are analyzed after each continuing calibration verification.

Acceptance Criteria: Results for the calibration blanks must be less than the RL. Note that some programs require control of method blanks to a concentration equal to 2X the MDL.

Corrective Action: If the calibration blank exceeds acceptance limits, then the possibility of instrument contamination should be examined, particularly the possibility of carry-over from high level samples. The blank can be reanalyzed, and if successful, analysis can continue. However, samples tested after high-level samples should be retested. If the reanalysis is not successful, then the analysis should be terminated. After the problem is corrected, recalibrate and reanalyze all samples tested since the last acceptable CCB.

10.5.7 Reporting Limit (RL) Verification Standard

Because the ICP calibration does not include multiple calibration levels, an independent standard is analyzed after the ICV to monitor the lab's

ability to produce reliable results at RL-level concentrations. The RL verification standard (see Section 7.2.6) is analyzed after the daily ICB.

Acceptance Criteria: For project reporting limits at or above two times the MDL, the results should be within 50% of the expected value. Some programs may require tighter control, in which case the RLs will need to be three or more times the MDL concentration.

Corrective Action: If the RL verification fails to meet acceptance limits, data for the associated samples must be assessed. For example, if the results are high, consider blank contamination, and if the results are low, consider MDL verifications. At a minimum, sample results must be qualified in the final report.

10.5.8 Lower Limit of Quantitation Check (LLQC)

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. The difference between the LLQC and the RLSTD is that this standard is carried through the entire preparation and analytical procedure.

Acceptance Criteria: LLQC is verified when all analytes are detected within ± 30% of their true value.

Corrective Action: If the LLQC fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.5.9 Low-Continuing Calibration Verification (LLCCV) Standard

A low-level CCV standard is analyzed after every set of ten samples and at the end of the analytical sequence.

Acceptance Criteria: The CCV recovery must be within 70-130%. In addition, the IS recovery must be within method limits: ≥70%. If CCV results are not within these limits, the CCV can be reanalyzed, but it must be successful twice in succession. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. TestAmerica will not hold samples with concentrations greater than 10x the reporting limit to the 30% acceptance criteria.

Corrective Action: If the CCV fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCV.

10.5.10 Mid-Continuing Calibration Verification (CCV) Standard

A 50 µg/L CCV standard is analyzed after every set of ten samples and at the end of the analytical sequence.

Acceptance Criteria: The CCV recovery must be within 90-110%. In addition, the IS recovery must ≥70%. If CCV results are not within these limits, the CCV can be reanalyzed, but it must be successful twice in succession or further corrective action must be taken.

Corrective Action: If the CCV fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCV.

10.6 Sample Analysis

10.6.1 Report the average of at least three integrations for all field and QC samples analyzed.

10.6.2 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

10.6.3 Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element.

10.6.4 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the RL. (The sample should be diluted to the approximate midrange of the analytical curve.)

10.6.5 The analytical run sequence should be performed as follows to meet all quality control criteria:

Instrument initialization / Warm-Up
Tune instrument
Perform mass calibration
Perform resolution check
Validate tuning criteria
Calibration blank
Calibration standard
ICV
ICB
LLICV
RL verification standard
LLQC(as needed)
ICSA
ICSAB

CCV
CCB
LLCCV
10 Samples (which can include all sample types)
CCV
CCB
LLCCV
Reslope
CCV
CCB
LLCCV

11.0 Calculations / Data Reduction

11.1 ICV percent recoveries are calculated according to the equation:

$$\%R = \left(\frac{\text{ICV Found Value}}{\text{ICV True Value}}\right) \times 100\%$$

11.2 CCV percent recoveries are calculated according to the equation:

$$\%R = \left(\frac{\text{CCV Found Value}}{\text{CCV True Value}}\right) \times 100\%$$

11.3 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{SSR - SR}}{\text{SA}}\right) \times 100\%$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

NOTE: When the sample concentration is less than the detection limit, use SR = 0 for the purpose of calculating %R.

11.4 The relative percent difference (RPD) between sample duplicates is calculated according to the following equation:

$$RPD = \left[\frac{DU1 - DU2}{\frac{1}{2}(DU1 - DU2)} \right] \times 100$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

11.5 The final concentration for an aqueous sample is calculated as follows:

$$\text{Result } (\mu g/L) = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

11.6 The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result } (\mu g/kg) = \frac{C \times V \times D}{W}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight, in g, of wet sample digested

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Prepare and analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.

- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy # DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 Instrument Detection Limit Study

Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each wavelength used for analysis in accordance with Policy DV-QA-014.

- Prepare seven reagent blank solutions.
- Digest the standards.
- Analyze the IDL standards on three non-consecutive days.
- For each day, the standard deviations for the seven standards are calculated. The final IDL concentration is the average of the three daily standard deviation values.

12.3 Linear Dynamic Range (LDR)

Linear range standards (see Section 7.2.7 for preparation) must be analyzed quarterly.

Acceptance Criteria: The highest standard must produce a recovery within 90-110% of the expected value.

Correction Action: Samples producing results above the LDR must be diluted reanalyzed.

12.3.1 Linear Range Verification

The LDRs should be verified whenever, in the judgment of the analyst, a change in the analytical performance caused by either a change in instrument hardware or operating conditions would dictate the necessity to re-establish them.

Acceptance Criteria: The LDR verification standard must produce a result within 90-110% of the expected value.

Corrective Action: If this limit is not met, then a new LDR study is required.

Some programs (e.g., USACE) require verification of linear ranges in each analytical run. As described in 7.2.7, a lower concentration is used for the daily check than is used for the quarterly determination.

Acceptance Criteria: Results must be within 90-110% of the expected value.

Corrective Action: Samples producing results greater than the concentration of the daily check standard will be diluted and reanalyzed.

12.4 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

Four aliquots of the ICV are analyzed using the same instrumental conditions and procedures used to analyze samples. The analyst must employ ICV's from four distinct analytical sequences. Using these four ICV's demonstrates the analyst's ability to optimize and calibrate the instrument and to prepare analytical solutions. Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.5 Training Requirements

12.5.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.5.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually. Initial Demonstration of Capability

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produce when this method is carried out:

- Aqueous Acidic (Metals) - Corrosive - Waste Stream J
- Expired reagents and standards – Contact the Waste Coordinator.

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 Test Methods For Evaluating Solid Waste, EPA SW-846, Update IV, Method 6020A: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 1, February 2007.

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, March 2005.

15.3 U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 6020A	Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept on file with QA.
2	EPA 6020A	Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18megOhm) and by the analysis of blanks.
3	EPA 6020A	Corrective action for a PDS failure will be limited to generating an NCM indicating the failed analyte and the recovery rather than diluting and reanalyzing the sample.
4	EPA 6020A	Internal standard recoveries are based on the intensities of the internal standards in the most recent calibration blank rather than the intensities of the internal standards in the initial calibration standard.

17.0 Attachments

Attachment 1: Recommended Elemental Equations
Attachment 2: Contributions of Contaminant Elements when Resolution and Measurement Schemes Vary

Attachment 3: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes
Attachment 4: Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions
Attachment 5: Internal Standards and Corresponding Metals
Attachment 6: Interference Check Sample Components and Concentrations
Attachment 7: Sample Preservation and Holding Times
Attachment 8: Suggested Mass Choices
Attachment 9: Tuning Solution
Attachment 10: Suggested Tuning and Response Factor Criteria
Attachment 11: Summary of Quality Control Requirements
Attachment 12: Calibration, Calibration Verification, and Spike Concentrations
Attachment 13: ICP/MS Technical Data Review Checklist

18.0 Revision History

NA

Attachment 1

Recommended Elemental Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	(1.0000)(27M)
Sb	none	(1.0000)(121M)
As	ArCl, Se	(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)
Ba	none	(1.0000)(135M)
Be	none	(1.0000)(9M)
Cd	MoO, Sn	(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)
Ca	none	(1.0000)(44M)
Cr	none	(1.0000)(52M)
Co	none	(1.0000)(59M)
Cu	none	(1.0000)(65M)
Fe	none	(1.0000)(57M)
Pb	none	(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)
Mg	none	(1.0000)(25M)
Mn	none	(1.0000)(55M)
Ni	none	(1.0000)(60M)
K	none	(1.0000)(39M)
Se	Ar2	(1.0000)(78M) - (1.1869)(76M)
Ag	none	(1.0000)(107M)
Na	none	(1.0000)(23M)
Tl	none	(1.0000)(205M)
V	ClO, Cr	(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)
Zn	none	(1.0000)(66M)
6Li	Li (natural)	(1.0000)(6M) - (0.0813)(7M)
Sc	none	(1.0000)(45M)
Y	none	(1.0000)(89M)
Rh	none	(1.0000)(103M)
In	Sn	(1.0000)(115M) - (0.0149)(118M)
Tb	none	(1.0000)(159M)
Ho	none	(1.0000)(165M)
Bi	none	(1.0000)(209M)

Where M = Total ion count rate at the specified mass.

Attachment 2
Contributions of Contaminant Elements when Resolution and Measurement Schemes Vary
Concentrations listed are the approximate level (µg/L) measured when the interferent is present at 100 mg/L.

Analyte	Interferent Element	Peak Width at 10% of the Peak Height			
		1.0 amu Integration Width		0.8 amu Integration Width	
		0.9 amu	0.3 amu	0.9 amu	0.3 amu
^{121}Sb	^{120}Sn	820	5	10	1
^{121}Sb	^{122}Te	77	None	1	none
^{75}As	^{74}Se, ^{76}Se	910	4	3	none
^{9}Be	^{10}B	1,200	12	9	1
^{112}Cd	^{113}In	1,700	8	10	none
^{114}Cd	^{115}In	5,000	150	180	18
^{116}Cd	^{115}In	30	None	5	none
^{52}Cr	^{51}V	1.4	1.5	none	none
^{53}Cr	^{54}Fe	650	7	1	none
^{59}Co	^{58}Ni, ^{60}Ni	1,500	6	2	none
^{63}Cu	^{62}Ni, ^{64}Ni	190	1	none	none
^{63}Cu	^{64}Zn	4,000	14	9	none
^{65}Cu	^{64}Ni	1	1	none	none
^{65}Cu	^{64}Zn, ^{66}Zn	4,400	22	15	none
^{208}Pb	^{209}Bi	140	14	57	none
^{55}Mn	^{54}Fe, ^{56}Fe	900	8	4	none
^{58}Ni	^{59}Co	3,000	96	75	7
^{60}Ni	^{59}Co	9	4	10	5
^{62}Ni	^{63}Cu	8,500	690	4,500	16
^{107}Ag	^{106}Pd, ^{108}Pd	2,400	22	80	4
^{107}Ag	^{106}Cd, ^{108}Cd	130	3	5	2
^{109}Ag	^{108}Pd, ^{110}Pd	1,800	12	36	3
^{109}Ag	^{108}Cd, ^{110}Cd	1,600	10	37	3
^{51}V	^{52}Cr	2,100	45	410	1
^{64}Zn	^{65}Cu, ^{63}Cu	7,800	57	410	2
^{66}Zn	^{65}Cu	2	none	3	2

Attachment 3

Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}

Attachment 3(cont.)
Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN				
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Attachment 4
Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions**

	Molecular Interference	Nebulizer Flow Rate		
		High	Average	Low
Oxides	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO, Cl	0.00725	0.00227	0.00233
Hydroxides	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

** Information for this table is being determined by the EPA.

Attachment 5
Internal Standards and Corresponding Metals

Method 200.8			
ICP-MS 004		ICP-MS-024	
Sc	Be	Li^6	Be
Ge	V, Cr, Co, Mn, Cu, Zn, As, Se, Ni	Ge	V, Cr, Co, Mn, Cu, Zn, As, Se, Ni
In	Mo, Ag, Cd, Sn, Sb, Ba	In	Mo, Ag, Cd, Sn, Sb, Ba
H	Tl, Pb, U	H	Tl, Pb, U

Attachment 6

Interference Check Sample Components and Concentrations
(ICSAB minors are suggested spike levels)

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Mn	0.0	0.1
Ni	0.0	0.1
Se	0.0	0.1
Ag	0.0	0.1
V	0.0	0.1
Zn	0.0	0.1

Attachment 7

Sample Preservation and Holding Times

Measurement Parameter	Container (1)	Preservative (2)	Maximum Holding Time (3)
Waters:			
Metals (4)	P,G	HNO_3 to pH < 2	6 months
Soils/Sediments/Wastes:			
The preservation required for soil/sediment/waste samples is maintenance at 4°C (± 2°C) until digestion.			

Footnotes:

(1) Polyethylene (P) or glass (G).
(2) Sample preservation is performed by the sampler immediately upon sample collection.
(3) Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that sample may be held before analysis and still considered valid. Holding times are calculated from the date when the sample was collected.
(4) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved elements.

Attachment 8

Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data.

Mass	Element of Interest
"**27**"	Aluminum
121, "**123**"	Antimony
"75"	Arsenic
138, "137", 136, **135**, 134, 132, 130	Barium
"9"	Beryllium
114, 112, "111", 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium
"**52**", **53**, **50**, 54	Chromium
"**59**"	Cobalt
"**63**", **65**	Copper
56, **54**, **57**, 58	Iron
"**208**", "**207**", "**206**", 204	Lead
24, **25**, **26**	Magnesium
"**55**"	Manganese
58, "**60**", 62, **61**, 64	Nickel
39	Potassium
80, **78**, "**82**", **76**, **77**, 74	Selenium
"**107**", **109**	Silver
23	Sodium
"**205**", 203	Thallium
"**51**", **50**	Vanadium
64, "**66**", **68**, **67**, 70	Zinc
72	Germanium
139	Lanthanum
118	Tin
35, 37	Chlorine
"98", 96, 92, **97**, 94	Molybdenum

NOTE: It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Attachment 9: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Method 6020

Element	Concentration (μg/L)
Mg	10
Rh	10
Ba	10
Be	10
U	10
Cs	10
Y	10
Pb	10
Li	10
Co	10
In	10
Tl	10

Attachment 10: Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution:

Be	>1,000
Mg	>2,000
Rh	>20,000
Pb	>10,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Attachment 11: Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
LLQC	At the beginning of the run on an as needed basis	70 - 130% recovery. 6020 IS, ≥70% rec.	Terminate analysis; correct the problem; recalibrate.
LLICV	Beginning of every analytical run.	70 - 130% recovery. 6020 IS, ≥70% rec.	Terminate analysis; correct the problem; recalibrate.
ICV	Beginning of every analytical run.	90 - 110% recovery. 6020 IS, ≥70% rec.	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result is < RL. 6020 IS, ≥70% rec.	Terminate analysis; correct the problem; recalibrate.
LLCCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent. Beginning and end of each lot.	70 - 130% recovery. 6020 IS, ≥70% rec.	See Section 10.5.9. Reanalyze twice in succession. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.
CCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent. Beginning and end of each lot.	90 - 110% recovery. 6020 IS, ≥70% rec.	Reanalyze twice in succession. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.

Attachment 11: Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
CCB	Immediately following each CCV.	The result must be < RL. 6020 IS, ≥70% rec.	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCB.
ICSA	Beginning and every 12 hours.	Monitor for possible interferences.	See Section 9.7
ICSAB	Immediately following each ICSA.	Monitor for possible interferences.	See Section 9.7
Method Blank	One per lot of 20 field samples or fewer.	The result must be < RL. Sample results greater than 10x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis.	Re-run once. If >RL, Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Serial Dilution	One per batch of 20 field samples or fewer.	90 - 110% recovery	See section 9.8 for additional requirements.
Post-Digestion Spike	One per batch of 20 field samples or fewer.	80-120% recovery	See section 9.9.
Matrix Spike	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See section 9.6 for additional requirements.

Attachment 12: Calibration, Calibration Verification, and Spike Concentrations

Element	Initial Calibration (µg/L)	LLICV / LLQC (µg/L)	ICV (µg/L)	LLCCV (µg/L)	CCV (µg/L)	LCS (µg/L)	MS/MSD (µg/L)
Aluminum	100	30	40	30	50	40	40
Antimony	100	2	40	3	50	40	40
Arsenic	100	5	40	5	50	40	40
Barium	100	1	40	1	50	40	40
Beryllium	100	1	40	1	50	40	40
Cadmium	100	1	40	1	50	40	40
Chromium	100	2	40	2	50	40	40
Cobalt	100	1	40	1	50	40	40
Copper	100	1	40	1	50	40	40
Lead	100	1	40	1	50	40	40
Manganese	100	1	40	1	50	40	40
Nickel	100	2	40	2	50	40	40
Silver	100	5	40	5	50	40	40
Thallium	100	1	40	1	50	40	40
Zinc	100	1	40	1	50	40	40

This procedure has been developed for thirty-five elements (See Attachment 8). Additional elements may be included in the calibration solution at the above levels. Levels may be adjusted to meet specific regulatory or client programs.

THE LEADER IN ENVIRONMENTAL TESTING

ICP/MS Technical Data Review Checklist

Lab Project ID Number(s): see attached cover sheet Check Method/SOP Used: ☐6020/DV-MT-0018 ☐200.8/DV-MT-0002

Review Items	--- Level 1 ---			Level 2	Comments & Samples Affected
	Yes	No	N/A		
Tune					
1. Tune solution analyzed min. of 4 times for 6020 or 5 times for 200.8?					
2. Tune RSD <5%?					
2. Resolution ≤ 0.9 AMU full width at 10% peak height? **NOTE**: This also satisfies 200.8, 1.0 AMU at 5% peak height					
Initial Calibration					
1. Done with a minimum of 3 integrations of a high standard and blank?					
2. ICV/CCV run at beginning of run, 10% frequency, and end of run? Results with 10% of expected value?					
3. ICB/CCB run at beginning of run, 10% frequency, and end of run? Results +/- RL					
4. ICSA/AB analyzed at beginning of run and every 12 hours and results 80-120% of TV?					
5. RL Std analyzed at beginning of run and results +/- 50% of TV(for AFCEE 4.0, DoD V3 +/- 20% of true value)?					
Client Samples & QC Sample Results					
1. Were all samples within linear range, ≤ 90% of LDR for 200.8?					
2. Dilutions due to target elements?____ Dilutions for other reasons?___					
3. All reported results bracketed by in control QC?					
4. All 6020 internal standards for all analyses 30-120% of intensities in blank or all 200.8 internal standards 60-125%?					
5. Was a 5X serial dilution analyzed for 6020 and, if so, are results ± 10% of original result, if original ≥ 100x MDL?					
6. LCS included in batch and within QC limits?					
7. Method blank included and <1/2RL?					
8. MS and MSD included in batch?					
9. PDS analyzed and recovery 75-125%?					
10. Manual calculations documented properly and checked?					
11. Are non-conformances documented on an NCM?					
12. Is the appropriate raw data included?					
13. Are all results manually entered into LIMS verified? Are all electronic data files archived to the appropriate network locations?					
14. Were special client requirements met?					

1st Level Reviewer: _____ Date: _____

2nd Level Reviewer: Date:

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Nitrate, Nitrite by Automated Cadmium Reduction [EPA 353.2]

Approvals (Signature/Date):

Dave Elkin — Date Wet Chemistry Supervisor	Adam Alban — Date Health & Safety Manager / Coordinator
Karen Kuoppala — Date Quality Assurance Manager	Robert C. Hanisch — Date Laboratory Director

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1.0 Scope and Application

1.1 This method determines nitrate plus nitrite as nitrogen. It can also be used to determine nitrite only, or, by difference, nitrate. This SOP is based on EPA Method 353.2.

1.2 This method is applicable to the analysis of drinking waters, surface waters, and domestic and industrial wastes. Solid samples may also be analyzed following extraction with de-ionized water (SOP DV-WC-0036).

1.3 The reporting limit is 0.10 mg/L for waters and 1.0 mg/kg for solids.

2.0 Summary of Method

Nitrate is reduced quantitatively to nitrite by passing through a column containing granulated copper-cadmium. The nitrite thus formed plus any originally present in the sample is determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. A separate component value is obtained for nitrite SM 4500 NO2 B. Nitrate can be determined by subtracting nitrite from nitrate plus nitrite from the procedure in this SOP.

3.0 Definitions

There are no terms requiring definition unique to this procedure. Refer to the Glossary of the Quality Assurance Manual (QAM) for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 High concentration of iron, copper and other metals can cause low results. It is possible to compensate for this effect to some extent by the addition of EDTA.

4.2 Build up of suspended matter in the reduction column will restrict sample flow. Particulates may be removed be filtration.

4.3 Oils and greases will coat the surface of the cadmium. Water samples containing a separate organic phase or an oil sheen should not be tested without removing the organic material by pre-extracting the sample with an organic solvent.

4.4 Samples collected from chlorinated sources should be checked for free chlorine by the analyst using KI test strips. If free chlorine is detected, it must be neutralized by adding sodium thiosulfate solution. Residual chlorine can produce a negative interference by limiting reduction efficiency.

4.5 Color or turbidity at measurable levels, especially color at 540 nm, can produce false positive results. Samples with turbidity must be filtered, while colored samples may need to be diluted prior to analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and

health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Cadmium	Carcinogen	50 ug/m3-TWA	Inhalation of dust or fume can cause severe lung irritation and pulmonary edema, which may be fatal. Chronic exposure can also cause kidney damage. Ingestion causes severe gastrointestinal irritation.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Ammonium Hydroxide	Corrosive Poison	50 ppm (TWA)	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Phosphoric Acid	Corrosive	1 mg/m3 (TWA)	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

5.3 Nitrate + nitrite waste may contain cadmium, which is toxic and carcinogenic; it must not be poured into the sinks. Wear gloves when handling cadmium. Eye protection that satisfies ANSI Z87.1 (as per the Environmental Health and Safety Manual), laboratory coat, and Nitrile gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Reduction column contain cadmium and must not be disposed of in the trash.

6.0 Equipment and Supplies

6.1 Instrumentation

- Auto-analyzer equipped with the proportioning pump, autosampler, and colorimeter with 540 nm filter
- The laboratory uses open tubular cadmium reactor (OTCR) from a commercial vendor.
- Degassing system to remove air from reagent water

6.2 Supplies

- Disposable auto-sampler vials
- Volumetric flasks, Class A, various sizes
- Volumetric pipettes, Class A, various sizes
- Mechanical pipettors, various sizes
- 0.45 micron syringe filters and syringes for filtration of turbid samples

7.0 Reagents and Standards

All reagents must be ACS Reagent Grade or better.

7.1 ASTM Type II Water (Milli-Q or equivalent)

7.2 Brij-35, 30% w/v. This reagent is available from a commercial vendor.

7.3 **Concentrated Ammonium Hydroxide**, available commercially

7.4 **Potassium Nitrate (KNO_3)**. This reagent is available from a commercial vendor.

7.5 **Potassium Nitrite (KNO_2)**. This reagent is available from a commercial vendor.

7.6 **Ammonium Chloride (NH_4Cl).** This reagent is available from a commercial vendor.

7.7 **Phosphoric Acid (H_3PO_4)**. This reagent is available from a commercial vendor.

7.8 **Cupric Sulfate, Pentahydrate ($CuSO_4 \cdot 5H_2O$)**. This reagent is available from a commercial vendor.

7.9 **Sulfanilamide ($C_6H_8N_2O_2S$)**. This reagent is available from a commercial vendor.

7.10 **Ethylene diaminetetraacetic acid, Disodium salt dihydrate (Disodium EDTA)**. This reagent is available from a commercial vendor.

7.11 **Ammonium Chloride- Disodium EDTA Buffer**
Dissolve 170.0 g ammonium chloride and 0.2 g disodium ethylenediamine tetraacetic acid dihydrate in about 1800 mL of deionized water. Adjust the pH to 8.5 by drop-wise addition of concentrated ammonium hydroxide and dilute to 2 liters with de-ionized water using a volumetric flask. Degas this solution and then add 4.0 mL of Brij-35 before use.

7.12 Color Reagent.

Cautiously add 100 mL 85% phosphoric acid to about 600 mL de-ionized water and mix. Add 40.0 g sulfanilamide and 2.0 g N-1-naphthylethylenediamine dihydrochloride and mix until dissolved. Do not allow to mix in air for a long period of time as discoloration may occur. Dilute to 1 liter with deionized water in a volumetric flask. This solution is stable for several months and should be kept in an amber container and stored in the dark when not in use. If precipitates form in the container, the reagent should be discarded and a fresh portion prepared before analysis.

7.13 Start-up Solution

Add approximately 2 mL of Brij-35, 30% (w/v) to approximately 1 L of deionized water.

7.14 Regeneration reagent for Cadmium-Copper Reduction Column:

7.14.1 Hydrochloric Acid, 0.5 N

Carefully add 4.15 mL concentrated hydrochloric acid to 70 mL deionized water in a 100 mL volumetric flask. Mix well, and dilute to the mark.

7.14.2 Copper Sulfate, 2%

Dissolve 20 g $CuSO_4 \cdot 5H_2O$ in deionized water and dilute to 1000 mL.

7.15 Cadmium Column Activation

Using 10 to 50cc plastic syringe fitted with a union, flush the OTCR with each solution using the following procedure (this procedure is performed on each side of the column). It is important to prevent the introduction of air into the cadmium reactor during this process.

7.15.1 Deionized water

7.15.2 Hydrochloric acid, 0.5 N (7.14.1)

7.15.3 Deionized water (this should be immediately after the hydrochloric acid flush)

7.15.4 Copper Sulfate, 2% (7.14.2). This phase should be rinsed slowly. Precipitate may be seen exiting the reactor.

7.15.5 Deionized water. Use sufficient force to wash out any clogs of precipitate that may have formed.

7.16 Sulfuric Acid, 0.2%

Slowly and with constant mixing add 4 mL concentrated sulfuric acid to 2 liters of de-ionized water.

7.17 Nitrate Calibration Stock Standard, 1000 mg/L as N

Dissolve 7.218 g potassium nitrate in de-ionized water and dilute to 1000 mL. Add 2 mL chloroform as a preservative. This solution may also be purchased from commercial sources.

7.18 Nitrite Stock Standard, 1000 mg/L as N

Dissolve 6.072g potassium nitrite in de-ionized water and dilute to 1000 mL. Add 2 mL chloroform as a preservative. This solution may also be purchased from commercial sources.

7.19 Nitrate Calibration Intermediate Standard, 100 mg/L as N

Dilute 10.0 mL of 1000 mg/L Calibration Stock Standard (see Section 7.17) to 100 mL with 0.2% sulfuric acid and mix. This solution is stable for one month.

7.20 Working Standards

The working standards are prepared using the 100 mg/L intermediate nitrate standard and 0.2% sulfuric acid. The following table is the recommended preparation of the calibration standards used for initial calibration:

Calibration Levels

LEVEL	VOLUME OF INTERMEDIATE STANDARD (ML)	CONCENTRATION OF INTERMEDIATE STANDARD (MG/L)	FINAL VOLUME (ML)	FINAL CONCENTRATION (MG/L)
BLANK	0	0	100	0
1	0.05	100	100	0.05
2	0.10	100	100	0.10
3	0.50	100	100	0.50
4	1.0	100	100	1.0
5	5.0	100	100	5.0
6	10.0	100	100	10.0

These standards must be prepared daily. Note that the low point on the calibration curve must be at or below the project reporting limits. Note that mixed nitrate/ammonia standards may be used if both nitrate and ammonia are being run on the sample.

7.21 Nitrate ICV Stock Standard, 1000 mg/L as N.

Dissolve 7.218 g potassium nitrate in de-ionized water and dilute to 1000 mL. Add 2 mL chloroform as a preservative. This solution may also be purchased from commercial sources. This solution is from a different vendor than that used to prepare the Nitrate Calibration Stock Standard (see Section 7.17).

7.22 Nitrate ICV Intermediate Standard, 100 mg/L as N.

Dilute 10 mL of Nitrate ICV Stock Standard (see Section 7.21) to 100 mL with deionized water in a volumetric flask. This solution is stable for one month.

7.23 Nitrate ICV Working Standard, 2 mg/L as N.

Dilute 2 mL of Nitrate ICV Intermediate Standard (see Section 7.22) to 100 mL with 0.2% sulfuric acid in a volumetric flask. This solution has a true value of 2 mg/L nitrate as N.

7.24 Column Efficiency Check Standard, 5 mg/L as N.

A 5 mg/L nitrite as N solution is by diluting 0.5 ml of the 1000 mg/L nitrite stock standard (see Section 7.18) to 100mL in a volumetric with de-ionized water.

7.25 Laboratory Control Standard (LCS)/Continuing Calibration Verification
The LCS is prepared identically to Calibration Standard 5 (see Section 7.20). It has a true value of 5 mg/L.

7.26 Kleenflow Solution - Basic
Add 50 mL of Isopropyl Alcohol to a 1 liter flask. Carefully add approximately 950 mL of 1N Sodium Hydroxide (NaOH).

8.0 Sample Collection, Preservation, Shipment and Storage

- Samples are to be collected in plastic or glass containers, acidified with sulfuric acid to pH < 2, and refrigerated to 4° ± 2°C. If only nitrate is required, or if nitrite is required, a separate sample must be submitted that has not been preserved with sulfuric acid.
- Sodium thiosulfate (0.1 mL of 5% solution) is added to samples at the time of collection if the samples are being collected from a chlorinated source.

Note: The laboratory must supply the thiosulfate solution separate from the acid in the bottle; sulfuric acid and thiosulfate cannot be mixed together in the collection bottle prior to shipping containers to the field.

- The holding time for nitrate + nitrite is 28 days if preserved with sulfuric acid. If the sample is unpreserved (except for refrigeration), the holding time is 48 hours.

9.0 Quality Control

The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

- The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.
- Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.
- Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.
- Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.1 Sample QC - The following quality control samples are prepared with each batch of samples.

9.1.1 Preparation Batch

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD). As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.1.2 Method Blank (MB)

One method blank (MB) must be processed with each batch. The MB consists of reagent water that is carried through the entire analytical procedure, including preparation and analysis. When analyzing soils, the MB is prepared in the same manner as the samples by performing a DI water leach in accordance with SOP DV-WC-0036 using washed Ottawa sand. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

Acceptance Criteria: The MB should not contain any analyte of interest at or above the reporting limit (RL).

Corrective Action: If the analyte level in the MB exceeds the reporting limit for the test, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data must be taken in consultation with the client and must be addressed in the project narrative.

If the analyte concentration is greater than the reporting limit (RL) in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

If all samples associated with a blank greater than the RL are greater than 10 times the blank value, the samples may be reported with an NCM to qualify the high blank value.

9.1.3 Laboratory Control Sample (LCS)

At least one LCS must be processed with each batch. The LCS for aqueous sample batches consists of reagent water to which a known amount of target analyte has been added. The LCS for soil batches consists of 10 grams of Ottawa sand to which a known amount of the target analyte is added. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process.

Acceptance Criteria: Maximum control limits for LCS recoveries in water by Method 353.2 are 90-110%. In-house control limits, set at ± 3 standard deviations around the historical mean, are used as long as they are at least as tight as the regulatory limits. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

Corrective Action: If LCS recoveries are outside established control limits, the analytical system is out of control and corrective action must be taken.

If recoveries are above control limits and nitrate is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.1.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) that is prepared and analyzed along with the sample and matrix spike.

One MS/MSD pair must be processed for every 10 samples.

The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing on only the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

Prepare the MS/MSD by adding 0.2 mL of the Nitrate Calibration Intermediate Standard, 100 mg/L as N (7.19) to 5 mL of sample before analysis. The spiking concentration is 4 mg/L.

Acceptance Criteria: In-house control limits, set at ± 3 standard deviations around the historical mean, are used for recovery acceptance as long as they are at least as tight as the regulatory limits.

Corrective Action: If the calculated recovery or relative percent difference (RPD) is outside the acceptance range, the recovery of that analyte in the LCS must be within the established control limits. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.2 Instrument QC

9.2.1 Initial Calibration Verification (ICV)

Analyze a second-source ICV standard (Section 7.23) immediately after the initial calibration (ICAL).

Acceptance Criteria: The recovery must be within the 90 -110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, and then recalibrate.

9.2.2 Continuing Calibration Verification (CCV)

Analyze the CCV standard, which is prepared from the same source and at the same concentration as the midrange 5 mg/L calibration standard (Section 7.20), after every ten samples and at the end of the analytical sequence.

Acceptance Criteria: The recovery must be within the 90 -110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, recalibrate, and rerun all samples analyzed since the last successful CCV.

9.2.3 Initial and Continuing Calibration Blank

System cleanliness is checked at the beginning (with an initial calibration blank or ICB), and after every ten samples and at the end of the analytical sequence using a continuing calibration blank (CCB).

Acceptance Criteria: Results must be less than the reporting limit.

Corrective Action: If the blank is greater than the reporting limit, check for carry-over from high level samples, clean the system, recalibrate, and rerun all samples analyzed since the last successful CCB.

9.2.4 Column Efficiency Check

The efficiency of the cadmium reduction column is checked by analyzing a 5 mg/L nitrite check standard (7.24). The recovery must be 85 -115%. If the recovery is outside of this range, this indicates that the column is not properly converting nitrate to nitrite. In this case the column must be regenerated or replaced and the instrument recalibrated.

NOTE: The column is regenerated daily before the beginning of analysis. See section 7.15 for the regeneration procedure.

9.2.5 Linear Calibration Range (LCR)

The LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ± 10%, the linearity must be re-established.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.1 Sample Preparation

10.1.1 Nitrate/nitrite in soils is extracted using de-ionized water (see SOP # DV-WC-0036).

10.1.2 The pH of all samples are checked in log-in at the time of receipt. If the pH is above 2.0, samples must be tested within 48 hours of collection. If this is not done, results may not be acceptable – A Condition Upon Receipt (CUR) form is completed to notify the laboratory Project Manager.

10.1.3 All drinking water samples and any samples from chlorinated sources (see special instructions from PM) must be checked for residual chlorine using KI test strips. If residual chlorine is detected, results may not be acceptable - prepare a Nonconformance Memo and notify the laboratory Project Manager.

10.2 Calibration

Instrument Set Up

The instrument is to be set up and operated in accordance to the manufacturer's instructions. Before running samples, the pump should be allowed to pump start-up water through the system for approximately 5 minutes to remove any air bubbles from the lines. Additional calibration information can be found in the Corporate TestAmeica's Calibration Curve document CA-Q-S-005.

10.2.1 The ICAL is performed automatically by the instrument at the beginning of each day's use.

10.2.2 Load the calibration standards (Section 7.20) into the autosampler so that they are analyzed before any samples. A series of six concentrations plus zero is used to establish this curve. All the standards and blanks are processed exactly as the samples.

10.2.3 The instrument software processes the calibration data and generates a calibration function that is used to calculate sample results. The instrument software uses a least squares linear regression to relate the concentration of nitrogen in each standard and the associated absorbance reading, as follows:

$$y = mx + b$$ **Equation 1**

Where:

y = *Absorbance of standard at 540 nm.*
x = *Nitrogen (as N) of standard, mg/L.*
m = *Slope of the fitted straight line.*
b = *Y-intercept of the fitted straight line.*

10.2.4 The instrument software uses the calibration function to calculate the concentration of each sample that is analyzed. The instrument software

prints a calibration report for review, which includes the calibration equation and correlation coefficient. The correlation coefficient of the calibration line must be ≥ 0.995. If this cannot be achieved, then check the calibration standards, correct any problems, and repeat the ICAL.

10.2.5 The instrument software automatically calculates the concentration of each unknown sample using the sample absorbance and the calibration curve.

10.3 Sample Analysis

10.3.1 Set up cartridge as shown in SFA diagram (See Attachement 1). Turn power on to all units. Place reagent lines in start up solution, tighten the platens and start the pump flow. Allow to flow for at least 5 minutes until a stable flow is established. Do not install OTCR at this time.

10.3.2 Move reagent lines from startup solution to the appropriate reagent bottles and allow reagents to flow through the system until a stable baseline is achieved. If nitrate-nitrite is to be determined, replace the jumper between ports #1 and # 10 with the activated OTCR. If nitrite is to be determined, leave the jumper in place.

10.3.3 Load the calibration standards, ICV, ICB, samples and CCVs and CCBs into the autosampler. Initiate the analytical sequence. The instrument will first analyze the calibration standards and generate a calibration function. This calibration function will then be used by the instrument to calculate sample concentrations based on measured abosrbances. Use the following analytical sequence:

- Sync Peak
- Calibration standards
- Column Efficiency Check
- Second-source ICV standard
- Initial Calibration Blank (ICB)
- LCS
- Method Blank
- Samples
- CCV
- CCB
- 10 Samples
- CCV
- CCB

10.3.4 Any sample results that exceed the working range should be diluted with deionized water and reanalyzed.

10.3.5 Samples may be diluted prior to analysis if screening with test strips indicates a high level of nitrate is possible, or if historical data indicates a

possible dilution. Samples with > 100 mg/L of nitrate may cause precipitation of solids in the cartridge lines and so should be diluted prior to analysis to avoid ruining a large portion of the analysis run.

10.3.6 After analysis is complete, the OTCR must be removed prior to removing the buffer solution. Replace the OTCR with the jumper. The OTCR should be filled with DI water for proper storage.

10.3.7 Disconnect the reagent lines and put all of them into DI water, EXCEPT the buffer line. The buffer line should be placed into bridge solution.

10.3.8 Rinse all tubes for at least 5 minutes, and then rinse with Kleenflow Base for 5 minutes. Rinse all tubes with the appropriate rinses for another 5 minutes.

10.3.9 Turn off the instrument and pump, rinse platens, and empty waste when finished.

11.0 Calculations / Data Reduction

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Concentration

$$\text{NO3+NO2 Result (mg N /L)} = \frac{(C \times DF)}{V}$$

Where:

C = Concentration measured at the instrument
DF = Dilution factor
V = Volume of sample used for analysis

- Normally this calculation is performed automatically by the instrument data system.
- If an extract of a non-aqueous sample was analyzed, multiply the result obtained by the prep dilution factor to obtain the final result.
- If nitrite was measured, nitrate may be calculated by subtracting the nitrite result from the nitrate + nitrite result.

11.4 **Anomalies:** Document any non-standard procedures or anomalies. Some common anomalies are:

- Sample diluted for color interference.
- Sample pH was neutral preserved with sulfuric acid before analysis.

11.5 All results are subject to two levels of data review, which are documented on the checklist shown in Attachment 2.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial method detection limit study is performed for each analyte and each sample matrix type in accordance with Policy DV-QA-005P. An MDL verification is performed once a year to satisfy NELAC 2003 requirement. For DoD and AFCEE projects, an MDL verification is performed quarterly. MDLs are stored in the LIMS.

The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 Demonstration of Capabilities

An initial demonstration of capability for each method must be performed prior to analyzing samples.

- For the standard analyte list, the initial demonstration consists of the preparation and analysis of a QC check sample containing all of the standard analytes for the method, as well as a method detection limit (MDL) study.
- Four aliquots of the QC check sample (independent source from the calibration) are analyzed with the same procedures used to analyze samples, including sample preparation.
- The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples.
- For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is successful analysis of an extracted standard at the reporting limit and a single point calibration.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and

the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

13.1 In general, the quantity of chemicals purchased by TestAmerica Denver is based on expected usage during its shelf life. The volume of reagents and standards prepared for this procedure reflects anticipated usage.

13.2 Source reduction is achieved through the use of automation that reduces the volume of hazardous waste generated by this procedure.

13.3 The volume of hazardous waste is minimized through proper segregation and management of the various waste streams generated by this procedure

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams have been identified for this method:

- Alpkem process waste – Aqueous Acidic (F)
- Contents of sampler cups (preserved) – Aqueous Acidic (F)
- Spent cadmium reduction columns - Contact Waste Coordinator

Note: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Method 353.2, "Methods for Chemical Analysis of Water and Wastes", USEPA, EPA-600/4-79-020.

15.2 Method 4500-NO2 and 4500-NO3, 20th Edition of Standard Methods for the. Examination of Water and Wastewater, AWWA.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 353.2	The source method has been expanded to include soils and wastes through the use of a de-ionized water leach.
2	EPA 353.2	The source methods state to place the calibration standards in the sampler "in order of decreasing concentration." The standards are placed in the sampler in increasing concentration per the instrument manufacturer's specifications.

17.0 Attachments

Attachment 1: Instrument Flow Diagram
Attachment 2: Example Data Review Checklist

18.0 Revision History

- Revision 6, dated 24 August 2009
  - Fixed spelling and section reference errors.
  - Added standard expiration to section 7.22.
  - Changed standard concentration for the LCS (section 7.25) and CCV (section 9.2.2)
  - Changed pH check to be performed by log-in (section 10.1.2)
  - Fixed section 10.2.3 to reflect nitrogen instead of phosphorus.
  - Added attachment reference to section 10.3.1
  - Added Kleenflow Base to section 7.

- Revision 5.1, dated 15 May 2009
  - Updated working calibration concentrations (section 7.20)
  - Added instrument shut down information (sections 10.3.6 to 10.3.9)
  - Added method modifications (section 16.0)
  - Updated method references
  - Updated formatting

- Revision 5, dated 01 February 2008
  - Integration for TestAmerica and STL operations.
  - Updated formatting
  - Document number changed from DEN-WC-0007 to DV-WC-0007

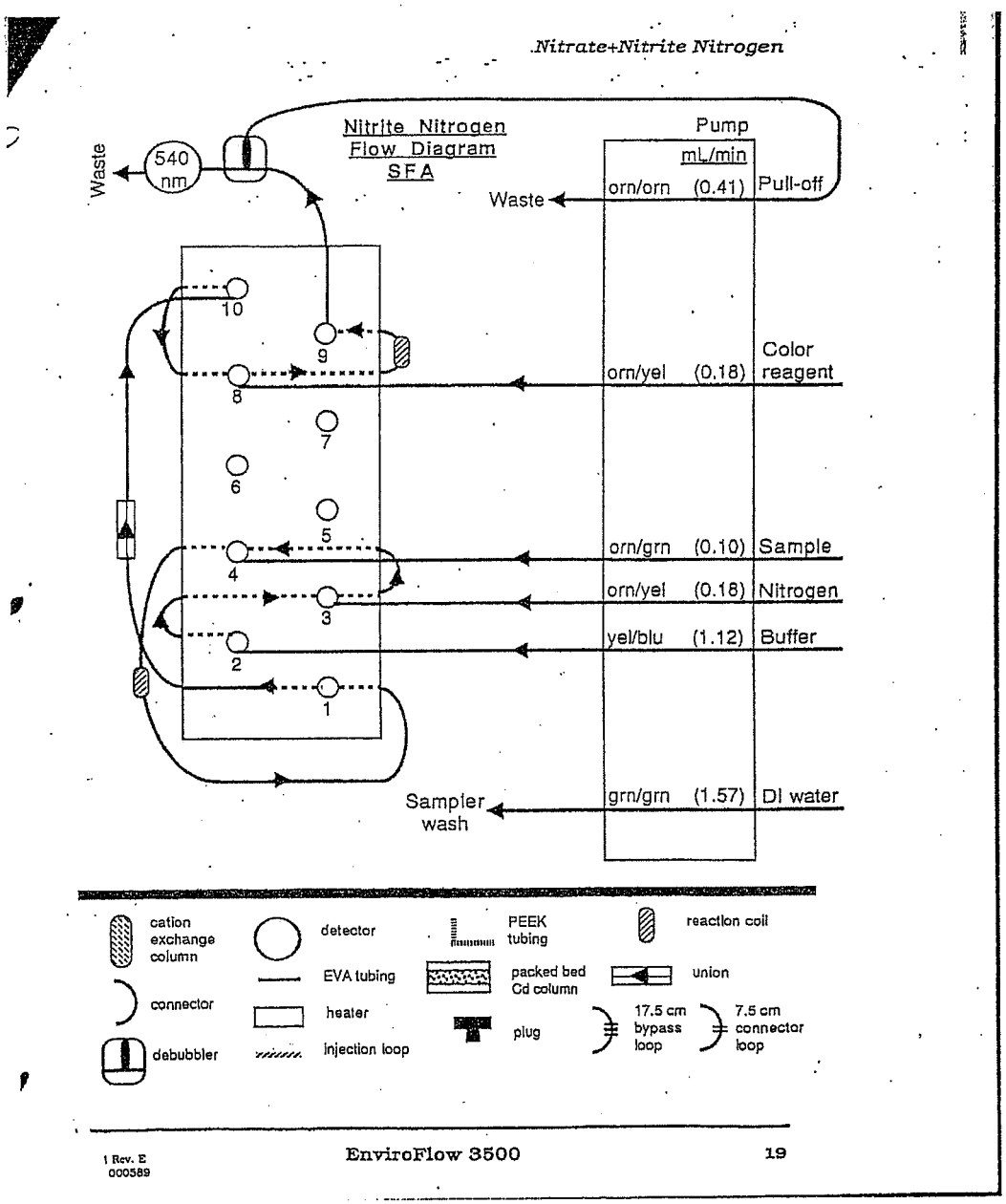
- Revision 4, dated 06 July 2007
  - Removed adjustment of pH of sample to between 5 and 9 as the buffer in the automated method performs this function.
  - Removed the instruction to degas the start-up solution.
  - Changed standards table to current format.
  - Updated Quality Control, Calibration and Standardization, Calculations, and Method Performance to new format.
  - Changed matrix spike preparation to accurately match current practice.
  - Added the analytical sequence.
  - Minor grammatical corrections.

- Revision 3, dated 04 August 2004
  - Safety Section 5 and Waste Management Section 15 were updated to current STL Corporate standards.
  - The Quality Control Section 9 now includes outer bounds for the LCS and MS/MSD control limits. The format of the section has been updated to current STL Denver requirements.
  - The MDL verification process is now described in Section 13.2.
  - The instrument flow diagram was added in Attachment 1.

- Revision 2, dated 04 August 2004
  - Addition of waste information
  - Document number changes from DEN-WC-007 to DEN-WC-0007.

Attachment 1.

Instrument Flow Diagram



Attachment 2.

Example Raw Data Review Checklist

TESTAMERICA Denver

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Wet Chemistry Data Review Checklist
For Tests with Calibration Curves

Test Name/ Method #: _____ **SOP #** _____

Instrument: _____ **Analyst:** _____ **Analysis Date:** _____

Lot / Sample Numbers	Matrix	Batch	Method	QC	Special Inst

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Minimum of five standards in ICAL or as specified in method?				
2. Correlation coefficient ≥ 0.995 ?				
3. Second-source ICV analyzed, and recovery 90-110%?				
4. ICB analyzed immediately after the ICV & results < the RL				
5. CCV analyzed after every ten samples & recovery ± 10% of true value?				
6. CCB analyzed after every CCV & results < RL?				
7. Absolute value of the intercept is < ± ½ the RL?				
B. Sample Results				
1. All samples greater than highest calibration standard diluted and reanalyzed?				
2. Do associated RLs/MDLs reflect dilutions or limited sample volume?				
3. All reported results bracketed by in control CCV results?				
4. Sample analyses done within holding time?				
5. Initial pH check documented for all samples?				
6. Preparation benchsheet completed and included in package?				
7. Client requirements reviewed and met?				
8. Were data manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures and correct units?				
9. Do the prep and analysis dates in QuanTIMS reflect the actual dates? Lots/Dates report checked?				
10. Are all data being reported highlighted on the benchsheet?				
11. Raw data copies prepared and scanned?				
12. Manual integrations done properly and initialed and dated?				
13. STD/True Value sheet is updated and included?				
C. Preparation/Matrix QC				
1. Method blank < RL or all reported samples > 10x blank have NCM?				
2. Method blank < ½ RL or NCM provided?				
3. LCS/LCSD run for batch and within QC limits?				
4. MS/MSD run at required frequency and within limits or NCM written?				
5. DUP run at required frequency and RPD within 20% or NCM written?				

Analyst: _____ **Date:** _____

_____

_____

2nd Level Reviewer : _____ **Date:** _____

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Anions by Ion Chromatography

[EPA 300.0, SW 9056 and 9056A]

Approvals (Signature/Date):

Dave Elkin 12/3/09 Date Wet Chemistry Supervisor	Adam W. Alban 03Dec09 Date Adam Alban Health & Safety Manager / Coordinator
Karen Kuoppala 12-4-09 Date Quality Assurance Manager	Robert C. Hanisch 12/4/09 Date Robert C. Hanisch Laboratory Director

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1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This procedure describes the determination of the anions fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate, and sulfate in water samples by ion chromatography, based on EPA Method 300.0 and SW-846 Methods 9056 and 9056A.

1.1.2 This procedure can also be applied to leachates from soil samples. The soil leaching procedure is described in SOP DV-WC-0036.

1.1.3 The anions included in this procedure and their routine working ranges for interference-free samples are as follows:

Analyte	CAS Number	Working Range (mg/L)	Working Range (mg/kg)
Fluoride	66-30-0	1.0 – 10	10 – 100
Chloride	1-00-3	3.0 – 50	30 – 500
Nitrite as N	15-90-0	0.5 – 10	5 – 100
Bromide	28-20-0	0.2 – 10	2 – 100
Nitrate as N	25-90-0	0.5 – 10	5 – 100
Phosphate as P	226750-80-0	0.5 – 10	5 – 100
Sulfate	3-03-5	5.0 – 50	50 – 500

Note: The working range can be extended by dilution of the sample.

1.1.4 The reporting limits for the following analytes are based on a 25 µL injection volume:

Analyte	Water RL (mg/L)	Soil RL (mg/kg)
Fluoride	0.5	5
Chloride	3.0	30
Nitrite	0.5	5
Bromide	0.2	2
Nitrate	0.5	5
Phosphate	0.5	5
Sulfate	5.0	50

NOTE 1: Report nitrite (NO_2^-) as N, nitrate (NO_3^-) as N, and phosphate (PO_4^{-3}) as P.

NOTE 2: Depending client or project requirements, reporting limits may be higher than those shown above.

NOTE 3: Reporting limits for soils are based on the DI Leach procedure using a soil to water ratio of 1:10. Client-specific soil to water ratios may differ.

2.0 Summary of Method

2.1 Aqueous samples are measured directly, unless visible particulate is present or the measured concentration exceeds the calibration. Samples with particulate must be filtered before they are injected into the ion chromatograph. High concentration samples must be diluted for analysis. Soil samples are leached using deionized water in accordance with SOP DV-WC-0036, and the water leach is analyzed.

2.2 A small volume of sample is introduced into the ion chromatograph to flush and fill a constant volume loop. The sample is injected into a stream of carbonate-bicarbonate or hydroxide eluent.

2.3 The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids.

2.4 The separated anions in their acid forms are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3.0 Definitions

3.1 This procedure includes the drinking water QC terminology from Method 300.0 and the solid waste terminology from SW-846 Methods 9056 and 9056A. Where there are two terms for the same concept, the cross reference is explained below. The frequency and evaluation of these QC samples are discussed in Sections 9 and 10.

3.2 **Calibration Blank (CB)** - A volume of reagent water fortified with the same matrix as the calibration standards, but without the addition of any of the analytes of interest.

3.3 **Laboratory Reagent Blank (LRB, also referred to as a Method Blank)** - For water samples, which do not require any preparation steps, the calibration blank and the method blank are the same thing. When soils are being analyzed, the method blank consists of the same reagents and preparation steps as applied to samples.

3.4 **Field Duplicates (FD)** - Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures. The laboratory project managers are responsible for informing clients of the relevant regulatory requirements for field duplicates.

3.5 **Laboratory Fortified Blank (LFB, also referred to as a Laboratory Control Sample, LCS)** - An aliquot of reagent water or other blank matrix to which known quantities of method analytes are added in the laboratory. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is

in control and whether the laboratory is capable of measurements the meet data quality objectives for accuracy and precision.

3.6 **Laboratory Fortified Sample Matrix (LFM, also referred to as a Matrix Spike, MS)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix affects the accuracy of the analytical result. The background concentrations of the analyte in the sample matrix must be determined if method analytes or other interference is present in the laboratory environment, the reagent, or the apparatus.

3.7 **Instrument Performance Check Solution (IPC, also referred to as Continuing Calibration Verification Standards, CCV)** - The CCV serves to monitor instrument drift from the beginning to the end of a given analytical sequence.

3.8 **Linear Concentration Range (LCR)** - The concentration range over which the instrument response is linear.

3.9 **Quality Control Sample (QCS)** - The QCS provides an independent verification of the accuracy of calibration standards and instrument performance. For the purposes of this SOP, the second-source ICV provides this verification.

3.10 Other quality control terms (e.g., MDL and PE sample) are defined in the Glossary Section of the Quality Assurance Manual.

4.0 Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent to 100 mL of each standard and sample. However, for routine samples, this problem is not severe enough to require this procedure.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

4.4 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate (with carbonate/bicarbonate eluent) and other low molecular weight organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium Nitrite	Oxidizer Toxic	None established	**Danger - strong oxidizer. Contact with other material may cause fire.** Toxic by inhalation; causes irritation to the respiratory tract and systemic poisoning, including intense cyanosis, nausea, dizziness, vomiting, collapse, spasms of abdominal pain, rapid heart beat, irregular breathing, coma, convulsions, and death due to circulatory collapse. Causes irritation, redness, and pain in contact with skin. May be absorbed through the skin causing systemic poisoning. Causes irritation, redness, and pain in contact with eyes.
Sodium Nitrate	Oxidizer	None established	**Danger - strong oxidizer. Contact with other material may cause fire.** Inhalation of dust irritates respiratory tract; symptoms may include coughing and shortness of breath. May cause irritation, redness, itching, and pain in contact with skin and eyes.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium Fluoride	Poison	2.5 mg/m3 (TWA as F)	**Highly Toxic!** Inhaled or swallowed, this compound can cause fluoride poisoning. Early symptoms include nausea, vomiting, diarrhea, and weakness. Later effects include central nervous system effects, cardiovascular effects, and death. Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation in contact with skin, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
1 – Always add water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- **Balance:** Analytical, capable of accurately weighing to the nearest 0.0001 g. Checked for accuracy each day of use in accordance with DV-QA-0014.
- Conductivity meter
- **Ion Chromatograph:** Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed gases, and detectors.
- **Anion guard column:** A protector of the separator column. If omitted from the system, the retention times will be shorter. Usually packed with a substrate that is the same as on the separator column. Dionex AG14, 4 x 50 mm, Dionex AG17-C, or equivalent.
- **Anion separator column:** The separation shown in Figure 1 was generated using a Dionex AS14 column. An alternate column, e.g., Dionex AS17-C, may be used if comparable resolution of the peaks is obtained, and all QC requirements can be met.
- **Anion suppressor device:** Dionex Anion Self-Regenerating Suppressor, or equivalent.
- **Detector:** Conductivity cell, approximately 1.25 µL internal volume, Dionex, or equivalent.
- Dionex ion chromatography software.
- Interfaced computer with printer.
- **Computer Software and Hardware:** Please refer to the master list of documents and software located on G\QA\Read\Master List of Documents\Master List of Documents and Software.xls for the current software to be used for data processing.

6.2 Supplies

- Volumetric Flasks (Class A): various sizes
- Eppendorf Pipettes, varying volumes
- Autosampler vials and caps
- 0.2 micron nylon syringe filters, and other miscellaneous filtration materials
- Disposable plastic beakers
- Other miscellaneous laboratory supplies

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all materials listed below must be reagent grade, unless listed otherwise.

7.1 Reagent Water

Deionized water, Milli-Q grade, ≥ 18 Megohm-cm.

7.2 Eluent for New Generation ICs with column AS17-C

New chromatographs use the Dionex RFIC™ systems, which employs an eluent generator. The eluent generators are purchased from Dionex. The eluent generators use electrolysis to generate a potassium hydroxide eluent, the concentration of which is controlled by the instrument software.

7.3 Eluent Concentrate:

The eluent concentrate for IC 3 (column AS14) is prepared at concentrations of the eluent species that are 100 times greater than used in the eluent solution. Dissolve 37.12 g of sodium carbonate (Na_2CO_3) and 8.4 g of sodium bicarbonate ($NaHCO_3$) in reagent water and dilute to 1 liter. This solution may be purchased commercially.

NOTE: A small amount of eluent concentrate, i.e., 50 µL in 5 mL of sample, is added to each sample, QC sample, and standard injected to eliminate the water dip. The eluent concentrate is not added to samples and standards analyzed on newer generation ion chromatographs that employ an eluent generator.

7.4 Eluent Solution:

Dilute 20 mL of the eluent concentrate (7.3) in reagent water to 2 liters.

NOTE: The bicarbonate/carbonate eluent solution is used in older generation ion chromatographs. New chromatographs use the Dionex RFIC™ systems, which employs an eluent generator. The system uses electrolysis to generate a potassium hydroxide eluent, the concentration of which is controlled by the instrument software.

7.5 Stock Solutions (1,000 mg/L)

All stock solutions are purchased from commercial sources.

WARNING! Sodium fluoride is highly toxic. Exercise extreme caution when working with sodium fluoride. See Section 5.2.

7.5.1 Fluoride Stock Solution (1.00 mg of F^- in 1.00 mL of solution)

In a 1-liter volumetric flask, dissolve 2.21 g of sodium fluoride (NaF) in reagent water, and dilute to volume with reagent water. Store in chemical-resistant glass or polyethylene.

7.5.2 Chloride Stock Solution (1.00 mg of Cl^- in 1.00 mL of solution)
Dry sodium chloride (NaCl) for 1 hour at 600 °C, and cool in a desiccator. In a 1-liter volumetric flask, dissolve 1.6484 g (weigh to the nearest mg), of the dry salt in reagent water and dilute to volume with reagent water.

7.5.3 Nitrite Stock Solution (1.00 mg of NO_2^- as N in 1.00 mL of solution)
Place approximately 10.0 g of sodium nitrite ($NaNO_2$) in a 125 mL beaker and dry to a constant weight (about 24 hours) in a desiccator. In a 1-liter volumetric flask, dissolve 4.9257 g (weigh to the nearest mg) of the dried salt in reagent water and dilute to volume with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

- Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used each day.
- Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170 °C in an air oven.

7.5.4 Bromide Stock Solution (1.00 mg Br^- in 1.00 mL of solution)
Dry approximately 5.0 g of sodium bromide (NaBr) for 6 hours at 150 °C, and cool in a desiccator. In a 1-liter volumetric flask, dissolve 1.2877 g (weigh to the nearest mg) of the dried salt in reagent water and dilute to volume with reagent water.

7.5.5 Nitrate Stock Solution (1.00 mg NO_3^- as N in 1.00 mL of solution)
Dry approximately 10.00 g of sodium nitrate (NaNO3) at 105 °C for 24 hours. In a 1-liter volumetric flask, dissolve 6.0679 g (weigh to the nearest mg) of the dried salt in reagent water and dilute to volume with reagent water.

7.5.6 Phosphate Stock Solution (1.00 mg PO_4^{-3} as P in 1.00 mL of solution)
Dry approximately 10.0 g of potassium dihydrogen phosphate (KH2PO4) for 1 hour at 105 °C and cool in a desiccator. In a 1-liter volumetric flask, dissolve 4.3937 g (weigh to the nearest mg) of the dry salt in reagent water and dilute to volume with reagent water.

7.5.7 Sulfate Stock Solution (1.00 mg SO_4^{-2} in 1.00 mL of solution)
Dry approximately 5.00 g of potassium sulfate (K2SO4) at 105 °C for 1 hour and cool in a desiccator. In a 1-liter volume flask, dissolve 1.8141 g (weigh to the nearest mg) of the dried salt in reagent water and dilute to volume with reagent water.

NOTE: The stability of the stock standards is at least 1 month when stored at 4 °C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

7.6 Second Source Stock Solutions (1,000 mg/L)
Stock solutions for each anion of interest are purchased at the same concentration but from a vendor other than the one that supplied the Stock Solutions described in Section 7.5. The second source stock solutions are used to prepare the ICV Intermediate Stock Solution (Section 7.8).

7.7 Calibration (CAL) Intermediate Stock Solution

Prepare the intermediate stock solution by combining the prescribed aliquots of each of the stock solutions described in Section 7.5(see table below) in a 100 mL volumetric flask. Dilute to volume with reagent water. Include all anions of interest, but omit all others.

Analyte	mL of Stock	Final Volume (mL)	Final Concentration (mg/L)
Fluoride	5.0	100	50
Chloride	25.0	100	250
Nitrite as N	5.0	100	50
Bromide	5.0	100	50
Nitrate as N	5.0	100	50
Phosphate as P	5.0	100	50
Sulfate	25.0	100	250

NOTE: The aliquots and final concentrations shown above are only recommended and assume a 1000 mg/L stock solution. Other aliquots and final concentrations may be used.

7.8 ICV Intermediate Stock Solution

Prepare the intermediate ICV stock solution by combining the prescribed aliquots of the second source (ICV) stock solutions (Section 7.6) in a 10 mL volumetric flask. Dilute to volume with reagent water. Include all anions of interest, but omit all others. The following table prescribes aliquot sizes for the individual anion stock solutions.

Analyte	mL of Stock	Final Volume (mL)	Final Concentration (mg/L)
Fluoride	0.5	10	50
Chloride	2.5	10	250
Nitrite as N	0.5	10	50
Bromide	0.5	10	50
Nitrate as N	0.5	10	50
Phosphate as P	0.5	10	50
Sulfate	2.5	10	250

NOTE: The aliquots and final concentrations shown above are only recommended and assume a 1000 mg/L stock solution. Other aliquots and final concentrations may be used.

7.9 Working Standards

Prepare working standards by pipetting 10mL aliquots of the CAL Intermediate Stock Solution (Section 7.7) into 100 mL volumetric flasks. Dilute to volume with reagent water. Refer to the following tables for the concentration of each analyte in the calibration standard.

7.9.1 Calibration Standard #1

Dilute 10 uL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	0.1
Chloride	0.5
Nitrite as N	0.1
Bromide	0.1
Nitrate as N	0.1
Phosphate as P	0.1
Sulfate	0.5

7.9.2 Calibration Standard #2

Dilute 50 uL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	0.5
Chloride	2.5
Nitrite as N	0.5
Bromide	0.5
Nitrate as N	0.5
Phosphate as P	0.5
Sulfate	2.5

7.9.3 Calibration Standard #3

Dilute 100 uL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	1.0
Chloride	5.0
Nitrite as N	1.0
Bromide	1.0
Nitrate as N	1.0
Phosphate as P	1.0
Sulfate	5.0

7.9.4 Calibration Standard #4

Dilute 0.4 mL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	4.0
Chloride	20.0
Nitrite as N	4.0
Bromide	4.0
Nitrate as N	4.0
Phosphate as P	4.0
Sulfate	20.0

7.9.5 Calibration Standard #5

Dilute 0.8 mL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	8.0
Chloride	40.0
Nitrite as N	8.0
Bromide	40.0
Nitrate as N	8.0
Phosphate as P	8.0
Sulfate	40.0

7.9.6 Calibration Standard #6

Dilute 1 mL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	10.0
Chloride	50.0
Nitrite as N	10.0
Bromide	10.0
Nitrate as N	10.0
Phosphate as P	10.0
Sulfate	50.0

NOTE: The aliquots and final concentrations shown above are recommended for calibration. Other aliquots and final concentrations may be used.

7.9.7 Lower Limit of Quantitation (LLOQ)
Dilute 20 uL of the CAL Intermediate Stock Solution (Section 7.7) to 5 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	0.2
Chloride	1.0
Nitrite as N	0.2
Bromide	0.2
Nitrate as N	0.2
Phosphate as P	0.2
Sulfate	1.0

7.10 Initial Calibration Verification (ICV)
Dilute 1.0 mL of the second source ICV Intermediate Stock Solution (Section 7.8) to 25 mL using reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	2.0
Chloride	10.0
Nitrite as N	2.0
Bromide	2.0
Nitrate as N	2.0
Phosphate as P	2.0
Sulfate	10.0

7.11 Continuing Calibration Verification (CCV) and Laboratory Control Sample (LCS) Solution
Prepare the CCV and LCS spike solution by diluting 10.0 mL of the ICAL Intermediate Stock Solution (Section 7.7) to 100 mL with reagent water.

Analyte	Final Concentration (mg/L)
Fluoride	5.0
Chloride	25.0
Nitrite as N	5.0
Bromide	5.0
Nitrate as N	5.0
Phosphate as P	5.0
Sulfate	25.0

NOTE: The aliquots and final concentrations shown above are recommended. Other aliquots and final concentrations may be used.

7.12 Stock Spiking Solutions (5000 mg/L chloride, sulfate and 1000 mg/L fluoride, bromide, nitrate, phosphate/1000 mg/L nitrite)

For the spiking solution, solids are dried and desiccated as listed in Section 7.4 for each individual component of the solution. Two solutions are made as summarized in the following two tables. Alternatively, a commercially prepared solution may be used.

Stock Spiking Solution #1

Analyte	Mass of Solid (g)	Final Volume (mL)	Anion Conc. (mg/L)
Sodium Fluoride	2.21	1000	1000
Sodium Chloride	8.2424	1000	5000
Sodium Bromide	1.2876	1000	1000
Sodium Nitrate	6.068	1000	1000
Potassium Dihydrogen Phosphate	4.3936	1000	1000
Potassium Sulfate	9.0704	1000	5000

Stock Spiking Solution #2

Analyte	Mass of Solid (g)	Final Volume (mL)	Anion Conc. (mg/L)
Sodium Nitrite	4.9256	1000	1000

7.13 Spikes for the Matrix Spike and Matrix Spike Duplicate (MS/MSD)

A working solution consisting of 10 mL of Stock Spiking Solution #1 and 10 mL of Stock Spiking Solution #2 is used. The MS is prepared by adding 50 µL of this working solution to a 5 mL aliquot of the selected sample. The MSD is prepared by adding 50 µL of this working solution to a second 5 mL aliquot of the same sample. This will result in the following anion concentrations ("true values") in the spiked sample: 25 mg/L for chloride and sulfate, and 5 mg/L for fluoride, nitrite, bromide, nitrate, and phosphate.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Analyte	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Fluoride	HDPE	50 mLs	Cool 4 ± 2°C	28 days	40 CFR Part 136.3
Chloride	HDPE	50 mLs	Cool 4 ± 2°C	28 days	40 CFR Part 136.3
Nitrite as N	HDPE	50 mLs	Cool 4 ± 2°C	48 hours	40 CFR Part 136.3
Bromide	HDPE	50 mLs	Cool 4 ± 2°C	28 days	40 CFR Part 136.3
Nitrate as N	HDPE	50 mLs	Cool 4 ± 2°C	48 hours	40 CFR Part 136.3
Phosphate as P	HDPE	50 mLs	Cool 4 ± 2°C	48 hours	40 CFR Part 136.3
Sulfate	HDPE	50 mLs	Cool 4 ± 2°C	28 days	40 CFR Part 136.3

NOTE: Soil leachates follow the same preservation and holding times as the water samples, starting from the time of extraction.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. The process of establishing control limits, and the use of control charts are described more completely in DV-QA-003P, Quality Assurance Program. Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.3 Attachment 1 reconciles the various QC requirements specified in the reference methods with the QC requirements specified in this SOP.

9.4 Before analyzing samples, the laboratory must establish a method detection limit (MDL) as described in Section 12.1 and the linear concentration range (LCR) as described in Section 9.7.6. In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument they will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 12 for more details.

9.5 Batch Definition
Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See Policy DV-QA-003P for further details.

9.6 **Sample QC** - The following quality control samples are prepared with each batch of samples.

9.6.1 Method Blank (same as Laboratory Reagent Blank, LRB)
A method blank (MB) is required with every batch of 20 or less samples. The MB is deionized water taken through the procedure as if it were a sample.

Acceptance Criteria: The MB must not contain anions of interest above the reporting limit or above one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL).

Corrective Action: If the method blank exceeds allowable levels, laboratory contamination is suspected and corrective action must be taken before continuing. All samples associated with the failed blank must be reanalyzed

9.6.2 Laboratory Control Sample (same as Laboratory Fortified Blank, LFB)

One Laboratory Control Sample (LCS) is required with each analytical batch. Depending on client or project requirements, an LCS duplicate may also be analyzed. The LCS and LCSD are prepared as described in Section 7.11. An LCS that is determined to be within acceptance criteria effectively demonstrates that the analytical system is in control and validates system performance for the samples in the associated batch.

Acceptance Criteria: For Method 300.0, the LCS recovery for each analyte of interest must be within 90-110%. For Method 9056, the LCS recovery for each analyte of interest must be within statistical control limits, not to exceed 85-115%. For Method 9056A, the LCS recovery for each analyte of interest must be within statistical control limits, not to exceed 80-120%.The absolute value of the relative percent difference (RPD) between the LCS and LCSD must be ≤10%. Statistical control limits are set at ± 3 standard deviations around the historical mean. The process of establishing control limits is described in more detail in Policy DV-QA-003P. Control limits are maintained in the LIMS.

Corrective Action: If the LCS recovery falls outside of the established control limits, and/or when the RPD for the LCS/LCSD exceeds the RPD limit, then check instrument conditions and the standards being used for problems. Correct any problems before continuing. Reanalyze all samples associated with the failed LCS.

9.6.3 Matrix Spike / Matrix Spike Duplicate (MS/MSD, same as Laboratory Fortified Matrix)

For Method 9056, one MS/MSD pair is required with each analytical batch of 20 or fewer samples. For Method 300.0, one MS is required for every 10 routine samples. Also note that some programs (e.g., North Carolina and South Carolina) require an MS/MSD pair for every 10 samples. The MS and MSD are prepared as described in Section 7.13.

Acceptance Criteria: The recovery of each anion of interest must be within the established statistical control limits. Statistical control limits are set at ± 3 standard deviations around the historical mean, and must be within 80-120%. The relative percent difference (RPD) between the MS and MSD must be less than 20%, or less than the established control limit, depending on project requirements. The process of establishing control limits is described in more detail in Policy DV-QA-003P. Control limits are maintained in the LIMS.

Corrective Action: The information obtained from MS data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If the MS

and/or MSD recovery falls outside of the established control limits, the bracketing CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly;
- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses); and
- Document the failure in an NCM and note it on the final report.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and document the failure in an NCM.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

9.7 **Instrument QC** - The following quality control samples are prepared with each analytical instrument run.

9.7.1 Initial Calibration Verification (ICV)

The second-source ICV, as described in Section 7.10, is analyzed immediately following the ICAL.

Acceptance Criteria: The ICV recovery for each anion must be 90-110%. The retention time for each analyte in the ICV must be within ± 10% of the established retention time for that analyte.

Corrective Action: If the recovery and/or retention time is outside of the acceptance limits, repeat the test. If the test fails on the second attempt, then the problem must be investigated and the instrument recalibrated for the failed analyte(s).

9.7.2 Initial Calibration Blank (ICB)

An ICB is analyzed following the ICV.

Acceptance Criteria: The result must be less than the reporting limit.

Corrective Action: If the blank is above the acceptance limit, check for carryover or the need for instrument

maintenance. The instrument must be recalibrated.

9.7.3 Continuing Calibration Verification (CCV, same as IPC in Method 300.0)
A CCV is required after every 10 or fewer samples and after the last sample.

Acceptance Criteria: The CCV recovery must be 90-110%. The retention time for each analyte in the CCV must be within ± 10% of the established retention time for that analyte.

Corrective Action: If the recovery and/or retention time is outside of the acceptance limits, the instrument must be recalibrated, and all samples analyzed since the last successful CCV must be reanalyzed.

9.7.4 Continuing Calibration Blank (CCB)
A CCB is analyzed after each CCV.

Acceptance Criteria: The result must be less than the reporting limit.

Corrective Action: If the blank is above the acceptance limit, check for carryover or the need for instrument maintenance. The instrument must be recalibrated, and all samples analyzed since the last successful CCB must be reanalyzed.

9.7.5 Lower Limit of Quantitation (LLOQ)
A LLOQ is required for method 9056A to verify the data reporting limit for each analyte.

Acceptance Criteria: The LLOQ recovery must be ± 50% of the true value.

Corrective Action: If the recovery is outside of the acceptance limits, the instrument must be recalibrated.

9.7.6 Linear Concentration Range (LCR)

9.7.6.1 The LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or a significant change (eg. Change to column type, eluent or instrument pressures) in instrument configuration is made.

9.7.6.2 The initial demonstration of linearity must use a sufficient number of standards to ensure that the resulting curve is linear.

9.7.6.3 The semi-annual verification of linearity must use a minimum of a blank and three standards. If the recovery for any analyte falls outside of 90-110%, linearity must be reestablished.

9.7.6.4 Linearity study data are maintained by the Wet Chemistry group leader.

9.7.7 Retention Time Study

The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms. See Section 10.3.4 for detailed instructions on performing the retention time study.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.1 Sample Preparation

10.1.1 Screen the conductivity of samples prior to analysis to determine whether the samples require dilution using a conductivity meter. Record the conductivity on a sample observation benchsheet if the conductivity is > 3000 μmhos/cm.

10.1.2 If the conductivity is > 3000 μmhos/cm, dilute as necessary with reagent water, based on the following calculation, rounding up to the smallest round

$$\text{dilution factor} = \frac{conductivity}{3000}$$

dilution that will bring the conductivity of the dluted sample to under 3000.

NOTE: If a sample requires filtration, prior to being loaded on the instrument, the method blank **must** also be filtered.

10.2 Calibration

10.2.1 An initial calibration is performed every three months, or as needed, based on instrument performance and maintenance.

10.2.2 Calibrate the instrument at six levels. See Section 7.9 for preparation of calibration standards.

NOTE: It is generally NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. The only exception is that a level may be removed from the calibration if the reason is clearly documented, for example a cracked tube, and a minimum of five levels remain.

10.2.3 Construct a calibration curve using a weighted linear regression. Additional calibration information can be found in the Corporate TestAmeica's Calibration Curve document CA-Q-S-005.

Acceptance Criteria: The absolute value of the correlation coefficient must be 0.995 or greater.

Corrective Action: If the correlation coefficient is less than the acceptance limit, recheck instrument conditions and calibration standards. Samples cannot be analyzed until the initial calibration is successful.

10.2.4 Attachment 2 summarizes the recommended operating conditions for the ion chromatograph.

10.2.5 Attachment 3 is an example chromatogram. Included in this chromatogram are example retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the data quality objectives can be met.

10.2.6 Check system calibration daily by analyzing an ICV and ICB (see Sections 9.7.1 and 9.7.2) and, if required, recalibrate.

10.3 Sample Analysis

10.3.1 When using the older generation ion chromatographs that do not employ eluent generation, add 50 µL of eluent concentrate (Section 7.3) to 5 mL of each standard, sample, and QC sample prior to injecting.

10.3.2 Load samples into the autosampler according to the schedule. The instrument will flush and load the sample loop for injection. See Attachment 2 for sample loop specifications. The instrument software detects and integrates peaks in the resulting chromatograph.

10.3.3 Following is a typical analytical sequence:

ICAL
ICV and ICB
LCS and LCSD (if LCSD required)
Method Blank
10 injections
CCV and CCB
10 injections
CCV and CCB
10 injections
CCV and CCB

10.3.4 Retention Times and Anion Identification

10.3.4.1 The width of the retention time window used to make identifications is based on measurements of actual retention time variations of standards over 72 hours. (This should be done prior to analysis of samples since the retention time window must be entered into the software before starting the run). The retention time windows should be re-evaluated and a retention time study run when significant changes (eg. Change to column type, eluent or instrument pressures) are made to the instrument.

10.3.4.2 Record the retention time of each calibration standard on at least 3 different days. Calculate the standard deviation for each analyte. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.3.4.3 The calibration curve is verified each working day or whenever the eluent is changed by analyzing an ICV and ICB, and after every 10 injections by analyzing a CCV and CCB. If the retention time for any analyte varies from the expected values (±5% for phosphate and sulfate and ± 10% for fluoride, chloride, nitrite, bromide and nitrate) a new calibration curve must be prepared.

10.3.4.4 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze. The addition of one to two times the sample concentration normally provides the best peak height for analyte identification.

NOTE: Concentration can affect retention time and cause peak migration. Late eluting species, e.g., nitrate and sulfate, exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration may produce poor resolution or misidentification. If a peak has shifted outside of its retention time window (as confirmed by a CCV or Matrix Spike), change the window in the software and reprocess the chromatogram. Document the reason for reprocessing the chromatogram along with the date and initials.

10.3.4.5 Should more complete resolution be needed between peaks, the eluent can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

10.3.5 If the response for the peak exceeds the working range of the system, dilute the sample with reagent water and reanalyze.

11.0 Calculations / Data Reduction

11.1 Using the computer and the Dionex software package, prepare a linear calibration curve for each analyte by plotting instrument response against standard concentration. The software calculates a calibration function in the following form:

$$Y_i = SX_i + I$$

Where:

Y_i = Instrument response (peak area) for specific anion in the ith calibration standard.
X_i = Concentration of anion in the ith calibration standard, mg/L.
S = Slope of calibration curve determined by linear regression analysis.
I = Intercept of calibration curve determined by linear regression analysis.

11.2 The anion concentration in the injected sample is calculated by solving the calibration function for Xi as follows:

$$X_i = \frac{Y_i - I}{S}$$

Where:

X_i = Calculated concentration of the ith sample at the instrument, mg/L.
Y_i = Instrument response for the ith sample (peak area).
I = Intercept of the calibration curve.
S = Slope of the calibration curve.

11.3 If the sample was diluted, the final anion concentration in the original sample is calculated as follows:

$$X_f = X_i \times DF$$

Where:

X_f = Anion concentration in original sample, mg/L.
X_i = Calculated concentration of sample at the instrument, mg/L.
DF = Dilution factor.

11.4 For soil leachates, the concentration in the original soil sample is calculated as follows:

$$X_s = X_i \times DF \times \frac{V}{M_s}$$

Where:

X_s = Anion concentration in original soil sample, mg/kg.
X_i = Calculated concentration of sample at instrument, mg/L.
DF = Dilution factor, if applicable.
V = Volume of leachate, L.
M_s = Mass of original soil sample, kg.

11.5 Report only those values that are less than the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

11.6 Use the appropriate data qualifier (i.e., "flag") to indicate when a sample requires dilution due to high conductivity. In most cases, a "G" flag denotes dilution due to matrix effects, and a "Q" indicates dilution to bring the sample into the calibration range. Special flagging conventions may apply depending on client or project requirements.

11.7 All results are subject to two levels of review, which are documented on the form shown in Attachment 4.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

Method Detection Limit Study an initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Prepare and analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy # DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

NOTE: EPA method 300.0 requires an MDL study to be performed every 6 months.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of capability (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows:

- Initially the analyst must perform an MDL study (see section 12.1).
- Four aliquots of the QC check sample (independent source from the calibration) are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration standard.
- Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

12.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.3.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive ICVs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

The use of ion chromatography eliminates the need to use a variety of hazardous reagents required by the other approved methods for the determination of the same anions.

Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

- IC process waste from older generation ion chromatographs – aqueous carbonate/bicarbonate eluent waste: Non-hazardous
- IC process waste from new generation ion chromatographs with hydroxide eluent generating system: Excess Sample – Aqueous – Waste Stream W

- Expired aqueous reagents/standards – Contact Waste Coordinator
- Expired solid chemicals – Contact Waste Coordinator

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW846, 3rd Edition, Final Update IIIB (December 1996), Method 9056, "Determination of Inorganic Anions by Ion Chromatography", Revision 0, September 1994.

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW846, 4th Edition, Final Update IV, Method 9056A, "Determination of Inorganic Anions by Ion Chromatography", Revision 1, February 2007.

15.3 Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 300.0	Method 300.0 includes a requirement for a second-source quality control standard (QCS), which is to be run quarterly and be within ±10% of the expected value. This SOP establishes calibration accuracy every day of operation using a second-source initial calibration verification (ICV) standard.
2	EPA 300.0	Method 300.0 specifies that target analytes must be less than the MDL in the Laboratory Reagent Blank. TestAmerica Denver QA policy (Policy DV-QA-003P) defines the acceptance limit for the method blank as the laboratory reporting limit (RL) and not the MDL. If specified in client or project requirements, the method blank acceptance limit may be set at the MDL.
3	EPA 300.0, SW 9056 and SW 9056A	Methods 9056 and 9056A specifies bomb combustion for solid waste samples. Method 300.0 specifies water leaching for solid samples. This SOP specifies water leaching and references SOP DV-WC-0036 for the deionized water leach procedure. In this respect, this SOP complies with Method 300.0, but deviates from Method 9056A.

17.0 Attachments

Attachment 1: Quality Control Summary
Attachment 2: Suggested Standard Instrument Operating Parameters
Attachment 3: Example Ion Chromatogram
Attachment 4: Example Data Review Checklist

18.0 Revision History

- Revision 7.1, dated 04 December 2009
  - Added bullet in section 6.1 concerning the Master List of Documents.
  - Added note on filtration to section 10.1.
  - Updated Attachment 4

- Revision 7, dated 19 June 2009
  - Added Lower limit of quantitation information.
  - Updated reagent and standard preparation information.
  - Made minor formatting and grammatical corrections.
  - Added 6 month MDL requirement note to section 12.1
  - Updated Attachment 4.

Revision 6, dated 22 February 2008

  - Update the recipes for the eluent concentrate and eluent solution to current practices.
  - Added the information concerning the eluent generators and need to purchase them from Dionex.

- Revision 5, dated 22 February 2008
  - Integration for TestAmerica and STL operations.
  - Updated formatting.
  - Moved the reporting limit table to Section 1.
  - Updated attachments with the TestAmerica logo.

- Revision 4, dated 24 July 2007
  - The method Reference has been changed for SW846 from Method 9056 to method 9056A.
  - The company name has been changed from STL to TestAmerica.

- Revision 3, dated 28 February 2006
  - Revised Sections 5, 14, and 15 (Safety, Pollution Prevention, and Waste Management, respectively) to comply with STL Corporate requirements.
  - Updated formatting to comply with current STL Denver guidance (Policy QA-001).
  - Updated the reporting limit table in Section 1.1.4 to reflect current reporting limits.
  - Expanded discussion of the matrix spike quality control criteria (Section 9.6.3) to be consistent with Policy QA-003, Quality Control Program.
  - Removed details concerning Method Performance, and included references to the applicable STL Denver SOPs.
  - Expanded Attachment 1, Quality Control Summary, to include references to the source methods.

- Revision 2, dated 6 September 2002
  - Calibration standards updated and includes addition of eluent concentrate to working standards.
  - Eluent concentrate recipe added.
  - Changed reporting limit tables to reflect current reporting limits.

- Added requirement for MS/SD pair per 10 samples for certain clients or agencies.
- The spike concentration was increased to avoid overly diluting the unspiked sample when matrix spikes are prepared.
- The Method Performance Section 13 was expanded.
- A Data Review Checklist was added to the end of the SOP.

- Revision 1, dated 9 June 1999
  - The size of the injection loop for low level analysis is changed from 300 uL to 25 uL, which is the manufacturer's recommendation for the latest equipment.

Attachment 1.

Quality Control Summary

QC Samples	Frequency	Acceptance Criteria	Corrective Action	Reference Method Equivalent
Initial Calibration Verification (ICV)	Immediately following the initial calibration, and at the start of each day prior to sample analysis, or whenever the eluent is changed.	90 - 110% of true value RT must be ± 10% of established RT	Repeat once, and recalibrate and reanalyze if it fails a second time.	QC Reference Sample (9056A) IPC and QCS (300.0)
Initial Calibration Blank (ICB)	After the ICV and prior to sample analysis.	≤ the Reporting Limit	Re-prepare and reanalyze	Calibration Blank (300.0)
Laboratory Control Sample (LCS)	1 per QC batch	Within laboratory historical limits	Recalibrate and reanalyze all samples associated with unacceptable LCS	LFB (300.0)
Matrix Spike Sample (MS/MSD)	1 MS/MSD pair per QC batch for 9056. 1 MS/MSD pair per 10 samples for 300.0.	%R within laboratory historical limits and RPD ≤ laboratory historical limits.	If LCS and CCVs are in control, then document in an NCM, unless project requires reanalysis.	Matrix Spike (9056A) LFM (300.0)
Continuing Calibration Verification (CCV)	Between each group of 10 injections and at the end of the analytical sequence.	90 - 110% of true value	Repeat. If repeat fails, recalibrate and reanalyze all samples since the last acceptable CCV.	Mid-range Calibration Standard (9056A) IPC (300.0)
Continuing Calibration Blank (CCB)	Between each group of 10 injections and at the end of the analytical sequence	< the Reporting Limit	Repeat. If repeat fails, recalibrate and reanalyze all samples since the last acceptable CCB.	Calibration Blank (300.0)
Method Blank (MB)	1 per QC batch	≤ the Reporting Limit	See Section 9.6.1 or Policy QA-003.	LRB (300.0)

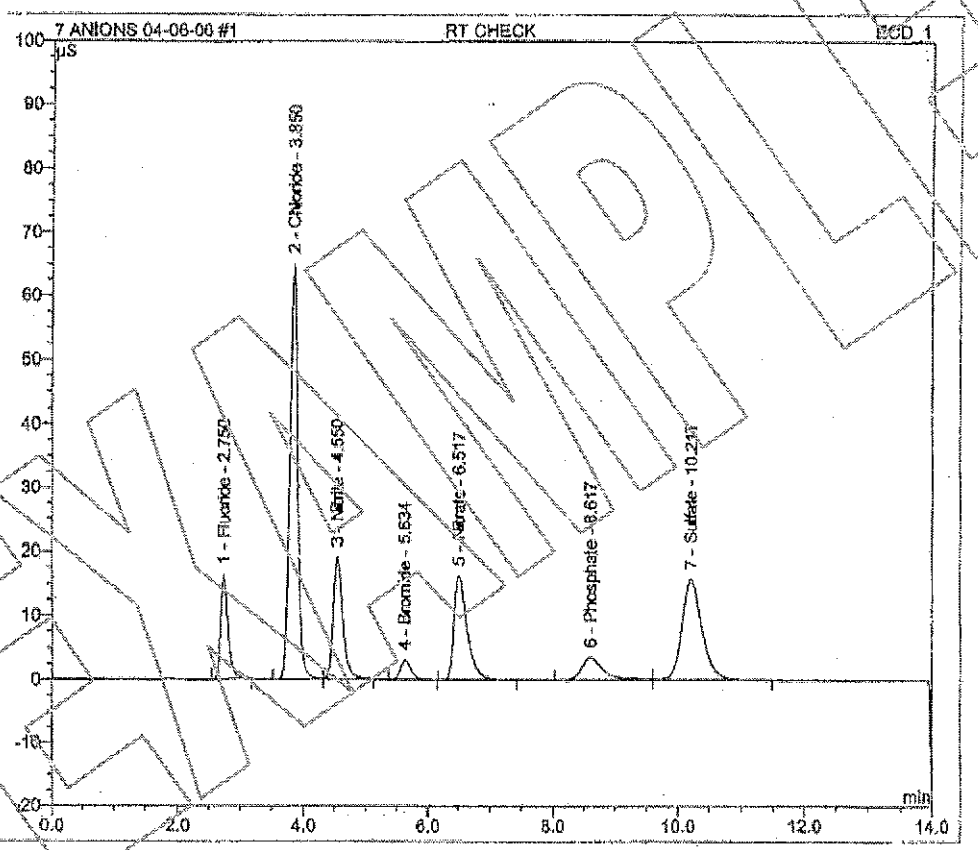
Attachment 2.

Suggested Standard Instrument Operating Procedures

Instrument Conditions	
Anion Guard Column	Dionex AG 4A or AG17-C
Anion Separator Column	Dionex AS4A or AS17
Supressor Device	SRS Ultra II Self-Regenerating Suppressor
Pump Rate	1.2 mL/min or 1.0 mL (depending on specific instrument used)
Sample Loop	10 µL
Eluent	Older Generation Instruments: 1.0 mM sodium bicarbonate, 3.5 mM sodium carbonate Dionex RFIC™ Systems: Potassium hydroxide, generated by electrolysis of water, in the range of 10 to 40 mM
Detector Output	Baseline conductivity should be between 15 - 16 µS prior to sample analysis.

Attachment 3.

Example Ion Chromatogram



EXAMPLE

Attachment 4.

Example Data Review Checklist

TESTAMERICA Denver

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Wet Chemistry Data Review Checklist
For Tests with Calibration Curves

Test Name/ Method #: _____ **SOP #** _____

Instrument: _____ **Analyst:** _____ **Analysis Date:** _____

Lot / Sample Numbers	Matrix	Batch	Method	QC	Special Inst

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Minimum of five standards in ICAL or as specified in method?				
2. Correlation coefficient ≥ 0.995 ?				
3. Second-source ICV analyzed, and recovery 90-110%?				
4. ICB analyzed immediately after the ICV & results < the RL?				
5. CCV analyzed after every ten samples & recovery ± 10% of true value?				
6. CCB analyzed after every CCV & results < RL?				
7. Absolute value of the intercept is < ± ½ the RL?				
B. Sample Results				
1. All samples greater than highest calibration standard diluted and reanalyzed?				
2. Do associated RLs/MDLs reflect dilutions or limited sample volume?				
3. All reported results bracketed by in control CCV results?				
4. Sample analyses done within holding time?				
5. Initial pH check documented for all samples?				
6. Preparation benchsheet completed and included in package?				
7. Client requirements reviewed and met?				
8. Were data manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures and correct units?				
9. Do the prep and analysis dates in QuanTIMS reflect the actual dates? Lot Dates report checked?				
10. Are all data being reported highlighted on the benchsheet?				
11. Raw data copies prepared and scanned?				
12. Manual integrations done properly and initialed and dated?				
13. STD/True Value sheet is updated and included?				
C. Preparation/Matrix QC				
1. Method blank < RL or all reported samples > 10x blank have NCM?				
2. Method blank < ½ RL or NCM provided?				
3. LCS/LCSD run for batch and within QC limits?				
4. MS/MSD run at required frequency and within limits or NCM written?				
5. DUP run at required frequency and RPD within 20% or NCM written?				

Analyst: _____ **Date:** _____

2nd Level Reviewer : _____ **Date:** _____

SAMPLE

TestAmerica Denver

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TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Title: Sulfate, Turbidimetric

[EPA 375.4, SW 9038, ASTM D516-02]

Approvals (Signature/Date):

Dave Elkin — Date Wet Chemistry Supervisor	Adam Alban — Date Health & Safety Manager / Coordinator
Karen Kuoppala — Date Quality Assurance Manager	Robert C. Hanisch — Date Laboratory Director

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1.0 Scope and Application

1.1 This procedure describes the analysis of samples for sulfate by ASTM D516 and EPA375.4, SW 9038. This method is applicable to drinking water, surface water, domestic and industrial wastes. Non-aqueous samples may be analyzed following an appropriate extraction (e.g., DI Leach SOP DV-WC-0036).

1.2 The reporting limit using this method is 5 mg/L for waters. For soils, assuming a 10 g sample was leached into 100 mL DI water, the reporting limit is 50 mg/kg. The upper end of the working range is 35 mg/L for

1.3 water samples and 350 mg/kg for soil samples. Samples with more than 35 mg/L require dilutions.

2.0 Summary of Method

Sulfate ion is converted to a barium sulfate suspension under controlled conditions using a conditioning reagent. This suspension absorbs light in proportion to the sulfate concentration. The absorbance is measured at 420 nm by UV-Vis and 405 nm by Konelab instrumentation.

3.0 Definitions

There are no terms requiring definition unique to this procedure. Refer to the Glossary of the QAM for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Color and suspended matter will cause positive interferences. Remove suspended solids by filtration. If samples are colored, run color blanks that include the use of conditioning reagent but do not contain BaCl2.

4.2 Silica in excess of 500 mg/L will interfere.

4.3 In waters containing large quantities of organic material it may not be possible to precipitate barium sulfate (BaSO4) satisfactorily.

4.4 Carbonates will cause bubbles in the sample and erratic absorbance readings. The absorbance will initially be high instead of low.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Glycerol is incompatible with strong oxidizers. In the event of a fire the glycerol releases a toxic gas (Acrolein).

5.1.2 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, and reagents.

Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Barium Chloride	Poison Irritant	0.5 mg/m3 TWA	May be fatal if swallowed. Harmful if inhaled. Avoid contact with eyes, skin, and clothing. Avoid breathing dust. Keep container closed and when in use adequate ventilation.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Konelab spectrophotometer which uses 405 nm, with light path of 4-5 mm
- For manual procedure: spectrophotometer for use at 420 nm, with a light path of 1 cm
- For manual procedure: Stopwatch or timer
- For manual procedure: magnetic stirrer and Teflon bars

6.2 Supplies

- Volumetric Flasks (Class A): varying volumes
- Eppendorf Pipettes, varying volumes
- For manual procedure: glass or disposable beakers or vials with at least 50 mL capacity
- For manual procedure: measuring spoon, 100 mg capacity
- Disposable cuvettes for the Konelab
- Disposable sample cups for the Konelab

7.0 Reagents and Standards

All chemicals listed below should be reagent grade or manufactured specifically for this analysis.

7.1 Barium chloride crystals, $BaCl_2$, 20 to 30 mesh. Available commercially.

7.2 10% Barium Chloride solution:
Place 10 g $BaCl_2$ crystals in a 100 mL volumetric flask and dilute to volume. This solution is prepared on a daily basis.

7.3 Conditioning Reagent:
To 300 mL of reagent water, slowly and carefully add 30 mL of concentrated hydrochloric acid (HCl), 75 g of sodium chloride (NaCl), and 100 mL of isopropyl alcohol. Stir to dissolve the NaCl. Add 50 mL of glycerol and mix. This solution is also commercially available.

7.4 Sulfate Stock Standard, 1000 mg/L:
Dissolve 1.479 g anhydrous sodium sulfate (Na_2SO4) in reagent water and dilute to volume in 1L volumetric flask. This solution expires annually. Note: This standard may be purchased commercially

7.5 Working Standards
Dilute the 1000 mg/L Stock Standard as follows (prepare fresh monthly):

Calibration Standard (mg/L)	Intermediate Standard added (mL)	Concentration of Stock Std(mg/L)	Final Volume (mL)
2.5	0.25	1000	100
5.0	0.5	1000	100
10	1.0	1000	100
15	1.5	1000	100
20	2.0	1000	100
25	2.5	1000	100
30	3.0	1000	100
35	3.5	1000	100

7.6 Initial Calibration Verification Stock Standard
Dissolve 1.479 g anhydrous sodium sulfate (Na_2SO_4) in reagent water and dilute to volume in 1L volumetric flask. This solution expires annually. Note: This standard may be purchased commercially. This is a second-source standard and must be from a different vendor from the stock prepared in 7.4.

7.7 Initial Calibration Working Standard (ICV), 20 mg/L
Prepare before by diluting 2.0 mL of a 1000 mg/L stock sulfate standard (7.6) to 100 mL with de-ionized water.

7.8 Continuing Calibration Verification Standard (CCV), 15 mg/L
Dilute 1.5 mL of the Sulfate Stock Standard (7.4) to 100 mL with deionized water. This is identical to the 15 mg/L calibration standard in 7.5.

7.9 Laboratory Control Sample (LCS), 25 mg/L
Dilute 2.5 mL of the sulfate stock standard (7.4) to 100 mL with deionized water. This is identical to the 25 mg/L calibration standard in 7.5.

7.10 Matrix Spike/Matrix Spike Duplicate (MS/MSD), 25 mg/L
Samples are spiked by adding 0.5 ml of 1000 mg/L stock sulfate solution (7.4) to 20 mL of sample.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	HDPE	50 mLs	Cool 4 ± 2°C	28 Days	40 CFR Part 136.3

9.0 Quality Control

The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

- The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.
- Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.
- Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.
- Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.1 Sample QC - The following quality control samples are prepared with each batch of samples.

9.1.1 Preparation Batch
A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch

must contain a method blank, a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD). As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.1.2 Method Blank (MB)

One method blank (MB) must be processed with each batch. The MB consists of reagent water that is carried through the entire analytical procedure, including preparation and analysis. When analyzing soils, a soil MB is prepared using washed Ottawa sand. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB is prepared in the same manner as the samples using a DI water leach in accordance with SOP DV-WC-0036.

Acceptance Criteria: The MB should not contain any analyte of interest at or above the reporting limit (RL).

Corrective Action: If the analyte level in the MB exceeds the reporting limit for the test, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data must be taken in consultation with the client and must be addressed in the project narrative.

If the analyte concentration is greater than the reporting limit (RL) in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

If all samples associated with a blank greater than the RL are greater than 10 times the blank value, the samples may be reported with an NCM to qualify the high blank value.

9.1.3 Laboratory Control Sample (LCS)

At least one LCS must be processed with each batch. The LCS for aqueous sample batches consists of reagent water to which a known amount of target analyte has been added. The LCS for soil batches consists of 1 gram of Ottawa sand to which a known amount of the target analyte is added. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process.

Acceptance Criteria: In-house control limits, set at ± 3 standard deviations around the historical mean, are used as long as they are at least as tight as the regulatory limits. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

Corrective Action: If LCS recoveries are outside established control limits, the analytical system is out of control and corrective action must be taken.

If recoveries are above control limits and sulfate is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.1.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) that is prepared and analyzed along with the sample and matrix spike.

- One MS/MSD pair must be processed for every 10 samples.
- The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing on only the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.
- Preparation of the MS/SD is described in Section 7.10

Acceptance Criteria: In-house control limits, set at ± 3 standard deviations around the historical mean, are used for recovery acceptance as long as they are at least as tight as the regulatory limits.

Corrective action: If the calculated recovery or relative percent difference (RPD) is outside the acceptance range, the recovery of that analyte in the LCS must be within the established control limits. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.2 Instrument QC

9.2.1 Initial Calibration Verification (ICV)

Analyze a second-source ICV standard (Section 7.7) immediately after the initial calibration (ICAL).

Acceptance Criteria: The recovery must be within the 90 -110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, and then recalibrate.

9.2.2 Continuing Calibration Verification (CCV)

Analyze the CCV standard, which is prepared from the same source and at the same concentration as the midrange calibration standard (Section 7.8), after every four samples and at the end of the analytical sequence. The CCV at a frequency of every 4 samples is required by method 9038. Methods ASTM D516 and EPA 375.4 only require a CCV frequency of every 10 samples.

Acceptance Criteria: The recovery must be within the 90 -110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, recalibrate, and rerun all samples analyzed since the last successful CCV.

9.2.3 Initial and Continuing Calibration Blank

System cleanliness is checked at the beginning (with an initial calibration blank or ICB), and after every CCV and at the end of the analytical sequence using a continuing calibration blank (CCB). The blanks consist of deionized water.

Acceptance Criteria: Results must be less than the reporting limit.

Corrective Action: If the blank is greater than the reporting limit, check for carry-over from high level samples, clean the system, recalibrate, and rerun all samples analyzed since the last successful CCB.

10.0 Procedure

One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager (see SOP DV-QA-0031 for details). If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.1 Sample Preparation

Particulates and/or suspended matter in field samples may be removed by filtration.

10.2 Calibration

10.2.1 Konelab Instructions:

- Check waste containers and dispose of waste properly.
- Check water reservoir and fill with DI water if needed.
- Turn the instrument and computer on and click on the "startup" button at the main screen. The instrument will warm up and go through a series of self-checks.
- Reagents should be replaced daily and will not be stored in the Konelab.

- When the analysis of samples is complete, click the "standby" button and the instrument will go to shutdown mode.

10.2.2 Spectrophotometer Instructions:

- Turn on the instrument and allow it to warm up for 20 minutes
- Set the wavelength to 420 nm and zero on the blank standard. Follow manufacturer procedures for instrument set-up.

NOTE: All tubes must be wiped dry with Kim-wipes before inserting in the spectrophotometer. Cover with the light shield while taking readings.

10.2.3 Initial Calibration (either method)

The instrument is calibrated with eight concentration levels, as shown in Section 7.5. Certain programs (such as South Carolina) require that the calibration curve must be established by least-squares linear regression, with a minimum correlation coefficient of $r > 0.995$.

Corrective Action: If the linearity criterion is not met, reprepare standards and/or optimize the instrument and recalibrate.

10.2.4 Additional calibration information can be found in the Corporate TestAmeica's Calibration Curve document CA-Q-S-005.

10.3 Sample Analysis

10.3.1 Programming and analysis instructions for the Konelab:

The instrument set up screen for sulfate is shown in Attachment 1.

10.3.1.1 An analytical run will consist of the following sequence:

Calibration Curve or a saved calibration curve
ICV
ICB
LCS
4 absorbance readings (method SW 9038)
10 absorbance readings (methods EPA 375.4 & ASTM D-516)
CCV
CCB
4 absorbance readings (method SW 9038)
10 absorbance readings (methods EPA 375.4 & ASTM D-516)
CCV
CCB...

10.3.1.2 Dilute and reanalyze samples that have concentrations greater than the high standard in the curve. Dilutions should be made to obtain concentrations on the mid- to upper part of the calibration curve whenever possible

NOTE: The last absorbance is usually used for test results; this usually translates to the highest concentration. If the first absorbance is the highest, this may be indicative of carbonate interference.

10.3.1.3 There are two sets of readings taken for the Konelab turbidimeteric sulfate procedure.

10.3.1.3.1 The kinetic readings are 9 separate readings taken over a 4 minute interval. The points are plotted and provided in the raw data. These points tend to be in line with the instrument generated graph.

NOTE: When there are two or more points that are not on the instrument generated graph than the sample is diluted and re-analyzed.

10.3.1.3.2 The second reading is a single point reading taken at 4 minutes and is used to provide the actual concentration value. This value is compared to the kinetic readings to see that it is in line with the absorbances.

10.3.2 <u>Alternate Procedure for UV-VIS spectrophotometer use:</u>

10.3.2.1 Place a 20 mL or an aliquot diluted to 20 mL, of each calibration standard, ICV, ICB, LCS, LCSD, prep blanks, samples and MS/MSD into individual glass beakers.

10.3.2.2 Add 1.0 mL of conditioning reagent.

10.3.2.3 Mix the sample using a magnetic stirrer. If the sample is effervescent, indicating carbonate interference, stir for 2 minutes before adding BaCl2.

10.3.2.4 Add one scoop of barium chloride crystals and begin timing immediately.

10.3.2.5 Stir for exactly 60 seconds at constant speed.

10.3.2.6 Immediately after stirring time is finished, pour solution into absorbance cell (pre-rinse cell with 2-5 mL of sample before filling).

10.3.2.7 Measure and record turbidity at 30 second intervals for 4 minutes.

10.3.2.8 The maximum reading obtained in the 4-minute period will be used to calculate the final results. If the absorbance decreased due to high carbonate, use the lowest absorbance.

10.3.2.9 To correct for sample color and/or turbidity, run a sample blank using steps 10.3.2.1 through 10.3.2.8 without the addition of barium chloride crystals.

10.3.2.10 Follow the run sequence and dilution instructions given in 10.3.1.1 and 10.3.1.2.

10.3.2.11 Data are recorded on the benchsheet (see example in Attachment 2).

11.0 Calculations / Data Reduction

11.1 Accuracy

ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Calculate net sample absorbances as follows, if using a color blank:

$$Abs_{net} = (A - B)$$

Where:

Abs_{net} = Net sample absorbance, mg/L
A = Absorbance of sample, mg/L
B = Absorbance of color blank, mg/L

Note: Sample matrix can cause positive interference which must be accounted for by use of a color blank.

11.4 Compute sample concentrations by comparing net sample absorbances against the standard curve and calculate as follows:

$$\text{Sulfate (mg/L)} = S_A \times DF$$

Where:

S_A = instrument reading (mg/L)
DF = dilution faction

11.5 All results are subject to a second-level review by the Wet Chemistry supervisor or designee. The review is documented on the form shown in Attachment 3.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial MDL study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven standards at three to five times the estimated MDL concentration.
- Analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in mg/L, and the standard deviation of the concentration(s) in mg/L. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy DV-QA-005P).
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 MDL Verification (MDLV)

Calculated MDLs from the annual studies are subject to quarterly verification by analyzing an MDLV standard prepared at 1-2 times the calculated MDL concentration. An MDLV standard is analyzed immediately after each MDL study and quarterly thereafter. This standard is subject to the entire preparation and analysis process. The calculated MDL is verified if the MDLV standard is detected, nominally signal to noise ratio > 3, under routine instrument conditions.

Corrective Actions: If the first MDLV is not detected, the MDLV standard will be reprepared and analyzed at twice the original concentration. The lowest concentration that produces a detectable signal will then be reported as the MDL.

12.3 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows"

- Four aliquots of the QC check sample (independent source from the calibration) are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.
- Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.4 Training Requirements

12.4.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has

the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.4.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

13.1 In general, the quantity of chemicals purchased by TestAmerica Denver is based on expected usage during its shelf life. The volume of reagents and standards prepared for this procedure reflects anticipated usage.

13.2 Source reduction is achieved through the use of automation that reduces the volume of hazardous waste generated by this procedure.

13.3 The volume of hazardous waste is minimized through proper segregation and management of the various waste streams generated by this procedure

13.4 In order to reduce the amount of reagents used and to minimize waste, the amount of sample and reagents has been reduced to one-fifth of the method values

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program".

14.2 Waste Streams Produced By This Method

14.3 The following waste streams are defined in "Collection and Accumulation of Hazardous Waste" (DV-HS-0002). Further details about the management of these wastes are given in the SOP.

- Prepared sample and absorbance cell waste – Acidic Aqueous (F).
- Expired Chemicals/Reagents – Contact Waste Coordinator
- Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Method 9038, "Sulfate (Turbidimetric)", 3rd Edition, Final Update II, Sept. 1994.

15.2 ASTM Method D516 – 02, Standard Test Method for Sulfate Ion in Water.

15.3 U.S. EPA, Method for Chemical Analysis of Water and Waste, EPA 600/4-79-020, Method 375.4, March 1983.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 375.4, SW 9038 & ASTM-D516-02	The method for the Konelab requires the barium chloride to be a solution instead of dry crytals. The Konelab also uses a wavelength of 405nm.
2	SW 9038	SW 846 Method 9038 requires a calibration to be performed every hour of continuous sample analysis and an ICV every 15 samples. Due to advances in technology the method performed calibrates the instrument once prior to any analysis and verified with a second source (ICV) once. Continuing calibration verification (CCV) is performed fresh every 4 samples. If the CCV fails the instrument is then re-calibrated.
3	EPA 375.4, SW 9038 & ASTM-D516-02	There are two sets of readings taken for this turbidimeteric sulfate procedure. The kinetic readings are 9 separate readings taken over a 4 minute interval. The points are plotted and provided in the raw data. These points tend to be in line with the instrument generated graph. When there are two or more points that are not on the instrument generated graph than the sample is diluted and re-analyzed. The second reading is a single point reading taken at 4 minutes and is used to provide the actual concentration value. This value is compared to the kinetic readings to see that it is in line with the absorbances. These separate readings are a modification from the source methods and are performed due to the limitation of the instrument software. The method was set up with the instrument specifications for the turbidimeteric sulfate procedure provided by the manufacturer (Konelab).

17.0 Attachments

Attachment 1: Example Konelab Setup Screen
Attachment 2: Example Turbidimeteric Sulfate Benchsheet
Attachment 3: Example Data Review Checklist

18.0 Revision History

- Revision 7.2, dated 24 August 2009
  - Changed the CCV concentration from 25mg/L to 15mg/L.

- Revision 7.1, dated 16 February 2009
  - Corrected minor grammatical and formatting errors.
  - Added method modification #2.
  - Added MS/MSD requirement for every 10 samples.

- Revision 7, dated 28 November 2008
  - Deleted references to SM 4500-SO_4^2 E throughout the SOP.
  - Added the method modifications for the instrument measurements.

- Revision 6, dated 22 February 2008
  - Integration for TestAmerica and STL operations.
  - Updated formatting.
  - Added MDL information location.

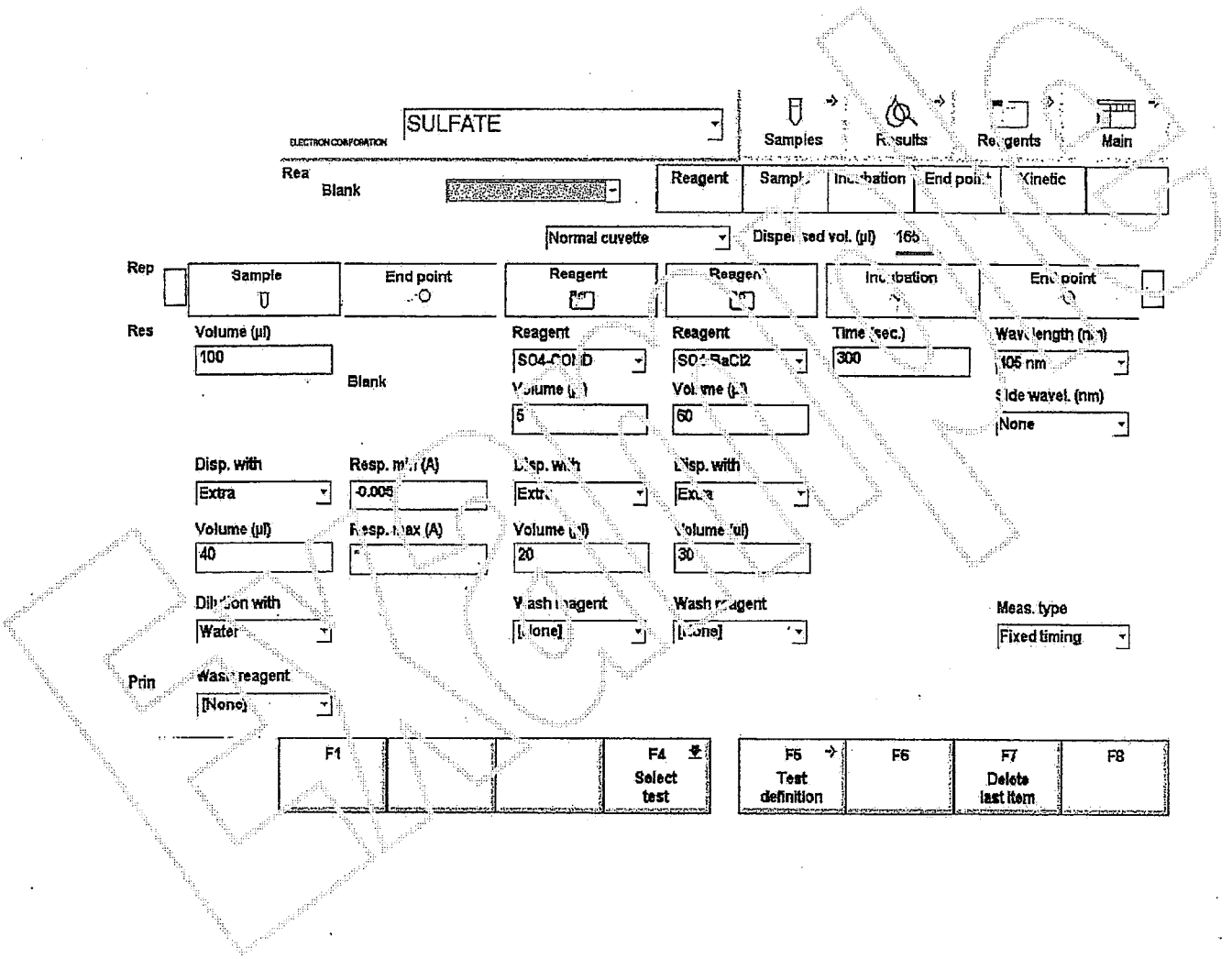
- Revision 5, dated 25 July 2007
  - Minor grammatical errors have been corrected.
  - Changed references from STL to TestAmerica.
  - Updated method references.

- Revision 4, dated 25 June 2004
  - An intermediate stock solution was added to prepare the calibration curve.
  - The calibration curve was adjusted for use in the Konelab.
  - The ICV, CCV, LCS and spike concentrations were updated to be at the mid-point of the curve.
- Revision 3, dated 16 August 2002
  - MS/SD per 10 client samples for specific client/agencies added.
  - South Carolina specific calibration curve information added.
  - Changed CCV/CCB frequency to every 4 samples.
  - Reading interval changed from 1 minute to 30 seconds for South Carolina samples.
  - The upper end of the working range was changed to 35 mg/L. The calibration curve was also changed to reflect this.
  - Equipment and supplies that were no longer needed due to the use of the Konelab, were deleted.
  - Instructions to make a 10% BaCl2 solution were added.
  - The spike solutions were updated using a lower concentration stock solution.
  - The ability to use second order least squares regression for the calibration curve was eliminated.
  - Instructions for the manual analysis of samples were deleted. Reference was added for the Konelab Instructions.

- Revision 2, dated 14 February 2002
  - The company name is changed from Quanterra to STL.
  - Calibration standards in section 7.4 were adjusted to include a 2.5 mg/L standard instead of a blank.
  - Section 7.5 was adjusted so that dilution instructions on how to prepare the ICV are present.
  - Detail was added in section 15 on Waste Disposal.
  - Data review checklist added to appendices.

Attachment 1.

Example Konelab Setup Screen



Attachment 2.

Example Turbidimeteric Sulfate Benchsheet

Laboratory Bench Sheet
Colorimetric Analysis
Revision 2 - July 2007

TestAmerica Denver

Turbidimetric Sulfate Analysis

		Cal. Curve Standards			SOP Information		Instrument Information	
Analyst:		Conc.(mg/L)		ABS.	Number:	DEN WC-0022	Instrument:	SPEC 301
Date:					Revision:	3	Wavelength:	420
QC Lot:		Std. 1	5		Cal. Curve Statistics		Parameter:	Sulfate
MS Run:		Std. 2	10		Corr. Coeff:	#DIV/0!	Rep. / Detection Limits	
SECOND SOURCE ICV		Std. 3	15		Slope:	#DIV/0!	MDL	1.000000
Source/Ver-Lot#:		Std. 4	20		Intercept:	#DIV/0!	Rep. Limit	5.000000
LOT #		Std. 5	25		LCS/MS/MSD/CCV	INFROMATION		
Made By:		Std. 6	30		LOT #	Made By:		
Concentration:	1000 mg/L	Std. 7	35		Source/Ver-Lot#: 10605	Spike True Value:		20.00
Expiration					Concentration: 1000 mg/L	LCS/DCS TRUE VALUE		20.00
ICV TRUE VALUE	20.00	DATE OF	CURVE	12/13/2002	Exp. Date:	CCV True Value:		20.00

Time Notes	LIMS ID	pH	Smp Amt (mL,g)	ABS.	Color Blk. ABS.	Concentration (mg/L-mg/Kg)	Prep Dilution Factor	Anal. Dil. Factor	Final Conc. (mg/L-mg/Kg)	% Rec.
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	
		N/A					1	1	0.00	

rev 06/17/04

Attachment 3.

Example Data Review Checklist

TESTAMERICA Denver

Wet Chemistry Data Review Checklist
For Tests with Calibration Curves

Test Name/ Method #: _____ **SOP #:** _____

Instrument: _____ **Analyst:** _____ **Analysis Date:** _____

Client	Lot / Sample Numbers	Matrix	Batch Number	Special Instructions
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Minimum of five standards in ICAL or as specified in method?				
2. Correlation coefficient ≥ 0.995 ?				
3. Second-source ICV analyzed, and recovery 90 - 110%?				
4. ICB analyzed immediately after the ICV & results < the RL?				
5. CCV analyzed after every ten samples & recovery ± 10% of true value?				
6. CCB analyzed after every CCV & results < RL?				
B. Sample Results				
1. All samples greater than highest calibration standard diluted and reanalyzed?				
2. Do associated RLs/MDLs reflect dilutions or limited sample volume?				
3. All reported results bracketed by in control CCV results?				
4. Sample analyses done within holding time?				
5. Initial pH check documented for all samples?				
6. Preparation benchsheet completed and included in package?				
7. Special client requirements met?				
8. Were data manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures?				
9. Do the prep and analysis dates in QuanTIMS reflect the actual dates?				
10. Are all data being reported highlighted on the benchsheet?				
11. Raw data copies prepared and scanned?				
12. Manual integrations done properly?				
C. Preparation/Matrix QC				
1. Method blank < RL or all reported samples > 20x blank have NCM?				
2. LCS run for batch and within QC limits ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within 10%?				

Analyst: _____ **Date:** _____

2nd Level Reviewer : _____ **Date:** _____

2/11/09 Version
QA\Edit\Forms\Wet Chemistry\Calib Curve Checklist

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Chloride Analysis (Alpkem) [EPA 325.2, SM 4500- CL E, SW 9251]

Approvals (Signature/Date):

Dave Elkin 5/4/09	Adam W. Alban 04 May 09
Dave Elkin — Date	Adam Alban — Date
Wet Chemistry Supervisor	Health & Safety Manager / Coordinator
Karen Kuoppala 5-1-09	Robert C. Hanisch 5/1/09
Karen Kuoppala — Date	Robert C. Hanisch — Date
Quality Assurance Manager	Laboratory Director

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1.0 Scope and Application

1.1 This method is applicable to the determination of chloride (CAS#: 1-00-3).

1.2 This method is applicable to the analysis of potable, surface and saline waters, and domestic and industrial wastes.

1.3 This method is also applicable to the analysis of soils and wastes following a DI leach (SOP DV-WC-0036).

1.4 The reporting limit for chloride is 3.0 mg/L for aqueous samples and 30.0 mg/kg for soils and wastes.

1.5 The method covers the range from 3.0 mg/L to 100.0 mg/L in aqueous samples and 30.0 to 1000 mg/kg in soils and wastes. The range may be extended by making dilutions for higher concentrations.

1.6 The approximate analysis time is 2 hours for a batch of 20 samples.

2.0 Summary of Method

2.1 Samples are analyzed on the Alpkem Flow IV autoanalyzer which performs an automated colorimetric analysis.

2.2 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.

3.0 Definitions

There are no terms requiring definition unique to this procedure. Refer to the Glossary of the Quality Assurance Manual for definitions of general analytical and QA/QC terms.

4.0 Interferences

Sample color or turbidity may interfere. Turbid samples should be filtered prior to analysis. Strongly colored samples that absorb in the 580 nm range must be diluted prior to analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 Mercury compounds are highly toxic and must be handled with extreme care.

5.1.3 Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol (MeOH)	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Mercuric Thiocyanate	Poison	0.1 mg/m^3 (TWA)	**Danger! May be fatal if swallowed. Average lethal does for inorganic mercury salts in about 1 gram.** Causes irritation to the respiratory tract, with symptoms including sore throat, coughing, pain, tightness in chest, breathing difficulties, shortness of breath, and headache. Can be absorbed through inhalation with symptoms parallel to ingestion. May cause redness, pain, and burns in contact with skin. Can be absorbed through the skin with symptoms parallel to ingestion. Causes irritation to eyes, and may cause burns and damage to eyes. Chronic exposure through any route can produce central nervous system damage.
Nitric Acid, HNO_3	Corrosive Oxidizer Poison	2 ppm (TWA) 4 ppm (STEL)	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

1 – Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- The ALPKEM Autoanalyzer:
  - Autosampler.
  - Proportioning pump.
  - Colorimeter equipped with 5 mm tubular flow cell and 480 nm filter.
  - An interfaced computer with the WinFlow software.

6.2 Supplies

- Volumetric Flasks (Class A): Varying volumes
- Eppendorf Pipettes, varying volumes

7.0 Reagents and Standards

7.1 Mercuric thiocyanate solution

Dissolve 4.17 g Hg(SCN)2 in 500 mL methanol. Dilute to 1 liter with methanol, mix, and filter through a Whatman 41 filter paper.

7.2 Ferric nitrate solution, 20.2%

Dissolve 202 g Fe(NO3)3•9 H2O in 500 mL reagent water. Add 31.5 mL concentrated nitric acid, mix, and dilute to 1 liter with reagent water. Store in an amber or foil-covered bottle.

7.3 Reagent water (Milli-Q or equivalent)

7.4 Chloride Color Reagent

Add 150 mL mercuric thiocyanate solution to 150 mL ferric nitrate solution. Mix the solution and dilute to 1 liter with reagent water. Add 0.5 mL polyoxyethylene 23 lauryl ether (ICI Americas Brij 35™ or equivalent). Alternatively, a commercially available color reagent can be purchased.

7.5 Chloride Stock Standard (1000 mg/L)

Dry 2-3 g of sodium chloride at 140°C. Dissolve 1.6482 g in 600 mL of reagent water, and dilute to 1000 mL with reagent water. This solution may also be obtained from a commercial vendor. This standard is used to produce the working standards in section 7.7.

7.6 Chloride ICV Standard (1000 mg/L)

Dry 2-3 g of sodium chloride chloride at 140°C. Dissolve 1.6482 g in 600 mL of reagent water, and dilute to 1000 mL with reagent water. This solution may also be obtained from a commercial vendor. This solution should be prepared or purchased from a separate source from section 7.5.

7.7 Working Standards/Recommended Calibration Standards:

Volume of Standard	Concentration of Standard Diluted	Final Volume	Final Concentration
1 mL	5 ppm	2 mL	2.5 ppm
0.5 mL	1000 ppm	100 mL	5 ppm
1 mL	1000 ppm	100 mL	10 ppm
2.5 mL	1000 ppm	100 mL	25 ppm
4 mL	1000 ppm	100 mL	40 ppm
6 mL	1000 ppm	100 mL	60 ppm
10 mL	1000 ppm	100 mL	100 ppm

7.8 Initial Calibration Verification (ICV), 25 mg/L

The initial calibration verification (ICV) is prepared by diluting 2.5 mL of the 1000 mg/L ICV stock standard (7.6) to 100 mL in reagent water.

7.9 Continuing Calibration Verifications (CCVs), 40 and 60 mg/L

The 40 ppm and 60 ppm working standards in section 7.7 are used as the CCVs.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	HDPE	150 mLs	Cool 4 ± 2°C	28 Days	40 CFR Part 136.3
Soils	Glass	4 oz	Cool 4 ± 2°C	28 Days	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS QC program code and special instructions to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial method proficiency studies, as described in section 12 must be completed before analyzing samples.

9.3 Control limits for LCS and MS/MSD spikes are initially set to 90-110%, with historical limits applied when sufficient data are available. Details about setting control limits and general guidelines for evaluating QC data are described in the TestAmerica Denver QC Policy (DV-QA-003P). Control limits are stored in QuantIMS, the laboratory LIMS system.

9.4 Method Blank (MB)

The laboratory must analyze at least one MB with each batch of 20 samples. Data produced are used to assess contamination from the laboratory environment.

Acceptance Criteria: The method blank results must be less than the reporting limit (RL) or less than one-tenth of the concentration measured in samples. If the method blank exceeds these levels, the problem should be investigated and all associated samples reanalyzed. If elevated blank levels are encountered and ferrous iron is not detected in samples, it may be possible to report the samples results together with an NCM.

Corrective Action: If the Method Blank concentration is more than the reporting limit, rerun all samples associated with the unacceptable blank unless the sample concentration is > 10 times the blank concentration.

9.5 Laboratory Control Sample (LCS)

One LCS is analyzed with every batch of 20 or fewer samples. The recommended LCS is the 25 ppm working standard prepared in section 7.7.

Acceptance Criteria: The LCS recovery must fall within the established control limits, which are set at ± 3 standard deviations around the historical mean.

Corrective Action: If the LCS recovery is outside of the laboratory historical control limits, investigate the problem and rerun all associated samples.

9.6 Sample Matrix Spike and Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair is analyzed with every batch of 20 or fewer samples. The 50 mg/L MS/MSD are prepared by taking 0.5 mL of 1000 mg/L chloride standard (7.5) and diluting to 10 mL with sample.

Acceptance Criteria: The MS and MSD recoveries and the relative percent difference between the MS and MSD must fall within established control limits.

Corrective Action: If the MS/MSD recovery or RPD is outside of acceptance limits, the associated sample results must be qualified in the final report case narrative.

9.7 Instrument QC

9.7.1 Initial Calibration (ICAL)

Prepare a series of 7 calibration standards as described in Section 7.7.

9.7.2 Initial Calibration Verification (ICV), 25 mg/L

Analyze a second-source ICV standard (Section 7.8) immediately after the initial calibration (ICAL).

Acceptance Criteria: The recovery must be within the 90-110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, and then recalibrate.

9.7.3 Continuing Calibration Verifications (CCVs), 40 and 60 mg/L

Analyze a CCV standard, which is prepared from the same source and at the same concentration as the midrange calibration standards (Section 7.7), after every ten samples and at the end of the analytical sequence. The CCV should be alternated between the two concentrations of 40 and 60 mg/L.

Acceptance Criteria: The recovery must be within the 90-110% range.

Corrective Action: If it is outside the acceptance limits, check the equipment and standards, recalibrate, and rerun all samples analyzed since the last successful CCV.

9.7.4 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

System cleanliness is checked at the beginning (with an initial calibration blank or ICB), and after every ten samples and at the end of the analytical sequence using a continuing calibration blank (CCB). The blanks consist of deionized water.

Acceptance Criteria: Results must be less than the reporting limit.

Corrective Action: If the blank is greater than the reporting limit, check for carry-over from high level samples, clean the system, recalibrate, and rerun all samples analyzed since the last successful CCB.

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.1 Sample Preparation

10.1.1 Soils and wastes must be taken through the D.I. Leach procedure before analysis. (SOP#: DV-WC-0036)

10.1.2 If particulate matter is present, the sample must be filtered prior to analysis. The sample may be centrifuged in place of filtration.

10.2 Calibration

The instrument is to be set up and operated in accordance to the manufacturer's instructions. Before running samples, the pump should be allowed to pump start-up water through the system for approximately 5 minutes to remove any air bubbles from the lines. Additional calibration information can be found in the Corporate TestAmeica's Calibration Curve document CA-Q-S-005.

10.2.1 The ICAL is performed automatically by the instrument at the beginning of each day's use.

10.2.2 Load the calibration standards (Section 7.7) into the autosampler so that they are analyzed before any samples. A series of seven concentrations are used to establish this curve. All the standards and blanks are processed exactly as the samples.

10.2.3 The instrument software processes the calibration data and generates a calibration function that is used to calculate sample results. The instrument software uses a quadratic regression to relate the concentration of chloride in each standard and the associated absorbance reading, as follows:

$$x = cyy + by + a \qquad \textbf{Equation 1}$$

Where:

x = *analyte concentration*
y = *analyte height*
c = *definition of the curve*
b = *Slope.*
a = *Y-intercept.*

10.2.4 The instrument software uses the calibration function to calculate the concentration of each sample that is analyzed. The instrument software prints a calibration report for review, which includes the calibration equation

and correlation coefficient. The correlation coefficient of the calibration line must be ≥ 0.995. If this cannot be achieved, then check the calibration standards, correct any problems, and repeat the ICAL.

10.2.5 The instrument software automatically calculates the concentration of each unknown sample using the sample absorbance and the calibration curve.

10.3 Sample Analysis

10.3.1 Fill cups on the sample tray with the standards and samples, taking care to ensure the tray is properly loaded. Enter dilution factors into the sample table if they are used.

10.3.2 Monitor the baseline, and when a steady baseline is obtained, start the analysis.

10.3.3 Analyze the standards, followed by the ICV, ICB, Method Blank, LCS, and then the samples.

10.3.4 The CCVs (both the 40 and 60 mg/L concentrations) and a CCB should be analyzed after every 10 samples and at the end of the run.

11.0 Calculations / Data Reduction

11.1 The calculations are performed by the WinFlow software in the computer.

11.2 Any samples with concentrations above the highest standard require dilution and re-analysis.

11.3 Accuracy

ICV / CCV, LCS % Recovery $= \frac{\text{observed concentration}}{\text{known concentration}} \times 100$

MS % Recovery $= \frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spiked concentration}} \times 100$

11.4 Precision (RPD)

Matrix Duplicate (MD) $= \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$

11.5 Concentration = mg/kg or L $= \frac{C \times V \times D}{W}$

Where:

C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor

W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

11.6 Reporting

11.6.1 Reporting units are mg/L for aqueous samples and mg/kg for non-aqueous samples.

11.6.2 Samples less than the reporting limit are reported as ND.

11.6.3 All data are subject to two levels of review, which is documented on the checklist shown in Attachment 2.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 Method Detection Limit Study an initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Prepare and analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy # DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

- Four aliquots of the QC check sample (independent source from the calibration) are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.
- Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

12.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.3.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

- Expired Chemicals/Reagents/Standards – Contact Waste Coordinator
- Aqueous waste containing mercury compounds – Aqueous Mercury (Acidic) - Waste Stream G

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Method 4500-Cl- E, "Automated Ferricyanide Method", Standard Methods of the Examination of Water and Wastewater, 20th Edition, 1998.

15.2 Methods for the Chemical Analysis of Water and Wastes, (MCAWW), U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, ORD Publication Offices of Center for Environmental Research Information, 1978.

- Method 325.2, Chloride (Colorimetric, Automated Ferricyanide).

15.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW846, 3rd Edition, Final Update IIIB (December 1996), Method 9251, "Chloride (Colorimeteric, Automated Ferricyanide AAII)", Revision 0, September 1986.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 4500CL E	The source method has been expanded to include soils and wastes through the use of a deionized water leach.

17.0 Attachments

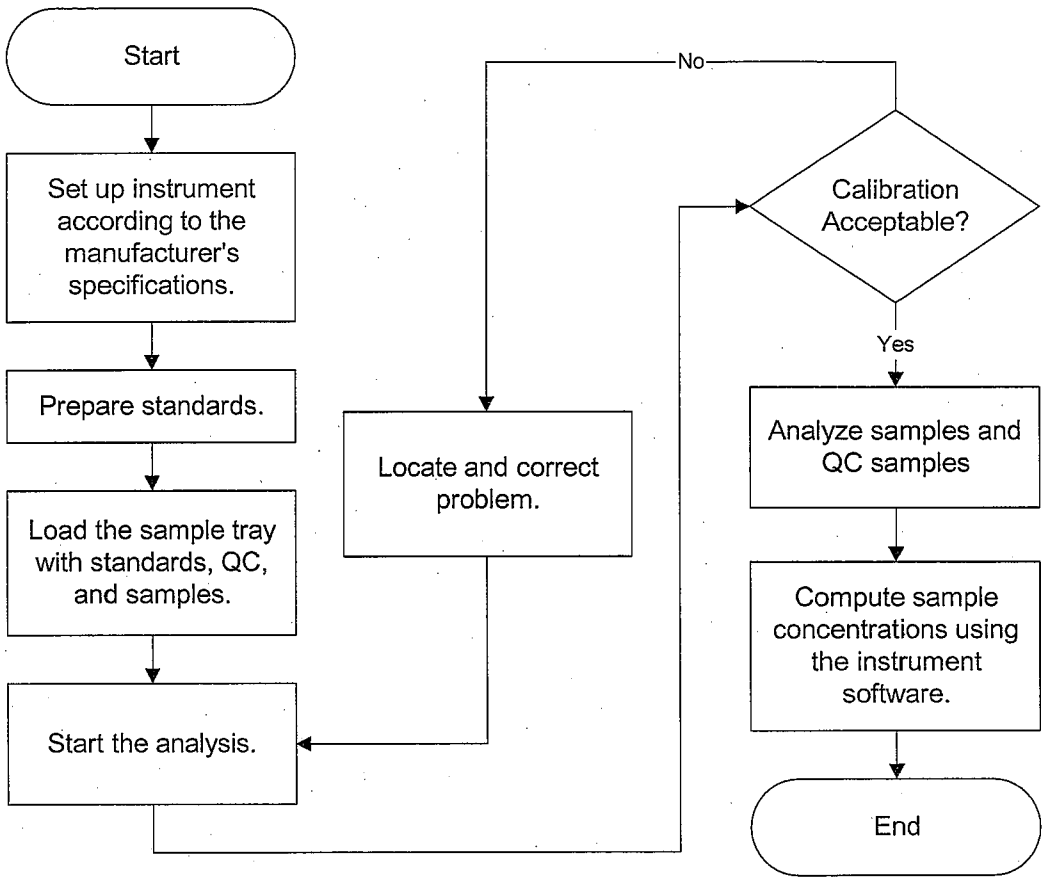
Attachment 1: Flow Chart
Attachment 3: Example Data Review Checklist

18.0 Revision History

- Revision 2.1, dated 01 May 2009
  - Deleted attachment 1 – Chloride manifold.
  - Added the method references SW 9251 and EPA 325.2.
  - Made minor formatting and grammatical corrections.
- Revision 2, dated 07 March 2008
  - Integration for TestAmerica and STL operations.
  - Removed all reference to retired EPA method 325.2 due to the MUR update.
  - Added attachment 3 Example Data Review Checklist.
- Revision 1.1, dated 20 November 2006
  - For this minor revision, the technical content of this SOP was not reviewed or updated. The purpose of this minor revision is to incorporate the Safety Bulletin information to ensure compliance with STL Corporate requirements. In addition, Section 9.1 was revised to reference Policy QA-024 for specific QC requirements for federal programs, any existing interim changes were incorporated, and formatting was updated consistent with Policy QA-001.

Attachment 1.

Flow Chart



Attachment 3.

Example Data Review Checklist

TESTAMERICA Denver

Wet Chemistry Data Review Checklist
For Tests with Calibration Curves

Test Name/ Method #: _____ **SOP #** _____

Instrument: _____ **Analyst:** _____ **Analysis Date:** _____

Client	Lot / Sample Numbers	Matrix	Batch Number	Special Instructions
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Minimum of five standards in ICAL or as specified in method?				
2. Correlation coefficient ≥ 0.995 ?				
3. Second-source ICV analyzed, and recovery 90-110%?				
4. ICB analyzed immediately after the ICV & results < the RL?				
5. CCV analyzed after every ten samples & recovery ± 10% of true value?				
6. CCB analyzed after every CCV & results < RL?				
B. Sample Results				
1. All samples greater than highest calibration standard diluted and reanalyzed?				
2. Do associated RLs/MDLs reflect dilutions or limited sample volume?				
3. All reported results bracketed by in control CCV results?				
4. Sample analyses done within holding time?				
5. Initial pH check documented for all samples?				
6. Preparation benchsheet completed and included in package?				
7. Special client requirements met?				
8. Were data manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures?				
9. Do the prep and analysis dates in QuanTIMS reflect the actual dates?				
10. Are all data being reported highlighted on the benchsheet?				
11. Raw data copies prepared and scanned?				
12. Manual integrations done properly?				
C. Preparation/Matrix QC				
1. Method blank < RL or all reported samples > 20x blank have NCM?				
2. LCS run for batch and within QC limits ?				
3. MS run at required frequency and within limits ?				
4. MSD or DUP run at required frequency and RPD within 10%?				

Analyst: _____ **Date:** _____

2nd Level Reviewer : _____ **Date:** _____

2/11/09 Version
QA\Edit\Forms\Wet Chemistry\Calib Curve Checklist

SAMPLE

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THE LEADER IN ENVIRONMENTAL TESTING

Title: Determination of solids in waters and wastes [EPA160.1, EPA160.2, EPA160.3, EPA160.4,SM 2540B, SM 2540C, SM 2540D, and SM 2540E]

Approvals (Signature/Date):

David M. Elkin 6/16/09 Dave Elkin Date Wet Chemistry Supervisor	Adam W. Alban 16 June 09 Adam Alban Date Health & Safety Manager / Coordinator
Karen Kuoppala 06.17.09 Karen Kuoppala Date Quality Assurance Manager	Robert C. Hanisch 6/17/09 Robert C. Hanisch Date Laboratory Director

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1.0 Scope and Application

1.1 This SOP is applicable to the determination of total solids, total suspended solids, total dissolved solids, volatile solids, volatile dissolved solids, and volatile suspended solids using gravimetric techniques. This SOP is applicable to drinking, surface, and saline waters and domestic and industrial wastes.

1.2 The methods cover a practical range of 10 mg/L to 20,000 mg/L (TSS: 4 mg/L - 20,000 mg/L). As a practical matter, the final residue weight should be limited to about 200 mg.

1.3 The procedure for settleable solids is in SOP # DV-WC-0032.

1.4 The procedure for percent moisture in solid samples is in SOP # DV-WC-0023.

2.0 Summary of Method

2.1 **Total Solids (TS):** A well-mixed aliquot of the sample is quantitatively transferred to a preweighed evaporating dish and evaporated to dryness at 103-105 °C. The increase in weight over that of the empty dish represents the total solids.

2.2 **Total Dissolved Solids (TDS):** A well-mixed sample is filtered through a glass fiber filter. The filtrate is quantitatively transferred into a preweighed evaporating dish and is evaporated to dryness and then dried to constant weight at 180 °C. The increase in weight over that of the empty dish represents the total dissolved solids. The filter from this procedure may also be used for TSS/VSS determination.

2.3 **Total Suspended Solids (TSS):** A well-mixed sample is filtered through a pre-weighed glass fiber filter. The residue on the filter is dried to constant weight at 103-105 °C. The increase in weight over that of the pre-weighed filter represents the TSS content. The filtrate from this procedure may be used for TDS determination. The filter from this procedure may also be used for VSS analysis.

2.4 **Volatile Solids (VS):** The residue obtained from the determination of total solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile solids.

2.5 **Volatile Dissolved Solids (VDS):** The residue obtained from the determination of total dissolved solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile dissolved solids.

2.6 **Volatile Suspended Solids (VSS):** A well-mixed sample is filtered through a glass fiber filter to separate the suspended material. The filter is dried and weighed, then ignited at 550 °C and reweighed. Volatile suspended solids is determined from the weight loss after ignition. The filter from the analysis of TSS may be used for the determination of VSS.

3.0 Definitions

3.1 **Total Solids (TS):** The term applied to the residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at 103-105 °C.

Total solids includes "total suspended solids," the portion of solids retained by a filter, and "total dissolved solids," the portion that passes through the filter. The reporting limit is 10 mg/L.

3.2 **Total Dissolved Solids (TDS):** Those solids capable of passing through a glass fiber filter and dried to constant weight at 180 °C. TDS is also referred to as filterable residue.

3.3 **Total Suspended Solids (TSS):** Those solids which are retained by a glass fiber filter and dried to constant weight at 103-105 °C. TSS is also referred to as non-filterable residue.

3.4 **Volatile Solids (VS):** The portion of total solids which is lost on ignition at 550 °C.

3.5 **Volatile Dissolved Solids (VDS):** The portion of total dissolved solids which is lost on ignition at 550 °C.

3.6 **Volatile Suspended Solids (VSS):** The portion of suspended solids which is lost on ignition at 550 °C.

3.7 **Aliquot:** A representative portion of a sample.

3.8 **Reagent Water:** Deionized water which is free of the analyte(s) of interest.

4.0 Interferences

4.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of analysis by running method blanks.

4.2 Non-homogeneous samples may give erroneous results. Samples should be mixed as thoroughly as possible before removing an aliquot for analysis.

4.3 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the benchsheet.

4.4 Samples containing large amounts of solids may filter slowly. Prolonged filtration times resulting from filter clogging may produce high TSS results due to increased colloidal materials captured on the clogged filter.

4.5 Oil and grease in the samples will cause unreliable results due to difficulty in drying to constant weight. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

4.6 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperatures are specified because these variables have been shown to affect the results.

4.7 The temperature at which the residue is dried has an important bearing on the results because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

4.8 Each sample requires close attention to desiccation after drying. Minimize opening the desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.9 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

4.10 Samples containing high concentrations of bicarbonate may require careful and possibly prolonged drying to ensure that all the bicarbonate is converted to carbonate.

4.11 Too much residue in the drying vessel will crust over, entrapping water that will not be driven off during drying. Total residue should be limited to about 200 mg.

4.12 Some samples may have fine suspended solids which will pass through the glass fiber filter causing high TDS results.

4.13 Aluminum pans should not be used for TS or TDS analyses. Components in some samples may react to form aluminum compounds, causing unreliable results.

4.14 For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material prior to TSS determination.

4.15 The volatile solids tests are subject to many errors due to the loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts during combustion. The results should not be considered an accurate measure of organic carbon in the sample.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1 (as per the Environmental Health and Safety Manual), laboratory coat, and nitrile or latex gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves

that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2 Primary Materials Used

There are no materials used in this method that have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

6.1 Analytical balance capable of weighing to 0.0001 g. The balance calibration is checked each day of use with three Class 1 weights that bracket the range of use. Details for this procedure are covered in SOP DV-QA-0014.

6.2 Vacuum filtration apparatus.

6.3 Vacuum pump equipped with moisture trap.

6.4 Glass fiber filter disks, 47 mm, without organic binder (Gelman Type A/E) or equivalent.

6.4.1 Preparation of Glass Fiber Filter Disc for TSS/VSS

6.4.1.1 Place the glass fiber filter discs, one at a time, on the membrane filter apparatus with wrinkled surface up.

6.4.1.2 While vacuum is applied, wash the disc with three successive (approximately) 20 mL volumes of distilled water.

6.4.1.3 Remove all traces of water by continuing to apply vacuum after water has passed through and discard washings.

6.4.1.4 Remove filter from membrane filter apparatus and place in a labeled, aluminum weighing dish and dry in an oven at 103-105 °C for one hour.

6.4.1.5 Remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

6.4.1.6 Weigh the cooled filter and aluminum weighing dish to the nearest 0.1 mg using an analytical balance. Record the weight and the dish identification number on the benchsheet.

6.5 Glass beakers for TDS, minimum 150 mL volume, must be thoroughly cleaned, rinsed with de-ionized water and baked at 180 ± 2 °C for TDS and 104 ± 2 °C for TS at least one hour before use. Transfer to a desiccator and allow to cool completely before use.

Note: Glass beakers may not be used for procedures requiring a muffle furnace. In that case, porcelain dishes, pre-dried and weighed, must be used.

6.6 Desiccators providing sufficient space for storage of samples in process separate from filters and evaporating dishes.

6.7 Desiccant containing a color indicator of moisture concentration or an instrumental indicator.

6.8 Drying ovens set at 103-105 °C and 180 ± 2 °C. Separate ovens should be maintained at appropriate temperatures if possible.

6.9 Muffle furnace (550 °C ± 50 °C).

6.10 Thermometers, NIST traceable.

6.11 Conductivity meter and associated apparatus.

6.12 Graduated cylinders, assorted sizes.

6.13 Volumetric flasks, Class A, assorted sizes.

6.14 Aluminum weighing dishes large enough to hold a 47 mm filter.

6.15 Forceps for handling filters.

6.16 Crucible tongs.

6.17 Zetex gloves or other gloves capable of providing protection at 550 °C.

7.0 Reagents and Standards

7.1 Reagent water must be produced by a Millipore DI system or equivalent (see also Section 10.1.3).

7.2 **LCS solution (500 mg/L TDS):**

Place 500.0 mg of sodium chloride into a 1000 mL volumetric flask and dilute to volume with deionized water. Mix well. Prepare fresh every three months. Alternatively, a commercially available LCS solution may be used.

7.3 Commercially available reference materials are used for the TSS/TS LCS.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Method	Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
TS	Waters	HDPE	100 mLs	Cool 4 ± 2°C	7 Days	40 CFR Part 136.3
TDS	Waters	HDPE	100 mLs	Cool 4 ± 2°C	7 Days	40 CFR Part 136.3
TSS	Waters	HDPE	100 mLs	Cool 4 ± 2°C	7 Days	40 CFR Part 136.3
VS	Waters	HDPE	100 mLs	Cool 4 ± 2°C	7 Days	40 CFR Part 136.3

Method	Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
VDS	Waters	HDPE	100 mLs	Cool 4 ± 2°C	7 Days	40 CFR Part 136.3
VSS	Waters	HDPE	100 mLs	Cool 4 ± 2°C	7 Days	40 CFR Part 136.3

9.0 Quality Control

9.1 Before analyzing samples, the laboratory must establish a method detection limit (MDL) as described in Section 12.1.

9.2 In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument they will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 12.2 for more details.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See QC Policy (DV-QA-003P) for further details.

9.4 Method Blank

A method blank is required with every batch of 20 or less samples. The blank is deionized water taken through the procedure like a sample. The general requirement is that the method blank result must be less than the reporting limit or one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL). Note that some agencies (e.g., South Carolina) require that the blank must be less than the MDL – see special requirements in LIMS to determine which criterion applies.

Corrective Action: If the method blank exceeds allowable levels, all associated samples must redigested and reanalyzed

9.5 Laboratory Control Sample (LCS)

One LCS is required with each analytical batch. Historical control limits are based on three standard deviations of past results, and must be 80-120% or tighter. The process of establishing control limits is described in more detail in the QC Policy DV-QA-003P.

Corrective Action: If the LCS exceeds allowable levels, all associated samples must be redigested and reanalyzed.

9.6 Duplicate Sample Analysis

Two duplicate pairs are required with each analytical batch. Historical control limits are based on three standard deviations of past results, and must be 20% RPD. Note that the control limits only apply to samples with results greater than 5 times the RL. The process of establishing control limits is described in more detail in the QC Policy DV-QA-003P.

Corrective Action: If the RPD is greater than 20 the sample should be reanalyzed.

10.0 Procedure

- One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo (see SOP # DV-QA-0031 for details) and must be approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.
- Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.
- All samples are to be checked out of sample control with the chain of custody documentation filled out completely.
- Proper sample identification is extremely important in any analytical procedure. Labeling of evaporating dishes and filters holders must be done in a manner to ensure connection with the proper sample.
- If possible, analyze all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.
- Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the benchsheet.
- If samples are visibly oily, this should be noted on the benchsheet.
- If there is limited sample volume or high solids content, smaller amounts of sample may need to be processed than detailed in the following sections. This occurrence must be noted on the benchsheet and reporting limits must be adjusted appropriately.

10.1 Calibration

10.1.1 Since this method is based on gravimetric techniques, there is no calibration in the usual sense. Proper balance operation will be verified daily or prior to sample analysis by following the lab-specific balance calibration SOP. Analytical balance calibration must be performed daily (every 24 hours).

10.1.2 Oven temperature must be checked daily and recorded either on the benchsheet or in an oven temperature logbook.

10.1.3 Conductivity of the water must be monitored and recorded in the Conductivity Logbook daily. The maximum permissible conductivity is 1.0 umhos/cm (at 25 °C). If the conductivity reading on the water system exceeds this level, do not use the water for these procedures and notify the supervisor immediately.

10.2 Sample Preparation

10.2.1 Total Solids

10.2.1.1 If only total solids are to be measured, heat clean dish to 103-105 °C for one hour. If volatile solids are to be measured in addition to total solids, ignite the clean evaporating dish at 550 °C for one hour in a muffle furnace.

10.2.1.2 Remove the dish from the muffle furnace using tongs and heat resistant gloves.

10.2.1.3 Cool and store dish in desiccator until dish reaches room temperature or until needed.

10.2.1.4 Weigh immediately before use to the nearest 0.1 mg. Record the weight on the benchsheet.

10.2.2 Total Dissolved Solids

Preparation of beakers/evaporating dishes.

- If only total dissolved solids are to be measured, heat clean beakers to 180 ± 2 °C for one hour. If volatile dissolved solids are to be measured in addition to TDS, ignite the clean evaporating dish at 550 ± 50 °C for one hour in a muffle furnace.
- Heat resistant gloves and tongs must be used when removing items from the muffle furnace.
- Store and cool dish in desiccator until dish reaches room temperature or until needed.

Note: Analyst must transfer the dish with gloves or tongs to prevent added weight due to oil from fingerprints.

- Weigh immediately before use to the nearest 0.1 mg. Record the weight of the dish on the benchsheet.

10.2.3 Total Suspended Solids

Preparation of the glass fiber filters is described in Section 6.4.

10.3 Sample Analysis

10.3.1 Total Solids

10.3.1.1 Transfer a measured aliquot of well-mixed sample to the pre-weighed, labeled dish. Record the volume of sample (to the nearest mL) on the benchsheet.

10.3.1.2 Choose an aliquot of sample sufficient to contain a residue of at least 10 mg but less than 200 mg.

10.3.1.3 If the sample is known to contain > 2000 mg/L dissolved solids, it should be diluted. Prescreening should be performed using a conductivity meter to determine the required sample volume or dilution. Dilution should be the smallest dilution sufficient to bring the approximate conductivity to under 3000 umho/cm.

10.3.1.4 For the LCS, measure 100 mL of the LCS Solution (Section 7.2) and pour into the dish.

10.3.1.5 For the MB, measure 100 mL of reagent water and pour into the dish.

10.3.1.6 Place the tray of samples into a drying oven and evaporate to dryness.

10.3.1.7 Dry the evaporated sample for at least one hour at 103-105 °C.

10.3.1.8 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.3.1.9 Remove the tray of weighing dishes from the oven using heat-resistant gloves. Place in a desiccator and cool to room temperature.

10.3.1.10 Weigh the dish to the nearest 0.1 mg. Record the weight on the benchsheet.

10.3.1.11 Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight difference is less than 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

Note: When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation.

10.3.1.12 If volatile solids are to be determined, treat the residue according to Section 10.3.4.

10.3.1.13 Calculate results according to the equation provided in Section 11.3.1. Use the lowest final weight achieved for calculating TS.

10.3.2 **Total Dissolved Solids**

10.3.2.1 Thoroughly rinse the entire filtration apparatus with reagent water before filtering each sample.

10.3.2.2 Assemble the filtering apparatus, place a glass fiber filter in the apparatus, pre-wet the filter using reagent water, and begin suction.

Note: If the sample also requires TSS, pre-weigh the prepared filter and refer to Section 10.3.3 for additional guidance.

10.3.2.3 Transfer 100 ml or a larger volume to yield between 10 and 200 mg dried residue to the funnel by means of a graduated cylinder. If more than 10 minutes are required to complete filtration, decrease sample volume or increase filter size.

Note: Multiple filters may be used if performing only TDS analysis.

10.3.2.4 The conductance of each sample may be used to determine the appropriate sample volume to process.

Note: TDS is typically 55-90% of the conductance result. The exact relationship depends on the compounds present in the samples and may not hold for very high concentrations or samples containing non-ionic species or samples with conductance greater than 10,000 umho/cm or less than 50 umho/cm.

10.3.2.5 If the sample has a conductance less than 3,000 umhos/cm, 100 mL should be used.

10.3.2.6 If the conductance is > 3,000 umhos/cm, the smallest dilution that would bring the conductance to under 3,000 umhos/cm should be used.

10.3.2.7 A smaller amount should be filtered if the sample is high in TSS or is otherwise slow to filter. Filter 25 mL at a time until filtration slows. Record on the benchsheet the reason that a smaller volume had to be used and any sample observations.

10.3.2.8 Record the volume of sample used (to the nearest mL) on the benchsheet.

10.3.2.9 For the method blank, process 100 mL of reagent water as the sample. Blank result should be less than method detection limit.

10.3.2.10 For the LCS, process 100 mL of the LCS Solution. Refer to Section 7.2 for instructions on how to prepare the LCS.

10.3.2.11 Filter the sample through the glass fiber filter.

10.3.2.12 Rinse the graduated cylinder, funnel walls, and filter with three successive 10 mL portions of reagent water and allow for complete drainage between washings. Continue to apply vacuum until the filter is completely dried.

10.3.2.13 Transfer the filtrate (including the washings) to a pre-weighed evaporating dish on a tray. Rinse the receiving

flask with 10-25 mL of reagent water and transfer washings into the dish to ensure complete transfer of the sample.

10.3.2.14 Evaporate the samples to dryness in a drying oven.

10.3.2.15 Dry the evaporated sample in an oven for at least one hour at 180 ± 2 °C.

10.3.2.16 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.3.2.17 Use heat resistant gloves to remove the tray of samples from the oven. Place in a desiccator and cool to room temperature.

10.3.2.18 Weigh the dish to the nearest 0.1 mg. Record the combined weight of the dried residue and the dish on the benchsheet.

10.3.2.19 Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating and weighing cycle until a constant weight is obtained or weight difference is less than 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.3.2.20 Calculate results according to the equation in Section 12.2. Use the lowest final weight achieved for calculating TDS.

10.3.3 **Total Suspended Solids**

10.3.3.1 Assemble the filtering apparatus, place the pre-weighed glass fiber filter in the apparatus, pre-wet the filter using reagent water and begin suction.

Note: Handle the filters only with forceps.

10.3.3.2 Selection of Sample Volume

- For a 47 mm diameter filter, sufficient sample to yield between 10 mg and 200 mg of dried residue. Some clients or agencies (e.g. South Carolina) require increasing standard volume from 250 mL up to 1L to achieve a minimum residue of between 10 and 200 mg.
- Because it can be difficult in some samples to determine the amount of TSS present visually, record on the benchsheet all observations on samples for which the entire volume could not be filtered due to slowing of filtration.
- If during filtration of this initial volume, the filtration rate drops rapidly or if filtration time exceeds 5-10 minutes, a smaller volume of sample should be processed.

Note: If the sample appears high in TSS, start with a smaller sample volume.

10.3.3.3 Shake the sample vigorously and quickly aliquot the sample. It is important to pour out the sample immediately after shaking so that the solids do not have time to settle. A smaller amount should be filtered if the sample is high in TSS or is otherwise slow to filter. Filter 25 mL at a time until filtration slows. Record the volume of sample filtered (to the nearest mL) on the benchsheet.

Note: If Total Dissolved Solids (TDS) is also required, the filtrate may be used. Refer to Section 10.3.2 for additional guidance.

10.3.3.4 Remove all traces of water by continuing to apply vacuum after the sample has passed through.

10.3.3.5 With suction on, rinse the graduated cylinder, filter, suspended solids residue, and filter funnel wall with three 10 mL portions of reagent water allowing complete drainage between washings.

10.3.3.6 Remove all traces of water by continuing to apply vacuum for about three minutes after the sample has passed through.

10.3.3.7 Carefully remove the filter from the filter support and transfer to an aluminum weighing dish. If the filter is torn or damaged during this process, the sample must be reanalyzed. Take care to keep the filter face-up during the transfer so that the residue does not fall off.

10.3.3.8 Dry the filter at least one hour at 103-105 °C.

10.3.3.9 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.3.3.10 Use heat resistant gloves to remove the tray of dishes from the oven. Place in a desiccator and cool to room temperature.

10.3.3.11 Cool the samples in a desiccator, weigh (to the nearest 0.1 mg), and record the weight on the benchsheet.

10.3.3.12 Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight difference is less than 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.3.3.13 If volatile suspended solids are to be determined, treat the residue according to Section 10.3.6.

10.3.3.14 Calculate the results using the formula given in Section 11.3.2. Use the lowest final weight achieved for calculating TSS.

10.3.4 **Volatile Solids**

10.3.4.1 Heat muffle furnace up to temperature (550 ± 50 °C).

10.3.4.2 Place evaporating dish containing residue generated by Total Solids protocol (Section 10.3.1) in muffle furnace to ignite the residue.

10.3.4.3 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.3.4.4 Typically, 15-20 minutes ignition are required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.3.4.5 Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace.

10.3.4.6 Let dish cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling.

10.3.4.7 Return the samples to the muffle oven for another cycle repeating steps 10.3.4.2 – 10.3.4.6 until a constant weight is obtained or weight difference is less than 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.3.4.8 Calculate the results using the formula given in Section 11.3.4. Use the lowest final weight achieved for calculating VS.

10.3.5 **Volatile Dissolved Solids**

10.3.5.1 Heat muffle furnace up to temperature (550 ± 50 °C).

10.3.5.2 Place evaporating dish containing residue generated by Total Dissolved Solids protocol (Section 10.3.2) in muffle furnace to ignite the residue. The dish used should be a ceramic weighing dish, not a glass beaker.

10.3.5.3 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.3.5.4 Typically, 15-20 minutes ignition are required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.3.5.5 Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace.

10.3.5.6 Let dish cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling to room temperature.

10.3.5.7 Return the samples to the oven for another cycle of weighing. Repeat steps 10.3.5.2 to 10.3.5.6 until a constant weight is obtained or weight difference is less than 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.3.5.8 Calculate the results using the formula given in Section 11.3.5. Use the lowest final weight achieved for calculating VDS.

10.3.6 Volatile Suspended Solids

10.3.6.1 Heat muffle furnace up to temperature (550 ± 50 °C).

10.3.6.2 Place glass fiber filter disc containing residue generated by Total Suspended Solids protocol (Section 11.12) in muffle furnace to ignite the residue.

10.3.6.3 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.3.6.4 Typically, 15-20 minutes ignition are required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.3.6.5 Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace.

10.3.6.6 Let dish cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling to room temperature.

10.3.6.7 Return the samples to the oven for cycle of weighing, repeating steps 10.3.6.3 – 10.3.6.6 until a constant weight is obtained or weight difference is less than 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.3.6.8 Calculate the results using the formula given in Section 11.3.6. Use the lowest final weight achieved for calculating VSS.

11.0 Calculations / Data Reduction

- If smaller or larger sample volumes are processed than are specified in the method, the reporting limit must be adjusted accordingly.
- All data are subject to two levels of review, which is documented on a checklist (see example Data Review Checklist in Attachment 3).

- If multiple weighing cycles are required, the lowest final sample weight is used for calculating solids content.

11.1 Conversion equation

All sample are weighed in grams but reported in milligrams. Use the following equation before computing further calculations:

Weight in grams X 1000 = Weight in milligrams

11.2 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.3 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.4 Concentration

11.4.1 Total Solids =

$$\text{Total Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

11.4.2 Total Dissolved Solids =

$$\text{Total Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

11.4.3 Total Suspended Solids =

$$\text{Total Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of filter + residue (mg)
B = weight of filter (mg)
C = volume of sample filtered (mL)

11.4.4 Volatile Solids =

$$\text{Volatile Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of residue + dish before ignition (mg)
B = weight of residue + dish after ignition (mg)
C = volume of sample (mL)

11.4.5 Volatile Dissolved Solids = $\text{Volatile Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{C}$

Where: A = weight of residue + dish before ignition (mg)
B = weight of residue + dish after ignition (mg)
C = volume of sample (mL)

11.4.6 Volatile Suspended Solids = $\text{Volatile Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$

Where: A = weight of residue + filter before ignition (mg)
B = weight of residue + filter after ignition (mg)
C = volume of sample (mL)

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Digest and analyze the MDL standards as described in Section 11.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.
- The MDL studies and concentrations can be found at L:\QA\Read\MDL.
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy # DV-QA-005P for further details concerning MDL studies.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows"

- Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.
- Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need

to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP# DV-QA-0024.

13.0 Pollution Control

Prescreening is performed to determine the required sample volume or dilution in order to minimize laboratory waste. In addition, standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents to be disposed.

14.0 Waste Management

All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

The following waste streams are produce when this method is carried out:

- Expired Chemicals/Reagents/Standards – Contact Waste Coordinator
- Acidic sample waste – Waste Stream F
- Filter and filter residue – nonhazardous waste

Note: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated from this procedure.

15.0 References / Cross-References

15.1 Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979: Methods 160.1, 160.2, 160.3, and 160.4.

15.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1992: Methods 2540A, 2540B, 2540C, 2540D, and 2540E.

16.0 Method Modifications:

None

17.0 Attachments

Attachment 1: Example TDS/TS/TSS Benchsheet

Attachment 2: Example VSS/VDS/VS Benchsheet

Attachment 3: Data Review Checklist

18.0 Revision History

- Revision 3.1, dated 19 June 2009
  - Corrected minor grammatical and formatting errors.
  - Technical and method review performed.

- Revision 3, dated 16 June 2008
  - Fixed formatting
  - Added EPA references to SOP

- Revision 2, dated 21 December 2007
  - Integration for TestAmerica and STL operations.
  - Updated formatting.
  - Updated to include the 10% sample duplicate requirement from Standard Methods.

- Revision 1.1, dated 30 December 2005
  - Safety and Waste section updates. The technical interim changes are maintained, and the revision was increased by "X.1"

- Revision 1, dated 26 August 2002
  - Definition for TS in 3.1 corrected to have drying temperature (103-105 degrees C) match text.
  - Standard volume for TSS and VSS changed from 250 ml to 100 ml.
  - Changed references to STL from Quanterra.
  - Updated references in Quality Control Section.
  - Added Appendices with bench sheet and data review checklist.
  - Changed volume required for TSS to be up to 1L of sample, to yield 1 mg of residue weight.
  - Added requirement of some clients for a duplicate 1 per 10 samples to 9.4.3.2.
  - Added requirement of some clients to control results down to the MDL to 9.4.1.1.
  - Added reference to the balance SOP to 6.1.
  - Changed "weight loss" to "weight difference" in description of cyclical weighings.
  - Removed commercially prepared filters for TSS from the procedure.
  - Update to section 13 to include information on MDLs & IDCs.
  - Removal of reference to MS and MSD.

Attachment 1.

Example TDS/TS/TSS Benchsheet

TestAmerica Denver

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Batch:

Analysis

Prep Date

Anal Date

Analyst

SOP Information		Standards Information	
Number:	DENWC 0064	Source/Ver. Lot#:	
Revision:	No. 1 8/02	LCS True Value:	500
Instrument Information		Expiration Date:	
Instrument:	Mettler	Volume:	100
Balance:	K80955		

BATCH # RUN #

	2		3	4
Oven Temp In (°C):				
Date In:				
Time In:				
Date Out:				
Time Out:				
Oven Temp Out (°C):				

	Sample No.	Tare wt (g)	Sample ml	Dillution Factor	Flags	wt1 g	wt 2 g	wt3 g	Final wt (g)	diff g	Result mg/L	Tare 3rd Weight	TDS/Cond 0.55-0.5	Crucible ID	Conductivity Screen
1	MB			#DIV/0!					0.0000	-66.4751	-8475		#DIV/0!	1	0
2	LCS			#DIV/0!					0.0000	-66.521	-66521		#DIV/0!	2	0
3	LCSD			#DIV/0!					0.0000	-66.3447	-663447		#DIV/0!	3	0
4				#DIV/0!					0.0000	-65.8[illegible]	#DIV/0!		#DIV/0!	4	
5				#DIV/0!					0.0000	-6[illegible].3607	#DIV/0!		#DIV/0!	5	
6				#DIV/0!					0.0000	-72.[illegible]612	#DIV/0!		#DIV/0!	6	
7				#DIV/0!					0.0000	-67.4[illegible]76	#DIV/0!		#DIV/0!	7	
8				#DIV/0!					0.0000	-[illegible].5022	#DIV/0!		#DIV/0!	8	
9				#DIV/0!					0.0000	-68.9017	#DIV/0!		#DIV/0!	9	
10				#DIV/0!					0.0000	-69.1186	#DIV/0!		#DIV/0!	10	
11				#DIV/0!					0.0000	-68.2941	#DIV/0!		#DIV/0!	11	
12				#DIV/0!					0.0000	-65.9714	#DIV/0!		#DIV/0!	12	
13				#DIV/0!					0.0000	-66.3788	#DIV/0!		#DIV/0!	13	
14				#DIV/0!					0.0000	-69.5109	#DIV/0!		#DIV/0!	14	
15				#DIV/0!					0.0000	-67.5462	#DIV/0!		#DIV/0!	15	
16				#DIV/0!					0.0000	-75.8229	#DIV/0!		#DIV/0!	16	
17				#DIV/0!					0.0000	-69.6923	#DIV/0!		#DIV/0!	17	
18				#DIV/0!					0.0000	-68.0323	#DIV/0!		#DIV/0!	18	
19				#DIV/0!					0.0000	-66.7626	#DIV/0!		#DIV/0!	19	
20				#DIV/0!					0.0000	-68.775	#DIV/0!		#DIV/0!	20	
21				#DIV/0!					0.0000	-70.1337	#DIV/0!		#DIV/0!	21	
22				#DIV/0!					0.0000	-66.0608	#DIV/0!		#DIV/0!	22	
23				#DIV/0!					0.0000	-66.4472	#DIV/0!		#DIV/0!	23	
24				#DIV/0!					0.0000	-67.8151	#DIV/0!		#DIV/0!	24	

EXAMPLE ONLY

Attachment 2.

Example VSS/VS/VDS Benchsheet

TestAmerica Denver

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Batch:

Analysis

Prep Date

Anal Date

Analyst

SOP Information		Standards Information	
Number: DEN-WC-0064		Source/Ver. Lot#:	5164-07
Revision:	No. 2.1 12\99	LCS True Value:	100
Instrument Information		Expiration Date:	Feb-08
Instrument:	K80955	BATCH #	
Balance:	28	RUN #	

	1	2	3	4	5
Oven Temp In (°C):					
Date In:					
Time In:					
Date Out:					
Time Out:					
Oven Temp Out (°C):					

Sample No.	Tare wt (g)	Sample ml	Dillution Facto	Flags	wt 1 g	wt 2 g	wt 3 g	Final wt (g)	Take 3rd Weight	TSS	wt 1 after ignition (g)	wt 2 after ignition (g)	wt 3 after ignition (g)	Take 3rd	Final residue (g)	Result (mg/L)
								0.0000		#DIV/0!						
								0.0000	0	#DIV/0!						
								0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						
			#DIV/0!					0.0000	0	#DIV/0!						

Example

Attachment 3.

Data Review Checklist

TestAmerica Denver

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

WET CHEMISTRY DATA REVIEW CHECKLIST FOR GRAVIMETRIC METHODS

Test Name/Method #: _____ **Analysis Date:** _____

SOP #: _____ **Analyst:** _____ **Instrument:** _____

Client	Lot / Sample Numbers	Matrix	Batch Number	Special Instructions
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD

	Yes	No	N/A	2nd Level
A. Balance, Oven, and DI Water QC Checks				
1. Was the balance calibration verified before and after processing samples and noted in the "Balance Calibration Log" for the date(s) the samples were processed?				
2. Was the oven temperature within method requirements and recorded in the "Oven Temperature" logbook for the date(s) the samples were processed?				
3. Was the daily conductivity check of the deionized water recorded in the "Conductivity Logbook"?				
B. Method Requirements				
1. If sample is visibly oily, was this noted on the benchsheet?				
2. Was final residue weight within minimum/maximum requirements?				
3. Were the initial and final drying dates and times recorded on the benchsheet and were all samples dried for at least one hour?				
C. Sample Results				
1. Were sample analyses done within holding time?				
2. Were special client requirements met?				
3. Were data that were manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures?				
4. Do the prep and analysis dates in QuanTIMS reflect the actual dates?				
5. Are all data being reported highlighted on the benchsheet?				
Are raw data copies prepared and scanned?				
D. Preparation/Matrix QC				
1. Method blank < RL for all reported samples > 10 X RL?				
2. LCS run for batch and within QC limits?				
3. DU run for batch and RPD < 20% for samples >5 X RL?				

Analyst: _____ **Date:** _____

Comments: _____

2nd Level Reviewer : _____ **Date:** _____

Comments: _____

L:\QA\Edit\FORMS\Wet Chemistry\Gravimetric Review Checklist 12-08-07

Draft

TestAmerica Denver

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TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Title: Total Cyanide by EPA Method 335.4 and Amenable Cyanide by EPA 335.1.

Approvals (Signature/Date):

David M. Elkin 2/1/10	Adam W. Alban 03 Feb 10
Dave Elkin — Date	Adam Alban — Date
Wet Chemistry Supervisor	Health & Safety Manager / Coordinator
Karen Kuoppala 02-02-2010	Robert C Hanisch 2/5/10
Karen Kuoppala — Date	Robert C. Hanisch — Date
Quality Assurance Manager	Laboratory Director

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Facility Distribution No. _____ **Distributed To:** _____

1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This procedure is for the determination of:

Analyte	CAS Number
Total Cyanide	57-12-5

1.1.2 This procedure is applicable to drinking, ground, surface and saline waters, domestic and industrial wastes.

1.1.3 This procedure detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine total cyanide as described in EPA 335.4 and amenable cyanide as described in EPA 335.1.

1.1.4 This procedure describes the reduced volume version of the methods and uses the same reagents and molar ratio to meet the quality control and performance requirement stated in the method.

1.1.5 Dynamic Range
The approximate working range extends from 0.01 mg/L to 0.4 mg/L (0.5 mg/kg to 20 mg/kg). Samples with higher concentrations are analyzed with dilution. Current method detection limits are given in the laboratory LIMS system.

2.0 Summary of Method

2.1 Cyanide, as hydrocyanic acid (HCN) is released from samples by means of reflux-distillation under acidic condition and absorbed in a scrubber containing sodium hydroxide (NaOH) solution. The cyanide concentration in the scrubber solution is determined using an automated analyzer. The cyanide is converted to cyanogen chloride by reactions with Chloramine-T that subsequently reacts with pyridine and barbituric acid to give a red-colored complex. The color intensity which is proportionate to the cyanide concentration is measured at 570 nm.

3.0 Definitions

3.1 Cyanide: The term "cyanide" refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN- by the various chemical methods. These compounds include both simple and complex cyanides.

4.0 Interferences

4.1 Oxidizing agents such as chlorine will destroy cyanide. Sodium arsenite is used to remove chlorine interferences.

4.2 Some unidentified organic compounds may oxidize or form decomposition products during chlorination, giving higher results for cyanide after chlorination

than before chlorination; this gives a negative value for cyanide amenable to chlorination. Examples include samples from petroleum refineries, the steel industry, and pulp from paper processing. The weak acid dissociable method should be used for these samples.

4.3 Samples that contain sulfide compounds may produce hydrogen sulfide during the distillation and interfere with color development. This is treated by adding an excess of cadmium chloride to the sample prior to distillation, which removes sulfur by precipitation as cadmium sulfide. Filter the sample before analysis.

4.4 Chlorine added to the sample for amenable cyanide must be completely destroyed before distillation. Otherwise, it may distill over and destroy the non-amenable cyanide. Chlorine present in samples from chlorinated sources will also destroy cyanide and must be destroyed before distillation.

4.5 Nitrate and/or nitrite may react with organic compounds during distillation to form cyanide. Sulfamic acid is added to remove the nitrate and/or nitrite interference.

4.6 Samples containing surfactants may foam excessively during distillation.

4.7 High carbonate concentrations may react violently when sulfuric acid is added to the samples during distillation.

4.8 Aldehydes, glucose, and other sugars may convert cyanide to cyanohydrin during distillation.

4.9 Amino acids may distill with the cyanide and interfere with the analysis.

4.10 Fatty acids may interfere by forming soaps in the absorption solution.

4.11 Thiocyanate greater than 10 mg/L may interfere.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Potassium cyanide and sodium cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, and dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Potassium Hydroxide	Corrosive Poison Reactive	2 mg/m3 - ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting and diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness and swelling. Greater exposures cause severe burns with possible blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm - ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat and upper respiratory tract and in severe cases, pulmonary edema, circulatory failure and death. Can cause redness, pain and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric acid	Corrosive Poison Irritant	1mg/m3 TWA	Inhalation symptoms may include irritation of the nose and throat, and labored breathing. Swallowing can cause severe burns of the mouth, throat, and stomach, leading to death. Can cause sore throat, vomiting, and diarrhea. Skin contact can cause redness, pain, and severe burn. Eye contact can cause blurred vision, redness, pain and severe tissue burns.
Calcium hypochlorite	Strong oxidizer	None listed	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting.
Glacial acetic acid	Corrosive Poison Flammable Irritant	10 ppm TWA	Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Swallowing can cause severe injury leading to death. Skin contact may include redness, pain, and skin burns. Eye contact may cause severe eye damage followed by loss of sight.
Sulfamic acid	Corrosive Irritant	None listed	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting.
Chloramine-T	Irritant	None listed	May cause irritation to the mucous membranes and upper respiratory tract, skin and eyes.
Barbituric acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as a potential health hazard; do not ingest.
Bismuth Nitrate	Oxidizer	None	May cause irritation to the respiratory tract, skin and eyes.
Silver Nitrate	Corrosive Poison Oxidizer	0.01 mg/m3 (TWA) for silver metal dust and fume as Ag	Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns, and eye damage.
Sodium Asenite	Poison/ Carniogen	0.01 mg/m3 TWA	Ingestion symptoms may include abdominal pain. burning sensation in the throat and chest, vomiting, diarrhea, dizziness, headache, or shock or collapse. Inhalation can cause coughing. headaches. laboured breathing and sore throats. This chemical MAY BE ABSORBED and cause redness and pain. Arsenic compounds are know human carcinogens with chronic exposeure.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3 Build-up of pressure in the distillation apparatus will cause the hot, acidic solution to spray out of the thistle tube. In case vacuum is lost, the condensers must be opened to prevent build-up of pressure. If the solution overflows onto the heating block, turn it off. Unplug and replace the heating mantle when it cools.

5.4 All distillations are to be performed with adequate ventilation.

5.5 Exposure to chemicals must be maintained as low as reasonable achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit. For cyanide amenable to chlorination, the chlorination step will also be performed in a fume hood.

5.7 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Denver associate. The situation must be reported immediately to a laboratory supervisor and the Health and Safety Officer.

6.0 Equipment and Supplies

6.1 Instrumentation

- Alpkem Automated Segmented Flow Analyzer
  - Autosampler
  - Proportioning pump
  - Injection module
  - Colorimeter with 570 nm filter and 10 mm flow cell
  - WinFlow Software
  - Debubblers
  - Miscellaneous tubing and reaction coils.
- Midi-distillation apparatus consisting of 100 mL distillation tubes, cold-finger condensers, absorption tubes, and associated apparatus.
- Vacuum pump.
- Recirculating chiller.

6.2 Supplies

- Disposable auto-sampler vials or culture tubes for samples.
- Eppendorf pipettes, various sizes.
- Volumetric flasks, class A, various sizes.
- Volumetric pipettes, class A, various sizes.
- Miscellaneous laboratory apparatus and glassware.

7.0 Reagents and Standards

All Standards purchased from vendors are NIST traceable. Reagents used in the lab for standard preparation must meet ACS specifications.

7.1 Cyanide Calibration Stock Standard, 1,000 mg/L

7.1.1 This standard is purchased commercially.

7.1.2 Alternatively, it can be made as described here.

7.1.2.1 Dissolve 2.51 g of dried (103 °C) potassium cyanide and 2.0 g potassium hydroxide in water and dilute to 1,000 mL.

7.1.2.2 This stock solution will be standardized initially and every 30 days thereafter as described below.

7.1.2.3 All intermediate and working standard concentrations are adjusted from the nominal concentrations shown below to the exact concentrations based on the results of the monthly standardization.

7.2 Standardization of the Stock Cyanide Solution

7.2.1 Indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 mL acetone. This indicator is purchased commercially.

7.2.2 Silver nitrate (AgNO3) titrant: 0.0192 N: Obtain a commercially prepared certified standard.

7.3 Cyanide Standardization

7.3.1 Add 10 mL of the 1000 mg/L Cyanide Stock Standard (Section 7.1) solution to a 500 mL Erlenmeyer flask. Dilute to 250 mL with deionized water.

7.3.2 Add 5-7 drops of p-dimethylaminobenzalrhodanine indicator solution.

7.3.3 Titrate with standard silver nitrate, AgNO3, to the first change in color from a canary yellow to a salmon hue.

7.3.4 Prepare a blank in a similar fashion. Add 250 mL of deionized water to a 500 mL Erlenmeyer flask.

7.3.5 Add 5-7 drops of p-dimethylaminobenzalrhodanine indicator solution. Titrate with standard AgNO3 to the first change in color from a canary yellow to a salmon hue. The standardization should be done in duplicates.

7.3.6 Calculate the true stock cyanide concentration as follows:

$$\text{mg/L Stock Cyanide} = \frac{[(A - B) \times 1000]}{\text{mL of sample}}$$

A = Volume of $AgNO_3$ for titration of sample, mL
B = Volume of $AgNO_3$ for titration of blank, mL

7.3.7 If the verification result is within 97% of the initial value, place the date and initials of the analyst verifying the standard in the Comment box of the standard in the Standards Log. A new Standards Log entry is not required.

7.3.8 If the verification result is less than 97% of the initial value, place the date and initials of the analyst verifying the standard in the Comment box of the standard in the Standards Log.

7.3.9 Create a "new" standard in the Standard Log for this standard using the new concentration from the verification process.

7.3.10 Prepare a label for the stock solution with the name of the analyst, date of verification, expiration date (one month beyond the date of re-

standardization), lot number, 1% (0.25N) NaOH, and the actual stock cyanide concentration.

7.3.11 The true concentration of the stock cyanide solution after standardization with silver nitrate is used to prepare intermediate and working standards. This concentration does not always equal 1000 mg/L. The dilution factor relative to the stock standard is provided to aid in the calculations, where:

[True Working] = [True Stock] / dilution factor

7.4 Intermediate Standard I, 50 mg/L (20x dilution from stock):
Pipette 5.0 mL 1,000 mg/L calibration stock standard (Section 7.1) into a 100 mL volumetric flask. Dilute to volume with 1% (0.25 N) sodium hydroxide. Prepare every 7 days.

7.5 Calibration Standards

7.5.1 Working Standard, 1.0 mg/L

7.5.1.1 Pipette 2.0 mL intermediate standard I (Section 7.4) into a 100 mL volumetric flask.

7.5.1.2 Dilute to volume with 1% (0.25N) sodium hydroxide and mix. Prepare daily.

7.5.2 Initial Calibration Standards

Dilute the 1.0 mg/L cyanide working standard with 1% (0.25N) sodium hydroxide as follows:

Standard Level	Intermediate	Aliquot (mL)	Final Volume (mL)	Concentration (mg/L)
1	1 mg/L	10.0	25	0.40
2	1 mg/L	10.0	50	0.20
3	1 mg/L	5.0	50	0.10
4	0.1 mg/L	2.0	4.0	0.05
5	1 mg/L	1.0	50	0.02
6	1 mg/L	0.5	50	0.01
7	N/A	0	50	0.00 (Blank)

Calculate the exact concentration for each calibration curve standard by dividing the exact working cyanide standard concentration by the dilution factors shown above if stock concentration is different from 1.0 mg = 1.0 ml.

7.6 Continuing Calibration Verification Standard (CCV), 0.2 mg/L:
The level 2 calibration standard described in Section 7.5.2 is used as the working CCV standard.

7.7 Second-Source Standards

7.7.1 Initial Calibration Verification (ICV) Stock Standard, 1,000 mg/L:

The second-source standard is obtained from a different source than the calibration standards. It is prepared and standardized as described in Section 7.2 for the primary standard. This standard is available commercially.

7.7.2 Intermediate ICV (second-source) Standard, 10 mg/L:
Pipette 1.0 mL 1,000 mg/L ICV stock into a 100 mL volumetric flask. Dilute to volume with 1% (0.25N) sodium hydroxide. Prepare every 7 days.

7.7.3 Working ICV (second-source) Standard, 0.10 mg/L
Spike 1 mL of the 10 mg/L intermediate into a 100 mL volumetric flask and fill to the mark with 1% (0.25N) NaOH.

7.8 Pyridine-Barbituric Acid Solution (per OI Manual)

7.8.1 In a hood, place 15 g barbituric ($C_4H_4N_2O_3$) acid in a 1000 mL volumetric flask and add about 100 mL deionized water, rinsing down the sides of the flask.

7.8.2 Place on a magnetic stirrer and add a stir bar.

7.8.3 Add 75 mL pyridine while mixing.

7.8.4 Carefully add 15 mL concentrated hydrochloric acid while mixing.

7.8.5 Add 500 mL of DI water and stir until the barbituric acid is dissolved.

7.8.6 Dilute to volume with deionized water and filter through a 0.45 µm filter.

7.8.7 Store in an amber bottle.

7.8.8 Expires 6 months from preparation.

7.9 Phosphate Buffer Solution 1M (per OI Manual)
Dissolve 138 g sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_20$) in deionized water and dilute to 1000 mL.

7.9.1 Add 4 mL of Brij-35 to the solution and mix gently.

7.9.2 Store at 4°C.

7.9.3 Filter the solution through a 0.45 µm filter.

7.9.4 This solution expires 3 months from preparation.

7.10 Chloramine-T (per OI Manual)

7.10.1 Dissolve 1.0 g Chloramine-T in deionized water and dilute to 250 mL.

7.10.2 Prepare fresh daily.

7.11 Sodium Hydroxide, 10N

7.11.1 Dissolve 400 g sodium hydroxide in deionized water.

7.11.2 Cool to room temperature, dilute to 1000 mL, and mix well.

7.11.3 Store in a plastic bottle. Solution is commercially available

7.12 Sodium Hydroxide, 2% wt/wt (0.5N)

7.12.1 Dissolve 20 g sodium hydroxide in deionized water.

7.12.2 Cool to room temperature, dilute to 1000 mL, and mix well. Store in a plastic bottle.

7.13 Sodium Hydroxide Dilution Solution, 1% wt/wt (0.25N)

7.13.1 Dissolve 10 g sodium hydroxide in deionized water.

7.13.2 Cool to room temperature, dilute to 1000 mL, and mix well. Store in a plastic bottle.

7.14 Sulfuric acid, concentrated.

7.15 Sulfuric acid, 0.02 N

7.15.1 In a 2000 mL volumetric flask, carefully add 1 mL concentrated sulfuric acid to approximately 1900 mL deionized water.

7.15.2 Dilute to final volume of 2000 mL with deionized water and mix. Solution is commercially available.

7.16 Bleach
Fragrance free commercial liquid bleach is purchased and used in place of the Calcium Hypochlorite solution.

7.17 Magnesium Chloride solution
This reagent is purchased though an approved vendor.

7.18 Acetate buffer

7.18.1 Dissolve 410 g sodium acetate trihydrate in approximately 450 mL deionized water.

7.18.2 Adjust the pH to 4.5 with glacial acetic acid and dilute to final volume of 500 mL with deionized water.

7.19 Ascorbic acid crystals.

7.20 pH test strips.

7.21 Lead acetate test paper.

7.22 Potassium iodide-starch test paper.

7.23 Boiling chips.

7.24 Sulfamic Acid, 10% wt/wt
Dissolve 10 g sulfamic acid in 100mL of deionized water. Mix well. Expires 1 year from preparation.

7.25 Cadmium carbonate powder; used to remove sulfide interference.

7.26 Brij-35 Start-Up Solution:
Concentrated Brij-35 is a buffer solution obtained from the equipment vendor. The start-up solution is prepared by diluting 1 mL of the Brij-35 concentrate to 500 mL with reagent water.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters[1]	HDPE, Glass	500 mLs	Cool 4 ± 2°C	48 hours ** 14 Days	40 CFR Part 136.3
Waters[1]	HDPE, Glass	500 mLs	NaOH, pH > 12; Cool 4 ± 2°C	14 Days	40 CFR Part 136.3

[1] Add 1.2 g of ascorbic acid per liter of sample if residual chlorine is present.

** **NOTE:** If the client sample arrives unpreserved the sample need to be checked for interferences (Section 10.1). If there are interferences, treat the sample and preserve immediately. If there are no interferences preserve with NaOH to a pH of >12 and follow the 14 day holding time. Document the preservation using an observation Nonconformance Memo (see SOP# DV-QA-0033).

9.0 Quality Control

9.1 Sample QC: The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< Rpt. Limit or < 5% of sample concentration
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples	Statistical Limits [4], but no more than 85-115% recovery.
Matrix Spike (MS)[2]	1 in 10 or fewer samples	Statistical Limits [4],but no more than 75-125% recovery.
MS Duplicate (MSD)[2]	1 in 10 or fewer samples	Statistical Limits [4],but no more than 75-125% recovery.
High Distilled Standard (HDS) (0.4 mg/L)	1 in 20 or fewer samples	± 10% of true value
Low Distilled Standard (LDS) (0.10 mg/L)	1 in 20 or fewer samples	± 10% of true value

[1] LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] The sample selection for MS/MSD are randomly selected, unless specifically requested by a client....predetermined by the extraction lab.
[3] Analytical and QC samples (MB, LCS, MS/MSD)
[4] Statistical control limits are updated annually and are updated into LIMS.

9.1.1 Method blank: Add 50 mL of 1% (0.25N) NaOH into a distillation flask immediately prior to distillation. For solid samples, weigh 1.0 g of Ottawa Sand into a distillation flask and add 50 mL 1% (0.25N) NaOH.

Corrective Action: The corrective action for method blank failures is redistillation and reanalysis of all samples in the batch. If there is insufficient sample for reanalysis, a Nonconformance Memo must be prepared and the client contacted by the laboratory Project Manager.

9.1.2 LCS: Spike 5 mL of the 1.0 mg/L working standard (7.5.1) into a distillation flask filled with 50 mL 1% (0.25N) NaOH. For solid samples, weigh 1.0 g of Ottawa Sand into a distillation flask and add 50 mL 1% (0.25N) NaOH.

Corrective Action: If the LCS fails, redistill and reanalyze all samples in the batch. If reanalysis is not possible, a Nonconformance Memo must be prepared and the client contacted by the laboratory Project Manager. See the TestAmerica Denver Policy, Quality Assurance Program, DV-QA-003P for additional guidance.

9.1.3 MS/MSD: Measure 50 mL of sample into a distillation flask. Spike the aliquot with 5 mL of the 1.0 mg/L cyanide standard (7.5.1). The matrix spike and matrix spike duplicate are prepared in the same manner. Both the matrix spike and matrix spike duplicate are taken through the distillation and analysis process.

Corrective Action: If MS/MSD recoveries exceed LIMS historical limits for total cyanide, the Method of Standard Additions may be employed to analyze all samples associated with a particular QC batch. Consult your Supervisor, a Technical Specialist, QA Manager, or if contractually required, the client before proceeding. Because MS/MSD results may not have a direct bearing on other samples in the batch, the appropriate corrective action is generally governed by specific project requirements. At a minimum, QC failures will be noted as anomaly and discussed in the final report.

9.1.4 High and Low Distilled Standards (HDS & LDS), 0.4 mg/L and 0.10 mg/L Standards are distilled to monitor the efficiency of the distillation process and verify the linearity of the curve. The high distilled standard is prepared by spiking 20 mL of the 1.0 mg/L working standard (7.5.1) into a volumetric flask that is then filled to 50 mL with 1% (0.25N) NaOH. The low distilled standard is prepared by spiking 5 mL of the 1.0 mg/L working standard (7.5.1) into a volumetric flask that is then filled to 50 mL with 1% (0.25N) NaOH.

Corrective Action: Distilled standard failure results in re-distillation and reanalysis of all associated samples. One possible

exception is the situation in which recoveries are greater than 110% and cyanide was not detected in the samples. In that case, a Nonconformance Memo should be prepared and the failure noted in the report together with the sample results without taking other corrective action.

9.1.5 Linear Calibration Range (LCR) standard (0.05 mg/L)
The LCR is performed initially by each analyst and then verified every six months. The linear calibration range standard is distilled. The standard is prepared by spiking 2.5 mLs of the 1.0 mg/L working standard (7.5.1) into a volumetric flask that is then filled to 50 mL with 1% (0.25N) NaOH.

Acceptance Limits: The acceptance limits for the LCR standard are ± 10% of the true value.

9.2 Instrument QC

9.2.1 Initial Calibration Verification (ICV) / ICB

9.2.1.1 Immediately after the initial calibration, the calibration is verified using a second-source ICV standard (see preparation in Section 7.7) and an initial calibration blank ICB (1% NaOH).

9.2.1.2 The measured result for the ICV must be within 10% of the expected value, and the ICB must be less than the reporting limit.

Corrective Action: If these criteria are not met, check the accuracy of the standards and recalibrate.

9.2.2 Continuing Calibration Verification (CCV) / CCB

9.2.2.1 A blank CCB (1% NaOH) and standard check CCV (see preparation in Section 7.5) are required after every 10 or fewer samples and at the end of the run.

9.2.2.2 Standard checks (ICV/CCV) must be within 10% of the expected value.

9.2.2.3 Blanks must be less than the reporting limit.

Corrective Action: If either continuing calibration check fails, all samples since the last successful calibration check must be reanalyzed.

10.0 Procedure

10.1 Sample Preparation and Pre-Treatment for Sulfide

10.1.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample

matrix, radioactivity, and chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo (see SOP# DV-QA-0033) and is approved by a Technical Specialist and QA Manager. Depending on the severity of the change and prior arrangements, the client shall be notified.

10.1.2 Check aqueous samples for sulfide prior to distillation using lead acetate paper.

10.1.2.1 Moisten the paper with 2 or 3 drops of acetate buffer, and then place 1 drop of sample on the paper.

10.1.2.2 A dark color indicates a positive test for sulfide.

10.1.2.3 Record the result as "positive" or "negative" on the bench sheet.

10.1.3 If the samples test positive using lead acetate paper, treat 75 mL of the stabilized sample (pH > 12) with powdered cadmium chloride.

10.1.3.1 Transfer approximately 75 mL of the sample to a 150 ml beaker.

10.1.3.2 Add approximately 1 g of cadmium chloride and stir to mix.

NOTE: Yellow cadmium sulfide precipitates if the sample contains sulfide.

10.1.3.3 Allow the precipitate to settle.

10.1.3.4 Test another drop of the treated sample with lead acetate paper.

10.1.3.5 If the paper indicates the presence of sulfide, repeat the addition of cadmium chloride and re-test.

10.1.3.6 Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper.

10.1.3.7 Filter the solution through a dry filter paper and from the filtrate, measure the sample aliquot to be used for analysis.

NOTE: Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

10.1.4 It is not imperative that all standards be distilled in the same manner as the samples (noted in EPA method 335.4 Sect. 10.2).

10.1.5 The filter papers are contaminated with cadmium. Use the designated disposal container for these filters.

10.1.6 If the client has specifically indicated that aldehydes may be present, 2 mL of 3.5% ethylenediamine is added to the sample upon receipt.

10.2 Cyanide Amenable To Chlorination Sample Preparation

10.2.1 Two sample aliquots are required for the determination of cyanide amenable to chlorination. The first aliquot is distilled for total cyanide (see Section 10.3), the second aliquot is chlorinated under an alkaline condition prior to distillation and is used to determine cyanide not amenable to chlorination.

10.2.1.1 Check the pH of samples with pH test strips. Record the results on the bench sheet.

10.2.1.2 Measure the sample aliquots to be chlorinated (including all quality control samples) into 100 mL beakers.

10.2.1.3 For water samples, use 50 mL of sample.

10.2.1.4 For soil samples, use 1.0 g of sample and add 50 mL 1% (0.25N) NaOH.

10.2.1.5 Clearly label the samples with the proper identification and "chlorinated" as appropriate.

Note: The chlorination process must be performed in a fume hood.

10.2.1.6 Adjust the pH of the samples in the beakers to between 11 and 12 with the 10 N Sodium hydroxide solution.

10.2.1.7 Test the samples with KI-Starch paper and add calcium hypochlorite drop-wise to sample while mixing until a positive test is obtained. A positive test is indicated by a blue or black color on the paper.

10.2.1.8 Maintain the excess chlorine level in the sample for 1 hour while keeping the pH of the samples between 11 and 12 with constant mixing (use a magnetic stirrer). Add calcium hypochlorite and sodium hydroxide as necessary.

10.2.1.9 After 1 hour, add 0.1 g portions of ascorbic acid crystals until a negative test is obtained with KI-Starch paper. Add an additional 0.1 g of ascorbic acid crystals to the sample to ensure an excess of the reagent

10.2.1.10 Transfer the contents of the beakers into distillation flasks quantitatively, rinsing with deionized water.

10.2.1.11 Proceed to section 10.3 for the distillation process.

10.3 Total Cyanide Sample Preparation and Distillation

10.3.1 Check the pH of aqueous samples with pH test strips. Record the results on the bench sheet.

10.3.2 Check the samples for oxidizing agents such as chlorine.

10.3.2.1 Place one drop of sample on a strip of potassium iodide (KI)-starch test paper.

10.3.2.2 A blue color indicates the need for treatment. Record the result as "positive" or "negative" on the benchsheet.

10.3.2.3 If a positive test is obtained, add a few crystals at a time of ascorbic acid.

10.3.2.4 Mix the sample.

10.3.2.5 Retest until a drop of sample produces no color on the indicator paper.

10.3.2.6 Add an additional 0.1 g of ascorbic acid in excess.

10.3.3 Measure 50 mL of the sample into the distillation flask.

Note: 0.25g of sodium arsenite is added to the sample, and batch QC at this time for a specific clients requirement (for matrix interferences)

10.3.4 Place 25 mL of 2% sodium hydroxide into the absorption tubes.

10.3.5 Assemble the distillation apparatus. All distillations are to be performed under the slot hood.

10.3.6 Turn on the vacuum pump and chiller. Also be sure that the slot hood is operating.

10.3.7 Adjust the vacuum to provide a flow rate of approximately 2-3 bubbles per second (i.e., this is approximately 1/8-1/4 inch of foam in the scrubber) in the distillation flask.

10.3.8 Verify that there are no leaks in the system by observing the flow into the absorber tube. The flow rate may not remain constant during the distillation; readjust as necessary.

10.3.9 Add 2 mL of 10% sulfamic acid solution (7.24) through the thistle tube. Allow to mix for 3 minutes.

10.3.10 Slowly and carefully, add 2.5 mL concentrated sulfuric acid through the thistle tube. Rinse the tube with a little deionized water and allow to mix for 3 minutes.

10.3.11 Add 2 mL of magnesium chloride solution (7.17) and mix. If excessive foaming is observed, add additional magnesium chloride.

10.3.12 Turn on the controller and heat the samples to boiling. While distilling the samples, carefully watch to make sure that vacuum is maintained on all of the stills. Adjust the flow as necessary.

10.3.13 Allow samples to reflux for 1.5 hours.

10.3.14 After 1.5 hours of refluxing,-allow the samples to cool for 15 minutes while air is flowing.

10.3.15 Remove the absorption tube from the distillation apparatus. Rinse the inside and outside of the bubbler into the tube with deionized water.

10.3.16 Remove the flask and rinse their contents into waste stream F. Residue not removed by this method must be scrubbed out.

10.3.17 Dilute the sodium hydroxide in the absorption tube to 50 mL with deionized water and store in plastic vials.

10.3.18 Place each batch of distillates in a box and store the samples at 4°C until they are analyzed.

10.3.19 At the end of the day, turn off the hood, vacuum, and chiller.

10.3.20 Proceed to Section 10.4 for colorimetric analysis of the distillates.

10.4 Instrument Set-Up & Calibration

10.4.1 Instrument Stabilization (per Alpkem)

10.4.1.1 Connect the reagent pump tubes to a reagent bottle containing the Brij-25 start-up solution (7.26).

10.4.1.2 Start the pump, allowing the start-up solution to flow through the entire system.

10.4.1.3 Make sure that the flow cell of the detector is purged of all bubbles and the flow is stable and free from surging.

10.4.1.4 Once a stable flow is achieved, connect the reagent pump tubes to their respective reagent bottles, as shown in the schematic in Appendix IV.

10.4.1.5 Allow the reagents to flow through the entire system, then, once again, verify that the flow cell of the detector is purged of all bubbles.

10.5 Initial Calibration

10.5.1 Calibration is performed daily or each time the instrument is set up using the standards shown in Section 7.5.

10.5.2 A minimum of five standards and a blank are required for the calibration (the high standard may be dropped if needed and sample dilutions performed appropriately).

10.5.3 The calibration function is calculated by least-squares linear regression, and the correlation coefficient must be > 0.995 and the absolute value of the intercept must be lower than ± 1/2 the value for the reporting limit.

Corrective Action: If the correlation coefficient is < 0.995 or the absolute value of the intercept is too large, locate and correct the problem and re-calibrate the instrument.

10.5.4 The peak height of the synchronization (sync) standard must be > 150,000.

Corrective Action: If the peak height is < 150,000, the flow cell of the instrument must be cleaned (consult manufacturer's instructions), and then the instrument must be recalibrated.

10.5.5 Additional calibration information can be found in the Corporate TestAmeica's Calibration Curve document CA-Q-S-005.

10.5.6 Initial Calibration Checks

10.5.6.1 Immediately after the initial calibration, the calibration is verified using a second-source ICV standard and an initial calibration blank (ICB, 1% NaOH).

10.5.6.2 The measured result for the ICV must be within 10% of the expected value, and the ICB must be less than the reporting limit.

Corrective Action: If these criteria are not met, check the accuracy of the standards and recalibrate.

10.5.7 Continuing Calibration Checks

10.5.7.1 A blank CCB (1% NaOH) and standard check CCV are required after every 10 or fewer samples and at the end of the run.

10.5.7.2 Standard checks (ICV/CCV) must be within 10% of the expected value. Blanks must be less than the reporting limit.

Corrective Action: If either continuing calibration check fails, all samples since the last successful calibration check must be reanalyzed.

Calibration Controls	Sequence	Control Limit
Calibration Standards	5-point (minimum) linearity	≥0.995 correlation coefficient
Initial Cal. Verification (ICV)	Immediately after the calibration	± 10% of the expected value
Initial Cal. Blank (ICB)	Immediately after the calibration	Less than the reporting limit
Cont. Cal. Verif. (CCV)	Prior to / after every 10 injections	± 10% of the expected value
Cont. Cal. Blank (CCB)	Prior to / after every 10 injections	Less than the reporting limit
Matrix Spike & Matrix Spike Duplicate (MS/MSD)	1 in 20 or fewer samples	≤ 20% RPD

10.6 Sample Analysis

10.6.1 Following instrument set up and calibration, the sample distillates are analyzed in exactly the same manner as the calibration standards. The routine run sequence is as follows:

Cal 0.00 ppm
Cal 0.01 ppm
Cal 0.02 ppm
Cal 0.05 ppm
Cal 0.10 ppm
Cal 0.20 ppm
Cal 0.40 ppm
Second-source ICV
ICB
High concentration distilled standard
Low concentration distilled standard
LCS / LCSD
Method blank
6 samples (may include MS/SD)
CCV
CCB
10 samples (may include MS/SD)
CCV

CCB
Additional cycles of 10 samples with CCV/CCB
Closing CCV
Closing CCB

10.7 Instrument Shut-Down

10.7.1 Disconnect the reagent lines and put all of them into the DI water, except the buffer line.

10.7.2 The Buffer line should be put into the bridge.

10.7.3 Rinse all tubes for at least 5 min.

10.7.4 Rinse with Kleenflow Base for 5 min.

10.7.5 Rinse tubes with appropriate rinses for 5 min.

10.7.6 Turn off instrument and pump.

10.7.7 Raise platens.

10.7.8 Empty Waste

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{ICV / CCV, LCS/ HDS, LDS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.3 Cyanide Amenable to Chlorination:

Amenable Cyanide = Total CN Unchlorinated Result – Treated Result

If the chlorinated aliquot shows more cyanide than the unchlorinated aliquot, a corrective action and/or a discussion in the final report is required. Iron-cyanides can cause this to occur. Weak acid dissociable cyanide would be a better method for these types of samples.

11.4 Total Cyanide Calculation

11.4.1 All routine calculations for total cyanide are performed by the instrument data system, provided dilutions and other information have been correctly entered.

11.5 Reporting Final Results

Final results are routinely reported in mg/L for aqueous samples and in mg/kg for solid samples. Results can also be reported as ug/L or ug/kg if there are special project instructions requiring it.

Note: Unless special instructions indicate otherwise, samples less than the reporting limit are reported as ND.

11.6 All data are subject to two levels of review, which is documented on the checklist shown in Attachment 2.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted every 6 months as follows:

12.1.1 Prepare seven samples at three to five times the estimated MDL concentration.

12.1.2 Digest and analyze the MDL standards as described in Section 10.

12.1.3 Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.

12.1.4 MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS. See Policy # DV-QA-005P for further details concerning MDL studies.

12.1.5 The current MDL value is maintained in the TestAmerica Denver LIMS.

NOTE: All personnel must perform an MDL study as part of their initial demonstration of capability (IDOC)

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of capability (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows:

12.2.1 Four aliquots of the QC check sample (independent source from the calibration) are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration standard.

12.2.1.1 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.1.2 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.2 A linear calibration range must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected (See Section 9.1.5).

Note: This requirement is fulfilled by the analysis of the method blank, high distilled sample, low distilled sample, and the linear calibration range standard.

12.2.3 MDL study must be performed per analyst.

12.2.4 A Quality Control Standard (QCS) must be performed initially and on a quarterly basis thereafter. This requirement is fulfilled by the use of the ICV that is performed daily.

12.2.5 Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use, has the required experience, and has successfully analyzed initial demonstration samples (see SOP # DV-QA-0024 for details).

13.0 Pollution Control

13.1 In general, the quantity of chemicals purchased by Test America Denver is based on expected usage during its shelf life. The volume of reagents and standards prepared for this procedure reflects anticipated usage.

13.2 Bismuth Nitrate is substituted for cadmium carbonate in the procedure.

13.3 Source reduction is achieved through the use of micro-distillation followed by an automated colorimetric determination.

13.4 The volume of hazardous waste is minimized through proper segregation and management of the various waste streams generated by this procedure

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees

will abide by this method and the policies in section 13 of the Environmental Health and Safety Manual for "Waste Management and Pollution Prevention."

14.2 The following waste streams have been identified for this method:

- Cyanide standardization waste – Aqueous Alkaline (E)
- Distilled sample – Aqueous Acidic (F)
- Distillate – Aqueous Alkaline (E)
- Alpkem process waste – Aqueous Alkaline, contains pyridine (E)
- Contents of sampler cups – Aqueous Alkaline (E)
- Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

Note: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 USEPA Method 335.4, Determination of Total Cyanide by Semi-Automated Colorimetry, Revision 1.0, August 1993.

15.2 USEPA Method 335.1, Cyanides, Amenable to Chlorination (Titrimeteric; Spectrophotometric), Approved for NPDES, 1974.

16.0 Method Modifications:

N/A

17.0 Attachments

Attachment 1: Cyanide Preparation Example Bench Sheet
Attachment 2: Data Review Checklist
Attachment 3: Cyanide Distillation Apparatus
Attachment 4: Alpkem Manifold Schematic

18.0 Revision History

- Revision 0, dated 23 February 2009

- Revision 1, dated 05 February 2010
  - Basic Annual Review
  - Added sodium arsenite to the hazardous chemical table in section 5.
  - Added client method change note to section 10.3.
  - Changed waste disposal to correct waste stream in section 10.3.16.

Attachment 1.

Cyanide Preparation Example Bench Sheet

TestAmerica Denver

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

CYANIDE PREPARATION BENCHSHEET
Rev Date: 6/11/2008

Analyst:		SOP# :	DV-WC-0003	LCS/MS/MSD Information *	
Date:		Rev # :		Source:	
Batch #:				Verification/Lot #:	
MS #:		Balance ID:		Concentration:	
Prep Time:				Expiration Date:	

Reagent/Standard Preparation: See attached *Laboratory Bench Sheet for Cyanide Standards*

SAMPLE PREPARATION INFORMATION

☐ **Water** Initial sample volume = 50 mL

☐ **Solid** Initial sample weight is 1.0 ± 0.1 grams
Actual sample weight is recorded below.**

Lot #	Work Order	pH	Sulfide Check (+ or -)	Cl_2 Check (+ or -)	Initial Wt/Vol** (grams)	Final Volume mL	Prep Dilution	Comments (Standard True Value)
						50		
						50		
						50		
						50		
						50		
						50		
						50		
						50		
						50		
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						50		
						50		

* The sample for the MS & MSD is chosen by the prep analyst.

QA\Edit\Logbooks\Wet Chemistry\CN Preparation Benchsheet 6-11-08

Attachment 2.

Data Review Checklist

TESTAMERICA Denver

Wet Chemistry Data Review Checklist
For Tests with Calibration Curves

Test Name/ Method #: _____ **SOP #** _____

Instrument: _____ **Analyst:** _____ **Analysis Date:** _____

Client	Lot / Sample Numbers	Matrix	Batch Number	Special Instructions
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Minimum of five standards in ICAL or as specified in method?				
2. Correlation coefficient ≥ 0.995 ?				
3. Second-source ICV analyzed, and recovery 90-110%?				
4. ICB analyzed immediately after the ICV & results < the RL?				
5. CCV analyzed after every ten samples & recovery ± 10% of true value?				
6. CCB analyzed after every CCV & results < RL?				
B. Sample Results				
1. All samples greater than highest calibration standard diluted and reanalyzed?				
2. Do associated RLs/MDLs reflect dilutions or limited sample volume?				
3. All reported results bracketed by in control CCV results?				
4. Sample analyses done within holding time?				
5. Initial pH checks documented for all samples?				
6. Preparation bench sheet completed and included in package?				
7. Special client requirements met?				
8. Were data manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures?				
9. Do the prep and analysis dates in QuanTIMS reflect the actual dates?				
10. Are all data being reported highlighted on the benchsheet?				
11. Raw data copies prepared and scanned?				
12. Manual integrations done properly?				
C. Preparation/Matrix QC				
1. Method blank < RL or all reported samples > 20x blank have NCM?				
2. LCS run for batch and within QC limits ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within 10%?				

Analyst: _____ **Date:** _____

_____

_____

_____

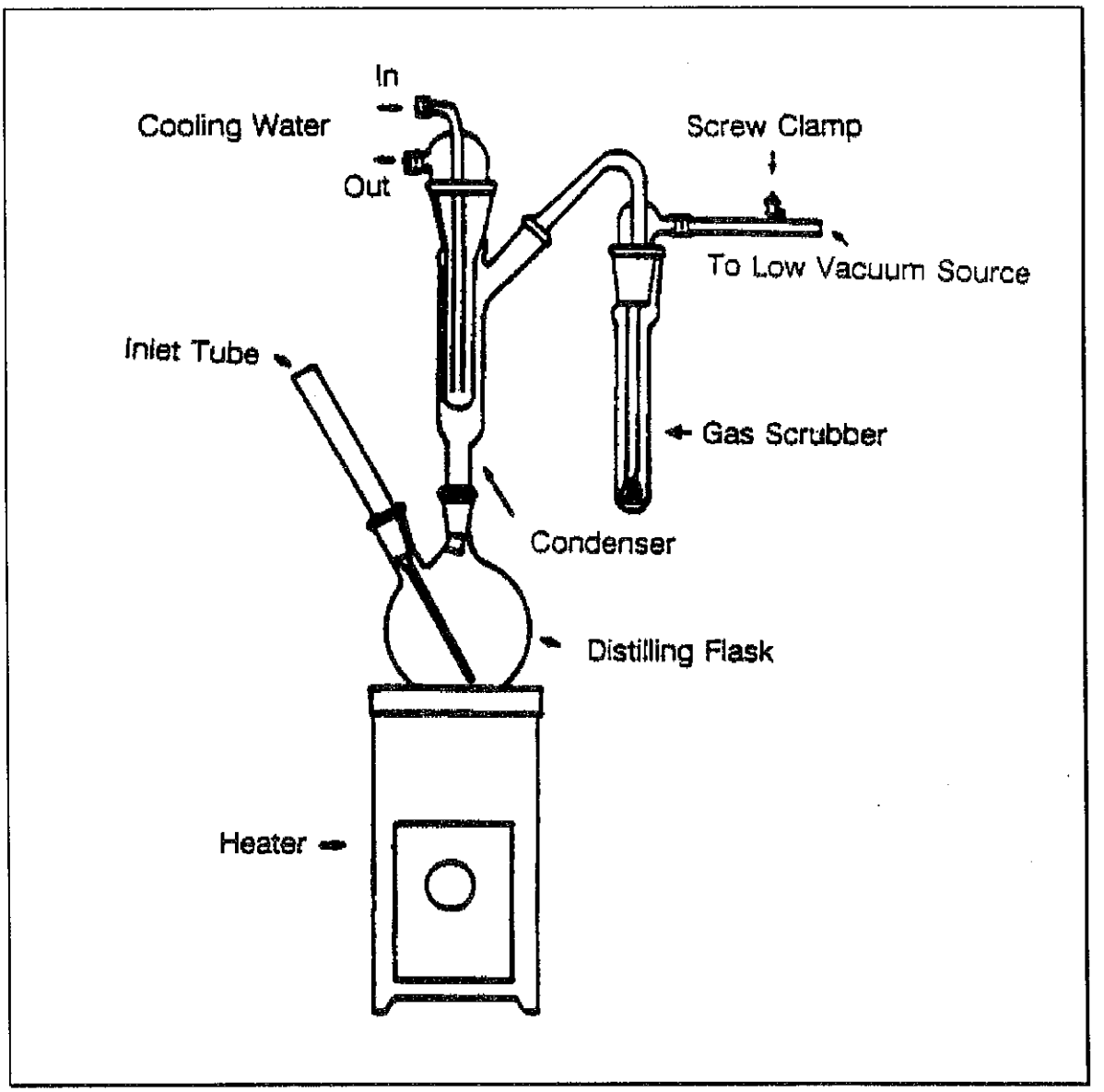
2nd Level Reviewer : _____ **Date:** _____

2/11/09 Version
QA\Edit\Forms\Wet Chemistry\Calib Curve Checklist

Company Confidential & Proprietary

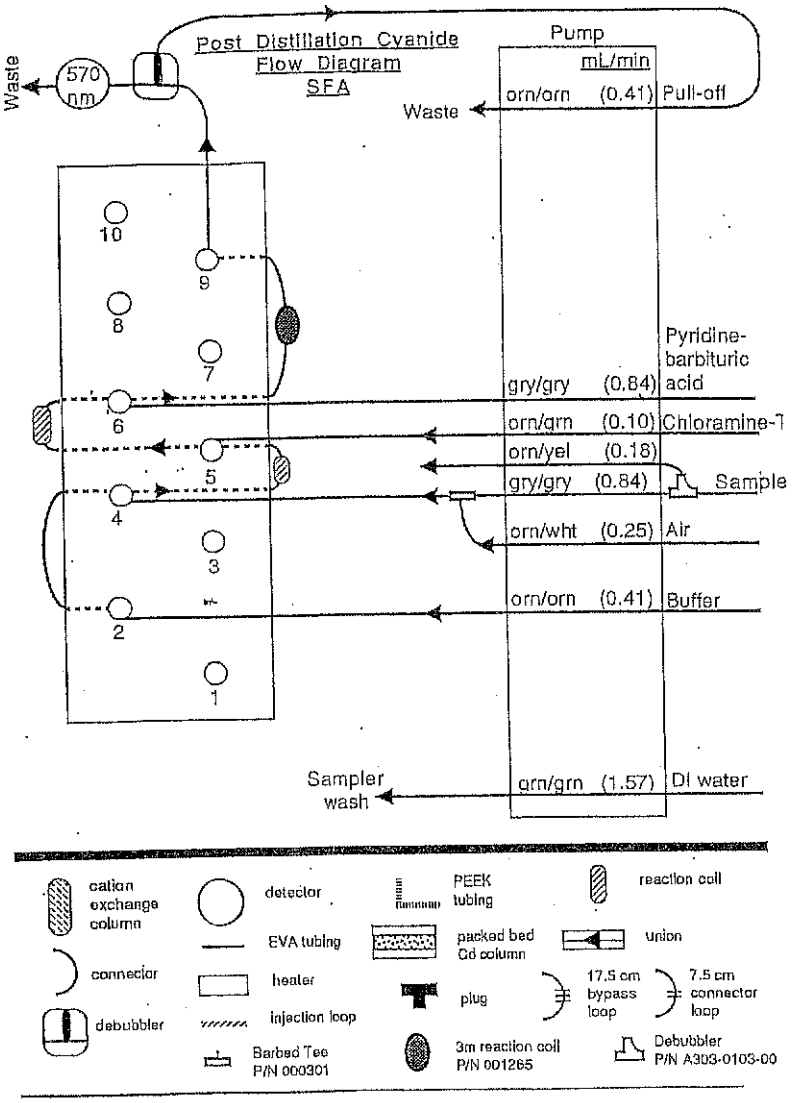
Attachment 3.

Cyanide Distillation Apparatus



Attachment 4.

Alpkem Manifold Schematic



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Title: Alkalinity by Manual Titration [EPA 310.1, SW9040B, SM2320B, SM4500-H+ B]

Approvals (Signature/Date):

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Dave Elkin — Date
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Richard Clinkscales — 3/31/09
Richard Clinkscales — Date
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Robert C. Hanisch — Date
Laboratory Director

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1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This procedure is to be used for the determination of alkalinity. The different forms of alkalinity (total, bicarbonate, carbonate, and hydroxide) can also be calculated.

Analyte	CAS Number
Alkalinity	N/A

1.1.2 This method is applicable to samples with an alkalinity greater than about 1200 mg/L as calcium carbonate require a reduced volume or stronger titrant in order to keep the titrant volume to a reasonable amount.

2.0 Summary of Method

2.1 Samples are analyzed by each method simultaneously on an automated titrator as follows:

2.1.1 The pH is determined electrometrically with a glass electrode in combination with a reference electrode. The special glass used in the electrode develops a voltage across it that depends on the pH of the solution being analyzed. The voltage is measured and converted to pH by calibration against buffers of known pH.

2.1.2 Alkalinity is determined by titration of the sample with a standardized acid to specified endpoints (pH 8.3 and 4.5). Alkalinity is calculated from the volume of acid required to reach the endpoints and is traditionally reported as calcium carbonate. Samples for alkalinity should not be altered (i.e., filtered or diluted).

3.0 Definitions

3.1 **pH** - At a given temperature, the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Because of the ionic interactions in all but very dilute solutions, it is necessary to use the "activity" of the hydrogen ion and not its molar concentration. The approximate equivalent to molarity can be presumed only in very dilute solutions. A logarithmic scale is used for pH in order to express a wide range of hydrogen ion activities. Neutral pH is 7.0 at 25 °C, while acidic pH's are <7 and basic pHs are >7.

3.2 **Alkalinity** – A measure of the acid-neutralizing capacity of water.

4.0 Interferences

4.1 The pH response of most glass electrodes is imperfect at both ends of the scale. The indicated pH value of highly alkaline solutions, as measured with the glass electrode, will be too low. The indicated pH value of salts and strong acids having

a pH less than 1 will often be higher than the true pH value. Interferences can be minimized by the selection of the proper electrodes for these conditions. For example, sodium may interfere at pH > 10, and is controlled by using a "low sodium error" electrode.

4.2 The pH electrode may exhibit slow or noisy response with high purity waters due to the lack of ionic strength.

4.3 Coatings of oil and particulate matter may impair electrode response.

NOTE: If the electrode becomes coated with oil, immerse in a mild detergent solution, rinse well with deionized water, and recalibrate. If this fails, try rinsing in 10% HCl.

4.4 Temperature variations will change the pH of the samples and also affect electrode response. Electronic temperature correction must be used to correct for electrode response.

4.5 Salts of weak organic and inorganic acids will contribute to alkalinity. If the alkalinity is intended to be a measure of carbonate and bicarbonate only, the presence of these substances will cause high results.

4.6 The pH 4.5 is the routine endpoint for total alkalinity. This assumes the normal carbon dioxide/bicarbonate/carbonate/hydroxide mass action interrelationships for natural waters. Other types of waters can have other interrelationships that might dictate the use of a different endpoint.

4.7 Samples not in equilibrium with the atmosphere may exhibit changes in pH and in the distribution of the various forms of alkalinity when exposed to the atmosphere. The sample containers should be filled completely and kept closed until just prior to the analysis. The analysis should be performed as soon as possible.

4.8 Particulates in the sample may affect the alkalinity results. This interference can cause an error in the ion balance calculation.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m3 (TWA)	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Magnetic stirrer and stir bars.
- Beakers
- Burette
- Combination pH Electrode – Epoxy-covered glass, with temperature correction, Ross Sure-Flow or equivalent.
- Pipette calibrated to 10.0 mL, and disposable tips.
- Miscellaneous laboratory apparatus and glassware.

7.0 Reagents and Standards

7.1 All of the standard materials are obtained from commercial sources, and must be NIST traceable.

7.2 **pH Buffers:** 4, 7, and 10.

7.3 Alkalinity Standards:

7.3.1 Sodium Carbonate solution (1N)
This standard is purchased commercially.

7.3.2 Sodium Carbonate solution (200 mg/L as CaCO3)
Pipette 4mL of the 1N Sodium Carbonate Solution into a 1 liter volumetric flask. Bring to volume with de-ionized water.

7.3.3 Sodium Carbonate solution (2000 mg/L as CaCO3)
Pipette 40mL of the 1N Sodium Carbonate Solution into a 1 liter volumetric flask. Bring to volume with de-ionized water.

7.3.4 0.02 N Sulfuric Acid (Alkalinity Titrant)
Purchase from a commercially available source.

7.3.5 0.1 N Sulfuric Acid (Alkalinity Titrant)
Purchase from a commercially available source.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Method	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
2320B	HDPE	1 liter	Cool 4 ± 2°C	14 Days	40 CFR Part 136.3
9040B	HDPE	1 liter	None	Analyze Immediately	40 CFR Part 136.3

9.0 Quality Control

9.1 Sample QC - The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< Rpt. Limit
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	± 10% of the true value
Sample Duplicate - Alkalinity[1]	1 in 20 or fewer samples	≤ 10% RSD

[1] Some programs (e.g., South Carolina and North Carolina) require duplicates to be analyzed at a 10% frequency.

9.2 Instrument QC

Initial Check and Continuing Calibration Verification

- Calibration verification standard (CCV) and a continuing calibration blank (CCB) are to be analyzed after ten samples and at the end of the run.
- The 200 mg/L standard (7.3.2) is used for the alkalinity Initial check and CCV.
- The pH 7 buffer is used for the pH CCV.
- A blank is not appropriate for pH analysis.

10.0 Procedure

10.1 Sample Preparation

Allow the sample to come to room temperature before analyzing.

10.2 Calibration

10.2.1 Initial Calibration for pH

- The pH meter is calibrated each day of operation.
- Be sure that the reference electrode has been filled with 3M potassium chloride.
- Calibration of the pH meter is done using pH 4,7, and 10 buffers.
    - Fill the first four tubes in the autosamples with the following order of samples: pH 4 buffer, pH 7 buffer, pH 10 buffer, and deionized water.
    - Click on the button "PH CALIBRATION 4-7-10" and follow the screens to calibrate.
    - When calibration has finished, go to titrator and choose "examine calibrations." Print the calibration if it is valid.
    - Open up "documents" and select the bottom option (Alk-new) to update the buffers and standards. Update info and print this out.

10.3 Sample Analysis

10.3.1 Place 10 mL of sample into a suitable glass container and measure the pH.

10.3.2 If the pH is >8.3, titrate to pH 8.3 and record the volume of titrant.

10.3.3 Continue to titrate to pH of 4.5.

10.3.4 Record the volume of titrant.

10.3.5 Calculate the results according to the calculation section below.

11.0 Calculations / Data Reduction

11.1 Standardization of Alkalinity Titrant

$$N_{ACID} = \frac{N_{BASE} \times V_{BASE}}{V_{ACID}}$$

Where:

N_{ACID} = Normality of titrant
N_{BASE} = Normality of Sodium Carbonate
V_{BASE} = Volume of Sodium Carbonate titrated, mL
V_{ACID} = Volume of titrant needed for titration, mL

11.2 pH values are recorded directly from the titrator printout.

11.3 Three values for alkalinity will be printed if the pH is greater than 8.3. Record the values at pH 8.3 and 4.5 on the bench sheet. The third value is the difference and is ignored. Note that some results will be printed in scientific notation; be careful to check this when recording results.

11.4 If the pH is less than 8.3, only one value will be printed (at pH 4.5). Record this value on the bench sheet. P alkalinity is ND on these samples.

11.5 Calculate the concentration as follows:

$$\text{Total Alkalinity, mg/L } CaCO_3 = \left(\frac{(2B - C) \times N \times 50{,}000}{\text{mL of sample}} \right)$$

Where:

B = Volume of titrant to first recorded pH, in mL.
C = Total volume of titrant added to reach a pH level 0.3 units lower.
N = Normality of acid.

11.6 Calculate the individual forms of alkalinity as follows:

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P = ND	ND	ND	T
P < T/2	ND	2P	T - 2P
P = T/2	ND	2P	ND
P > T/2	2P - T	2(T - P)	ND
P = T	T	ND	ND

Where:

T = Total Alkalinity = Alkalinity at pH 4.5
P = Phenolphthalein Alkalinity = Alkalinity at pH 8.3

11.7 Record the values for Total, Bicarbonate, Carbonate, and Hydroxide Alkalinity.

11.8 Reporting

- Alkalinity results less than 5mg/L are reported as ND. All forms of alkalinity are reported in mg/L as Calcium Carbonate.
- Report case narratives for South Carolina must include date and time of collection.
- All data are subject to two levels of review, which is documented on the checklist shown in attachments 3 and 4.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

An initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

- Prepare seven samples at three to five times the estimated MDL concentration.
- Analyze the MDL standards as described in Section 10.
- Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte. Then, calculate the MDL (single-tailed, 99% confidence level, as described in Policy # DV-QA-005P) for each analyte.
- MDL studies are repeated annually, and MDL results are stored in the laboratory LIMS system. See Policy # DV-QA-005P for further details concerning MDL studies.
- The current MDL value is maintained in the TestAmerica Denver LIMS.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows."

- Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.
- Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test

need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

- Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use, has the required experience, and has successfully analyzed initial demonstration samples (see SOP # DV-QA-0024 for details).

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

The following waste streams are produced when this method is carried out:

- Expired Chemicals/Reagents/Standards – Contact Waste Coordinator
- Titrated sample waste – Aqueous Acidic - Waste Stream F

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 pH:

- Method 9040B, "pH Electrometric Measurement", Test Methods for Evaluating Solid Waste, EPA SW-846 Third Edition, 1/95.
- Method 4500-H+, pH Value, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.

15.2 Alkalinity:

- Method 2320B, Alkalinity – Titration Method, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.
- U.S. EPA, Method for Chemical Analysis of Water and Waste, Method 310.1, Approved 1978.

16.0 Method Modifications:

Item	Method	Modification
1	310.1 & SM 2320B	The method requires an initial verification of the sulfuric acid titrant. The laboratory purchases the titrant from a commercial source and therefore does not perform additional verification.

17.0 Attachments

Attachment 1: Example Titration Calculation/Bench Sheet
Attachment 2: Example Data Review Checklist for Titrations

18.0 Revision History

- Revision 0, dated 27 March 2009

Attachment 1.

Example Data Review Titration Calculation/Bench Sheet

Analyst:	MARCIA D.	SOP Information	Second Source Information		
Date:	8:00	Number: DV-WC-25	Vendor:	Lot #:	
Batch #:			pH True Value:	Alkalinity (mg/L):	200
MS Run #:		Revision: 1.0	Conductivity True Value (umho):		

Conductivity Standard Info		Titrant Information		PH Calibration Information			
Vendor		Titrant (N H_2SO_4):	0.02	Buffer	Vendor	Lot #:	Exp. Date:
Lot Number:		Vendor:	RICCA	pH 4 Buffer	RICCA	1711278	Oct-09
True Value:		LOT #:	4353-07	pH 7 Buffer	RICCA	1302894	Feb-10
Expiration Date:		Expires:	7/31/2009	pH 10 Buffe	RICCA	1708710	Feb-09

Sample Lot/ Work order	Sample pH	Buret Start (mL)	Vol (mL)	Buret at 8.3 (mL)	Buret at 4.5 (mL)	Alkalinities (mg/L) at pH 8.3	at pH 4.5	OH^- Alkalinity	$CO_3^=$ Alkalinity	HCO_3^- Alkalinity	Total Alkalinity	% Rec.	
LCS			20			0.00	0.00						PALK
LCSD			20			0.00	0.00						
BLANK			20			0.00	0.00						

DRAFT

Attachment 2.

Example Data Review Checklist for Titrations

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Denver Wet Chemistry Data Review Checklist
For Titration Methods

Test Name/Method #: _____ **Analysis Date:** _____

SOP #: _____ **Analyst:** _____ **Instrument:** _____

Client	Lot / Sample Numbers	Matrix	Batch Number	Special Instructions
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD
				No B J G s DCS MSQC RD

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Was the normality of the titrant verified and found acceptable?				
B. Sample Results				
1. Are all sample dilutions appropriate and do associated RLs/MDLs reflect required dilutions or limited sample volume?				
2. All reported results bracketed by in control LCS or QC Sample?				
3. Sample analyses done within holding time?				
4. Initial pH check documented for all samples (if required)?				
5. Preparation benchsheet completed and included in package (if applicable)?				
6. Special client requirements met?				
7. Was data manually transcribed from instrument printouts into QuanTIMS verified 100% including significant figures?				
8. Do the prep and analysis dates in QuanTIMS reflect the actual dates?				
9. Are all data being reported highlighted on the benchsheet?				
10. Raw data copies prepared and scanned?				
C. Preparation/Matrix QC				
1. Method blank < RL or all reported samples > 10x method blank result?				
2. LCS run for batch and within QC limits?				
3. MS and/or MSD run at required frequency and within limits (if applicable)?				
4. Sample DUP run at required frequency and RPD within 10%?				

Analyst: _____ **Date:** _____

Comments: _____

2nd Level Reviewer : _____ **Date:** _____

Comments: _____

SAMPLE

TEST AMERICA RICHLAND
STANDARD OPERATING PROCEDURES

Title: Determination of Actinides by Extraction Chromatography

Approvals (Signature/Date):

Steve Wheland Technical Manager	11/26/08 Date	Dave Harbinson Health & Safety Coordinator	11/26/08 Date
Tim Armstrong Quality Assurance Manager	11/26/08 Date	Jodie Carnes Laboratory Director	12/1/08 Date

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RL-ALP-001

REVISION 1

Facility Distribution No. _____ **Distributed To:**_____

1. SCOPE AND APPLICATION

1.1. This procedure describes a method for separation and measurement of isotopic Plutonium, Americium/Curium, Thorium and Uranium from water and a variety of environmental and bioassay samples. The sample preparation consist in either direct reduction of the sample or leachate to dryness or the performance of a calcium phosphate precipitation (RL-PRP-010)

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. After the initial sample preparation the various isotopes are separated from other actinides by chromatographic resins prior to measurement by alpha spectrometry. Tracers are used to monitor chemical recoveries and yield correct analyte results.

3. DEFINITIONS

3.1. Chromatography – A method of separating and analyzing mixtures of chemical substances by chromatographic adsorption.

4. INTERFERENCES

4.1. Actinides with unresolvable alpha energies such as Np-237 and Th-230 must be chemically separated to enable measurement. This method separates these isotopes effectively. It has been demonstrated that high levels of phosphate can cause problems with these analyses, especially thorium. This is to be considered when selecting the sample preparation method.

4.2 Samples with large amounts of iron require oxidation state readjustment prior to running the americium portion of the method. This adjustment is accomplished with sulfamic and ascorbic acid. Iron (III) competes for sites on TRU and thus can diminish americium yields.

4.3 Np-237 can interfere with the Pu-242 peak if not removed from the column before eluting Plutonium.

4.4 Thorium and Uranium will not be analyzed sequentially by this procedure.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

Company Confidential & Proprietary

5.1 Specific Safety Concerns or Requirements

A vigorous reaction occurs as Sodium Nitrite is added to the sample, with fizzing and evolution of a brownish gas. Perform in a fume hood.
Do not put Hydrofluoric acid into glass containers. Always dispense HF from its original, drip-free shipping bottle.

WARNING: Hydrofluoric acid (HF) is one of the strongest and most corrosive acids known. Do not assume that dilute solutions do not require special precautions! Always double check your personal protective equipment before each use of HF. A pinhole in a glove or leaky container can cause an accident. HF burns penetrate deeply into skin and muscle tissue and cannot be treated by simply flushing the area with water. HF causes delayed burns over several hours so immediate care is essential to prevent further harm.

FIRST AID MEASURES FOR HF ACID EXPOSURE

1. Flush area with cold water for at least 15 minutes.
2. Remove contaminated clothing immediately.
3. After washing exposed skin, use gloves to rub a generous amount of calcium gluconate gel into burn area.
4. For areas too large to apply gel, use an Epsom salts solution in a concentration of ½ to 1 cup of Epsom salts in one quart of iced water. Immerse the limb into a bucket of solution or soak the solution into gauze and apply to the wound. This dressing should be replaced or re-soaked every two minutes.
5. If area affected is greater than 2 inches by 2 inches, give 6 tablets of calcium gluconate orally.
6. If area affected is greater than 4 inches by 4 inches, assume significant inhalation injury and treat accordingly.

5.1.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Hydrofluoric Acid	Poison Corrosive Dehydrator	3 ppm-TWA	Severely corrosive to the respiratory tract. Corrosive to the skin and eyes. Permanent eye damage may occur. Skin contact causes serious skin burns, which may not be immediately apparent or painful. Symptoms may be delayed 8 hours or longer. **THE FLUORIDE ION READILY PENETRATES THE SKIN CAUSING DESTRUCTION OF DEEP TISSUE LAYERS AND BONE DAMAGE.**
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Nitrite	Oxidizer Poison Reactive	None	**Danger! Strong oxidizer and toxic material. Heat, shock, or contact with other material may cause fire or explosive decomposition.** Causes irritation to the respiratory tract and systemic poisoning. Can irritate the mouth, esophagus, stomach, etc. Excessive amounts affect the blood and blood vessels. Signs and symptoms of nitrite poisoning include intense cyanosis, nausea, dizziness, vomiting, collapse, spasms of abdominal pain, rapid heart beat, irregular breathing, coma, convulsions, and death due to circulatory collapse. Causes irritation, redness and pain to the skin and eyes. May be absorbed through the skin causing systemic poisoning.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Balance, capable of reading 0.01 g.

6.2. Beakers, various sizes.

6.3. Centrifuge tubes 50 mL conical (plastic)

6.4. Extension funnel for cartridge

6.5. Filters - Whatman

6.6. Hot plate.

6.7. Pipettors, adjustable volume, capable of measuring 0.1 through 5 mL, non-critical, with disposable plastic tips.

6.8. Syringe filters

6.9. Vacuum box with disposable pipet tips

6.10. Vacuum pump and tubing

6.11. Watch glasses, various sizes.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RL-RPL-001.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. Ammonium iodide – granular – NH_4I, FW 144.96 g/mol

7.3. Ammonium Hydrogen oxalate (0.1M $NH_4HC_2O_4$) – Dissolve 6.31 g of $H_2C_2O_4 \cdot 2H_2O$ (oxalic acid) and 7.11 g of $(NH_4)_2C_2O_4 \cdot H_2O$ (ammonium oxalate) in 900 mL of reagent water, and dilute to 1 L with reagent water.

7.4. Ascorbic acid powdered form is preferred.

7.5. Ascorbic acid solution - 2.5 g. dissolved in 10 ml of reagent water. **Prepare solution each day of use (i.e. within a 24 hour period)**

7.6. Hydrochloric acid (12M) – concentrated hydrochloric acid (sp gr 1.19)

7.7. Hydrofluoric acid (28M) - concentrated hydrofluoric acid (sp gr 1.2).

7.8. Sodium Nitrite (3M) – Dissolve 207.0 g of $NaNO_2$ in 500 mL water and dilute to 1L with reagent water. Or analyst can prepare according to sample load, i.e. 2.07g of $NaNO_2$ in 5 mL reagent water and dilute to 10 mL. **Prepare solution each day of use (i.e. within a 24 hour period)**

7.9. Sodium Nitrite – granular – ($NaNO_2$), FW 69.00 g/mol

7.10. Hydrochloric acid (4M HCl) - Add 333 mL of concentrated HCl to approximately 500 mL of reagent water. Dilute to 1 liter with reagent water and mix well. **CAUTION**: Corrosive.

7.11. Hydrochloric acid (4M HCl) – 0.1M Hydrofluoric acid (0.1M HF) - Add 333 mL of concentrated HCl to approximately 500 mL of reagent water. Add 3.6 mL of HF and dilute to 1L with reagent water and mix well. **Do not prepare or store solution in glass. CAUTION**: Corrosive.

7.12. Hydrochloric acid (8M HCl) - Add 667 mL of concentrated HCl to approximately 100 mL of reagent water. Dilute to 1L with reagent water and mix well. **CAUTION**: Corrosive.

7.13. Hydrochloric acid (9M HCl) - Add 750 mL of concentrated HCl to approximately 100 mL of reagent water. Dilute to 1L with reagent water and mix well. **CAUTION**: Corrosive.

7.14. Hydrochloric acid (0.1M HCl) - hydrofluoric acid (0.05M HF) – ammonium iodide (0.1M NH_4I) solution -- Add 8.33 mL concentrated HCl and 1.78 mL of concentrated HF and 14.49g NH_4I to 400 mL of water and dilute to 1L with water. **Do not prepare or store solution in glass. Prepare solution each day of use (i.e. within a 24 hour period)**

7.15. Hydrogen peroxide (30% H_2O_2). **WARNING**: Corrosive and Oxidizer.

7.16. Nitric acid (HNO_3) Concentrated. **CAUTION**: Corrosive and Oxidizer.

7.17. Nitric acid (3M HNO_3) - Add 191 mL of concentrated HNO_3 to approximately 700 mL of reagent water. Dilute to 1L with reagent water and mix well. **CAUTION**: Corrosive and Oxidizer.

7.18. Nitric acid (3M HNO_3) - Aluminum Nitrate solution (1M $Al(NO_3)_3$) - Dissolve 375 g of aluminum nitrate non-hydrate or 212 g anhydrous aluminum nitrate in approximately 500 mL of reagent water and add 191 mL of concentrated HNO_3. Dilute to 1L with reagent water and mix well. Pass solution through a UTEVA column prior to using, to extract any uranium present.

7.19. Nitric acid (0.5M HNO_3) - Add 32 mL of concentrated HNO_3 to approximately 900 mL of reagent water. Dilute to 1L with reagent water and mix well. **CAUTION:** Corrosive and oxidizer.

7.20. Sulfamic acid (NH_2SO_3H) Caution – causes severe irritation and burns upon contact.

7.21. Sulfamic acid solution Dissolve 2.0 grams sulfamic acid in 10 ml of reagent water.

7.22. Titanium trichloride, $TiCl_3$ (Titanous Chloride) 20% solution, commercially available.

7.23. TEVA resin - prepackaged cartridges.

7.24. TRU resin - prepackaged cartridges.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2. It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RL-DR-001 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Sample Preparation:

11.1.1. If calcium phosphate precipitation is preferred, refer to SOP RL-PRP-010 (Calcium Phosphate Precipitation) for sample preparation instructions. For example urine samples for Am, Pu and U iso and environmental samples for U iso are prepared by SOP RL-PRP-010. Then proceed with step 11.2.

11.1.2. Sample residues may be reduced to dryness by evaporation. **NOTE:** For some water samples, calcium sulfate formation may occur during evaporation. If this occurs, use the calcium phosphate precipitation option, step 11.1.1.

11.1.2.1 Gently evaporate the sample to dryness and redissolve in approximately 5 mL of concentrated HNO_3. Wet ash if necessary.

11.2. Actinide Separations using Eichrom resins:

11.2.1. Redissolve the sample residue with approximately 20 mL of 3M HNO_3-1M $Al(NO_3)_3$ (load solution) and swirl to dissolve the precipitate or residue. If necessary, the beakers may be lightly warmed, if covered with a non-ribbed watch glass. Cool to room temperature.

NOTE: An additional 5-10 mL may be necessary if the precipitate volume is large. Consult supervision if more than 30 mL is required

NOTE: When Thorium is requested, and significant amounts of phosphate are suspected, increased amounts of load solution may be necessary. 40 mL of load solution is recommended for urine.

NOTE: Some samples may need to be centrifuged or filtered at this point. If there are visible solids present or suspected silicates or the possibility of other interferents the solutions must be filtered or centrifuged, otherwise the very fine mesh of the TEVA cartridges will become clogged and flow will be diminished.

NOTE: The sample must be clear of any undissolved material at this time. If this material persists contact supervision.

If only thorium is required skip to 11.3

11.2.2. Add 1 mL ascorbic acid solution to the sample and warm for approximately 5 mins.

11.2.3. Add 1.5 mL of 3M Sodium Nitrite solution to each beaker, swirling to mix and warm for approximately 5 mins.

NOTE: If additional load solution was used, add 0.5 mL of 3M sodium nitrite solution for every 5 mL addition.

11.2.4. Remove samples from heat and let cool until they are near room temperature

11.3. Separation of Thorium and Plutonium isotopes from other actinides using TEVA resin:

11.3.1. For setup and operation of a vacuum box, see procedure RL-ALP-017.

11.3.2. For each sample solution, place a TEVA cartridge on the vacuum box. If Americium and/or Uranium is also required, attach a TRU cartridge beneath the TEVA cartridge (see NOTE below). Label each cartridge with the appropriate sample ID. Place a waste collecting container in box.

NOTE: If concerns about iron are present collect the load and first rinse from this step for oxidation state adjustment prior to passing through the TRU column, otherwise the TEVA and TRU columns can be used in tandem.

11.3.3. Just prior to loading the sample, add 5 mL of 3M HNO_3 into each reservoir (to condition the resin) and pass through the cartridge with vacuum at approximately 3 ml/minute.

11.3.4. Transfer each sample solution into the appropriate cartridge reservoir, filtering if necessary, by pouring and/or by using a disposable, plastic pipet. Allow the solution to pass through the cartridge at a flow rate of 1 mL/min.

11.3.5. Rinse each beaker with 5 mL of 3M HNO_3. Transfer each rinse into the appropriate cartridge.

11.3.6. Add 15 mL of 3M HNO_3 to each reservoir and allow to pass through the cartridge at a flow rate of 3 mL per minute.

11.3.7. If Americium and/or Uranium is required, remove the TRU cartridge and set aside for step 11.4.1.

11.3.8. For Thorium: Continuing with the TEVA cartridges, add 20 mL of 9M HCl into each reservoir and allow it to pass through and collect eluate for Th analysis.

NOTE: This rinse converts the resin to the chloride form. Some Np may be removed.

11.3.9. Add 5 mL of 6M HCl solution into each reservoir and allow it to pass through the cartridge at a flow rate of 3 mL per minute. Combine this rinse with the thorium elution.

NOTE: This rinse removes neptunium and thorium from the column. The 9M HCl and 6M HCl rinses also remove any residual ferrous ions that might interfere with electrodeposition.

11.3.10. Transfer the thorium HCl solution, with 5 ml of concentrated HNO_3. to a clean beaker and evaporate to near dryness. Proceed to either the electrodeposition or micro coprecipitation procedures.

11.3.11. Place a clean, labeled centrifuge tube under each cartridge.

11.3.12. **For samples high in Neptunium-237**, elute the Plutonium with 20 ml of 8M HCl and 0.4 ml of $TiCl_3$. Mix the HCl and the $TiCl_3$ by adding 10 ml of the 8 M HCl to the column, pipetting 0.4 ml of $TiCl_3$, and then adding the remaining 10 ml of 8 M HCl. Collect the eluant and proceed with micro-coprecipitation. Electrodeposition is not an option with this eluant since the Titanium would also electrodeposit.

11.3.13. **For routine Plutonium samples**: Pipet 20 mL of 0.1M HCl-0.05M HF-0.1M NH_4I solution into each reservoir to elute the plutonium. Allow the liquid to pass through cartridge at a flow rate of 1 mL per minute.

11.3.14. Transfer each sample to a small, labeled, beaker with small amounts of concentrated HNO_3 and evaporate to dryness.

11.3.15. Wet ash each sample with concentrated HNO_3 and 30% peroxide at least once. Proceed with SOP RL-ALP-015 (Electrodeposition) or RL-ALP-016 (Coprecipitation).

11.4. Separation of Americium from Uranium using TRU resin:

11.4.1. Attach the TRU cartridge from step 11.3.7 to the vacuum box and insert the waste container.

11.4.2. Rinse the funnel and/or reservoir with 5 ml of 3M HNO_3 and allow to drain to waste and then continue with step 11.4.3.

11.4.3. If concern about iron is present slowly add to the combined load and rinse from the TEVA column 2.5 ml of sulfamic acid solution with swirling. The solution will bubble as the nitrite in the sample reacts with the sulfamic acid.

11.4.3.1. After the solution quits bubbling, add 3 ml of the ascorbic acid solution and heat the solution for approximately 3 minutes.

11.4.3.2. Allow sample to cool to approximately room temperature.

11.4.3.3. For each sample solution, place a TRU cartridge on the vacuum box. Label each cartridge with the appropriate sample ID. Place a waste collecting container in box. Condition TRU cartridge with 5 ml HNO_3 at a flow rate of approximately 3 ml/minute.

11.4.3.4. Pass the solution from step 11.4.2 through the column at a flow rate of approximately 1 ml per minute.

11.4.4. Add 5 mL of 0.5M HNO_3 to the reservoirs and allow to pass through.

NOTE: 0.5M HNO_3 is used to lower the nitrate concentration prior to conversion to the chloride form and remove the nitrite ion.

11.4.5. Remove the waste container and place a clean labeled centrifuge tube under each column to elute the Americium. If electrodeposition is requested, add a pre-filter to the column.

11.4.6. Add approximately 20 mL of 4M HCl to each reservoir to elute the americium. Allow the 4M HCl to pass through the cartridge at a flow rate of 1 mL per minute.

11.4.7. Transfer each sample to a small, clean, labeled beaker and evaporate to dryness.

11.4.8. Wet ash each sample with concentrated HNO_3 and 30% peroxide at least once. Proceed with SOP RL-ALP-015 (Electrodeposition) or RL-ALP-016 (Coprecipitation).

11.4.9. If Uiso required, continuing with the TRU cartridge, place the waste container into the vacuum box.

11.4.10. Rinse the cartridge reservoirs with 25 mL of 4M HCL-0.1M HF and allow the solution to pass through the cartridge at a flow rate of 3 mL per minute.

NOTE: 4M HCL-0.1M HF is used to selectively remove any residual Thorium that may be present on the TRU cartridge and leave the Uranium.

11.4.11. Place clean, labeled centrifuge tubes below each cartridge.

11.4.12. Add 10 mL of 0.1M $NH_4HC_2O_4$ to elute the Uranium and allow to pass through the cartridge at a flow rate of 1 mL per minute.

11.4.13. Transfer each sample to a small, clean, labeled beaker and evaporate to dryness.

11.4.14. Wet ash each sample with concentrated nitric acid and 30% peroxide. Proceed with SOP RL-ALP-015 (Electrodeposition) or RL-ALP-016 (Coprecipitation).

11.4.15. Rinse each cartridge with 5-10 mL of water prior to disposal.

NOTE: Consult technical supervision prior to attempting the electrodeposition of Americium by this method. Special cleanup is need to remove organics that "poison" the electrodeposition procedure.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete computer calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. POLLUTION PREVENTION

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. This method produces only 120 mL of aqueous waste from the column separation steps. This method produces less than 10% of the waste volume produced by traditional actinide separation procedures. In addition, this method does not produce mixed organic waste as is produced by more traditional actinide separation procedures.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Health and Safety Coordinator should be contacted if additional information is required.

16. REFERENCES

16.1. Horwitz, E.P., et al., 1993, "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," **Analytica Chimica Acta**. 281, 361-372.

16.2. Horwitz, E.P., et al., 1992, "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography," **Analytica Chimica Acta**. 266, 25-37.

16.3. Maxwell, S.L., et al., October 1993, "High Speed Separations to Measure Impurities in Plutonium-238 Oxide and Trace Radionuclides in Waste," **34th ORNL-DOE Conference on Analytical Chemistry in Energy Technology,** Gatlinburg, TN.

16.4. Maxwell, S.L., et al., May 2002, "Rapid Separation Methods for Bioassay Samples," **Eichrom Technologies, Inc. North American Users' Group Workshop,** Westminster, CO.

16.5. Nelson, D., November 1992, "Improved Methods for the Analysis of Radioactive Elements in Bioassay and Environmental Samples," **38th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry**, Santa Fe, NM.

16.6. RadCalc DB, Users Guide, Richland, latest revision.

16.7. RL-QAM-001 Quality Assurance Manual, latest revision

16.8. Associated SOPs

16.8.1. RL-DR-001 Review of Bioassay and Environmental Data, latest revision.

16.8.2. RL-RPL-001 Reagent and Non-Radioactive Standard Labeling, latest revision

16.8.3. RL-ALP-016 Coprecipitation of Some Actinides on Neodymium Fluoride for Alpha-Particle Spectrometry, latest revision

16.8.4. RL-ALP-015 Electrodeposition of Actinides, latest revision

16.8.5. RL-PRP-010 Urine and Water Sample Preparation by Calcium Phosphate Precipitation, latest revision

16.8.6. RL-ALP-017 Chromatographic Column Preparation, latest revision

17. MISCELLANEOUS

17.1. Responsibilities

17.2. Analyst: Implements SOP as written.

17.3. Counting Room: Performs review on raw instrument data.

17.4. Technical Data Reviewer: Performs final data review.

17.5. Project Manager: Confirms final review and prepares data for reporting to client.

17.6. QA Manager: Performs product quality assessments as defined in the Quality Assurance policies.

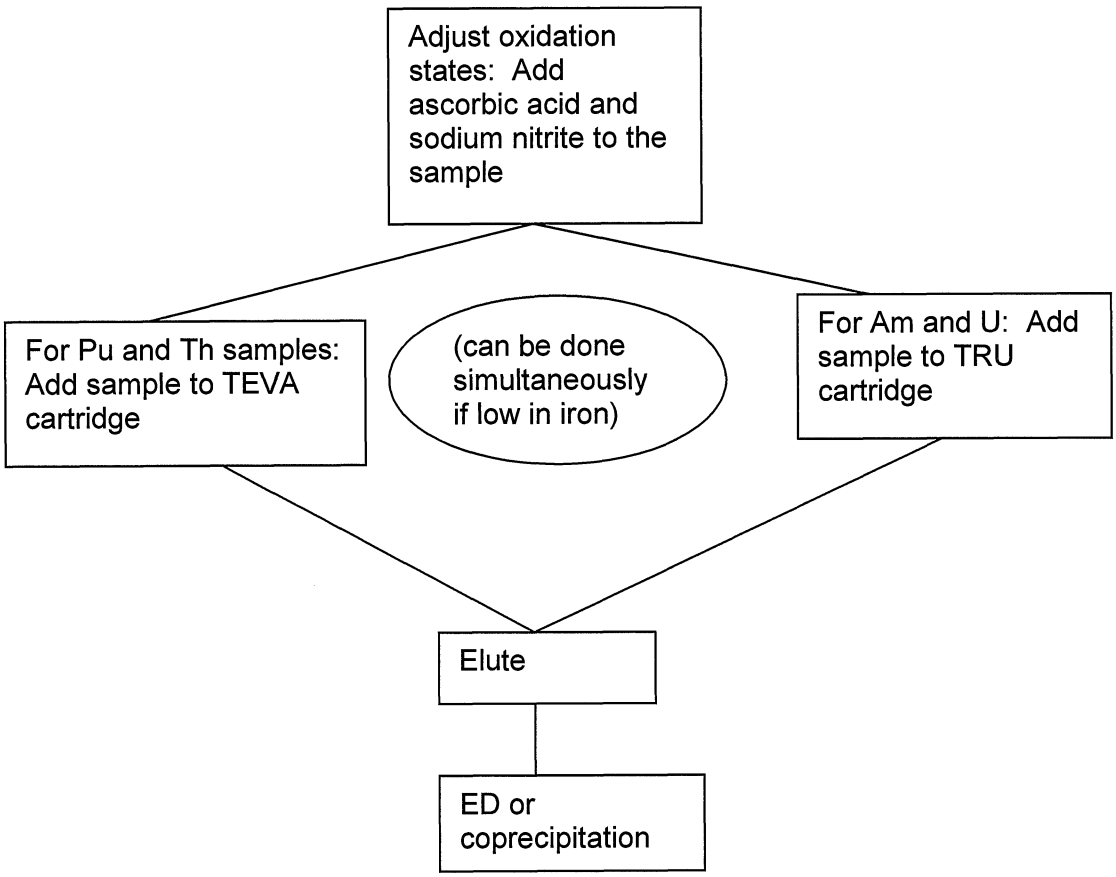
17.7. Records Management/Documentation

17.7.1. All records generated by this analysis will be filed and kept in accordance with the Richland facility of TestAmerica QA policies for records management and maintenance.

18. REVISION HISTORY

- Revision 1, 11/20/2008
  - Added sequential Uranium analysis steps.

19. PROCEDURAL FLOW CHART



Title: Separation of Uranium by Extraction Chromatography

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5067 Rev 8

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1. SCOPE AND APPLICATION

1.1. This procedure describes a method for separation and measurement of isotopic uranium (U-234, U-235 and U-238) from water, soil, digestates and urine.

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. An initial calcium phosphate precipitation concentrates and removes actinides from water, soil and urine samples. Uranium isotopes are separated from other actinides by chromatographic resins prior to measurement by alpha spectrometry. Tracers are used to monitor chemical recoveries and yield correct analyte results.

3. DEFINITIONS

3.1. Decant – To pour off supernate gently without stirring up the precipitate.

3.2. Supernate – Liquid standing above a precipitate.

4. INTERFERENCES

4.1. Actinides with unresolvable alpha energies such as Np-237 and U-234 must be chemically separated to enable measurement. This method separates these isotopes effectively.

4.2. Very high levels of phosphate in the sample may cause an interference. Adjusting the amount of phosphate added to coprecipitate the actinides may be necessary in these cases.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all associates. The following requirements must be met:

5.1.1. Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.1.2. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.1.2.1. The following materials are known to be **corrosive**: Ammonium hydroxide, hydrochloric acid, and nitric acid.

5.1.2.2. The following materials are known to be **oxidizers**: Aluminum nitrate, calcium nitrate and nitric acid.

6. EQUIPMENT AND SUPPLIES

6.1. Balance, capable of reading 0.01 g.

6.2. Beakers, various sizes and/or vials with caps.

6.3. Bottles, plastic, squirt for reagent use.

6.4. Centrifuge.

6.5. Centrifuge tubes (50 mL), plastic.

6.6. Columns, prepackaged 2 mL columns containing UTEVA resin.

6.7. Column rack, plastic.

6.8. Cover, plastic film or watch glass.

6.9. Extension funnel for column.

6.10. Hot plate.

6.11. Pipets, transfer, disposable, plastic.

6.12. Pipettors, adjustable volume, capable of measuring 4 through 20 mL, non-critical, with disposable plastic tips.

6.13. Rod, stirring.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. Ascorbic acid, powdered form is preferred.

7.3. 9M Hydrochloric acid (9M HCl) - Add 750 mL of concentrated HCl to approximately 100 mL of reagent water. Dilute to 1 L with reagent water and mix well. **CAUTION**: Corrosive.

7.4. 1.0M Hydrochloric acid (1.0M HCl) - Add 83 mL of concentrated HCl to approximately 900 mL of reagent water. Dilute to 1 L with reagent water and mix well.

7.5. 5M Hydrochloric acid - 0.05M oxalic acid solution - Dissolve 6.3 grams of oxalic acid dihydrate in approximately 400 mL reagent water. Add 417 mL of concentrated hydrochloric acid. Cool to room temperature. Dilute to 1 L with reagent water and mix well. **CAUTION**: Corrosive.

7.6. 3M Nitric acid (3M HNO_3) - Add 191 mL of concentrated HNO_3 to approximately 700 mL of reagent water. Dilute to 1 L with reagent water and mix well. **CAUTION**: Corrosive and Oxidizer.

7.7. 3M Nitric acid - 1.0M aluminum nitrate Solution - Dissolve 375 g of aluminum nitrate nine hydrate or 212 g anhydrous aluminum nitrate in approximately 500 mL of reagent water and add 191 mL of concentrated HNO_3. Dilute to 1 L with reagent water and mix well.

In order to achieve low level uranium results, the load solution should be stripped of the uranium contamination that can be present in some lots of aluminum nitrate.

Condition a column of UTEVA resin with 3M nitric acid.

Pass the above load solution through the UTEVA column and collect in a clean container. This solution has been stripped of uranium and is ready for use in the analysis of samples.

7.8. UTEVA resin - prepackaged 2 mL column, 0.7 g 100-150 μm particle size resin.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2. It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Sample Preparation

11.1.1. Refer to SOP RICH-RC-5086 for sample preparation instructions.

11.1.2. If plutonium is requested by RICHRC5010 the 8M nitric acid load and rinse fractions are collected and taken to dryness on a hot plate.

11.2. Actininde Separations using Eichrom resins:

11.2.1. Redissolve the calcium phosphate precipitate or the evaporated water sample:

11.2.2. Add 10 mL of 3M HNO_3-1.0M $Al(NO_3)_3$ (load solution) into each beaker and swirl to dissolve the precipitate or residue.

NOTE: An additional 5 mL may be necessary if the precipitate volume is large.

NOTE: Soil and urine samples may require up to 30 mL of load solution to ensure dissolution. If the sample does not completely dissolve in 30 mL of load solution, consult supervision.

11.2.3. Add approximately 200 mg of ascorbic acid (preferably powdered) to each solution, swirling to mix. Wait for 2-3 minutes. Visually confirm that all the ascorbic acid is dissolved before proceeding.

NOTE: If the sample is not extracted within a 24 hour period, add an additional 200 mg ascorbic acid.

NOTE: For samples that require more than 15 mL of load solution, add an additional 200 mg of ascorbic acid for each 10 mL of extra load solution used.

11.2.4. Any undissolved solids remaining in the sample must be removed. Transfer samples in beakers to clean, plastic centrifuge tubes without rinsing. Centrifuge at least 5 minutes at medium-high speed. Decant the supernate to a clean, small beaker and save. Slurry the solid residue in the tube with a few milliliters of reagent water and discard to an appropriate waste container.

NOTE: The use of filtration is also permitted, e.g. syringe filter.

11.3. Separation of Uranium isotopes from other actinides using UTEVA resin:

11.3.1. Flow rates can be maintained by the use of a vacuum box.

11.3.2. For each sample solution, place a UTEVA column in a column rack. Label each column with the appropriate sample ID. Place a waste collecting container under the column.

11.3.3. Snap off the bottom plug from each column, remove the cap from each column and allow the liquid to drain. Attach a plastic extension funnel to the top of the column.

11.3.4. Pipet 15 mL of 1.0M HCl into each column to elute any residual uranium that is present in the column material. Allow the liquid to drain.

11.3.5. Just prior to loading the sample, pipet 5 mL of 3M HNO_3 into each column to condition the resin and allow the liquid to drain.

11.3.6. Transfer each sample solution into the appropriate UTEVA column by pouring and/or by using a disposable, plastic pipet. If americium/curium is required, collect the sample load and following 3M HNO_3 rinse in a clean labeled beaker for analysis by RICHRC5072.

NOTE: Do not include extra Po rinses.

11.3.7. Rinse each beaker with 5 mL of 3M HNO_3. Transfer each rinse into the appropriate UTEVA column.

11.3.8. Repeat the preceding step once, rinsing the reservoir while transferring the wash to the column. Plutonium and Americium have been removed.

11.3.9. If polonium is suspected, further rinse the column three times with 10 mL of 3M HNO_3. This is necessary for soil samples. The polonium rinses are discarded to an appropriate waste container.

11.3.10. Pipet 5 mL of 9M HCl into each column and allow to pass through.

NOTE: This rinse converts the resin to the chloride form. Some Np may be removed here.

11.3.11. Pipet 20 mL of 5M HCl-0.05M oxalic acid solution into each column and allow it to pass through.

NOTE: This rinse removes neptunium and thorium from the column. The 9M HCl and 5M HCl-0.05M oxalic acid rinses also remove any residual ferrous ions that might interfere with electrodeposition.

11.3.12. Remove the waste collection container from under the column and discard the liquid to an appropriate waste container. Place a clean, labeled beaker, vial or tube under each column. Consult with supervision for which container type to use.

11.3.13. Pipet 15 mL of 1.0M HCl into each column to elute the uranium. Allow the liquid to drain.

11.3.14. Proceed with SOP RICHRC5039 (Electrodeposition) or RICHRC5003 (Coprecipitation).

12. DATA ANALYSIS AND CALCULATIONS

12.1. For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete computer calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. POLLUTION PREVENTION

14.1. This method produces only 40 mL of aqueous waste from the column separation steps. This method produces less than 20% of the waste volume produced by traditional actinide separation procedures. In addition, this method does not produce mixed organic waste as is produced by more traditional actinide separation procedures.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Health and Safety Coordinator should be contacted if additional information is required.

16. REFERENCES

16.1. Horwitz, E.P., et al., 1993, "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," **Analytica Chimica Acta**. 281, 361-372.

16.2. Horwitz, E.P., et al., 1992, "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography," **Analytica Chimica Acta**. 266, 25-37.

16.3. Maxwell, S.L., et al., October 1993, "High Speed Separations to Measure Impurities in Plutonium-238 Oxide and Trace Radionuclides in Waste," **34th ORNL-DOE Conference on Analytical Chemistry in Energy Technology,** Gatlinburg, TN.

16.4. Nelson, D., November 1992, "Improved Methods for the Analysis of Radioactive Elements in Bioassay and Environmental Samples," **38th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry**, Santa Fe, NM.

16.5. RadCalc DB, Users Guide, STL Richland, latest revision.

16.6. STL Quality Management Plan, latest revision.

16.7. STL Richland Laboratory Quality Assurance Manual, latest revision.

16.8. STL Richland Quality Assurance Summary, latest revision.

16.9. Associated SOPs

16.9.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16.9.2. RICHRC5003 - Coprecipitation of Some Actinides on Neodymium Fluoride for Alpha-Particle Spectrometry.

16.9.3. RICHRC5019 - Preparation and Dissolution of Sediment and Soil by Microwave Bomb Digestion.

16.9.4. RICHRC5039 - Electrodepostion of Actinides.

16.9.5. RICHRC5086 – *Urine and* Water Sample Preparation by Calcium Phosphate Precipitation

17. MISCELLANEOUS

17.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

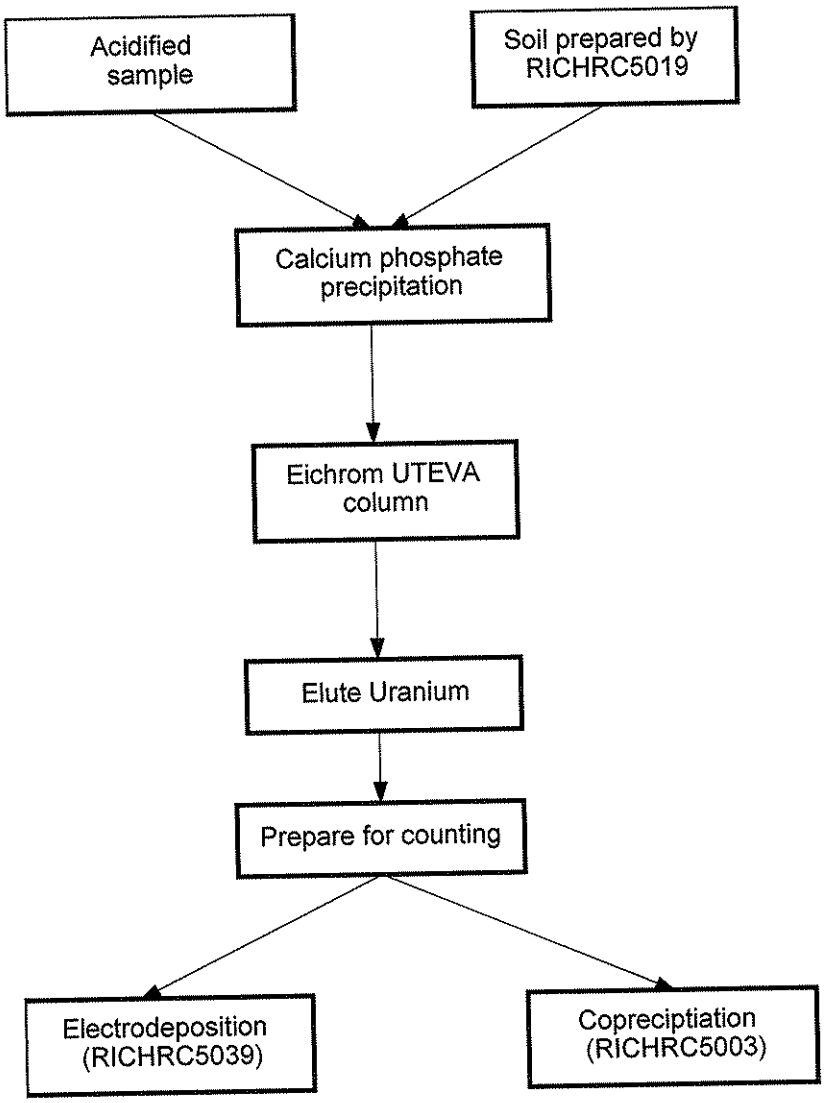
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance policies.

17.2. Records Management/Documentation

17.2.1. All records generated by this analysis will be filed and kept in accordance with STL QA policies for records management and maintenance.

17.3. Procedural Flow Chart



Title: Determination of Isotopic Thorium in Environmental Matrices

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5084 Rev 3

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1. SCOPE AND APPLICATION

1.1 This procedure describes the separation of thorium in water, air filter, sediment, and soil samples that have been digested according to the appropriate preparation procedure.

1.2 Due to the time required to perform this procedure, it is not appropriate for TAT less than 1 week.

1.3 The thorium isotopes typically reported with this method are: Th-228, Th-230 and Th-232.

1.4 Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. The residue or precipitate from the water, sediment, soil, and air filter samples are treated identically. The precipitate or residue is dissolved in strong HCl and introduced to a pre-conditioned anion-exchange column. The uranium, polonium, bismuth, and iron are adsorbed on the column while the thorium passes through. Lead is separated from thorium by passing the Th-Pb fraction (as a dilute HCl solution) through an anion-exchange column. The thorium is separated from other elements by passing the thorium fraction (as a dilute HNO_3 solution) through an anion-exchange column. At this point the thorium has been purified and is ready to be deposited for alpha spectrometry.

3. DEFINITIONS

3.1. LCS – Laboratory Control Sample

3.2. TAT – Turnaround Time

4. INTERFERENCES

4.1. None.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

- 16M HNO_3 and 30% H_2O_2 when mixed together will liberate large quantities of oxygen. If these are mixed together and the container is sealed, pressure may build up causing a pressure explosion. Always add nitric acid before adding 30% H2O2 to avoid possible vigorous reactions. Use extreme caution when wet-ashing samples.

5.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Collodion	Flammable	ACGIH 1000ppm TWA	May cause central nervous system depression. May cause liver and kidney damage. May be harmful if swallowed. Causes eye and skin irritation. May cause reproductive and fetal effects. May be harmful if absorbed through the skin. Causes respiratory tract irritation.
Ethyl Alcohol	Flammable	ACGIH 1000ppm TWA NIOSH 1000ppm TWA; 1900 mg/m^3 TWA	Causes severe eye irritation. May cause skin irritation. May cause central nervous system depression. May cause liver and kidney damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Iron Carrier	Oxidizer	ACGIH $1mg/m^3$ TWA NIOSH $1mg/m^3$ TWA	May cause severe eye irritation. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. May cause respiratory tract irritation.

Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Beakers - pyrex glass, various sizes.

6.2. Centrifuge.

6.3. Centrifuge tubes - glass or plastic, approximately 50 or 90 mL (250 mL optional).

6.4. Column - ion-exchange, straight, glass or plastic disposable with an extended reservoir.

6.5. Column rack - plastic to hold straight ion-exchange columns.

6.6. Filter paper - Whatman #1 or equivalent with a diameter to fit the planchet used.

6.7. Frit - porous polymer bed support supplied with disposable columns, used in place of glass wool.

6.8. Glass wool - pyrex brand borosilicate glass.

6.9. Graduated cylinders - various sizes.

6.10. Heat lamp.

6.11. Hot plate - variable heat.

6.12. Petri dish - plastic for holding planchets.

6.13. Pipets - transfer, plastic disposable, 2 mL volume recommended.

6.14. Pipettor - non-critical, 1 or 2 mL volume, with disposable tips.

6.15. Planchets - stainless steel, 1" or 1½", flamed or muffled overnight at 470^{0}C.

6.16. Planchet holder - cardboard, size to fit planchet.

6.17. Rods - stirring, glass, appropriate length.

6.18. Ruler - able to measure 12 cm.

6.19. Stir plate - magnetic with Teflon stir bars.

6.20. Thermometer - include range 40 - 100^{0}C.

6.21. Ultrasonic bath.

6.22. Vortex mixer.

6.23. Zeetex cloth or equivalent.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nanopure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. 14.7M Ammonium hydroxide (14.7M NH_4OH) - Concentrated. **CAUTION**: Corrosive.

7.3. 0.7M Ammonium hydroxide (0.7M NH_4OH) - Add 24 mL of concentrated NH_4OH to approximately 350 mL of reagent water. Dilute to 500 mL with reagent water and mix well. **CAUTION**: Corrosive.

7.4. Anion exchange resin - BioRad AG 1 x 8, 100-200 mesh, chloride form, or AG 1 x 8 200-400 mesh, chloride form.

7.5. Collodion (10% solution) - Add 50 mL of collodion to a mixture of 300 mL of diethyl ether and 150 mL of ethyl alcohol. Mix well. **WARNING**: Flammable.

7.6. Diethyl ether. **WARNING**: Flammable.

7.7. Ethyl alcohol, anhydrous. **WARNING**: Flammable.

7.8. 12M Hydrochloric acid (12M HCl) - concentrated. **WARNING**: Corrosive.

7.9. 8M Hydrochloric acid (8M HCl)- Add 660 mL of concentrated HCl to approximately 200 mL of reagent water. Dilute to 1L with reagent water and mix well. **CAUTION**: Corrosive.

7.10. 1.5M Hydrochloric acid (1.5M HCl) - Add 125 mL of concentrated HCl to about 500 mL of reagent water. Dilute to 1L with additional reagent water and mix well.

7.11. 30% Hydrogen peroxide (30% H_2O_2). **WARNING**: Corrosive and Oxidizer.

7.12. Iron carrier (0.3M $FeCl_3$, non-standardized) - Dissolve 81 g of ferric chloride-hexahydrate ($FeCl_3$.6H2O) to approximately 800 mL of reagent water. Dilute to 1L with reagent water and mix well.

7.13. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and Oxidizer.

7.14. 8M Nitric acid (8M HNO_3) - Add 500 mL 16M HNO_3 to approximately 400 mL reagent water. Dilute to 1L with reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.15. 18M Sulfuric acid (18M H_2SO_4) - Concentrated. **WARNING**: Corrosive.

8. SAMPLE COLLECTION, PRESERVATIVES AND STORAGE

8.1. The sample may be collected in glass or plastic containers using no preservatives. Storage of the sample prior to analysis should not exceed six months.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: *One time procedural* variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Samples are prepared by the appropriate method.

NOTE: Add 2 mL of lead carrier to each sample if lead carrier has not already been added.

11.2. If sample residue has not been wet ashed, wet ash the sample with 5-10 mL of concentrated HNO_3 and several drops of 30% H_2O_2 and evaporate to dryness. Dissolve the sample residue in 5 to 10 mL of 8M HCl and evaporate to dryness on a hot plate. Repeat once.

11.3. Separation of Thorium and Lead from Uranium and other Elements

11.3.1. Prepare an anion-exchange column, straight glass or disposable for each sample, using AG 1x8, 100-200 mesh with a bed height of 12 cm (12 mL). Follow the preparation instructions in RICHRC5018, omitting the top glass wool plug or frit.

NOTE: AG 1x8, 200-400 mesh resin may be used, but the bed height should be reduced to 6 cm (6 mL).

NOTE: All ion exchange columns used in this procedure run with stopcocks wide open. Resin of this mesh size will not dry out unless left for more than 30 minutes without any other liquid additions.

11.3.2. Condition the column by passing approximately 10 mL of 8M HCl through the column. Rinse any resin from the side of the column reservoir with 8M HCl from a wash bottle. When the acid has passed through the column, add approximately 20 mL of 8M HCl and allow to pass through the column.

11.3.3. Discard the conditioning liquid to an appropriate waste container. Place a clean, labeled beaker (250-mL size suggested) under the conditioned column.

11.3.4. **NOTE**: It may be necessary to use an ultrasonic bath to aid in the dissolution of the sample in the acid during this step and step 11.3.5. Samples may also be heated in a hot water bath to aid dissolution.

Add 20 to 30 mL of 8M HCl to the sample residue and warm on a hot plate to dissolve. Allow the sample to cool at least 10 minutes.

11.3.5. Pour the sample onto the column being careful to disturb the resin bed as little as possible. Rinse the sample beaker with three consecutive 5 to 10 mL portions of 8M HCl and add the rinses to the column. Use up to six rinses total if the salts are difficult to dissolve.

11.3.6. If undissolved salts clog the top of the resin column so that sample flow slows or stops, use a disposable plastic pipet to break up the salts, being careful to disturb the resin bed as little as possible. Be sure to use a clean pipet for each sample.

11.3.7. Wash the thorium through the column with three consecutive 20 mL portions of 8M HCl, allowing each portion to pass through the resin before adding the next. Be sure to rinse the inside of the reservoir at least once with 8M HCl during this step.

11.3.8. Evaporate the sample to dryness on a Zeetex covered hot plate to prevent spattering.

11.3.9. Dispose of the resin from the column and clean the column per procedure RICHRC5018.

11.4. Separation of Lead-210 from Thorium

11.4.1. Prepare an anion-exchange column, straight glass or disposable for each sample, using AG 1x8, 100-200 mesh with a bed height of 12 cm (12 mL). Follow the preparation instructions in RICHRC5018, omitting the top glass wool plug or frit.

NOTE: AG 1x8, 200-400 mesh resin may be used, but the bed height should be reduced to 6 cm (6 mL).

11.4.2. Condition the column by passing approximately 20 mL of 1.5M HCl through the column. Rinse any resin from the side of the column reservoir with 1.5M HCl from a wash bottle. When the acid has passed through the column, add approximately 40 mL of 1.5M HCl and allow to pass through the column.

11.4.3. Discard the conditioning liquid to an appropriate waste container. Place a clean, labeled beaker (250-mL size suggested) under the conditioned column.

11.4.4. Add 20 to 30 mL of 1.5M HCl to the sample residue and warm on a hot plate to dissolve. Allow the sample to cool at least 10 minutes.

11.4.5. Pour the 1.5M HCl sample onto the column being careful to disturb the resin bed as little as possible. Rinse the sample beaker with three consecutive 5 to 10 mL portions of 1.5M HCl and add the rinses to the column. If necessary, place in an ultrasonic bath and/or place briefly on a warm Zeetex-covered hot plate to assist in dissolution. Use up to six rinses total if the salts are difficult to dissolve.

11.4.6. Wash the thorium fraction through the column with approximately 20 mL of 1.5M HCl. Be certain to rinse the inside of the reservoir at least once. After the liquid level falls to the top of the resin bed, add **three** consecutive 20 mL portions of 1.5 M HCl. Allow each rinse to pass through the resin before adding the next.

11.4.7. Evaporate to dryness on a Zeetex covered hot plate without spattering.

11.4.8. Wet ash with 5 to 10 mL of 16M HNO_3 and several drops of 30% H_2O_2 and evaporate to dryness. Add 5 to 10 mL of 8M HNO_3 to the thorium fraction and evaporate to dryness.

11.5. Separation of Thorium from Radium and Other Salts.

11.5.1. Before proceeding, complete step 11.4.8, if not already completed.

11.5.2. Prepare an anion-exchange column, straight glass or disposable, for each sample using AG 1x8, 100-200 mesh with a bed height of 12 cm (12 mL). Follow the preparation instructions in RICHRC5018, omitting the top glass wool plug or frit.

NOTE: AG 1x8, 200-400 mesh resin may be used, but the bed height should be reduced to 6 cm (6 mL).

11.5.3. Condition the column by passing approximately 20 mL of 8M HNO_3 through the column. Rinse any resin from the side of the column reservoir with 8M HNO_3 from a wash bottle. When the acid has passed through the column, add approximately 40 mL of 8M HNO_3 and allow to pass through the column.

11.5.4. Add 20 to 30 mL of 8M HNO_3 to the sample residue and warm on a hot plate to dissolve. Allow the sample to cool at least 10 minutes.

11.5.5. Pour the 8M HNO_3 sample onto the column being careful to disturb the resin bed as little as possible. Rinse the sample beaker with three consecutive 5 to 10 mL portions of 8M HNO_3 and add the rinses to the column. If necessary, place in an ultrasonic bath and/or place briefly on a warm Zeetex-covered hot plate to assist in dissolution. Use up to six rinses total if the salts are difficult to dissolve.

11.5.6. Wash the column with three consecutive rinses of approximately 20 mL of 8M HNO_3. Be sure to rinse the reservoir with a minimum amount of 8M HNO_3. Allow each rinse to pass through the resin before adding the next. Discard the wash solution to an appropriate waste container.

11.5.7. Place a clean, labeled beaker (150-mL size suggested) under the column. Elute the thorium from the resin column with approximately 20 mL of 8M HCl. Rinse the sides of the reservoir with a minimum of 8M HCl. When liquid is within approximately 1 inch or less of the top of the resin bed, add a second 20 mL portion of 8M HCl. After the acid is within approximately one inch of the top of the resin, add a third 20 mL 8M HCl portion.

11.5.8. Place the thorium fraction on a Zeetex covered hot plate and evaporate to dryness without spattering.

11.5.9. Wet ash the residue with small portions of concentrated HNO_3 and 30% H_2O_2.

NOTE: If there is more than a slight visible residue after wet ashing, consult supervision about repeating the HNO_3 column.

11.5.10. When there is no change in the residue appearance after two successive wet ashings, proceed with RICHRC5003 to coprecipitate the sample.

NOTE: If Th-234 tracer is used, the sample must be counted by beta proportional and alpha spectrometry.

11.5.11. Dispose of the resin from the column and clean the column per procedure RICHRC5018.

12. DATA ANALYSIS AND CALCULATIONS

12.1.1. For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete computer calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1. Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in a Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in a Flammable waste container which is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. Anderson, R.F. and A.P. Fleer, 1982, "Determination of Natural Actinides and Plutonium in Marine Particulate Material", Analytica Chimica Acta, Vol. 54, pp. 1142-1147.

15.2. Beals, D.M., 1989, Development of the Procedure for the Sequential Determination of Isotopic Thorium and Lead-210 Activities in Water, Sediments, and Soil. U.S. Testing Internal Technical Report.

15.3. Beals, D.M. and J.R. Noyce, 1989, "Microwave Dissolution of Soils and Sediments with Subsequent Analysis of Some Uranium and Thorium Series Elements", U.S. Testing Technical Memorandum.

15.4. Koide, M.; Bruland, K.W. 1975, "The Electrodeposition and Determination of Radium by Isotopic Dilution in Seawater and in Sediments Simultaneously with Other Natural Radionuclides", Analytical Chemistry, Vol. 75, pp. 1-19.

15.5. Chieco, N.A., D.C. Bogen, and E.O. Knutson. eds. 1990 EML Procedures Manual, Th-01, HASL-300, 27th Edition, Volume 1. Environmental Measurements Laboratory, US Department of Energy, New York, New York.

15.6. RadCalc DB, Users Guide, STL Richland.

15.7. STL Quality Management Plan, latest revision.

15.8. STL Richland Laboratory Quality Manual, latest revision.

15.9. Associated SOPs

15.9.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

15.9.2. RICHRC5003 - Coprecipitation of Some Actinides on Neodymium Fluoride for Alpha-Particle Spectrometry.

15.9.3. RICHRC5018 - Ion-Exchange Preparation.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on all raw instrument data.

Technical Data Reviewer: Performs final data review checking of all data.

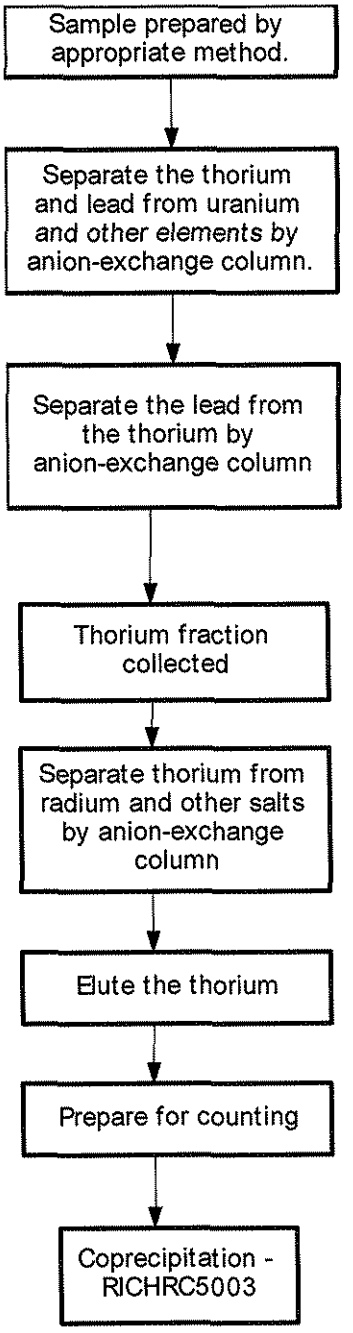
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

16.2. Records Management/Documentation

16.2.1. All records generated by this analysis will be filed and kept in accordance with STL policies and procedures for records management and maintenance.

16.3. Procedural Flow Chart



Title: Determination of Isotopic Neptunium-237 by Liquid-Liquid Extraction in all Matrices

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/4/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5009 Rev 5

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1. SCOPE AND APPLICATION

1.1. This procedure is applicable to the separation of neptunium-237 in aqueous samples and leachates from solid matrices. This procedure is valid for urine samples up to 1.5 L, and for fecal samples up to 150 g, wet weight. It has not been tested with leachates from soil samples larger than 2 g.

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. Initial coprecipitation of neptunium (Np) on lanthanum fluoride separates Np from many cations that do not form insoluble fluorides in dilute hydrofluoric acid-nitric acid.

2.2. The extraction of Np into 2-thenoyltrifluoroacetone (TTA) in xylenes depends on the quantitative reduction of Np with Fe(II) to form extractable Np(IV) while other interfering ions are stabilized in unextractable oxidation states. Trivalent actinides and lanthanides do not interfere in solutions of appropriate concentrations of nitric acid.

The Np-239 tracer is supported by an equal activity of its parent, Am-243. After separation the short lived Np-239 is counted within 36 hours. The Am-243 parent if effectively removed in the liquid-liquid extraction.

After sample preparation, neptunium is separated from the bulk of the matrix with a lanthanum fluoride precipitation. The precipitate is wet ashed with nitric and perchloric acids to remove fluoride and other anionic interferences. It is then dissolved in 1M HNO_3 from which it is extracted into TTA after reduction to Np(IV). Hexavalent uranium and Pu(III) remain in the aqueous phase. Trivalent actinides and lanthanides do not interfere. Elements extracted into the TTA along with Np(IV) are Fe(III), Zr(IV) and Pu(IV). They are separated from the Np(IV) by stripping the Np(IV) from the TTA into 8M HNO_3. The 8M HNO_3 phase is wet ashed prior to electrodeposition and alpha spectrometry analysis.

3. DEFINITIONS

3.1. Supernate – Liquid standing above a precipitate.

4. INTERFERENCES

4.1. The fluoride ion concentration must not be excessive for fecal, soil or similar samples, or very insoluble fluorides of other metals (calcium, for instance) will also precipitate and retain the Np.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.

- Do not use hand to stop centrifuge from spinning.

- WARNING: Hydrofluoric acid (HF) is one of the strongest and most corrosive acids known. Do not assume that dilute solutions do not require special precautions! Always double check your personal protective equipment before each use of HF. A pinhole in a glove or leaky container can cause an accident. HF burns penetrate deeply into skin and muscle tissue and can't be treated by simply flushing the area with water. HF causes delayed burns over several hours so the immediate care is essential to prevent further harm.

FIRST AID MEASURES

1. Flush area with water for at least 15 minutes.
2. Remove contaminated clothing immediately.
3. After washing exposed skin, use gloves to rub a generous amount of calcium gluconate gel into burn area.
4. For areas too large to apply gel, use an Epsom salts solution in a concentration of ½ to 1 cup of Epsom salts in one quart of iced water. Immerse the limb into a bucket of solution or soak the solution into gauze and apply to the wound. This dressing should be replaced or re-soaked every two minutes.
5. If area affected is greater than 2 inches by 2 inches, give 6 tablets of calcium gluconate orally.
6. If area affected is greater than 4 inches by 4 inches, assume significant inhalation injury and treat accordingly.

    - WARNING: Perchloric acid may cause fire or explosion when hot and in contact with oxidizable or combustible material. Do not contact perchloric acid with alcohols at any temperature. Use of perchloric acid requires a hood equipped appropriately with fan and running water to prevent production of explosive compounds.

    - CAUTION: Always add nitric acid to the sample first. DO NOT add perchloric acid to hot nitric acid.

5.1.1 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section.

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrofluoric Acid	Poison Corrosive Dehydrator	3 ppm-TWA	Severely corrosive to the respiratory tract. Corrosive to the skin and eyes. Permanent eye damage may occur. Skin contact causes serious skin burns, which may not be immediately apparent or painful. Symptoms may be delayed 8 hours or longer. **THE FLUORIDE ION READILY PENETRATES THE SKIN CAUSING DESTRUCTION OF DEEP TISSUE LAYERS AND BONE DAMAGE.**
Hydroxyl-amine Hydro-chloride	Corrosive Poison	None	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Corrosive to the eyes. Irritant and possible sensitizer. May cause burns to the skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Perchloric Acid	Corrosive Oxidizer Poison	None	**Unstable at ordinary temperature and pressure and can undergo explosive decomposition, especially at elevated temperatures or if allowed to dehydrate.** Inhalation of vapors or mists will cause irritation with coughing, choking, and inflammation of the nose, throat, and upper respiratory tract. Highly corrosive to tissue. Can cause severe burns with discoloration and pain. Permanent visual damage may occur.
Xylene	Flammable Irritant	100 ppm-TWA	Inhalation of vapors may be irritating to the nose and throat. Inhalation of high concentrations may result in nausea, vomiting, headache, ringing in the ears, and severe breathing difficulties, which may be delayed in onset. High vapor concentrations are anesthetic and central nervous system depressants. Skin contact results in loss of natural oils and often results in a characteristic dermatitis. May be absorbed through the skin. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Balance - readable to 10 mg or less.

6.2. Beakers - glass and Teflon, various sizes.

6.3. Centrifuge.

6.4. Centrifuge tubes - approximately 90 mL, plastic, preferably polycarbonate for large matrix samples, such as feces and soil.

NOTE: Do not let concentrated acids or bases and most organic solvents (for example, acetone) come into contact with polycarbonate. Mark tubes only with felt-tip pens which have ink that can be removed with ethanol. Do not soak tubes in nitric acid stronger than 4M, or for longer than overnight.

6.5. Graduated cylinders - various sizes.

6.6. Hot plate.

6.7. Microspatula.

6.8. Perchloric acid hood - for designated steps.

6.9. Pipets - transfer, plastic disposable, approximately 1 mL.

6.10. Rod - glass stirring.

6.11. Rubber gloves.

6.12. Separatory funnel - approximately 125 mL, glass or plastic.

6.13. Shaker - wrist action.

6.14. Vortex mixer.

6.15. Watch glassed - various sizes.

6.16. Weighing cups or dishes - disposable.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. Ferrous ammonium sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2.6H_2O$ - solid.

7.3. 1M Ferrous sulfamate ($Fe(NH_2SO_3)_2$)-Add 20 grams of NH_2SO_3H to approximately 80 mL of boiled reagent water in a beaker, heat to approximately 60°C, and add 6.0 grams of powdered iron in small increments until dissolved. (Sulfamic acid may decompose above 60^0C). Using a Whatman #54 filter or equivalent, filter the solution using a glass funnel, dilute to 100 mL with previously boiled reagent water. **NOTE**: PREPARE FRESH WEEKLY. STORE IN GLASS IN A REFRIGERATOR. KEEP BOTTLE CLOSED EXCEPT WHEN POURING.

7.4. Hydrofluoric acid (48% HF) - concentrated. Do not put HF into glass containers. **CAUTION**: Corrosive.

NOTE: Hydrofluoric acid (HF) can cause deep-seated burns. Incidents involving HF spills on the skin must receive prompt medical attention.

7.5. Hydroxylamine hydrochloride (NH_2OH HCl) - solid.

7.6. Lanthanum carrier (10 mg/mL) non-standardized - Dissolve 17.7 g of anhydrous lanthanum chloride ($LaCl_3$) in approximately 800 mL 2M HNO_3. Dilute to 1L with 2M HNO_3 and mix well. **NOTE**: Reclose the $LaCl_3$ container tightly.

7.7. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and Oxidizer.

7.8. 8M Nitric acid (8M HNO_3) - Add 500 mL 16M HNO_3 to approximately 400 mL reagent water. Dilute to 1L with reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.9. 2M Nitric acid (2M HNO_3) - Add 125 mL of 16M HNO_3 to 800 mL of reagent water. Dilute to 1L with reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.10. 1M Nitric acid (1M HNO_3) - Add 64 mL of 16M HNO_3 to approximately 500 mL of reagent water. Dilute to 1L with reagent water and mix well.

7.11. 12M Perchloric acid (12M $HClO_4$) - concentrated (70%), **WARNING**: Corrosive and oxidizing agent.

7.12. Xylenes - Mixture of ortho, meta, and para isomers. **WARNING**: Flammable.

7.13. 0.5M 2-Thenoyltrifluroacetone (TTA) in xylenes - Dissolve 100 g of 2-Thenoyltrifluoroacetone in 900 mL of xylenes and mix well. Store in a brown glass bottle. Replace after 3 months. (Smaller quantities may be prepared if only a few samples are to be analyzed. **WARNING**: Flammable.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers using no preservatives. Storage of the sample prior to analysis should not exceed six months.

8.2. It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequencies.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Perform volume reduction or leaching pre-separation process steps. Samples are prepared according to the appropriate SOP, as specified in the client specific QAS. If the sample residue is not dry after these steps, carefully evaporate it to dryness to minimize spattering. Cool, then add 2 mL (20 mg) of lanthanide carrier. Exception: For samples that are received in solution in 2-8M HNO_3, add 2 mL (20 mg) of lanthanide carrier and go to step 11.3.

11.2. For samples received that are not in solution:

11.2.1. For bioassay samples only, add 20 mL of reagent water to the sample salts and swirl or stir the sample. Add not less than 3 mL, nor more than 20 mL, of concentrated nitric acid to dissolve the salts. Heat and stir or swirl to speed the dissolving process. Additional 8M HNO_3 may be needed for fecal samples, up to a total of 1 mL of acid per gram of wet-weight feces.

11.2.2. For environmental samples only, dissolve the residue in up to 30 mL of 8M HNO_3. Heat and stir or swirl to speed the dissolving process. Add additional nitric acid only if needed.

For ALL samples from either step 11.2.1 or 11.2.2, cover with a watch glass and boil very gently for 10 to 15 minutes.

NOTE: Am-243 is added during the preparation procedure to each sample and the Np-239 beta progeny is counted within 36 hours of separation on the column. The tracers are added prior to continuing to step 11.3. Proceed to step 11.2.3 for the addition of the tracers.

11.2.3. Add the appropriate tracer to each beaker. To the LCS flask only, add the appropriate spike vial. Rinse the vials 3 times with 2M HNO_3, adding the rinses to the appropriate beaker. Remove the labels from the QC vials and place them on the analytical worksheet

11.3. Transfer the sample solution to a plastic centrifuge tube (preferably transparent polycarbonate for high-solids samples, such as feces or soil). Rinse the beaker or flask with 2M HNO_3 and add the rinsate to the tube. The final volume should be at least 35-40 mL (artificial feces salts usually will go into solution here if the tube is heated in a hot water bath). Centrifuge if undissolved salts are present, then decant the supernate to another labeled plastic tube. If only a slight cloudiness persists, such as suspended silica in urine, do not centrifuge and continue with step 11.5.

11.4. Take any precipitate from the centrifugation and add 2 mL (20 mg) of a lanthanide carrier. Repeat steps 11.2 and 11.3. Discard any solids still remaining after completing the repeat. The two portions of supernates of a sample may be combined if the total volume is less than half the capacity of one tube.

11.5. **NOTE:** The samples must be at room temperature before proceeding with step 11.5. Start step 11.6 only when enough time remains in the workday to complete steps 11.6 through 11.8.

If the sample volume in a tube is greater than half its capacity, pour approximately one half of the sample solution into a second, clean labeled tube. Add to each tube approximately 0.25 g ferrous ammonium sulfate and approximately 0.3 g hydroxylamine hydrochloride. Promptly stir with a vortex mixer for a minimum of 30 seconds to thoroughly dissolve the ferrous ammonium sulfate and hydroxylamine hydrochloride. DO NOT HEAT. Allow to stand for at least 5 minutes.

NOTE: A vortex mixer must be used to ensure thorough mixing and proper oxidation of the neptunium.

11.6. **WARNING:** Hydrofluoric acid (HF) is particularly hazardous because it numbs the skin upon contact, thereby preventing prompt detection of the contact and the subsequent severe burn. If you even suspect the possibility of contact with HF, flood the skin area with water and immediately obtain help and seek medical attention. Wear protective gear when using HF. Always dispense HF from its original, drip-free shipping bottle.

Add 1 mL of concentrated hydrofluoric acid (if supernates were combined in step 11.4, add 2 mL HF). Immediately mix thoroughly for at least 30 seconds on a mixer or with a plastic stir rod. A fine, translucent precipitate should begin to form. DO NOT HEAT. A large precipitate is neither needed nor desirable. If no precipitate forms, add 1 mL more of concentrated HF (0.5 mL HF for soil) and

mix thoroughly. If needed, repeat the 1 mL HF additions (0.5 mL HF for soil) and mixing up to 6 mL total. Allow to stand for at least 10 minutes at room temperature. If a precipitate still does not form, consult supervision.

NOTE: Five mL of concentrated HF may be used for reagent LCSs, blanks, and water matrix samples without going through the process of adding 1 mL increments.

11.7. **CAUTION:** The supernate will contain hydrofluoric acid. Wear gloves when handling this waste.

Centrifuge the sample tube(s). Carefully decant the supernate(s) to a plastic beaker. If any precipitate transfers with the supernate, recentrifuge the sample and re-decant. The supernate may be transferred to an acidic waste container after successful completion of this step.

11.8. Dissolve the precipitate(s) in 10 mL of 8M HNO_3 with stirring. If the precipitate does not dissolve, add an additional 5 mL of 8M HNO_3 and stir. Heat gently for several minutes. If the sample is still not completely dissolved proceed to the next step at this point even if the sample is still partially undissolved.

11.9. Dilute the (combined) sample to approximately 40 mL with 2M HNO_3. Repeat steps 11.6 through 11.8 once, except add the HF in 2 mL increments. Do not repeat step 11.8.

NOTE: Do NOT repeat steps 11.6 through 11.8 for urine, clear water or air filters designated for rapid analysis.

11.10. **WARNING:** Perchloric acid may cause fire or explosion when hot and in contact with oxidizable or combustible material. Do not contact perchloric acid with alcohols at any temperature. Use only in a hood designated for perchloric acid and run the hood-washing system during and for one-half hour after use. Always wear hand and eye protection when heating perchloric acid.

Add 15-20 mL of 8M HNO_3 to the precipitate in the tube. Mix well. Transfer the contents of the tube to a 150 or 250-mL beaker with small washes of 8M HNO_3. Add 3 mL of perchloric acid. Evaporate to dryness until dense, white fumes of perchloric acid have ceased. Do not bake. Allow to cool.

11.11. Dissolve the residue in about 20 mL of 1M HNO_3. Heat the covered sample briefly ONLY if needed to dissolve the sample. Transfer using 1M HNO_3, to a 125-mL separatory funnel so that the sample volume is about 30 mL. If the sample was heated, allow it to cool to room temperature before proceeding.

NOTE: Grease should not be used on the stopper or stopcock.

11.12. **NOTE:** Ferrous sulfamate is readily oxidized by air. Keep the bottle open for as short a time as feasible. Refrigerate when not in use. If a dark green precipitate forms (may appear black), warm the closed bottle in warm water and swirl to dissolve the precipitate. If a whitish precipitate forms, discard the reagent according to directions from supervision.

Add 1 mL of 1M ferrous sulfamate. Shake for 1-2 minutes. Vent the sample as needed to relieve pressure by halting the shaker and briefly loosening the stopper. Let stand for about 5 minutes.

11.13. Add 29 to 31 mL of 0.5M TTA in xylene and replace the stopper. Shake the sample for 5 to 7 minutes, venting it as before. The organic phase will turn orange-red due to iron.

11.14. Allow the phases to separate. Drain the aqueous (lower) phase into a beaker and discard.

NOTE: Do not let the upper organic phase into the stopcock during this or later drainings. If any organic phase gets into the beaker, return its entire contents to the separatory funnel. Let the phases re-separate, and drain the aqueous phase again.

11.15. Add 29 to 31 mL of 1M HNO_3 to the organic phase. Shake for 2 to 3 minutes. Allow the phases to separate. **Note the date and time as the separation time for the Np-239 tracer.**

11.16. Drain and discard the aqueous (lower) phase.

11.17. Add 29 to 31 mL of 8M HNO_3 to the separatory funnel. Shake for 5 to 7 minutes, then let the phases separate.

11.18. Drain the 8M HNO_3 (lower) phase to a clean, labeled, 150 or 250-mL beaker.

11.19. Add 14 to 16 mL of 8M HNO_3 to the separatory funnel. Shake for 2 to 3 minutes. Allow the phases to separate.

11.20. Drain this aqueous (lower) phase into the same beaker used in 11.18.

11.21. Evaporate the combined aqueous phases to dryness but do not bake.

11.22. Discard the organic phase to organic waste.

11.23. **CAUTION:** Use nitric acid with perchloric acid, and always add the nitric acid to the sample first. Do not add perchloric acid to hot nitric acid.

Wet ash the residue with 5 mL of concentrated HNO_3 and 3 mL of perchloric acid to remove traces of TTA and xylene. Evaporate to dryness until the dense white fumes of perchloric acid have disappeared. Use the perchloric acid hood and heed the warning in 11.10. Do not bake. Let cool. If the residue is dark colored, repeat this step once.

11.24. **NOTE:** Skip this step when processing samples designated for rapid analysis.

Repeat steps 11.12 through 11.24 once for high-solids samples, such as feces or soil, and whenever the residue after step 11.24 appears to be more than a few milligrams. Prior to repeating these steps, rinse the separatory funnels and their stoppers with 1M HNO_3 and discard the wash to an acidic waste container.

11.25. Proceed to the electrodeposition procedure for actinides, RICHRC5039. If there is still any dark residue (iron), then proceed to the coprecipitation procedure, RICHRC5003, instead. Electrodeposit at 0.6 ampere for one hour. For expedited samples, decrease the electrodeposition time to 40 minutes.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For calculation of the sample activity and its total propagated uncertainty (TPU), consult the latest revision of the RadCalc Users Guide. The complete computer calculation includes reagent blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container. Transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste

Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. Burney, G.A. and R.M. Harbour, 1974, The Radiochemistry of Neptunium. Nuclear Science Series. National Academy of Sciences - National Research Council. Springfield, VA: National Technical Information Service; NAS-NS-3060.

15.2. Schneider, R.A. 1962, Analytical Extraction of Neptunium Using Tri-iso-octylamine and Thenoyltrifluoroacetone. Anal. Chem. 34: 522.

15.3. RadCalc DB, Users Guide, STL Richland, latest revision.

15.4. STL Quality Management Plan, latest revision.

15.5. STL Richland Laboratory Quality Manual, latest revision.

15.6. STL Richland Quality Assurance Summary, latest revision.

15.7. Associated SOPs

15.7.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

15.7.2. RICHRC5003 - Coprecipitation of Some Actinides on Neodymium Fluoride for Alpha-Particle Spectrometry.

15.7.3. RICHRC5039 - Electrodeposition of Actinides.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

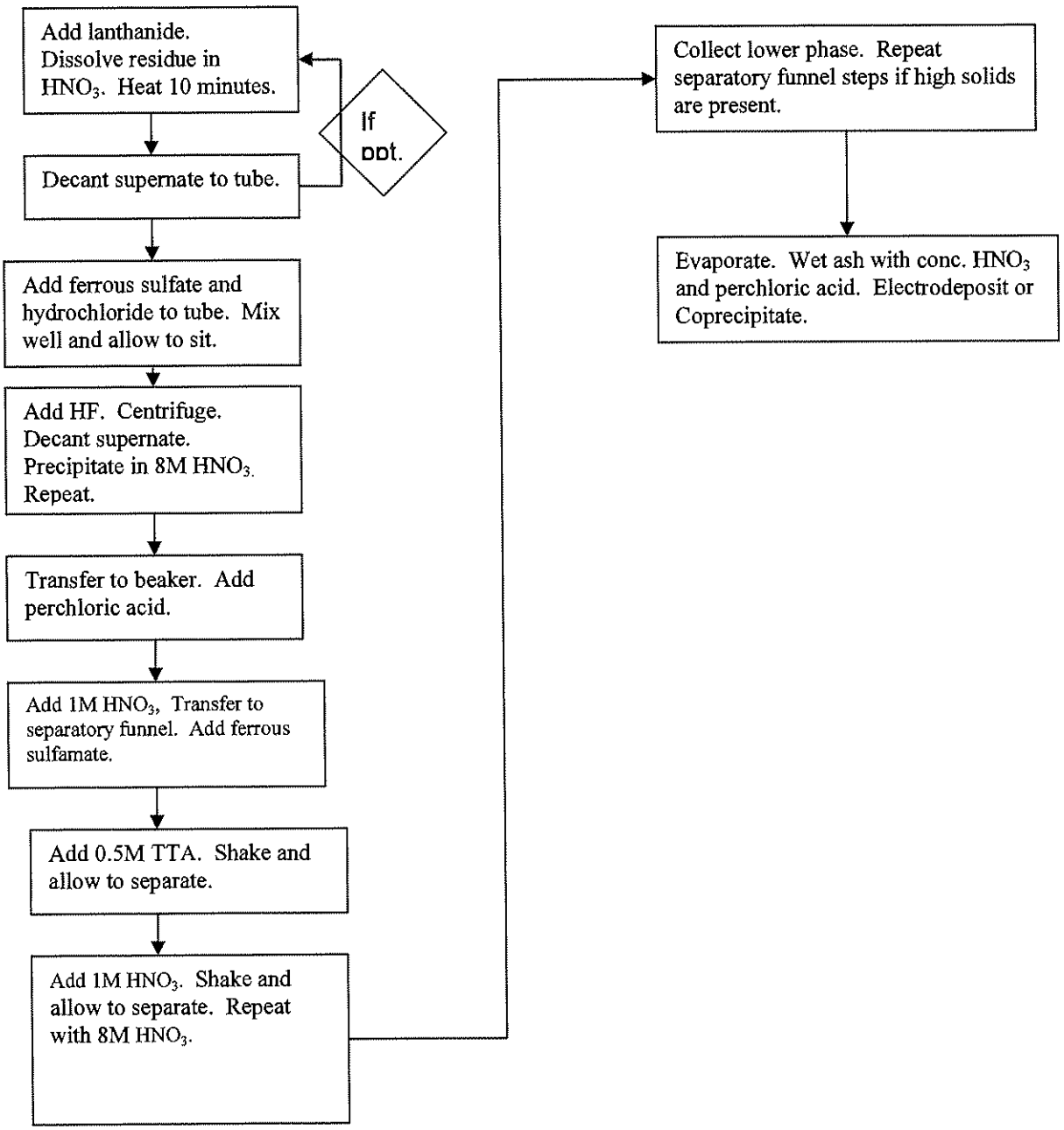
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

16.2. Records Management/Documentation

16.2.1. All records generated by this analysis will be filed and kept in accordance with STL QA policies for records management and maintenance.

16.3. Procedural Flow Chart



Title: Anhydrous Ether Extraction of Uranium

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5085 Rev 2

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1. SCOPE AND APPLICATION

1.1. Uranium is separated from other sample constituents by liquid-liquid extraction into anhydrous diethyl ether. This procedure is used prior to electrodeposition, for all matrices except soil, or prior to RICH-RC-5079 for soil samples. This procedure is applicable to all isotopic uranium analyses including U-234, U-235 and U-238.

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. The sample is dissolved in nitric acid. Uranium is extracted from the sample with diethyl ether. The ether phase is evaporated. The sample in the ether phase is electrodeposited using SOP RICH-RC-5039. For soils, the ether phase is separated by ion exchange using SOP RICH-RC-5079.

3. DEFINITIONS

3.1. Electrodeposition – Depositing made by an electric current.

4. INTERFERENCES

4.1. None.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.
- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.
- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.
- NOTE: Allow ether to evaporate in a well ventilated hood. If time is critical, evaporate in a hot water bath. DO NOT PUT ETHER ON A HOTPLATE!
- 16M HNO_3 and 30% H_2O_2 when mixed together will liberate large quantities of oxygen. If these are mixed together and the container is sealed, pressure may build up causing a pressure explosion.

Always add nitric acid before adding 30% H2O2 to avoid possible vigorous reactions. Use extreme caution when wet-ashing samples.

5.1.1 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ethyl Ether	Flammable Irritant Peroxide Former	400 ppm-TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of with six months.**
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Beakers - glass, various sizes.

6.2. Hot Water Bath

6.3. Hot Plate

6.4. Magnetic Stirrer

6.5. Teflon or Stainless Steel Stir Bars

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nanopure system. Label all reagents as outlined in procedure RICH-QA-5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them

7.2. Ethyl ether, anhydrous. **WARNING**: Flammable.

7.3. 12M Hydrochloric Acid (12M HCl) – concentrated. **WARNING**: Corrosive.

7.4. 30% Hydrogen peroxide (30% H_2O_2). **WARNING**: Corrosive and Oxidizer.

7.5. 16M Nitric acid (16M HNO_3) - concentrated. **WARNING:** Corrosive and Oxidizer.

7.6. 8M Nitric acid (8M HNO_3) - Add 500 mL of 16M HNO_3 to approximately 400 mL of reagent water. Dilute to 1L with reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.7. Ruthenium dye – Dissolve 2 g of ruthenium trichloride hydrate in approximately 950 mL of reagent water. Dilute to 1L with reagent water and mix well.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2. It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2 (15 ml 1N HNO_3 per liter of sample is usually sufficient).

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Complete the analytical worksheet(s) which accompany the sample.

11.2. **NOTE**: Refer to procedure RICH-RB-5002, RICH-RC-5016, RICH-RC-5013, RICH-RC-5019 or appropriate client specific procedures for appropriate bioassay or environmental sample preparation method.

Dissolve the sample in 20-30 mL of 8 M HNO_3 on a hot plate. Soil samples will require more acid (40-50 mL) to completely dissolve. Cool the sample to room temperature, add approximately 30 mL of anhydrous ether (40-50 for soil samples), 2-3 mL of ruthenium dye and a Teflon or approximately 3-4 stainless steel stir bars. Stir the sample for 2 minutes on a magnetic stirrer. DO NOT HEAT.

11.3. Allow the phases to separate for at least 2 minutes. Carefully decant most of the ether (top) phase into a clean, labeled beaker containing approximately 20 mL of reagent water.

WARNING: If less than 2 mL of water is in the beaker, sample behavior may become unstable.

11.4. Add approximately 30 mL of anhydrous ether (40-50 for soil samples) to the aqueous (acid) phase remaining in the original beaker. Stir for 2 minutes and carefully decant the ether phase (upper phase) to the labeled beaker from step 11.3.

11.5. Repeat step 11.4 once for a total of three repetitions.

11.6. Allow the ether to evaporate in a well ventillated hood. If time is critical, evaporate in a hot water bath.

NOTE: If samples are to be electrodeposited the same day, add more water to ensure the ether flashpoint is not exceeded.

11.7. After the ether has evaporated, heat the remaining water to dryness on a hot plate.

11.8. For soil samples add concentrated hydrochloric acid and take to dryness. Repeat this step.

11.9. Visually inspect the evaporated sample for any signs of yellow residual organic material. If necessary, wet ash the sample two times with a minimum of concentrated HNO_3 and 30% H_2O_2 on a hotplate and evaporate to dryness.

11.10. Proceed to the electrodeposition procedure RICH-RC-5039 or to the isotopic uranium procedure RICH-RC-5079 for soils.

12. DATA ANALYSIS AND CALCULATIONS

12.1 None.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container and transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap

- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

16. REFERENCES

16.1 Associated SOPs

16.1.1 RICH-QA-5002 – Reagent and Non-Radioactive Standard Labeling.

16.1.2 RICH-RB-5002 - Preparation of Urine and Blood Samples.

16.1.3 RICH-RC-5013 - Preparation of Soil Samples.

16.1.4 RICH-RC-5016 - Preparation of Environmental Matrices.

16.1.6 RICH-RC-5019 - Preparation and Dissolution of Sediments and Soil by Microwave Bomb Digestion.

16.1.7 RICH-RC-5039 - Electrodeposition of Actinides.

16.1.8 RICH-RC-5079 - Determination of Isotopic Uranium in All Matrices

17. MISCELLANEOUS

17.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

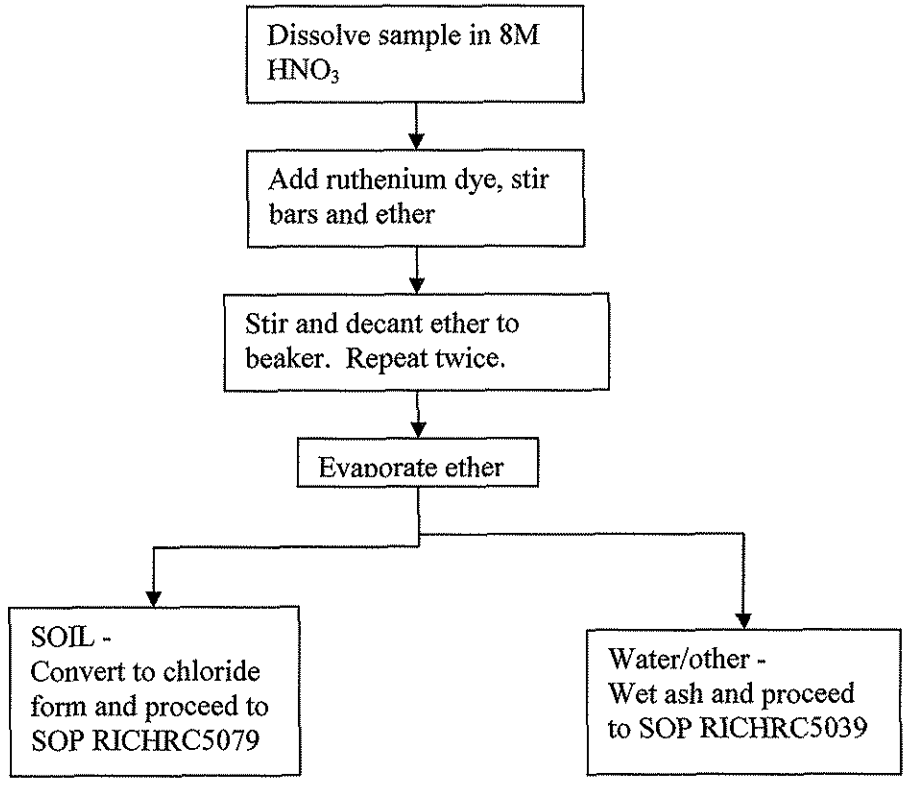
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the facilities Quality Assurance procedures.

17.2. Records Management/Documentation

17.2.1. All records generated by this analysis will be filed and kept in accordance with STL policies and procedures for records management and maintenance.

17.3. Procedural Flow Chart



Title: Preparation of All Matrices for Analysis by Gamma Spectroscopy

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5017 Rev 6

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RL-GAM-001

REVISION 0

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1. SCOPE AND APPLICATION

1.1 This procedure describes the preparation of a variety of matrices for analysis by gamma-ray spectroscopy. Depending on the isotopic request, samples are counted either on an Intrinsic (hyperpure) Germanium (HPGE) or Low Energy Photon Detector (LEPD).

1.2 The typical isotopes included in the ND library are listed in Appendix B.

1.3 This method includes the analysis of the drinking water isotopes, Cs-134, Cs-137 and I-131.

1.4 The drinking water detection limits for Cesium-134 and Cesium-137, which are 10 and 20 pCi/L respectively, are met by this procedure.

1.5 Refer to Policy P-R-01 for method detection limit information.

2 SUMMARY OF METHOD

2.1 A homogenous aliquot of the sample is transferred to a suitable container (matching a standard geometry) and submitted to the counting room for counting on the gamma detectors. HPGE detectors may be used to detect isotopes with gamma-ray energies between 60 and 2000 keV. The LEPD detectors are generally used for isotopes with gamma-ray energies less than 200 keV. Any sample matrix which can be mounted in one of the standard geometries may be analyzed for any of the isotopes included in the Nuclear Data (ND) system software library. Isotopes not included in the ND library may be evaluated manually.

2.2 The Low Energy Photon Detector (LEPD) is usually used to identify gamma isotopes with energies less than 200 keV such as I-129, U-238 (Th-234), U-235, Pb-210, Fe-55, Ni-59 and Am-241. Calibrations are developed for specific isotopes as needed. A styrene jar is used for nearly all LEPD counting. Exceptions include liquid geometries greater than 50 mL, some specialty solid geometries, and for some filter (FA) geometries where plastic disks (used to enclose the sample) are wrapped and counted directly on top of the detector.

2.3 The volume or weight of sample transferred to the appropriate geometry is recorded. If the sample is to be counted on a LEPD, a weighed aliquot is usually transferred to a styrene jar or the final analysis fraction is sandwiched between a 2" plastic disc and a single layer of plastic wrap for the most efficient geometry. If the sample is to be counted on a HPGE detector, a weighed aliquot is transferred to an appropriately sized container.

2.3.1 Milk: 1000 mL of milk is placed in a 1L Marinelli beaker.

2.3.2 Water: May be counted directly in an appropriate container as received. If a lower detection limit is required, the water is evaporated, transferred into a polyethylene bottle, and counted at a 100 mL (or greater) geometry or transferred to a styrene jar and counted at a 25 or 50 mL geometry.

2.3.3 Urine: urine and other liquids are transferred to an appropriate sized container and diluted, if necessary, to a standard volume. (These may also be concentrated to meet a lower detection limit, as for water, if requested).

2.3.4 All other samples for gamma spectroscopy analysis are transferred to an appropriately sized container and the nearest geometry is estimated and noted on the analytical work sheet.

3 DEFINITIONS

3.1 HPGE – Intrinsic (hyperpure) Germanium Detector

3.2 LEPD – Low Energy Photon Detector

4 INTERFERENCES

4.1 Whenever an isotope is quantified by the gamma emission of one of its progeny, the assumption of equilibrium between the parent and its progeny is necessary. The sample usually must be allowed some time after being transferred to the counting container to reattain equilibrium before counting. Ra-226, U-234, and U-238 are three isotopes for which it is necessary to specify ingrowth holding times after the sample is placed in the counting container. Ra-226 may be determined without an ingrowth holding time if the 186 keV line is used. The 186 keV line for Ra-226 may only be used with a limited number of geometries, and only if the proper library is specified. Caution must be exercised in using the 186 keV line to determine Ra-226, as U-235 may interfere. Associates should consult supervision if they are uncertain of how to proceed.

5 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.

Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Octanol	Flammable		Liquid may be irritating to skin and eyes. Store in a cool, dry, well-ventilated, flammable liquid storage area or cabinet. Vapors may flow along surfaces to distant ignition sources and flash back.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6 EQUIPMENT AND SUPPLIES

6.1 Aluminum cans - 95 mL capacity with lids and can sealer.

6.2 Bags - plastic.

6.3 Balance - top loading, able to read to nearest whole gram.

6.4 Beakers - glass, large enough to contain a water sample.

6.5 Bottles - polyethylene, wide mouth , 450 mL capacity and polyvinyl chloride, narrow mouth, 500 mL capacity, with screw caps. The 450 mL bottle is obtained from Quintex Corporation or equivalent.

6.6 Flasks - Erlenmeyer, various sizes.

6.7 Funnels.

6.8 Hot plate.

6.9 Marinelli beakers - 450 (MA) and 1000 (MB) mL capacity.

6.10 Petri dish - 60 mm, plastic.

6.11 pH paper - 0 to 14 range.

6.12 Plastic wrap.

6.13 Styrene jars - plastic 250 mL capacity, 2½" diameter by 3½" in height, wide mouth with lids.

6.14 Vinyl tape - various colors.

7 REAGENTS AND STANDARDS

7.1 Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nanopure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2 14.7M Ammonium hydroxide (14.7M NH_4OH) - Concentrated. **CAUTION**: Corrosive.

7.3 30% Hydrogen peroxide (30% H_2O_2). **WARNING**: Corrosive and Oxidizer.

7.4 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and Oxidizer.

7.5 8M Nitric acid (8M HNO_3) - Add 500 mL 16M HNO_3 to approximately 400 mL reagent water. Dilute to 1L with reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.6 10% Sodium bisulfite (10% $NaHSO_3$) - Dissolve 1.0g $NaHSO_3$ in 9 mL of reagent water. Prepared fresh for each use.

7.7 12M Sodium hydroxide (12M NaOH) Slowly dissolve 480 g of sodium hydroxide pellets in approximately 400 mL of reagent water. Dilute to 1 L with reagent water and mix well. Or, use the commercially prepared 50% NaOH solution. **WARNING**: Corrosive. Do not store for a long time due to CO_2 absorption which forms carbonate (CO_3^{2-}).

7.8 Phenolphthalein Indicator 0.1% - Dissolve 100 mg phenolphthalein in 60 mL of ethyl alcohol. Dilute to100 mL with reagent water. Mix well. **WARNING**: Flammable.

7.9 Octanol - **WARNING**: Flammable.

8 SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1 The sample may be collected in glass or plastic containers using no preservatives. Storage of the sample prior to analysis should not exceed six months.

8.2 It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2.

9 QUALITY CONTROL

9.1 All quality control data shall be maintained and available for easy reference.

9.2 Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.3 An appropriate blank shall be prepared in the same geometry as that of the batch of samples to be counted. The sample date on the analytical work sheet shall be the date of preparation of the blank sample.

9.4 An appropriate spike shall be prepared in the same geometry as that of the batch of samples to be counted. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate spike activity to use. The spike may be prepared in one of two ways.

9.4.1 The spike may be prepared by the addition of the contents of a spike vial to an aliquot of reagent water, which is then diluted to the appropriate geometry volume. For a spike prepared in this manner, the sample date on the analytical work sheet shall be the preparation date of the spike vial except for Sr-85 vials where the reference date is used. The proper vial code to be used in preparation of a spike will depend upon contract criteria.

9.4.2 A prepared spike may be reusable (as in the soil laboratory control sample containing Cs-134, Cs-137, Ra-226 and Ra-228). For this type of spike, the sample date on the analytical work sheet shall be the first day of the quarter of the year in which the sample being counted (ie., 1JanXX, 1AprXX, 1JulXX, 1OctXX).

9.5 Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10 CALIBRATION AND STANDARDIZATION

10.1 Germanium detectors are calibrated according to RICHQA5015, Efficiency Calibration of Germanium Spectroscopy Detectors.

11 PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: *One time procedural variations* are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1 **CAUTION**: When a sample has been placed in a container and sealed and labeled, the container should be kept in a upright position at all times. Tipping the sample container onto its side may cause some sample to be trapped up by the lid making the geometry different from the standard geometries for which calibrations have been performed.

Tables 1 and 2 in Appendix A, show the appropriate container, and volume/weight of sample for existing geometries for the HPGE and LEPD detectors.

11.1.1 Milk

11.1.1.1 Shake the sample container(s). Transfer 1000 mL of milk to a 1 L Marinelli beaker. Tap the lid to remove the air from above the sample and tape the lid securely with vinyl tape. Place the sample in the refrigerator. Record the sample volume and geometry on the analytical worksheet. Proceed to step 11.2.

11.1.2 Water, Urine, and other liquids

11.1.2.1 For Direct Counting:

11.1.2.1.1 The sample may be counted directly by transferring a sample aliquot to a counting container to match the largest standard geometry possible as directed by the client specific QAS and recording the aliquot weight/volume and geometry on the analytical worksheet. Proceed to 11.2.

NOTE: The detection limit can be significantly improved by concentrating the sample through evaporation.

11.1.2.2 For concentration of water and aqueous liquids:

11.1.2.2.1 Before concentrating, the pH must be less than 2. Verify that the pH is 2 or less in the original sample container. If the pH is greater than 2, acidify the samples using 16M HNO_3 until the sample pH is less than 2. If acidification was necessary, allow the sample to sit for at least sixteen hours in the original container before proceeding.

11.1.2.2.2 Mix the sample prior to measuring out an aliquot (specified in the client specific QAS) to an appropriately sized and labeled beaker. Evaporate the sample on a hot plate to a volume appropriate for the final geometry to be used. Consult the client specific QAS for geometry specifications. If the geometry is not specified in the QAS, consult supervision. Allow the sample to cool to room temperature. Proceed to 11.1.2.6.

11.1.2.3 For concentration of water and aqueous liquids for I-131:

11.1.2.3.1 Before concentrating, the pH must be less than 2. Verify that the pH is 2 or less in the original sample container. If the pH is greater than 2, acidify the samples using 16M HNO_3 until the sample pH is less than 2. If acidification was necessary, allow the sample to sit for at least sixteen hours in the original container before proceeding.

11.1.2.3.2 Mix the sample prior to measuring out an aliquot (specified in the client specific QAS) to an appropriately sized and labeled beaker. Add the appropriate spike and/or yield monitors to each beaker. Rinse the yield monitor vials 3 times with reagent water and the spike vials with 2M HNO_3. Remove the labels from the QC vials and place them on the analytical worksheet.

11.1.2.3.3 Add approximately 2 mL of freshly prepared 10% $NaHSO_3$ and approximately 3-4 mL of 12M NaOH to all the beakers except the LCS. Add a few drops of phemolphthalein indicator. The solution should be pink, pH>9. If not, add a few more drops of NaOH. Evaporate the sample on a hot plate to a volume appropriate for the final geometry to be used. Consult the client specific QAS for geometry specifications. If the geometry is not specified in the QAS, consult supervision. Allow the sample to cool to room temperature. Proceed to 11.1.2.6.

11.1.2.4 For concentration of Urine:

11.1.2.4.1 Pour the sample into a labeled flask/beaker and rinse the plastic collection bottle with concentrated HNO_3, unless already acidified. Add the rinses to the flask/beaker using a total volume of acid approximately equivalent to 10% of the sample volume.

11.1.2.4.2 Measure out an aliquot (specified in the client specific QAS) to an appropriately sized and labeled beaker. Add about 1%, by volume of 30% H_2O_2 and 1-2 drops of Octanol. Digest and evaporate the sample on a hot plate to a volume appropriate for the final geometry to be used. Consult the client specific QAS for geometry specifications. If the geometry is not specified in the QAS, consult supervision. Allow the sample to cool to room temperature. Urine samples may be taken just to dryness over gentle heat and the residue redissolved with 8M HNO_3. Proceed to 11.1.2.6.

11.1.2.5 **NOTE**: If Ra-226 is requested and the 186 keV Ra-226 gamma line is not used, the sealed Aluminum can geometry must be used. Samples must be held for seventeen days after sealing, for ingrowth, before counting.

If the sealed Aluminum can geometry is to be used, continue with this step, otherwise go to 11.1.2.6. The sample should be evaporated to approximately 50 mL. The pH of the sample shall be adjusted to a pH of 7 ± 0.5 with concentrated NH_4OH. Pour the sample into a labeled can and rinse the evaporation container with 2-3 small rinses of reagent water (total volume < 95 mL). Add reagent water till the total volume is 95 mL and seal the can. Proceed to step 11.2.

CAUTION: Do not overfill can or leakage during sealing will occur.

11.1.2.6 Pour the sample into the appropriate container. Rinse the evaporation container with 2-3 small rinses of reagent water and pour the rinsate into the counting container. Add reagent water to bring the total volume to the appropriate geometry. This volume is measured by comparing the sample container to a pre-marked container. Cap the container and seal the cap with vinyl tape. Clearly mark the sample container with the STL Richland sample number and place the container in a plastic bag (or double bag if so directed). Proceed to step 11.2.

11.1.3 Feces

11.1.3.1 Fecal samples may be counted as received, or may be digested prior to counting.

11.1.3.2 For counting as received, place a 450-mL wide mouth polyethylene bottle on the balance and tare the balance. Transfer the total fecal sample to the bottle and record the weight on the analytical sheet. Sample sizes less than 100 mL geometry equivalent should be placed in a styrene jar. If the sample is received in a plastic bag, place the sample, still in the bag, in the counting container. Compress the sample into the corners of the bottle and level by compressing or gently tapping. Seal the container with vinyl tape. Clearly mark the sample container with the STL Richland sample number. Estimate to the nearest standard geometry and record on the analytical worksheet. Proceed to step 11.2.

11.1.3.3 For counting after digestion, place a two-liter beaker on the balance and tare the balance. Transfer the sample to the beaker and record the sample weight on the analytical worksheet. Add sufficient octanol to just coat the surface of the sample. Add 200-300 mL of 8M HNO_3 and 40-50 mL of 30% H_2O_2 to the beaker. Heat over gentle heat until the sample just goes to dryness. Wet ash the sample with concentrated HNO_3 and 30% H_2O_2 until the sample is a whitish purple color. Add approximately 80 mL of 8M HNO_3 and warm gently. Transfer the sample to a counting container using reagent water and dilute to the desired standard geometry. This volume is measured by comparing the sample container to a pre-marked container. Cap the container and seal the cap with vinyl. Clearly mark the sample container with the STL Richland sample number and place the container in a plastic bag (or double bag if so directed). Record the geometry on the analytical worksheet and proceed to step 11.2.

11.1.4 Soil and vegetation

11.1.4.1 **NOTE**: If U-234 determination is requested by gamma spectrometry, consult supervision for the appropriate geometry.

NOTE: If Ra-226 if requested, hold the sample for 10 days after placing in the counting container but prior to counting for ingrowth.

Dry and sieve the sample as in RICHRC5016 or RICHRC5013, if requested. Place an empty container of the appropriate size as stated in the client specific QAS, usually a plastic Marinelli beaker (450-mL or 1000-mL, depending on sample size), on the balance and tare the balance. Transfer an aliquot large enough to fill the container to within ¾" of the top. Pack vegetation samples but allow to re-expand when adjusting to ¾" of the top and record the weight of sample on the analytical worksheet. Replace the lid and seal with vinyl tape. Write the STL Richland sample number on a piece of white vinyl tape and place it on the top of the lid. Record the appropriate geometry on the analytical worksheet and proceed to 11.2.

11.1.4.1.1 If the sample volume is less than that required to fill the appropriate client specific geometry, then use a wide mouth plastic bottle or styrene jar and fill to the largest geometry possible and record the sample weight on the analytical worksheet. Seal with vinyl tape and record the geometry on the

analytical work sheet. Clearly mark the STL Richland sample number on the bottle or jar and place in a plastic bag. Proceed to step 11.2.

11.1.4.1.2 Our experience has shown that for environmental levels of Ra-226 in soil, *a 10 day ingrowth period after drying and grinding will restore equilibrium.* Therefore, unless a sealed container is specified by contract or Ra-226 levels in excess of 10X environmental levels are expected, the sealed aluminum can geometry is not required.

If the sealed Aluminum can geometry is to be used, continue with this step. Weigh the empty can. Fill the can with sample and reweigh the filled can. Record the sample weight on the analytical worksheet. Seal the lid on the can and label the can. Proceed to step 11.2.

CAUTION: *Do not overfill can or leakage during sealing will occur.*

11.1.5 Air Filters (47mm)

11.1.5.1 For single filters: Label a 60 mm plastic petri dish and place the filter inside. Replace the lid and tape around the edge of the dish with vinyl tape. Clearly mark the sample container with the STL Richland sample number. Record the appropriate sample size analyzed (cubic meters, 1 sample, etc) and geometry on the analytical worksheet. Proceed the step 11.2.

11.1.5.2 For multiple filters: Label a styrene jar and place filters in the jar. Estimate the nearest geometry, 25 mL, 50 mL, depending on the number of filters analyzed. Seal the container with vinyl tape. Clearly mark the sample container with the STL Richland sample number. Record the appropriate sample size analyzed (cubic meters, 1 sample, etc) and geometry on the analytical work sheet. Proceed to step 11.2.

11.1.5.2.1 For certain clients, filters may be placed in a styrene jar with sufficient 2M HNO_3 to fill a specific geometry's volume. Allow several hours for leaching and swirl to distribute any leached material throughout the liquid prior to counting.

11.1.5.2.2 For certain clients, filters are digested and the resulting solution filtered. The filtrate is evaporated to a desired geometry and transferred to an appropriate counting container.

11.1.6 Charcoal

11.1.6.1 Place a charcoal filter, removed from its plastic bag, in a labeled, styrene jar. Make sure the filter flow arrow is pointing upward. Record the sample size in cubic meters and specify "charcoal filter" on the analytical work sheet. Charcoal filter samples are marked with the STL Richland sample number. Place the styrene jar in a plastic bag. Proceed to step 11.2.

11.1.7 Meat and Produce

11.1.7.1 Small sample sizes may be placed directly in a pre-weighed styrene jar and the appropriate geometry selected. Larger samples of meat and produce are cut into small sections and packed in a pre-weighed, Marinelli beaker to within ¾" of the top, or in a pre-weighed wide mouth plastic bottle or styrene jar to the largest geometry possible. Weigh the container with the sample and record the net weight of sample and the geometry on the analytical work sheet. Seal the sample container with vinyl tape. Clearly mark the STL Richland sample number on the sample container. Place styrene jars or bottles in plastic bags. Place samples in the refrigerator. Proceed to step 11.2.

NOTE: For egg samples, remove the shells and discard them (unless Sr or another analysis is requested on the shells) before placing sample in the container.

11.1.7.2 Produce - I-129

11.1.7.2.1 Wet and dry weights of the entire sample must be noted and recorded, as applicable, as described in RICHRC5016. A styrene jar is placed on the balance and the balance is tared. An appropriate aliquot of the sample is transferred to the styrene jar and compressed lightly. IV9 geometry is noted on the analytical work sheet.

11.1.7.2.2 Clearly mark the sample container with the STL Richland number of the sample. Seal with vinyl tape. Place the filled counting container in a plastic bag. Proceed to step 11.2.

11.1.8 Resin and Filters

11.1.8.1 The preparation of resin samples and filters are covered in RICHRC5045, Preparation of Resin and Filter Samples.

11.2 Verify that the analytical worksheets contain all necessary information (sample analyzed, sample date, geometry, detector type, and counting time). The completed analytical work sheets and samples (if not refrigerated) are submitted to the counting room. Refrigerated samples are removed from the refrigerator by the counting room personnel as needed and returned to the refrigerator after counting.

NOTE: If ingrowth is required, note the desired count date on the analytical worksheet before submitting to the counting room. Alert the counting room staff that ingrowth is required.

12 DATA ANALYSIS AND CALCULATIONS

12.1 Gamma activity calculations are performed by computer using Nuclear Data (ND) and/or internally developed software. Further information is provided in ND manuals software documentation files.

12.2 Wet Weight Conversion Equation:

$$\frac{D\ (g)}{1 - M} = W\ (g)$$

where:

D = dry weight of the sample aliquot.

M = percent moisture expressed as a decimal.

W = converted wet weight of the sample aliquot.

13 METHOD PERFORMANCE

13.1 The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2 Method Demonstration of Capability documentation is maintained in the quality files.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Aqueous acidic waste pH< 2. Waste is collected in an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in a Flammable waste container which is red with a self closing metal lid

Radioactive Waste

Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15 REFERENCES

15.1 National Council on Radiation Protection and Measurements. A Handbook of Radioactivity Measurement and Procedures. NCRP Report 58 and Edition, Washington, D.C., 1985.

15.2 American Society for Testing and Materials. Standard Practice for High-Resolution Gamma-ray Spectrometry of Water in Annual Book of ASTM standards. Philadelphia, PA: ASTM D3649-91, 1992.

15.3 Chieco, N.A., D.C. Bogen, and E.O. Knutson. eds. 1990 EML Procedures Manual, Gamma, HASL-300, 27th Edition, Volume1. Environmental Measurements Laboratory, US Department of Energy, New York, New York.

15.4 U.S. Environmental Protection Agency, August 1980, "Gamma Emitting Radionuclides in Drinking Water", Method 901.1, EPA-600/40-80-032, National Technical Information Services, Springfield, VA.

15.5 STL Quality Management Plan, latest revision.

15.6 STL Richland Laboratory Quality Manual, latest revision.

15.7 STL Richland Quality Assurance Summary, latest revision.

15.8 Associated SOPs

15.8.1 RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

15.8.2 RICHQA5015 - Efficiency Calibration of Germanium Spectroscopy Detectors.

15.8.3 RICHRC5013 - Preparation of Soil Samples.

15.8.4 RICHRC5016 - Preparation of Environmental Matrices.

15.8.5 RICHRC5045 - Preparation of Resin and Filter Samples.

16 MISCELLANEOUS

16.1 Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

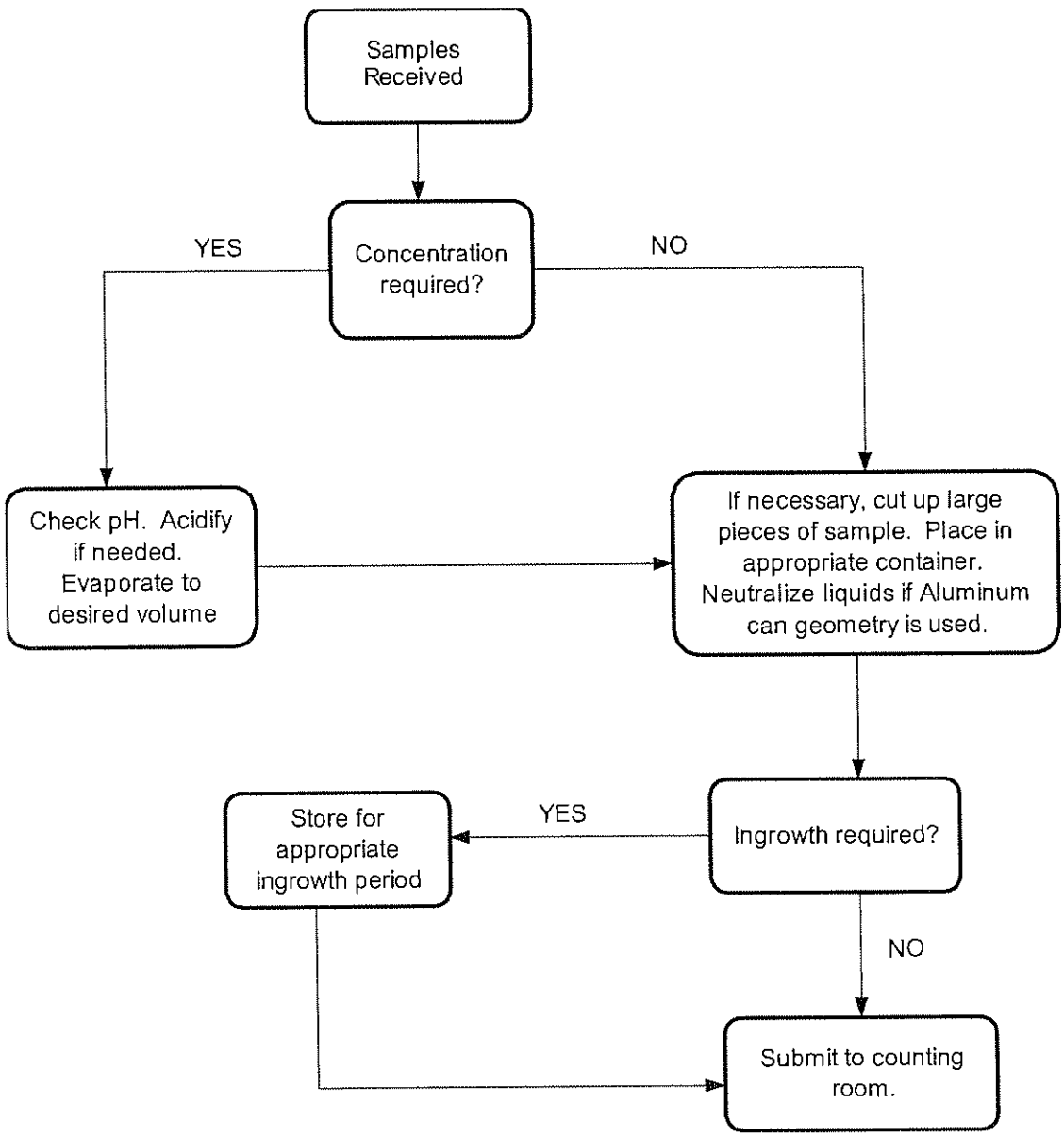
16.2 Records Management/Documentation

16.2.1 All records generated by this analysis will be filed and kept in accordance with STL Richland SOPs for records management and maintenance.

16.3 Drinking Water Method Variations

17.3.1 This procedure is compliant with Method 901.1. RICH-RC-5017 includes the use of HPGEs and LEPDs.

16.4 Procedural Flow Chart



APPENDIX A

Table 1. Geometries for the HPGE Detectors

Geometry	Description
FP	one filter in the bottom of a 60 mm Petri dish.
25 mL	25 mL of liquid in a styrene jar.
25 mL_SE75	Se-75 in 25 mL of liquid in a styrene jar.
50 mL	50 mL of liquid in a styrene jar
100 mL	100 mL of liquid in a 500 mL polybottle.
200 mL	200 mL of liquid in a 500 mL polybottle.
500 mL	500 mL of liquid in a 500 mL polybottle.
CHR	I-131 in a charcoal filter placed in a styrene jar.
MA	450 mL Marinelli beaker.
MB	1 L Marinelli beaker.
ROFS	200 mL of soil in a wide mouth plastic bottle.
25ROF	25 mL of soil in a styrene jar.
S25	25 mL of soil in a styrene jar.
S200	200 mL of soil in a 500 mL polybottle.
SMA	Soil in a 450 mL Marinelli beaker.
WALCAN	Sealed aluminum can for liquids.
ALCAN	Sealed aluminum can for soils.

NOTE: The 450 mL wide-mouth plastic bottle obtained from Quintex Corporation (P9-35) is considered equivalent to the 500 mL polybottle. The wide mouthed plastic bottle is used for counting dry matrices using the 100 mL through 500 mL HPGE geometries.

500 mL polybottle - polyvinyl chloride of 500 mL capacity, boston round shape, 78 mm outside diameter and 115 mm in height to the shoulder of the bottle.

Styrene jar - 250 mL capacity plastic jar, 60-63 mm inside diameter, 80-82 mm inside depth.

Table 2 - Geometries for the LEPD Detectors

Geometry	Description
FA	filter/plastic disc sandwich.
25 mL	25 mL of liquid in a styrene jar.
50 mL	50 mL of liquid in a styrene jar.
100 mL	100 mL of liquid in a 500 mL polybottle.
200 mL	200 mL of liquid in a 500 mL polybottle.
400 mL	400 mL of liquid in a 500 mL polybottle.
500 mL	500 mL of liquid in a 500 mL polybottle.
IC9 or IC5	I-129 and I-125 - charcoal filter in a styrene jar.
I_FA	I-129 in a filter/plastic disc sandwich.
IS9	I-129 in 50 grams of soil in a styrene jar.
IV9	I-129 in 50 grams of alfalfa in a styrene jar.
IW9	I-129 in 25 mL of water in a styrene jar.
PBA	Pb-210 in 25 grams of soil in a styrene jar.
PBC	Pb-210 in 90 gram geometry.
UGS	U-Nat in 100 grams of soil in a styrene jar.
X_RAY	Fe-55 and Ni-59 in a filter/plastic disc sandwich.

NOTE: The 450 mL wide-mouth plastic bottle, obtained from Quintex Corporation (P9-35), is considered equivalent to the 500 mL polybottle. The wide mouthed plastic bottle is used for counting dry matrices using the 100 mL through 500 mL HPGE geometries.

500 mL polybottle - polyvinyl chloride of 500 mL capacity, boston round shape, 78 mm outside diameter and 115 mm in height to the shoulder of the bottle.

Styrene jar - 250 mL capacity plastic jar, 60-63 mm inside diameter, 80-82 mm inside depth.

Filter/plastic sandwich - filter on a plastic disk and wrapped tightly in a single layer of plastic wrap.

Company Confidential & Proprietary

Gamma Isotopes from ND Library
(EXAMPLE)

ISOTOPE	HALF-LIFE	KEY LINE ENERGY
Be-7	53.44 days	477.59 keV
Na-22	2.60 years	1274.54 keV
Na-24	15.00 hours	1368.53 keV
K-40	1.28E+09 years	1460.81 keV
Sc-46	83.85 days	1120.51 keV
Cr-51	27.70 days	320.08 keV
Mn-54	312.70 days	834.83 keV
Co-57	270.90 days	136.48 keV
Co-58	70.80 days	810.76 keV
Fe-59	44.63 days	1099.22 keV
Co-60	5.27 years	1332.49 keV
Zn-65	244.40 days	1115.52 keV
Se-75	119.78 days	264.65 keV
Sr-85	64.84 days	513.99 keV
Y-88	106.61 days	1836.01 keV
Nb-94	20300.00 years	871.10 keV
Nb-95	35.06 days	765.79 keV
Tc-95M	61.00 days	204.12 keV
Zr-95	64.02 days	756.72 keV
ZrNb-95	64.40 days	765.82 keV
Mo-99	66.02 hours	140.50 keV
Ru-103	39.35 days	497.08 keV
Ru-106DA	368.20 days	621.84 keV
Ag-108M	127.00 years	433.93 keV
Ag-110M	249.85 days	884.67 keV
Sn-113DA	115.10 days	391.69 keV
Sb-124	60.20 days	602.72 keV
Sb-125	2.77 years	427.89 keV
Sn-126DA	1.00E+05 years	666.33 keV
I-131	8.04 days	364.48 keV
Ba-133	10.50 years	356.00 keV
Cs-134	2.06 years	604.70 keV
Cs-137DA	30.17 years	661.65 keV
La-138	1.06E+11 years	1435.80 keV
Ce-139	137.20 days	165.85 keV
Ba-140	12.79 days	537.32 keV
BaLa-140	12.79 days	1596.20 keV
La-140	40.22 hours	1596.49 keV
ISOTOPE	**HALF-LIFE**	**KEY LINE ENERGY**
Ce-141	32.50 days	145.44 keV
Ce-144	284.30 days	133.54 keV
CePr-144	284.20 days	133.53 keV
Pm-144	363.00 days	618.06 keV
Pm-146	5.53 years	453.89 keV

Eu-152	13.60 years	344.27 keV
Eu-154	8.80 years	1274.45 keV
Eu-155	4.96 years	105.31 keV
Hf-181	42.39 days	482.03 keV
Bi-207	33.40 years	569.67 keV
Tl-208	1.41E+10 years	583.14 keV
Bi-210M	3.00E+06 years	266.15 keV
Pb-212	1.41E+10 years	238.63 keV
Bi-214	4.47E+09 years	609.31 keV
Pb-214	4.47E+09 years	351.92 keV
Ra-223	21.77 years	269.46 keV
Ra-224DA	1.91 years	238.63 keV
Ra-226DA	1600.00 years	609.32 keV
Ac-227DA	21.77 years	236.00 keV
Ac-228	1.41E+10 years	911.07 keV
Ra-228DA	5.75 years	911.07 keV
Th-228DA	1.91 years	583.14 keV
Th-232DA	1.41E+10 years	338.32 keV
Th-234DA	4.47E+09 years	1001.03 keV
U-234DA	4.47E+09 years	295.22 keV
U-235HP	7.04E+08 years	143.76 keV
Np-237DA	2.14E+06 years	311.98 keV
U-238DA	4.47E+09 years	351.92 keV
U-238DHP	4.47E+09 years	63.28 keV
Am-241HP	432.20 years	59.54 keV

Title: Determination of Iodine-131 and 129 in Water by Solvent Extraction Method

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5025 Rev 4

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1. SCOPE AND APPLICATION

1.1. Iodine-131 and I-129 are determined in water by this procedure. A separate aliquot is analyzed for each isotope requested.

1.2. Iodine is separated from interferences by oxidation to I_2 with $NaNO_2$, and extraction into CCl_4 from a dilute acid media. The iodine is then reduced to iodide with $NaHSO_3$ (sodium bisulfite), back extracted into water, and then precipitated as AgI. Radiochemical purity and concentration at sampling time are determined by decay counting the sample. Chemical yields, determined gravimetrically, are normally about 89%.

1.3. Iodine-131 is determined with low background gas flow beta proportional counters having background counts of < 1.5 cpm. Isotopic purity can be determined by recounting the sample for radioactive decay. Iodine-129 is determined by counting with a low energy photon detector. There is negligible attenuation of the I-129 (39 keV) gamma rays from the precipitate.

1.4. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. A weighed iodine carrier is added to each aliquot to be analyzed. $NaHSO_3$ is added, and NaOH is added to make the solution basic. The volume is reduced. The sample is transferred to a separatory funnel and acidified with H_2SO_4. $NaNO_2$ is added and the iodine is extracted into CCl_4. The extraction is repeated, and then the CCl_4 washed with dilute HNO_3. $NaHSO_3$ is added and the iodide is back extracted into water. $AgNO_3$ is added and the solution is heated to precipitate AgI. If an I-131 analysis was requested, the precipitate is transferred to a tared planchet and counted on a low beta gas flow proportional detector. If an I-129 analysis was requested, the precipitate is collected on a filter and counted on a low energy photon detector.

3. DEFINITIONS

3.1. Decant – To pour off supernate gently without stirring up the precipitate.

3.2. Supernate – Liquid standing above a precipitate

4. INTERFERENCES

4.1. None.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.

- WARNING: Carbon Tetrachloride is a known Carcinogen.

- WARNING: Ether is flammable.

- Do not use hand to stop centrifuge from spinning.

5.1.1 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Collodion	Flammable	ACGIH 1000ppm TWA	May cause central nervous system depression. May cause liver and kidney damage. May be harmful if swallowed. Causes eye and skin irritation. May cause reproductive and fetal effects. May be harmful if absorbed through the skin. Causes respiratory tract irritation.
Ethyl Alcohol	Flammable	ACGIH 1000ppm TWA NIOSH 1000ppm TWA; 1900 mg/m^3 TWA	Causes severe eye irritation. May cause skin irritation. May cause central nervous system depression. May cause liver and kidney damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Silver Nitrate	Poisonous Corrosive Oxidizer		Silver Nitrate should never be mixed with ammonia compounds as it can form azides which are powerful explosives. Never mix with finely particulate metals such as aluminum or zinc. Also avoid contact with organics. Stains skin and can cause burns.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Nitrite	Oxidizer Poison Reactive	None	**Danger! Strong oxidizer and toxic material. Contact with other material may cause fire. Heat, shock, or contact with other material may cause fire or explosive decomposition.** Causes irritation to the respiratory tract and systemic poisoning. Can irritate the mouth, esophagus, stomach, etc. Excessive amounts affect the blood and blood vessels. Signs and symptoms of nitrite poisoning include intense cyanosis, nausea, dizziness, vomiting, collapse, spasms of abdominal pain, rapid heart beat, irregular breathing, coma, convulsions, and death due to circulatory collapse. Causes irritation, redness and pain to the skin and eyes. May be absorbed through the skin causing systemic poisoning.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Balance - analytical.

6.2. Beakers - glass, various sizes.

6.3. Buchner funnel - #2, 8.5 cm outside diameter.

6.4. Centrifuge.

6.5. Centrifuge tube - approximately 100 mL, glass.

6.6. Filter clamp and holder - for 0.45 micron filter.

6.7. Filters - for Buchner funnel, glass fiber.

6.8. Filters - 0.45 micron, 2 inch diameter.

6.9. Graduated cylinder - glass, various sizes.

6.10. Heat gun.

6.11. Heat lamp.

6.12. Hot plate.

6.13. pH paper - wide range.

6.14. Pipet - plastic transfer, disposable.

6.15. Pipettor - automatic, 1 mL and 5 mL capacity.

6.16. Planchet - 1: stainless steel with cardboard holder.

6.17. Plastic wafers - two inch diameter.

6.18. Plastic wrap - heat shrink recommended.

6.19. Separatory funnel - approximately 1 L.

6.20. Spatula - stainless steel blade for transferring dry reagents.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. Carbon tetrachloride (CCL_4). **WARNING**: Carcinogen.

7.3. Collodion (1% solution) - Add 5 mL of collodion to a mixture of 330 mL of ether and 165 mL of ethyl alcohol. Mix well. **WARNING**: Flammable.

7.4. Ethyl alcohol, anhydrous. **WARNING**: Flammable.

7.5. Ether, anhydrous (diethyl ether). **WARNING**: Flammable.

7.6. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and Oxidizer.

7.7. 4M Nitric acid (4M HNO_3) - Add 250 mL of concentrated HNO3 to approximately 700 mL of reagent water. Dilute to 1 L with reagent water and mix well.

7.8. Phenolphthalein Indicator 0.1% - Dissolve 100 mg phenolphthalein in 60 mL of ethyl alcohol. Dilute to100 mL with reagent water. Mix well. **WARNING**: Flammable.

7.9. 0.1M Silver nitrate (0.1M $AgNO_3$) in 8M HNO_3 -Dissolve 17 g of $AgNO_3$ in 500 mL of reagent water. Dilute to 1 L with concentrated HNO_3 and mix well.

7.10. 10% Sodium bisulfite (10% $NaHSO_3$) - Dissolve 1.0g $NaHSO_3$ in 9 mL of reagent water. Prepared fresh for each use.

7.11. 12M Sodium hydroxide (12M NaOH) Slowly dissolve 480 g of sodium hydroxide pellets in approximately 400 mL of reagent water. Dilute to 1 L with reagent water and mix well. Or, use the commercially prepared 50% NaOH solution. **WARNING**: Corrosive. Do not store for a long time due to CO_2 absorption which forms carbonate (CO_3^{2-}).

7.12. Sodium nitrite ($NaNO_2$) - crystals.

7.13. 18M Sulfuric acid (18M H_2SO_4) - Concentrated. **WARNING**: Corrosive.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers using no preservatives. Storage of the sample prior to analysis should not exceed six months.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Using a wide range pH paper, measure the pH of the sample and record the pH on the analytical work sheet. If the pH is 2 or less, consult supervision.

11.2. If the sample is to be aliquoted, ensure the sample has not been acidified and mix the sample well before splitting. Measure the appropriate aliquot to a clean labeled beaker. Add one vial of calibrated iodine carrier (20 mg/mL I) to each sample beaker. Rinse each vial with reagent water and add the rinse to the appropriate sample beaker. Add about one mL of freshly prepared 10% $NaHSO_3$ and one to two mL of 12M NaOH to each beaker. Add a few drops of phenolphthalein indicator. The solution should be basic (deep pink color persists, pH > 9). If not, add a few more drops of NaOH.

11.3. Place the sample on a hot plate and evaporate the sample to about 500 mL. If necessary, filter the sample through a glass fiber filter using a Buchner funnel. Cool the sample and transfer the sample or filtrate to a 1-L separatory funnel. Slowly and carefully acidify the sample with concentrated H_2SO_4; a maximum of 2 mL may be used. Check with pH paper to ensure the sample is between pH 1 - 2.

NOTE: If a large amount of fine white precipitate occurs during evaporation, filtering is usually not necessary, however, more than 2 mL of concentrated H_2SO_4 may be required to redissolve the precipitate.

NOTE: After filtering, the sample may be left for completion of analysis at a later time.

11.4. **WARNING**: Turn the separatory funnel upside-down and release the pressure occasionally through the stopcock. Avoid inhaling the CCl_4 fumes. All work should be performed in a hood.

NOTE: Lack of pink color in the lower CCl_4 layer could indicate that the no carrier was added.

Add 2 to 3 grams of $NaNO_2$, then 75 mL of CCl_4 (carbon tetrachloride) to the separatory funnel. Shake the separatory funnel vigorously, with periodic venting, for 3 minutes or until a deep pink color persists in the CCl_4 layer.

11.5. Allow the phases to separate. Drain the CCl_4 lower layer into a clean labeled beaker (600-mL recommended) containing about 100 mL of 4M HNO_3.

11.6. Extract the sample again by adding approximately 50 mL of CCl_4 to the separatory funnel. Shake the separatory funnel vigorously, with periodic venting, for 3 minutes or until a light pink color persists in the CCl_4 layer. Allow the phases to separate. Add the pink layer (CCl_4) to the same beaker as above. Discard the water phase to an appropriate waste container and rinse the funnel with water. Add the rinse to the appropriate waste container.

11.7. Transfer the CCl_4 plus 4M HNO_3 back to the separatory funnel. Shake the funnel vigorously and allow the phases to separate. Drain the CCl_4 (pink, lower layer) into the previously used beaker containing an equal volume of reagent water. Discard the acid phase to an appropriate waste container. Rinse the separatory funnel with water, discarding the rinse water to an appropriate waste container.

11.8. Transfer the CCl_4 plus reagent water back to the separatory funnel. Add 5 to 6 drops of freshly prepared 10% $NaHSO_3$ and shake for one minute. Allow the phases to separate.

NOTE: Add additional drops of $NaHSO_3$ if the pink color returns to the CCl_4 layer. The CCl_4 layer should be clear. If the CCl_4 layer is not clear, consult supervision prior to proceeding further.

11.9. Drain the CCl_4 (lower layer) into an appropriate waste container for recycling. Drain the aqueous layer to the previously used beaker. Slowly add 5 mL of 0.1M $AgNO_3$ reagent to the beaker while swirling the solution. Heat the sample on a hot plate until the precipitate coagulates (the solution turns clear).

11.10. If I-131 is requested, proceed to step 11.11. If I-129 is requested, proceed to step 11.12.

11.11. For Iodine-131:

11.11.1. Transfer the solution and precipitate to a 100 mL glass centrifuge tube with reagent water. Centrifuge for 5 minutes. Decant the supernate to an appropriate waste container. Wash the precipitate twice with about 20 to 30 mL of reagent water and decant each wash to an appropriate waste container.

11.11.2. Transfer the precipitate with a glass transfer pipet to a pre-weighed 1" planchet. Dry slowly under a heat lamp and weigh; record the precipitate weight (and other appropriate information) on the Analytical Work Sheet. Fix the sample with a few drops of 1% collodion. Mount the planchet on a mounting card and submit to the counting room.

NOTE: Two to four drops of 1% collodion should be sufficient. The sample should be allowed to sit for about one hour before counting is begun to allow for decay of any trapped radon daughters.

11.12. For Iodine-129:

11.12.1. Filter the precipitate through a pre-weighed two inch 0.45 micron filter which has been pre-wetted and dried. Wash the precipitate with reagent water. Place the filter on a 2" planchet and place in a planchet box. Place the planchet box next to a heat lamp to slowly dry the filter with the precipitate. Weigh the filter and precipitate, record the precipitate weight on the Analytical Work Sheet. Sandwich the filter with the precipitate between two plastic wafers. Wrap the wafers together in heat shrink plastic. Warm, using a heat gun, until the plastic securely collapses around the wafers.

NOTE: If heat shrink plastic is not available, wrap the wafers in plastic wrap as tight as possible and warm with a heat gun.

11.12.2. Complete the Analytical Work Sheet and submit the samples to the counting room for counting.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. Waste Management and Pollution Prevention

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1. Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container and transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. Armstrong, G. W.; Gill, H. H., Rolk, R. F. Treatise on Analytical Chemistry, Part II, Volume 7. New York: Interscience Publishers; 1961:358.

15.2. Glendenin, L. E.; Metcalf, R. P.; Coryell, C. D.; Sugarman, N. Radiochemical Studies: The Fission Products, NNES, Div. IV Vol. 9, paper 272. New York: McGraw-Hill 1952:1625.

15.3. RadCalc DB, Users Guide, STL Richland, latest revision.

15.4. Standard Test Methods for Radioactive Iodine in Water, ASTM, D2334-1979 (discontinued).

15.5. STL Quality Management Plan, latest revision.

15.6. STL Richland Laboratory Quality Manual, latest revision.

15.7. STL Richland Quality Assurance Summary, latest revision.

15.8. Associated SOPs

15.8.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance policies.

16.2. Carbon Tetrachloride Recycling

16.2.1. To a clean separatory funnel, add about 100 mL of reagent water, 5 – 6 drops of 10% $NaHSO_3$ and approximately 200 mL of used carbon tetrachloride. Shake for at least 1 minute. Allow the phases to separate.

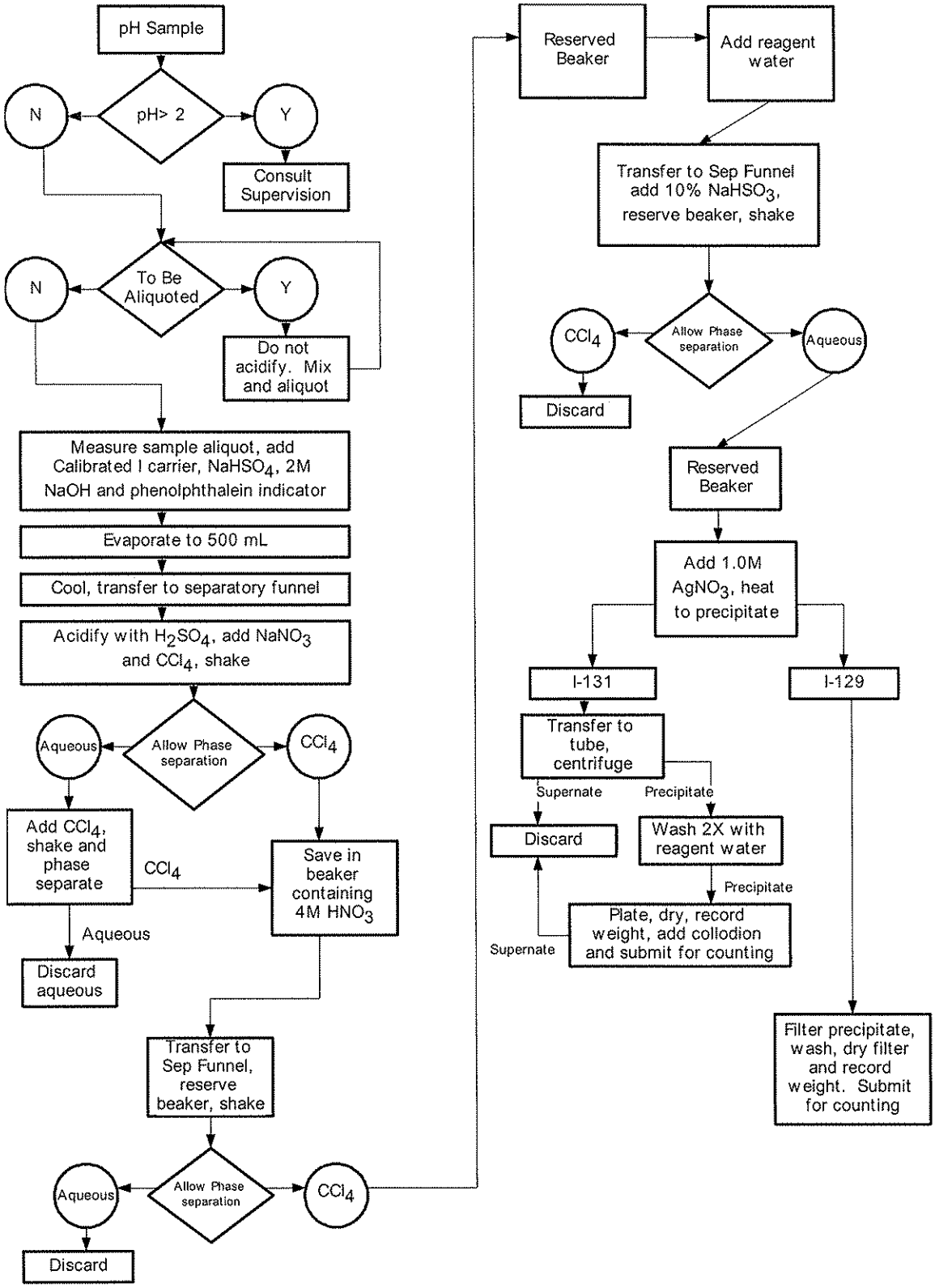
16.2.2. Drain the lower phase into a clean labeled CCL_4 bottle. Discard the upper water phase to an appropriate waste container.

NOTE: If the carbon tetrachloride remains cloudy, filter through a glass fiber filter

16.3. Records Management/Documentation

16.3.1. All records generated by this analysis will be filed and kept in accordance with STL QA policies for records management and maintenance.

16.4. Procedural Flow Chart



Title: Determination of Gross Alpha and Gross Beta in Water by Method 9310 and EPA Method 900.0

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/4/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5014 Rev 7

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RL-GPC-001 REVISION 0

Facility Distribution No. _____ **Distributed To:** _____

1. SCOPE AND APPLICATION

1.1. This procedure is applicable to the measurement of gross alpha and gross beta activity in drinking, surface, ground waters and leachates for alpha emitters with energy above 3.9 MeV and beta emitters with maximum energies greater than 0.1 MeV. This procedure complies with Method 9310 from EPA SW846, Third Edition (1986) which is very similar to Method 900.0 from EPA-600/4-032 (1980). The minimum detectable concentration varies with sample size, counting time, and counting systems.

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. The customer is advised to acidify samples at the time of collection. If this is not done, the sample is acidified at STL Richland. If requested, the sample is filtered. An aliquot of the sample is taken to near dryness. Concentrated HNO_3 is added, and the sample is taken to near dryness again. Dilute HNO_3 is added, and the sample is transferred to a pre-weighed planchet. The planchet is lightly flamed to convert the nitrates to oxides. The sample is weighed, and a collodion solution is added to secure the precipitate to the planchet.

3. DEFINITIONS

3.1. Hygroscopic – Pertaining to a substance whose physical characteristics are appreciably altered by effects of water vapor.

4. INTERFERENCES

4.1. The amount of solids left when a given sample volume is evaporated is a limiting factor in the sensitivity of the method. The largest sample aliquot that can be reasonably counted for gross alpha activity is one which gives a solid density of 5 mg/cm^2 on the planchet. For a 3.8-cm (1½") planchet, this is a total weight of 57 mg.

4.2. Radionuclides that are volatile under the sample preparation procedure are not measured.

4.3. Non-uniformity of the sample residue in the planchet is a source of error.

4.4. Hygroscopic samples present problems with self-absorption corrections.

4.5. For beta counting, a Whatman number one filter can be used as an absorber so that no correction for alpha particles counted on the beta plateau is necessary.

4.6. Am-241, selected by EPA as the recommended alpha calibration source, also emits a low energy gamma (59.5 KeV) which interferes with the beta contribution when generating the self absorption correction factors.

4.7. Non-uniformity of the sample residue on the counting planchet interferes with the accuracy and precision of the method.

5. SAFETY

5.1.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Specific Safety Concerns or Requirements

5.2.1. Extreme care must be exercised when flaming planchets. Gloves that provide thermal protection must be worn during this section of the procedure. Ensure that compressed flammable gas cylinders are secure to prevent them from falling over.

5.3. Primary Materials Used

5.3.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ethyl Ether	Flammable Irritant Peroxide Former	400 ppm-TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of within six months.**
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Balance - analytical, capable of weighing to at least 0.1 mg.

6.2. Beaker - glass, various sizes.

6.3. Dessicator - Equipped with desiccant or equivalent.

6.4. Drying oven - capable of maintaining 105°C.

6.5. Filter flask - various sizes.

6.6. Filter paper - Whatman No.1 or equivalent, diameter to fit the planchet used.

6.7. Funnel/support assemblies - 47 mm vacuum filtration apparatus.

6.8. Graduated cylinder - 10 mL.

6.9. Heat lamp.

6.10. Hot plate.

6.11. Meeker burner or propane gas cylinder.

6.12. Membrane filter - 47 mm diameter, 0.45 µm pore size, cellulose nitrate membrane.

6.13. pH paper - able to read pH 2.

6.14. Planchet - stainless steel, 3.8 cm (1.5") or 5.1 cm (2").

6.15. Planchet holder - cardboard.

6.16. Transfer pipets - disposable, plastic, approximately 3 mL.

6.17. Zetex cloth or equivalent.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. Alcohol - anhydrous ethyl, denatured. **WARNING**: Flammable, poisonous.

7.3. 10% Collodion (10% solution) - Add 50 mL of collodion to a mixture of 300 mL of diethyl ether and 150 mL of ethyl alcohol. Mix well. **WARNING**: Flammable.

7.4. 1% Collodion (1% solution) - Add 5 mL of collodion to a mixture of 330 mL of diethyl ether and 165 mL of ethyl alcohol. Mix well. **WARNING**: Flammable.

7.5. Diethyl ether. **WARNING**: Flammable.

7.6. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and oxidizer.

7.7. 2M Nitric acid (2M HNO_3) - Add 125 mL of 16M HNO_3 to approximately 800 mL of reagent water. Dilute to 1 L with reagent water and mix well.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. The container choice should be plastic over glass to prevent loss due to breakage during transportation and handling.

8.2. It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15 ml 1N HNO_3 per liter of sample is usually sufficient).

8.3. Storage of the sample prior to analysis should not exceed six months.

9. QUALITY CONTROL

9.1. *All quality control data shall be maintained and available for easy reference.*

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1.Complete the analytical worksheet which is prepared following login and will accompany the sample.

11.2. Soil digestates may be plated like a water sample. Proceed to step 11.4. **NOTE**: If the soil digestate precipitate weight is found to exceed the maximum precipitate weight, the planchet may be stripped as described in step 11.11.

NOTE: If Carbon-14, Iodine-129, Iodine-131, or Tritium analyses have been requested and the aliquots are to be taken from the same sample container, remove those aliquot(s) prior to acidification of the sample. Document on the chain of custody(s) that aliquots were removed prior to acidification.

Using a wide range pH paper, measure the pH of the sample and record the pH on the analytical worksheet. If the pH is 2 or less, proceed to 11.3.

NOTE: Some clients do not want samples analyzed if preservation is incorrect. If the pH is above 2, consult the client specific QAS or supervision to determine if the sample analysis may proceed after acidification.

To acidify the sample, add acid to the sample using approximately 1 mL of concentrated HNO_3 to each liter of sample. Mix the sample and recheck the pH. Continue to add acid in 1 mL increments until the sample pH is below 2. Hold the sample in the original container for a minimum of 16 hours before continuing with this procedure.

11.3. Filtration is not performed on samples unless specifically requested by the client. If excessive, visible particulate matter is suspended in the sample, the client may be contacted regarding filtration. If filtration is requested on a sample, remove a representative aliquot, but not more than 1 liter, and filter under vacuum using a 47-mm filtration apparatus equipped with a 47-mm diameter, 0.45-µm pore size, cellulose nitrate membrane filter.

NOTE: Screening residue weights may be used to determine the sample aliquot size required to produce an optimal planchet weight. If screening residue weights are available, calculate the sample size using the equation below, otherwise proceed with step 11.4.

Before optimizing sample aliquot size, consult QAS for residue weight restrictions. To determine the sample aliquot size required to produce an optimal residue weight, using a critical pipet, mix the sample and transfer a 10 mL aliquot of sample directly onto the appropriate pre-weighed planchet or into a small beaker. If the sample is transferred to a small beaker, heat the sample to near dryness and dissolve the residue with 2M HNO_3. Transfer sample to a pre-weighed planchet using three rinses of 2M HNO_3. Dry the planchet completely under a heat lamp, then cool. Weigh the planchet to determine the weight of the beta precipitate. The desired volume can be calculated using the equation shown below.

Aliquot volume (mL) =

$$\frac{Samplevolumeused(mL) \times desired\,alpha/beta\,weight(mg)}{sampleresidueweight(mg)}$$

desired weight for alpha or sequential alpha/beta determination = 50 mg

desired weight for beta only determination = 200 mg

desired weight for beta only determination with drinking water requirements = 100 mg

11.4. Mix the sample and transfer an appropriate aliquot of sample, as determined in 11.3. For alpha only or alpha and beta determination, not more than 57 mg of total solids (dissolved plus particulate) shall be contained. For beta, no more than 114 or 200 mg (consult QAS to determine residue limit) of total solids (dissolved plus particulate) shall be contained in the aliquot. For sample aliquots less than 75 mL, consult supervision. Procedure RICHRC5021, "Determination of Gross Alpha Activity in Water by Coprecipitation", should be used for samples with extremely high solids content.

11.5. Evaporate the aliquot to near dryness on a hot plate.

CAUTION: If samples will be left unattended while evaporating to near dryness, reduce the hot plate temperature. Do not allow samples to evaporate to dryness as this could cause loss of some activity due to volatilization.

11.6. If water samples are known or suspected to contain chloride salts, those chloride salts should be converted to nitrate salts before the sample residue is transferred to a stainless steel planchet.

NOTE: Chlorides will attack stainless steel and increase the sample solids, and no correction can be made for those added solids.

11.6.1.1. Chloride salts can be converted to nitrate salts by adding 5 mL portions of 16M HNO_3 to the sample residue and evaporating to near dryness. Two treatments are usually sufficient. Consult supervision for further information.

11.7. Weigh a planchet and record the weight on the appropriate planchet holder and on the back of the planchet. Quantitatively transfer the aliquot concentrate using 2M HNO_3, in small portions (not more than 5 mL at a time) to the pre-weighed planchet, evaporating each portion to dryness under a heat lamp or on a hot plate.

NOTE: Most types of water-dissolved solids, when converted to nitrate salts, are quite hygroscopic. Therefore, all sample planchets are flamed to convert the nitrate salts to oxides. Since it is possible to have a loss of cesium or other volatile betas during the flaming of the sample planchets, special care must be taken to only lightly flame, and not flame to a bright red appearance when analyzing for beta emitters. Planchets for alpha analysis may be flamed more vigorously.

For alpha/beta analysis on separate aliquots of sample, continue with 11.8. For sequential alpha/beta analysis on a single sample aliquot, continue with 11.9.

11.8. **For alpha/beta analysis on separate sample aliquots:**

11.8.1. Using forceps, gently flame the planchet over a gas flame. Allow the planchet to cool and then weigh the planchet to determine the sample residue weight. Record the planchet weight on the appropriate planchet holder. If the residue weight is greater than the desired weight, reflame the planchet, cool, and reweigh. If the residue weight is still too large, reprepare the sample.

11.8.2. After the residue weight has been recorded on the analytical work sheet, add a few drops of 1% collodion solution for alphas, or 10% collodion solution for betas, to secure the sample residue. Make sure the collodion is dry by placing the sample under a heat lamp, on a hot plate or in a drying oven set at 105°C. Proceed to step 11.10.

11.9. **For sequential alpha/beta analysis on a single sample aliquot:**

11.9.1. Using forceps, lightly flame the planchet over a gas flame. Allow the planchet to cool and then weigh the planchet to determine the sample residue weight. Record the planchet weight on the appropriate planchet holder. If the residue weight is greater than the desired weight, reflame the planchet, cool, and reweigh. If the residue weight is still too large, reprepare the sample.

11.9.1.1. Record the residue weight on the analytical worksheet.

11.9.1.2. Add a few drops of 10% collodion solution to secure the sample residue. Make sure the collodion is dry by placing the sample under a heat lamp or in a drying oven set at 105° C. Submit for beta counting with an absorber.

NOTE: If the samples cannot be counted within six hours, the sample planchet shall be stored in a desiccator or drying oven prior to counting. Excess moisture can cause erratic measurements and damage detectors.

11.9.1.3. Upon completion of the beta count, store the planchets in a desiccator until the beta data has been reviewed and accepted.

11.9.1.4. Following acceptance of the beta data, reflame the planchets vigorously. Allow the planchet to cool and then weigh the planchet to determine the sample residue weight. After the residue weight has been recorded, add a few drops of 1% collodion solution. Make sure the collodion is dry by placing the sample under a heat lamp, on a hot plate or in a drying oven set at 105°C.

11.9.1.5. Submit the samples to the counting room for alpha counting.

11.10. If the samples cannot be counted within six hours, the sample planchet shall be stored in a desiccator or drying oven prior to counting. Excess moisture can cause erratic measurements and damage detectors.

11.11. Planchet Stripping:

NOTE: This may not be performed on a planchet which has been vigorously flamed.

11.11.1. Place the planchet is a clean labeled beaker. Add 4M HNO_3 to cover the planchet.

11.11.2. Place the beaker on a hot plate and heat for 2 – 10 minutes.

11.11.3. Using forceps, lift the planchet and rinse the residue from the planchet with 4M HNO_3.

11.11.4. Dry the planchet.

11.11.5. Determine the appropriate aliquot as described in step 11.3 and proceed through the rest of the procedure.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.2. Waste Streams Produced by the Method

14.2.1. Aqueous acidic waste from planchet stripping.

14.2.1.1. Allow the 4M HNO_3 solution used in step 11.11 to cool to room temperature. Once cooled, empty the contents of the beaker into the Acid Waste container. This container is color coded with Yellow tape and a Yellow cap.

15. REFERENCES

15.1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. 703, Gross alpha and gross beta radioactivity (total, suspended, and dissolved). In: Franson, M.A.H., ed. Standard Methods for the Examination of Water and Wastewater. 16th Ed. Washington, D.C.: American Public Health Association; 1985.

15.2. Krieger, H.L.; Whittaker, E.L. Gross alpha and gross beta radioactivity in drinking water, method 900.0. In: Prescribed Procedures for Measurement of Radioactivity in Drinking Water. Cincinnati, OH: Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency; EPA-600/4-80-032; 1980.

15.3. Thatcher, L.L; Janzer, V.J.; Edwards, K.W. Gross alpha and beta radioactivity, dissolved and suspended residue method (R-1120-76). In: Techniques of Water-Resources Investigations of the United States Geological Survey, Chapter A5, Methods for Determination of Radioactive Substances in Water and Fluvial Sediments. Washington, D.C.: U.S. Government Printing Office; 1977.

15.4. U.S. Environmental Protection Agency. Method 9310, Gross alpha and gross beta. In: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846. 3rd Ed. Washington, D.C.: U.S. Government Printing Office; 1986.

15.5. RadCalc DB, Users Guide.

15.6. STL Quality Management Program, latest revision.

15.7. STL Richland Laboratory Quality Manual, latest revision.

15.8. STL Richland Site-Specific Quality Assurance Summary, latest revision.

15.9. Associated SOPs

15.9.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Review raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

16.2. Records Management/Documentation

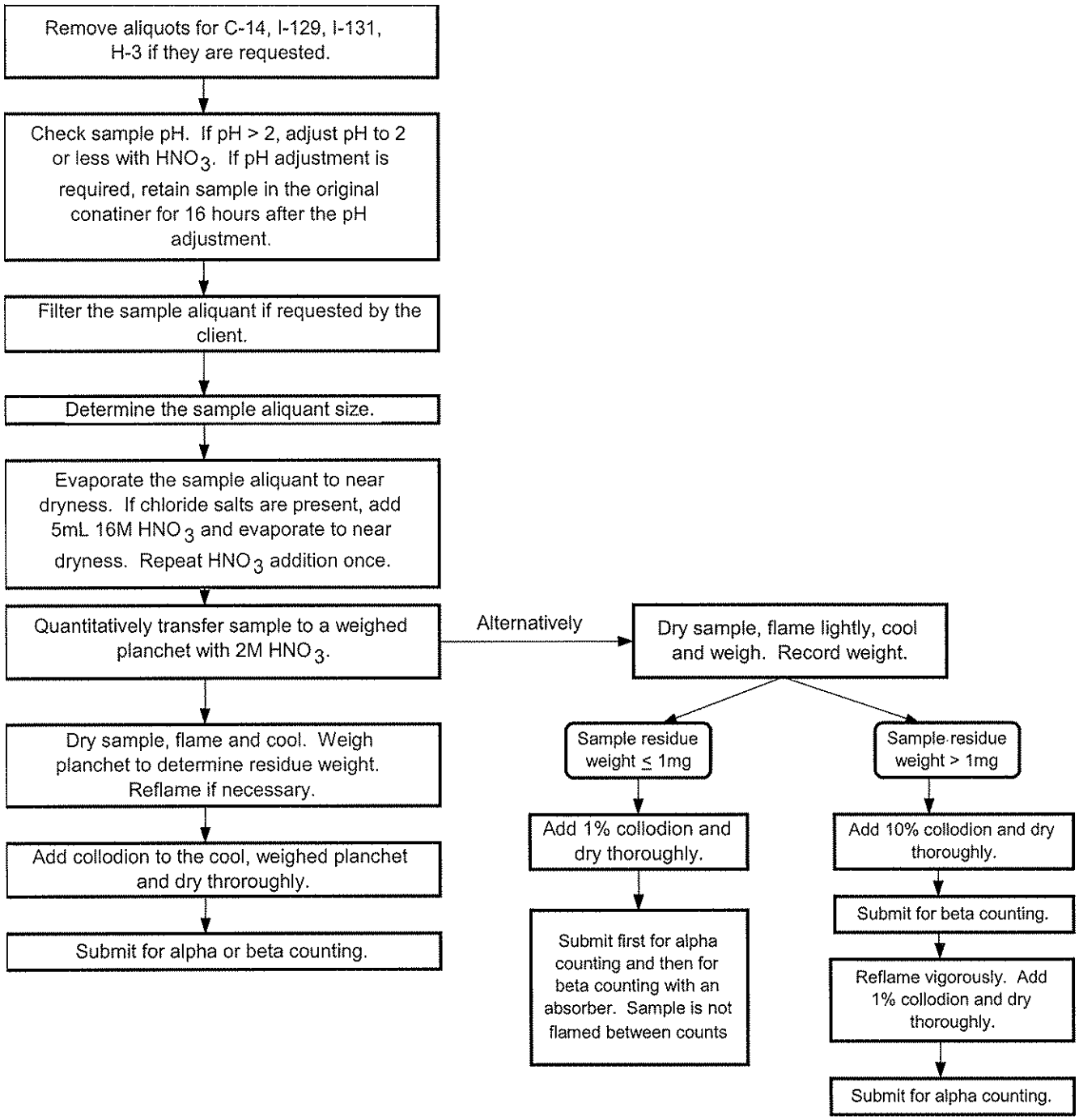
16.2.1. All records generated by this analysis will be filed and kept in accordance with STL QA policies for records management and maintenance.

16.3. Drinking Water Method Variations

16.3.1. Instead of using 10 ml 1M HNO_3 to transfer the sample to the planchet, several small portions of 2M HNO_3 are used to quantitatively transfer the sample.

16.3.2. This procedure allows for the use of heat lamps to dry the planchets in place of the drying oven.

16.4. Procedural Flow Chart



Title: Determination of Gross Alpha Activity in Water by Coprecipitation

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5021 Rev 5

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1. SCOPE AND APPLICATION

1.1. This procedure is used to prepare samples for the determination of gross alpha activity in water and urine by coprecipitation.

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. This method is applicable to the determination of gross alpha activity in water samples which have high dissolved solids. Alpha emitters such as actinides and radium are carried on the final precipitate.

3. DEFINITIONS

3.1. Decant – To pour off supernate gently without stirring up the precipitate.

3.2. Supernate – Liquid standing above a precipitate.

4. INTERFERENCES

4.1. Metal ions which form hydroxides near pH 7 can cause complications by coprecipitating with the iron hydroxide, mainly because they increase the weight of precipitate to be counted and make it difficult to obtain a uniform distribution of precipitate over the planchet. Anions such as citrate, dissolved CO_2, and phosphates can interfere by complexing alpha emitters and preventing them from being carried on the precipitate.

4.2. The typical sample size is 500 mL. Radon interferences are removed by boiling rapidly prior to analysis and then letting the sample sit for 3 hours for radon progeny to decay.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- Extreme care must be exercised when flaming planchets. Gloves that provide thermal protection must be worn during this section of the procedure. Ensure that compressed flammable gas cylinders are secure to prevent them from falling over.

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.

- Do not use hand to stop centrifuge from spinning.

5.1.1 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Collodion	Flammable	ACGIH 1000ppm TWA	May cause central nervous system depression. May cause liver and kidney damage. May be harmful if swallowed. Causes eye and skin irritation. May cause reproductive and fetal effects. May be harmful if absorbed through the skin. Causes respiratory tract irritation.
Iron Carrier	Oxidizer	ACGIH 1mg/m3 TWA NIOSH 1mg/m3 TWA	May cause severe eye irritation. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. May cause respiratory tract irritation.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Analytical balance.

6.2. Beakers - glass, various sizes.

6.3. Centrifuge.

6.4. Centrifuge tubes - plastic, approximately 100 mL.

6.5. Heat lamp.

6.6. Hot plate.

6.7. Magnetic stirrer with heating capabilities.

6.8. Meeker burner or propane gas cylinder.

6.9. pH paper - 0-14 range.

6.10. Pipets - transfer, plastic.

6.11. Planchets - 1 1/2" flamed or muffled with cardboard holders.

6.12. Plastic wrap.

6.13. Stir bars - 1 1/2" with stir bar remover.

6.14. Thermometer - able to read to 50°C, range 0°C -100°C.

6.15. Watch glass - various sizes.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. 6M Ammonium hydroxide (6M NH_4OH) - Add 400 mL of concentrated NH_4OH to approximately 500 mL of reagent water. Dilute to 1 L with reagent water and mix well. **CAUTION**: Corrosive.

7.3. Barium carrier (5 mg Ba^{++}/mL) - Dissolve 4.4 g $BaCl_2 \cdot 2H_2O$ in approximately 400 mL of reagent water. Dilute to 500 mL with reagent water and mix well.

7.4. 0.1% Bromocresol purple - Dissolve 100 mg of Bromocresol purple in approximately 80 mL of reagent water. Dilute to 100 mL with reagent water and mix well.

7.5. Collodion (1% solution) - Add 5 mL of collodion to a mixture of 300 mL of diethyl ether and 150 mL of ethyl alcohol. Mix well. **WARNING**: Flammable.

7.6. Iron carrier (5 mg Fe/mL) - Dissolve 17.5 g of ferric nitrate-nine hydrate ($Fe(NO_3)_3.9H_2O$) to 200 mL reagent water containing 2 mL of concentrated HNO_3 and mix. Dilute to 500 mL with reagent water and mix well. **WARNING**: Oxidizer.

7.7. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and Oxidizer.

7.8. 8M Nitric acid (8M HNO_3) - Add 500 mL 16M HNO_3 to approximately 400 mL reagent water. Dilute to 1L with reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.9. 1M Sulfuric acid (1M H_2SO_4) - Add 55 mL of concentrated H_2SO_4 to approximately 800 mL of reagent water. Dilute to 1 L with reagent water and mix well.

8. SAMPLE COLLECTION, PRESERVATIVES AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2. It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. If the sample is urine, go to step 11.3.1.

11.2. **NOTE**: If Carbon-14, Iodine-129, Iodine-131, or Tritium analyses have been requested and the aliquot to be taken from the same sample container, remove those aliquot(s) prior to acidification of the sample. Document on the analytical work sheet that aliquots were removed prior to acidification.

Using a wide range pH paper, measure the pH of the sample and record the pH on the analytical work sheet. If the pH is 2 or less, proceed to 11.3.

NOTE: Some clients do not want samples analyzed if preservation is incorrect. If the pH is above 2, consult the client specific QAS or supervision to determine if the sample analysis may proceed after acidification.

To acidify the sample, add acid to the sample using approximately 1 mL of concentrated HNO_3 to each liter of sample. Mix the sample and recheck the pH. Continue to add acid in 1 mL increments until the sample pH is below 2. Hold the sample in the original container for a minimum of 16 hours before continuing with this procedure.

11.3. Consult the QAS or supervision for client specific aliquots and requirements. Typically measure approximately 200 mL of sample into a labeled beaker. If it is necessary to use a sample size less than 500 mL, dilute to 500 mL with reagent water.

11.3.1. Wet ash muffled urine salts using concentrated HNO_3 and H_2O_2. Dissolve salts using approximately 5 mL of 2M HNO_3 and dilute to 500 mL with reagent water.

11.4. Measure the pH using pH paper with a 0-14 range. If the pH is less than 6.5, add 1 mL of bromocresol purple and 6M NH_4OH dropwise until the solution just turns purple.

11.5. Add 20 mL of 1M H_2SO_4. Bring to a vigorous boil on a hot plate and boil for 5 minutes. Remove from hot plate.

11.6. Wait for 3 hours before proceeding to allow radon daughters to decay.

11.7. Place the samples on a magnetic stirrer/heater with a thermometer in one sample. Turn on the heater and stirrer. When the sample reaches at least 40°C, add 1 mL of barium carrier.

11.8. Heat the sample to approximately 50°C while stirring for 30 minutes.

NOTE: If a temperature of 60°C is exceeded, the final iron hydroxide precipitate may not adhere to the planchet.

11.9. Add 1 mL of iron carrier and 1 mL of bromocresol purple reagent.

11.10. Continue stirring/heating and add 6M NH_4OH dropwise to the sample until the indicator color turns purple.

NOTE: It is important that the samples are brought just to the color change. Do not add any excess NH_4OH. If NH_4OH has been added in excess, add 8M HNO_3 dropwise until the indicator just returns to the yellow color. Then very carefully add 6M NH_4OH, one drop at a time, until the color change back to purple occurs.

11.11. Maintain the heat at 50°C and continue stirring for another 30 minutes.

11.12. Remove the sample from the heat source. Remove the stir bar using another stir bar or a stir bar remover and cover the sample with a watch glass or plastic wrap. Allow the precipitate to settle overnight.

11.13. Decant off most of the supernate, being careful not to lose the precipitate.

NOTE: If there is precipitate floating on top of the solution, transfer the floating precipitate to a labeled centrifuge tube with a transfer pipet before decanting the remaining liquid. Be careful not to lose any precipitate.

Decant the supernate to a basic waste container.

11.14. Transfer the precipitate to a labeled centrifuge tube. Rinse the beaker 3 times with a minimum volume of reagent water and add the rinses to the centrifuge tube.

11.15. Centrifuge at least 5 minutes. Decant the supernate to a basic waste container. Wash with about 5 mL reagent water. Centrifuge and decant the supernate to a basic waste container.

11.16. Transfer the precipitate to a previously flamed or muffled, labeled and tared 1 1/2" planchet using reagent water and a plastic transfer pipet. Dry under a heat lamp.

11.17. **NOTE**: If the precipitate weight is greater than 25 mg, flame the planchet. If the precipitate weight less than 25 mg, it is not necessary to flame the planchet.

Cool, weigh, and record the precipitate weight on the analytical work sheet and the planchet holder.

11.18. **NOTE**: If the planchet was flamed, re-weigh the planchet after it has cooled. Record the new weight.

Add three drops of 1% collodion to the planchet. Allow the planchet to air dry in a hood.

11.19. Complete the analytical work sheets and submit samples to the counting room for counting.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For calculation of the sample activity and its total propagated uncertainty (TPU), consult the latest revision of the RadCalc Users Guide. The complete computer calculation includes reagent blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1. Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container. Transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. Porter, Charles. Radiochemistry Procedures Manual, Environmental Protection Agency (EPA), Eastern Environmental Radiation Facility, EPA 520/5-84-006. Montgomery Alabama.

15.2. STL Quality Management Plan, latest revision.

15.3. STL Richland Laboratory Quality Manual, latest revision.

15.4. STL Richland Quality Assurance Summary, latest revision.

15.5. Associated SOPs

15.5.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

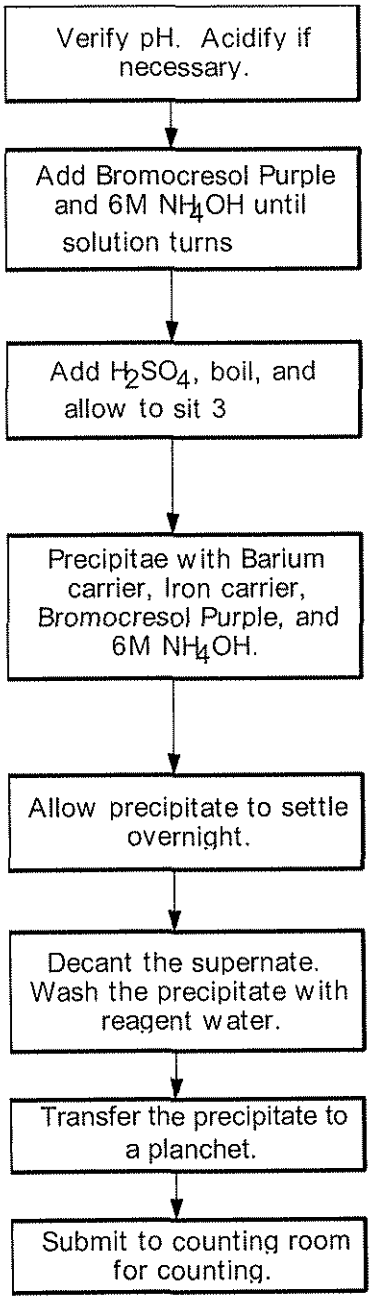
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance policies.

16.2. Records Management/Documentation

16.2.1. All records generated by this analysis will be filed and kept in accordance with STL QA policies for records management and maintenance.

16.3. Procedural Flow Chart



Title: Strontium Separation in Environmental Matrices

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5006 Rev 7

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1. SCOPE AND APPLICATION

1.1. This procedure is intended for the separation of Sr-89 and Sr-90, Sr-90 or total strontium in environmental matrices, including, but not limited to milk, soil, tissue, vegetation, surface and groundwater, drinking water, air filters, ion exchange resin, and high calcium content samples. Preliminary separations vary according to sample matrix, and then all samples undergo the same classical strontium chemistry.

1.2 The required drinking water detection limits for Sr-89 and Sr-90 are 10 pCi/L and 2 pCi/L respectively.

1.3 Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. Strontium is very effectively isolated from the sample matrix by first removing excessive chemical interferences through selective preliminary matrix separations, followed by more specific separation steps including nitrate and carbonate precipitations, and iron and barium scavenges. In particular, a fuming nitric acid precipitation separates Group II elements, including strontium, from all other elements.

2.2. A series of precise weight and activity determinations must be completed to verify the presence of strontium. Both a strontium and yttrium recovery must be established in this method. The strontium chemical yield is determined gravimetrically for the Sr-89 and Sr-90 or total strontium determinations. For Sr-90 determination only, the chemical yield is determined by counting of a Sr-85 tracer. Use of a radioactive tracer is deemed to be more accurate. After a period of ingrowth, the Yttrium-90 daughter is purified by successive hydroxide and oxalate precipitations, and the yttrium yield is determined gravimetrically. The Y-90 is beta counted at least two times to verify its decay. Sr-89, if requested, has a higher uncertainty associated with its value because it is established by subtracting the Sr-90 (Y-90) activity from the total strontium measurements.

2.3. After a specific matrix-dependent pre-separation, saturated sodium carbonate is added to the solution. The strontium carbonate is dissolved in dilute nitric acid. Iron and many fission products are removed by adding a mixed carrier, and precipitating them by raising the pH to alkaline. Radioisotopes of barium, radium, and lead are removed by adjusting the pH of the solution to 5-5.5, and adding barium carrier and sodium chromate solution to cause their precipitation. It may be necessary to perform an additional barium scavenge on difficult matrices. The strontium is reprecipitated as the carbonate, and then dissolved in fuming nitric acid. The precipitate is washed one or more times with concentrated nitric acid to remove calcium. The sample may then be counted for Sr-85 to determine the chemical yield, or the strontium carrier is precipitated by adding ammonium carbonate, weighed for gravimetric yield, and counted for Sr-89 and Sr-90.

2.4. After an appropriate ingrowth period, yttrium carrier is added. The yttrium is separated from strontium by successive hydroxide and oxalate precipitations. The yttrium oxalate is transferred to a tared counting dish. It is dried, converted to the oxide by flaming, and then weighed for chemical recovery. The sample is counted on a low background beta proportional counter to obtain the Y-90, and therefore Sr-90, activity of the sample. Decay counts are made to check the purity of the Y-90.

2.5. For strontium analysis, varying sample matrices require different preliminary separations to bring them to a common point for the Strontium Determination. According to the specific matrix or matrix interference, these preliminary separation steps are summarized below. These serve to remove excess organic material, calcium, sulfates, silicates, and phosphates.

2.6. Milk

2.6.1. Strontium is separated from milk and concentrated by equilibration with cation exchange resin using a batch technique. The resin after equilibration is washed with water to remove milk solids. Strontium is desorbed from the resin by equilibrating with 4M NaCl solution. Strontium is precipitated from the NaCl solution as the carbonate. The calcium is removed and strontium is precipitated by digestion in concentrated nitric acid and precipitated as the nitrate upon cooling.

2.7. Tissue (Organic Matrices)

2.7.1. Strontium is initially concentrated from tissue and other organic material such as meat, wildlife, and food samples (not requiring sequential analysis) by digestion in a mixture of nitric and sulfuric acids. Sulfuric acid increases the boiling point sufficiently to destroy all organic matter present in the sample. The strontium sulfate precipitate is converted to carbonate and excess calcium is removed.

2.8. Soil

2.8.1. The sample digestate residue following a fuming nitric acid precipitation (performed in the sample preparation procedure) is dissolved in water and filtered to remove silicates. The residue is examined for the presence of strontium salts and, if suspected to be present, the residue is metathesized with sodium carbonate. The carbonate precipitate is dissolved and combined with the filtrate fraction. A hydroxide precipitation is performed to remove iron and aluminum.

2.9. High Calcium Matrices

2.9.1. Strontium is initially separated from high calcium matrices such as eggshells, coral, and bone by dissolution and digestion in concentrated nitric acid. Strontium nitrate precipitates with cooling and agitation. Calcium will largely remain in solution under these conditions.

2.10. Vegetation (Pu/Sr Sequential Chemistry)

2.10.1. In the case of vegetation and produce requiring sequential analysis, for which the sulfuric acid digestion technique cannot be used (especially alfalfa and wheat), the water-insoluble residue of the fuming nitric acid salts may contain strontium, depending on the sulfate content of the sample. This residue is boiled with a saturated solution of sodium carbonate to metathesize the insoluble sulfate to the acid soluble carbonate. The carbonate is dissolved in nitric acid and combined with the water soluble fraction

2.11. Surface and Groundwater

2.11.1. Large volume water samples are concentrated by evaporation. All samples are neutralized with ammonium hydroxide. Some samples may require the removal of silicates and/or metal hydroxides.

2.12. Sequential Analysis (Water)

2.12.1. All water samples requiring other analyses (usually plutonium) must first have a fuming nitric acid separation performed as described in the sample preparation procedure, RICHRC5016.

2.13. Ion Exchange Resin Samples

2.13.1. The resin is transferred to a beaker and dried, then muffled for a week or more. The ashed resin is fused with sodium carbonate. The fusion "cake" is dissolved in water and hydrochloric acid, then reprecipitated as the carbonate.

2.14. Air Filter

2.14.1. The sample residue following a fuming nitric acid precipitation (performed in the sample preparation procedure, RICHRC5016) is dissolved in reagent water. Any undissolved residue is removed initially followed by hydroxide precipitation and rejection by filtration.

3. DEFINITIONS

3.1. Metathesis – The interchange of elements or radicals between compounds, as when two compounds react with each other to form two new compounds.

3.2. Precipitation – To cause a slightly soluble substance to become insoluble, as by heat or a chemical reagent, and separate out from a solution.

3.3. Scavenge – To add a substance to a mixture to remove or inactivate impurities or radioisotopes other than the isotope(s) of interest.

4. INTERFERENCES

4.1. This procedure is designed to remove radiochemical interferences. If they are suspected to be present upon review of the processed sample data, they can be removed by repetition of the strontium separation steps and/or through an yttrium remilking process.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1. Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

- Do not use hand to stop centrifuge from spinning.

- Never add anything to warm or hot H_2SO_4. Cool the sample completely before adding HNO_3.

- 16M HNO_3 and 30% H_2O_2 when mixed together will liberate large quantities of oxygen. If these are mixed together and the container is sealed, pressure may build up causing a pressure explosion. Always add nitric acid before adding 30% H_2O_2 to avoid possible vigorous reactions. Use extreme caution when wet-ashing samples.

- WARNING: Fuming nitric acid is a severe health hazard if not handled properly. Contact with skin and breathing of vapors must be avoided, and gloves and eye protection must be worn when handling. If fuming nitric acid contacts skin, immediately hold the exposed area under cool running water for fifteen minutes and call for help. Promptly report burns to supervision.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Ammonium Carbonate	Corrosive Poison	OSHA PEL 50ppm ACGIH TLV 25ppm 35ppm STEL	Harmful if swallowed or inhaled. Causes irritation to skin, eyes and respiratory tract. Ammonia vapors released upon decomposition may cause irritation of the upper respiratory tract, with coughing, vomiting and redness to the mucous membranes.
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Collodion	Flammable	ACGIH 1000ppm TWA	May cause central nervous system depression. May cause liver and kidney damage. May be harmful if swallowed. Causes eye and skin irritation. May cause reproductive and fetal effects. May be harmful if absorbed through the skin. Causes respiratory tract irritation.

Ethyl Alcohol	Flammable	ACGIH 1000ppm TWA NIOSH 1000ppm TWA; 1900 mg/m^3 TWA	Causes severe eye irritation. May cause skin irritation. May cause central nervous system depression. May cause liver and kidney damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Silver Nitrate	Poisonous Corrosive Oxidizer		Silver Nitrate should never be mixed with ammonia compounds as it can form azides which are powerful explosives. Never mix with finely particulate metals such as aluminum or zinc. Also avoid contact with organics. Stains skin and can cause burns.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Balance, capable of weighing to 100 grams.

6.2. Balance, capable of weighing to the nearest 0.001g.

6.3. Beakers, glass, various sizes.

6.4. Centrifuge.

6.5. Centrifuge tubes, 100 mL plastic and/or glass, 50 mL conical bottom with caps.

6.6. Filter paper, glass fiber GF/A or equivalent, with appropriate diameter.

6.7. Funnel, 60°, plastic or glass.

6.8. Heat lamp.

6.9. Hot plate.

6.10. Magnetic stirrer and Teflon stirring bar.

6.11. Meeker burner or equivalent.

6.12. Mixer, vortex or equivalent.

6.13. Muffle furnace, capable of reaching 500°C and 1000°C.

6.14. pH paper, measurable to 5-5.5 pH.

6.15. Pipettes, disposable, plastic.

6.16. Plastic jar, 250 mL or plastic vial, 25 mL.

6.17. Platinum crucible, 150 mL.

6.18. Stainless steel planchets pre-flamed, tared, 1½" or 1" with appropriate planchet holders.

6.19. Tech pen - containing ink that resists temperatures of 500°C or more.

6.20. Vacuum filtration system with Buchner funnel, suction pump, hoses and appropriately sized side arm flasks.

6.21. Volumetric flask.

6.22. Water bath, hot and ice.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. 1.5M Acetic acid - Add 86 mL 17.4M glacial acetic acid to approximately 800 mL reagent water. Dilute to 1 L with reagent water and mix well.

7.3. 3M Ammonium acetate (3M $NH_4C_2H_3O_2$) - Dissolve 231 g of $NH_4C_2H_3O_2$ in approximately 700 mL reagent water. Dilute to 1 L with reagent water and mix well.

7.4. Ammonium carbonate, saturated solution ($(NH_4)_2CO_3$) - Add water to solid ammonium carbonate in an appropriate container. (The 2.5 Kg size is convenient for this.) Let the mixture stand one day, with occasional agitation. Keep the bottle capped at all times, except when adding water or removing solution. An inventory of at least two inches (2") of solid ammonium carbonate shall be maintained at all times, if necessary add more reagent. **CAUTION:** Saturated ammonium carbonate solution decomposes when exposed to air.

7.5. Ammonium carbonate ($(NH_4)_2CO_3$) - Solid.

7.6. 14.7M Ammonium hydroxide (14.7 NH_4OH) - Concentrated. **WARNING:** Corrosive.

7.7. Barium carrier (10 mg Ba^{+2}/mL) - Dissolve 19 g $Ba(NO_3)_2$ in approximately 200 mL reagent water. Dilute to 1 L with reagent water and mix well. **WARNING**: Oxidizer.

7.8. Collodion (10% solution) - Add 50 mL of collodion to a mixture of 300 mL of diethyl ether and 150 mL of ethyl alcohol. Mix well. **WARNING**: Flammable.

7.9. Ethyl alcohol, anhydrous. **WARNING**: Flammable.

7.10. Diethyl ether. **WARNING**: Flammable.

7.11. Glacial acetic acid (17.4M CH_3OOH) -Concentrated.

7.12. 12M Hydrochloric acid (12M HCl) - Concentrated. **WARNING:** Corrosive.

7.13. 6M Hydrochloric acid (6M HCl) - Add 500 mL of concentrated HCl to approximately 400 mL of reagent water. Dilute to 1 L with reagent water and mix well. **WARNING:** Corrosive.

7.14. 30% Hydrogen peroxide (30% H_2O_2). **WARNING:** Corrosive and oxidizing.

7.15. Nitric acid (90% HNO_3) - Fuming. **WARNING:** Vapor and liquid are corrosive and oxidizing.

7.16. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING:** Corrosive and Oxidizer.

7.17. 8M Nitric acid (8M HNO_3) - Add 500 mL 16M HNO_3 to approximately 400 mL reagent water. Dilute to 1 L with reagent water and mix well. **WARNING:** Corrosive and Oxidizer.

7.18. 2M Nitric acid (2M HNO_3) - Add 125 mL of 16M HNO_3 to 800 mL of reagent water. Dilute to 1 L with reagent water and mix well.

7.19. 0.1% Phenolphthalein Indicator - Dissolve 1 gram phenolphthalein in a mixture of 700 mL of 95% ethyl alcohol. Dilute to 1 L with reagent water. Mix well. **WARNING**: Flammable.

7.20. Sodium carbonate (Na_2CO_3) - Saturated aqueous. Add 225 g Na_2CO_3 (granular) to 700 mL of reagent water and mix well.

7.21. Sodium carbonate (Na_2CO_3) - granular.

7.22. 0.15M Sodium chromate (0.15M Na_2CrO_4) - Dissolve 25 g of Na_2CrO_4 or 35.2 g $Na_2CrO_4 \cdot 4H_2O$ in approximately 100 mL of reagent water. Dilute to 1 liter with reagent water and mix well. **CAUTION:** Carcinogenic.

7.23. Sodium chromate (Na_2CrO_4) - solid. **CAUTION:** Carcinogenic.

7.24. Sodium hydroxide (NaOH) - Pellets. **WARNING**: Corrosive.

7.25. 12M Sodium hydroxide (12M NaOH) Slowly dissolve 480 g of sodium hydroxide pellets in approximately 400 mL reagent water. Dilute to 1 L with reagent water and mix well. Or, use the commercially prepared 50% NaOH solution. **WARNING:** Corrosive. Do not store for a long time due to CO_2 absorption which forms carbonate (CO_3^{2-}).

7.26. 18M Sulfuric acid (18M H_2SO_4) - Concentrated. **WARNING:** Corrosive.

7.27. Mixed Co, Ce, Cs, Mn, & Fe Hold back Carrier.

7.27.1. This solution contains 2 mg/mL Co and Ni, 1.0 mg/mL Cs, Mn, Fe and Ce. Transfer the following into a 250 mL beaker: 9.91 g $Ni(NO_3)_2 \cdot 6H_2O$ (Nickel nitrate),and 7.24 g $Fe(NO_3)_3 \cdot 9H_2O$ (Ferric nitrate), and 3.60 g $MnCl_2 \cdot 4H_2O$ (Manganous Chloride), and 8.07 g $CoCl_2 \cdot 6H_2O$ (Cobalt chloride), and 3.10 g $Ce(NO_3)_3 \cdot 6H_2O$ (Cerous nitrate), and 1.27 g CsCl (Cesium chloride).

Add 50 mL of reagent water and 5 mL 8M HNO_3. Warm gently until everything has dissolved, then transfer quantitatively to a 1 liter volumetric flask. Bring the volume to 1000.0 mL mark with reagent water, mix well, then pour into a storage bottle without rinsing the volumetric flask. **CAUTION**: Nickel nitrate is a carcinogen and an oxidizing agent. Ferric nitrate is an oxidizing agent.

7.28. Reagents for milk only:

7.28.1. Cation exchange resin - Dowex 50W-X8 (Na form), 50-100 mesh size, available from Bio-Rad Laboratories. (The commercially available H^+ form is converted into the Na^+ form by mixing 2 L of 4M NaCl and a 1 pound bottle of resin on a magnetic stirrer for 30 minutes. The resin is filtered in a large Buchner funnel and washed with reagent water until the wash water is chloride free when tested with 10% $AgNO_3$. If a white AgCl precipitate forms, additional water washings are necessary. (It is advantageous to prepare enough resin for several samples ahead of time.)

7.28.2. 4M Sodium chloride (4M NaCl) Dissolve 234 g NaCl in approximately 400 mL reagent water. Dilute to 1 L with reagent water and mix well.

7.28.3. 10% Silver nitrate (10% $AgNO_3$) -Dissolve 50 g of $AgNO_3$ in 500 mL of reagent water and mix well. Store in a dark bottle, away from light.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2 It is recommended that water samples be preserved with acid at the time of collection. For preservation, sufficient acid should be added to make the sample pH<2.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for QC acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate

notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1 For Sr-90 only, certain matrices may require the addition of increased amounts of strontium carrier; e.g. dried vegetation.

11.2 Pre-Separation Milk

11.2.1 Mix the samples well by shaking and inverting the original container several times.

NOTE: Milk must not be over 7 days from sample date.

11.2.2 Measure the milk sample into an appropriate sized clean labeled beaker. Add appropriate carrier/tracer (consult the QAS or supervision for specific vial activity and/or concentration) and rinse the vial three times with reagent water - not nitric acid, adding the rinses to the appropriate beaker. Remove the vial label and place on the corresponding analytical worksheet. Add approximately 100 mL of Dowex 50W-X8 resin (Na-form), equilibrated as described in the reagent section, to the milk sample aliquots. Stir for about three hours using a magnetic stirrer. Allow the resin to settle for 5-10 minutes. Decant as much of the milk as possible into an appropriate waste container without discarding any resin.

NOTE: If the sample appears curdled or otherwise unlike normal milk, contact supervision.

11.2.3 Add approximately 500 mL of reagent water to the beaker and stir for about one minute using a magnetic stirrer. Allow the resin to settle, decant, and discard the supernate to the appropriate waste container. Repeat this process until visible milk solids (cloudiness) have been removed from the resin.

11.2.4 Add approximately 400 mL of 4M NaCl solution to the resin sample and stir for about 15 minutes. Allow the resin to settle, then vacuum filter through a glass fiber GF/A filter and collect the filtrate in a 1000-mL side arm flask. Transfer the NaCl solution from the flask to a clean, labeled 1000-mL beaker. Transfer the resin from the filter reservoir back to the resin beaker using reagent water.

11.2.5 Add about 200 mL of 4M NaCl solution to the resin sample and stir for approximately 15 minutes, vacuum filter as before and rinse the resin with reagent water. Add this second NaCl solution and rinse from the flask to the 1000-mL beaker containing the 4M NaCl solution from the previous step. Discard the resin to an appropriate waste container.

11.2.6 Add 2-3 drops of 0.1% phenolphthalein indicator to the 4M NaCl solution, then add concentrated NH_4OH while stirring until the solution has reached endpoint (basic) pink.

11.2.7 Proceed to the section titled; Strontium Determination.

11.3 Tissue

11.3.1 Weigh an aliquot of the sample, as directed by the client specific QAS, in an appropriate sized clean labeled beaker (usually 1500-mL). Add the appropriate prepared carrier/tracer vial (consult the QAS or supervision for specific vial activity and/or concentration) and rinse the vial three times with reagent water, adding the rinses to the appropriate beaker. Remove the vial label and place on the corresponding analytical worksheet.

11.3.2 Add concentrated HNO_3 to cover the sample and warm the sample on a hot plate if necessary, to start digestion. Remove the beaker from the hot plate. Once the sample has dissolved, place the beaker on the hot plate and continue the digestion (adding nitric acid as necessary) until the brown fumes stop evolving. Remove the sample from the hot plate if the reaction becomes too vigorous, and reduce the heat to control the reaction. Repeat this step until only white salts remain.

11.3.3 The sample may be muffled at this time. Consult supervison to determine if the sample shall be muffled. If the sample is muffled, note on the analytical worksheet that muffling was performed and proceed to step 11.3.3.1. If the sample is not muffled, proceed to step 11.3.4.

11.3.3.1 After cooling, redissolve the salts in a minimum of 2M HNO_3. Add fuming HNO_3 until strontium begins to reprecipitate. Chill in an ice bath for at least 30 minutes. Transfer the sample to a clean labeled centrifuge tube with concentrated HNO_3. Centrifuge for approximately 5 minutes and decant the supernate to an appropriate waste container. Dissolve the strontium nitrate precipitate with reagent water. Proceed to the section titled; Strontium Determination.

11.3.4 **CAUTION:** Make sure the sample is completely cooled, then add the sulfuric acid, in this and other steps, slowly and carefully. Otherwise, the nitric and sulfuric acids will spatter violently. Do not add 30% H_2O_2 to a dry or nearly dry sample.

Evaporate the sample on a hot plate to near dryness. Remove the sample from the hot plate and allow the sample to cool to room temperature.

11.3.5 Add 30-50 mL of concentrated H_2SO_4 and about 200 mL of concentrated HNO_3. Heat the sample to boiling on a hot plate and continue the digestion. Reduce the volume until only sulfuric acid remains, indicated by the appearance of white wispy fumes.

11.3.6 **WARNING:** Never add anything to warm or hot H_2SO_4. Cool the sample completely before adding HNO_3.

Remove the sample from the hot plate and allow the sample to cool to room temperature. Add approximately 100 mL of concentrated HNO_3 the sample. About 3-5 mL of 30% H_2O_2 may also be added to complete the digestion. Heat the sample to boiling. (The black color disappears initially and will reappear after the HNO_3 is driven off, if organic material is still present.)

11.3.7 Remove the sample from the hot plate and allow to cool to room temperature. Add about 10 mL of concentrated HNO_3 and 1-2 mL of 30% H_2O_2 . Repeat this step until the sample does not turn black after the nitric acid has boiled away, and the solution remains yellow. White crystalline precipitate will be present at the bottom of the solution.

11.3.8 **NOTE:** Consult supervision for low calcium matrices where calcium carrier may be added.

Allow the sample to cool to room temperature and slowly add reagent water to a total volume of 300-400 mL. Strontium sulfate (soluble in concentrated H_2SO_4) will precipitate along with any calcium. Heat the sample just to boiling on a hot plate, remove from the hot plate, and allow the precipitate to settle. If no precipitate forms, warm the sample on a hot plate while stirring for one to two hours until precipitation is complete.

11.3.9 Vacuum filter the entire sample through a glass fiber GF/A filter (the size depending on the amount of precipitate), or decant most of the supernate to an appropriate waste container, and centrifuge the remaining sample. Wash the precipitate once with reagent water. Discard the wash to an appropriate waste container. Thoroughly rinse the digestion beaker with reagent water, adding the rinses to the filter or centrifuge tube. Transfer the precipitate to the digestion beaker with additional reagent water.

11.3.10 Metathesis - Add a few drops of 0.1% phenolphthalein indicator, and adjust the solution to the pink (basic) endpoint with concentrated NH_4OH. Add 200 to 300 mL of saturated Na_2CO_3 solution to the beaker and mark the initial level with a marker. Bring to a boil and boil on a hot plate the sample for at least 2 hours to fully convert the strontium sulfate to strontium carbonate. Add reagent water while digesting to maintain the original level of the sample. Use a Teflon stir bar and stirring hot plate if the sample bumps when heated.

11.3.11 Observe the amount of carbonate precipitate. If large amounts of precipitate, indicating high calcium content, are observed, proceed to the next step. If the precipitate is light, allow the precipitate to settle overnight and proceed to the section titled; Strontium Determination starting at step 11.11.2.

11.3.12 If the sample is high in calcium, vacuum filter through a glass fiber GF/A filter and rinse the precipitate with reagent water. Discard the solution in the filter flask to an appropriate waste container. Reset the flask under the Buchner funnel and add concentrated HNO_3 in small amounts to dissolve the precipitate. Rinse the filter with small amounts of 2M HNO_3, and transfer the acid solution to the labeled beaker. Rinse the flask with more concentrated HNO_3 adding the rinses to the beaker. Proceed to step 11.4.3 of High Calcium Matrices with the solution in the beaker. Discard the filter to an appropriate waste container.

11.4 High Calcium Matrices

11.4.1 Weigh an aliquot of the sample, as specified in the client specific QAS, in an appropriate sized clean labeled beaker. Add the appropriate prepared carrier/tracer vial (consult the QAS or supervision for specific vial activity and/or concentration) and rinse the vial three times with reagent water, adding the rinses to the appropriate beaker. Remove the vial label and place on the corresponding analytical worksheet.

11.4.2 Initially, without applying any heat add concentrated HNO_3 very slowly to completely cover the sample. Heat the sample gently on a hot plate until the sample is entirely dissolved. Remove the sample from the hot plate if the reaction becomes too vigorous. Organic samples, such as bone or eggshell, may require wet ashing with 30% H_2O_2 to completely digest the sample. If the

sample does not dissolve completely, add more concentrated HNO_3 but do not exceed 250-300 mL. Consult supervision if the sample does not dissolve.

11.4.3 Evaporate the sample on a hot plate until the volume is less than 100 mL. Remove the sample from the hot plate and allow the sample to cool to room temperature. Place the beaker in an ice water bath for at least 30 minutes. If a precipitate does not form, add a magnetic stirring bar and stir the sample until a precipitate begins to form. Then place in an ice bath again for at least 30 minutes. Add at least 15 mL of fuming nitric acid to the sample until a precipitate forms. If no precipitate forms, contact supervision.

NOTE: Strontium nitrate will precipitate in concentrated HNO_3 and calcium nitrate should stay in solution.

11.4.4 Allow the precipitate to settle. Decant most of the supernate to an appropriate waste container and transfer the remaining sample to a clean labeled centrifuge tube with concentrated HNO_3. Centrifuge for approximately 5 minutes. Decant the supernate to an appropriate waste container. (Vacuum filtration may be used in place of centrifugation.) If the precipitate is heavy add about 30 ml of concentrated HNO_3 to the precipitate, suspend the precipitate using a vortex mixer. Centrifuge and decant the supernate to an appropriate waste container. Repeat the wash one more time.

11.4.5 Dissolve the strontium nitrate precipitate in a minimum amount of reagent water, then transfer the sample to the beaker from the previous step using a total rinse of about 100 mL reagent water.

NOTE: If the volumes permit, samples may be dissolved in 15-20 mL of reagent water. Continue with step 11.11.4 of the Strontium Determination Section.

11.4.6 Add a few drops of 0.1% phenolphthalein indicator, and adjust the solution to the pink (basic) endpoint with concentrated NH_4OH. Continue with step 11.11.4 of the Strontium Determination Section.

11.5 Soil

11.5.1 Residue/Precipitation Dissolution

11.5.1.1 For the sample residue from RICHRC5013, go to step 11.5.2.

11.5.1.2 For the fuming nitric acid precipitate from RICHRC5013, go to step 11.5.3.

11.5.2 Dissolve the residue in an appropriate volume of 2M HNO_3 and warm on a hot plate to dissolve. Proceed to step 11.5.4. Consult supervision for the appropriate volume.

11.5.3 Transfer the fuming nitric acid precipitate from the Pu-Sr (RICHRC5013) separation to the original sample leaching beaker using about 100 mL reagent water. Warm the sample on a hot plate to dissolve the precipitate. Proceed to the next step.

11.5.4 Remove the sample silicates (sand) by vacuum filtration using a Buchner funnel equipped with a glass fiber GF/A filter. Rinse the filter with reagent water. Save the filtrate containing the strontium in the beaker used in the previous steps.

11.5.5 **NOTE:** If the insoluble material on the glass fiber GF/A filter has any crystalline material that look similar to table salt, continue with the next steps, otherwise go to step 11.5.7.

Transfer the undissolved residue to a clean labeled beaker with reagent water. Add 0.1% phenolphthalein indicator and adjust the pH to the pink (basic) endpoint using concentrated NH_4OH. Add 100 to 300 mL of saturated Na_2CO_3 solution and boil the solution on a hot plate for at least 2 hours to convert the strontium sulfate to the carbonate form.

11.5.6 Centrifuge or vacuum filter (using a glass fiber GF/A filter) the precipitate and discard the supernate/filtrate to an appropriate waste container. Dissolve the precipitate (in the centrifuge tube or on the filter) with a minimum amount of concentrated HNO_3 and dilute with reagent water. Combine this solution with the filtrate from the step 11.5.4.

11.5.7 Add 2-3 drops of 0.1% phenolphthalein indicator and adjust to the pink (basic) endpoint using concentrated NH_4OH, then add about 10 mL in excess to make it strongly alkaline. The sample will probably be gelatinous at this stage due to aluminum and iron hydroxides. If the sample solidifies, add more ammonium hydroxide and water, stir, and warm on a hot plate until the solution thins.

NOTE: Ammonium hydroxide should be added until the hydroxide precipitation is complete, then add 10 mL of ammonium hydroxide in excess.

11.5.8 Vacuum filter the sample through a glass fiber GF/A filter. Rinse the beaker and the filter with reagent water. Save the hydroxide precipitate until acceptable strontium yields have been achieved. If large quantities of phosphate are present in the soil, it may be necessary to perform a fuming nitric precipitation to recover the strontium. Proceed to the section titled, Strontium Determination.

11.6 Water - Surface and Groundwater and Drinking Water- Non sequential analysis.

11.6.1 Add an appropriate aliquot of sample, as specified by the client specific QAS, in an appropriately sized clean labeled beaker. If the sample was previously concentrated for a gamma analysis, transfer it to a beaker and dilute to about 500 mL with reagent water. Add a prepared carrier/tracer vial (consult the QAS or supervision for specific vial activity and/or concentration) if this has not already been done. Reduce the volume of larger volume samples by heating to about 500 mL. Samples of one liter or less do not require volume reduction.

11.6.2 Add 2-3 drops of 0.1% phenolphthalein indicator and adjust to the pink (basic) endpoint with concentrated NH_4OH. Then add 10 mL in excess.

11.6.3 If the samples have little hydroxide precipitate present (usually with smaller volume samples) proceed directly to the section titled; Strontium Determination.

11.6.4 If the samples have large amounts of hydroxide forming elements (i.e. Al, Fe), warm the sample for a few minutes on a hot plate. Remove the precipitate by vacuum filtration using a glass fiber GF/A filter paper. Wash the precipitate with reagent water. Save the filter until acceptable chemical recovery yields have been obtained as defined in the QAS. Return the filtrate to the beaker and proceed to the section titled; Strontium Determination.

NOTE: The samples may be centrifuged instead of filtering. If the sample is centrifuged, add the water wash to the initial supernate. The precipitate in the centrifuge tube should be saved.

11.7 Water - Sequential Analysis

11.7.1 If the sample has been prepared according to RICHRC5016, proceed to step 11.7.6. If the sample has not been prepared according to RICHRC5016, proceed to the next step.

11.7.2 Add an appropriate aliquot of sample, as specified in the client specific QAS, to an appropriately sized clean labeled beaker. Acidify the sample by increasing the volume by 5% with concentrated HNO_3 and add a prepared Pu-Sr tracer/carrier vial (consult the QAS or supervision for specific vial activity and/or concentration). Rinse the vial three times with reagent water, adding the rinses to the appropriate beaker. Remove the vial label and place on the corresponding analytical worksheet.

11.7.3 Evaporate the sample to approximately 200 mL on a hot plate. Transfer the sample to a 600 mL beaker and evaporate to just dryness. Allow the sample to cool to room temperature.

11.7.4 Add about 10 mL of reagent water and warm the beaker on a hot plate to dissolve the sample. Add an equal amount of concentrated HNO_3 to dissolve the precipitate off the bottom of the beaker. Evaporate most of the liquid on a hot plate but do not allow to splatter. Transfer this solution quantitatively to a 100-mL centrifuge tube with concentrated HNO_3. Be very careful to assure that the last drop transfers.

11.7.5 **CAUTION**: Add the fuming nitric very slowly at first to avoid sample loss due to the effervescence. Fuming nitric acid can be hazardous, especially when brought into contact with organics that may still be present in the sample. Exercise extreme care in the following step.

Carefully add approximately 40 mL fuming nitric acid to the beaker and carefully transfer this rinse into the 100-mL centrifuge tube. Add an additional 20-30 mL of fuming nitric acid to the beaker and transfer this rinse also to the 100-mL centrifuge tube. Centrifuge for about 5 minutes and transfer the fuming nitric acid supernate (Pu fraction) to a clean, labeled, 250-mL beaker. Evaporate to dryness and submit the supernate residue to the appropriate laboratory for further separation.

11.7.6 Dissolve the strontium nitrate precipitate in the centrifuge tube in 10-20 mL of reagent water. Transfer the sample to the beaker used in the previous step. Rinse the tube with reagent water to ensure complete transfer, adding the rinse to the appropriate beaker. Proceed to the section titled; Strontium Determination.

11.8 Air Filters

11.8.1 Dissolve the fuming nitric acid salts from the Pu-Sr separation (RICHRC5016) in about 15-20 mL of reagent water while vortexing. Place the sample in a hot water bath to assist dissolution. Centrifuge the sample to remove any undissolved residue. Decant the supernate to a clean labeled beaker. Save the residue until an acceptable chemical recovery is obtained by sufficient precipitate designated in the QAS or by supervision. The residue may be discarded to an appropriate waste container when sufficient chemical yield is obtained.

11.8.2 Add 2-3 drops of 0.1% phenolphthalein indicator to the solution. Adjust the pH to the pink (basic) endpoint using concentrated NH_4OH, then add 10 mL in excess to make the sample strongly alkaline. Transfer the sample to a clean, labeled centrifuge tube with reagent water and proceed to the Strontium Determination Section.

11.9 Produce

11.9.1 Samples (produce-wet) are prepared according to RICHRC5016.

11.9.2 Dissolve the residue from RICHRC5016 in approximately 500 mL of reagent water and approximately 10 mL of concentrated HNO_3. Warm on a hot plate to ensure total dissolution. Let the samples cool.

11.9.3 Add 2-3 drops of 0.1% phenolphthalein indicator and adjust to the pink (basic) endpoint with concentrated NH_4OH. Then add 10 mL in excess.

11.9.4 If the samples have little hydroxide precipitate present (usually with smaller volume samples) proceed directly to the section titled; Strontium Determination.

11.9.5 If the samples have large amounts of hydroxide forming elements (i.e. Al, Fe), warm the sample for a few minutes on a hot plate. Remove the precipitate by vacuum filtration using a glass fiber GF/A filter paper. Save the filter until acceptable chemical recovery yields have been obtained as defined in the QAS. Return the filtrate to the beaker and proceed to the section titled; Strontium Determination.

11.10 Dried Vegetation, Wheat, Leaves and Potatoes (produce-dry)

11.10.1 Samples are prepared according to RICHRC5016.

11.10.2 Sequential Pu/Sr: Transfer the fuming HNO_3 precipitate from RICHRC5016 to the digestion beaker using reagent water and heat the sample to assist dissolution on a hot plate. Proceed to step 11.10.6.

Non-Sequential Sr: Add approximately 100 mL of 2M HNO_3 to the sample residue from RICHRC5016. Warm on a hot plate to promote dissolution. Remove the sample from the hot plate and allow the sample to cool to room temperature. Proceed to step 11.10.3.

11.10.3 Add 30 - 50 mL of concentrated H_2SO_4 to the sample and about 200 mL of concentrated HNO_3. Heat the sample to boiling and continue boiling until only sulfuric acid remains. Continue the digestion until heavy white fumes appear and the volume is less than the amount of sulfuric acid

added.

NOTE: If the sample turned black during this boil down, allow the sample to cool to room temperature. Add an additional 200 mL of concentrated HNO_3 and heat to boiling and reduce the volume until only sulfuric acid remains. Repeat until the sample no longer turns black.

11.10.4 Allow the sample to cool to room temperature. Slowly add reagent water to a total volume of 300 - 400 mL. Strontium sulfate (soluble in concentrated sulfuric) will precipitate along with any calcium. Heat the sample just to boiling on a hot plate. Remove the sample from the hot plate and allow the precipitate to settle. If no precipitate forms, warm the sample on a hot plate while stirring for one to two hours until the precipitation is complete.

11.10.5 Vacuum filter the sample using a glass fiber GF/A filter or decant most of the supernate and centrifuge the remaining sample. Discard the filtrate or decanted supernate to an appropriate waste container. Wash the precipitate once with reagent water. Discard the rinse to an appropriate waste container. Transfer the precipitate (from the filter or centrifuge tube) into the digestion beaker with reagent water.

11.10.6 Metathesis:

11.10.6.1 Add a few drops of 0.1% phenolphthalein indicator and adjust the pH to the pink (basic) endpoint using concentrated NH_4OH. Add 200 to 300 mL of saturated Na_2CO_3 solution to the beaker, mark the level of the solution on the beaker, and place the beaker on a hot plate. Bring the solution to a boil and boil for at least 2 hours to fully convert the sulfate to carbonate. Maintain the level of the solution by adding reagent water as needed. Use a Teflon stir bar and a stirring hot plate if the sample bumps while being heated.

11.10.6.2 Remove the beaker from the hot plate and allow to cool.

11.10.6.3 Vacuum filter the solution using a glass fiber GF/A filter, then rinse the precipitate with reagent water. Discard the filtrate to an appropriate waste container. Reset the Buchner funnel on the filter flask. Add concentrated HNO_3 in small amounts to dissolve the precipitate. The entire filter should be in contact with the HNO_3. Rinse the filter with small amounts of 2M HNO_3 and transfer the acid solution to a clean labeled beaker. Rinse the filter flask with 2M HNO_3, adding the rinses to the appropriate beaker.

NOTE: Samples may be centrifuged using approximately 20 mL rinses. Discard the reagent water rinse and **save** the concentrated HNO_3 and 2M HNO_3 rinses to a clean labeled beaker as above. Dilute solution in beaker with reagent water to minimize reaction of the next step.

11.10.6.4 Add a few drops of 0.1% phenolphthalein indicator to the sample solution and adjust the pH to a basic (pink) endpoint with concentrated ammonium hydroxide.

11.11 Strontium Determination

CAUTION: Fuming nitric acid is used in this procedure. It is hazardous; especially when brought in contact with organics, therefore exercise extreme care.

NOTE: At the discretion of supervision, waste fractions may be saved until acceptable chemical recoveries are obtained.

11.11.1 To the solution obtained from the matrix pre-separation, add saturated Na_2CO_3 solution until a precipitate forms (usually about 100 mL is required). Heat the sample on a hot plate for 10-15 minutes. It may be necessary to stir the sample to prevent bumping and loss of sample. Remove from the heat and allow the carbonate precipitate to settle. Inspect the sample for high calcium. Allow to sit for a minimum of one hour.

11.11.2 **NOTE**: For more rapid analysis, the carbonate precipitate may be vacuum filtered, using a glass fiber GF/A filter paper, instead of centrifuged.

Decant most of the supernate to an appropriate waste container. Transfer the remaining sample to a 50 or 100 mL centrifuge tube using reagent water to rinse the beaker. Centrifuge and decant the remaining supernate to an appropriate waste container.

11.11.3 Rinse the beaker with a minimum amount of 2M HNO_3 and add the rinse to the centrifuge tube. If necessary, dissolve the carbonate precipitate in a minimum of concentrated HNO_3. Dilute the solution to about 10-15 mL with reagent water.

11.11.4 Add 3-4 drops of mixed holdback carrier. Add a few drops of 0.1% phenolphthalein indicator and mix, adjust the pH to the pink (basic) endpoint with concentrated NH_4OH. Allow the iron and other metal hydroxides to flocculate (form a rusty suspended precipitate).

11.11.5 Centrifuge (or vacuum filter using a glass fiber GF/A filter) and decant the supernate to a clean, labeled centrifuge tube (or beaker). If the precipitate appears heavy, rinse the precipitate with approximately 10 mL of reagent water, centrifuge and combine the supernates. If the hydroxide precipitate is very heavy, the precipitate should be saved until acceptable strontium yields have been achieved.

NOTE: Acceptable yields are determined by either the final yield monitor recovery or visual inspection of the precipitate volume at the conclusion of step 11.11.8.2.

Strontium may have been lost at this point as either a phosphate or sulfate. A fuming nitric acid precipitation is required for phosphate and a metathesis with sodium carbonate is required if sulfate is present. Contact supervision.

NOTE: If advised by supervision, it may be necessary to repeat the above step, depending upon the suspected levels of radioactive contaminants.

11.11.6 To the supernate, add 10 mL of freshly prepared buffer solution, made by mixing equal amounts of 1.5M acetic acid and 3M ammonium acetate. Using pH paper, verify the pH of the sample is 5-5.5.

NOTE: (Methyl red indicator may be used as an initial guide to adjusting pH. However, the final pH must be determined using pH paper.)

If the pH is outside the limit, use concentrated HNO_3 or concentrated NH_4OH to adjust the solution (lower concentrations of HNO_3 and NH_4OH may be used if necessary).

11.11.7 Add approximately 1 mL of barium carrier and about 1 mL of 0.15M Na_2CrO_4 (sodium chromate) solution. If the precipitate does not form, recheck the pH of the solution, readjust if necessary, and add 2 drops of Ba carrier and 2 drops of Na_2CrO_4 solution down the sides of the centrifuge tube. Allow 20 minutes for precipitation. Consult supervision if a precipitate still does not form.

11.11.8 Centrifuge at least five minutes and/or filter the $BaCrO_4$ through a 60° funnel (using glass fiber GF/A filter paper) into a clean, labeled centrifuge tube.

11.11.8.1 For vegetation, soil, and filter samples: Repeat the above step if advised by supervision.

11.11.8.2 **NOTE:** If either a small or large amount of precipitate forms during the following step, save the supernate and contact supervision.

Fill each centrifuge tube containing the $BaCrO_4$ supernate with 2-3 mL of NH_4OH and then at least 40 mL of saturated $(NH_4)_2CO_3$. If this is not possible, split the sample solution between two or more tubes. Allow the precipitate to settle for 20-30 minutes. Centrifuge for at least 10 minutes and decant the supernate to an appropriate waste container. Vacuum filtration may be used for large volume samples.

11.11.8.3 **CAUTION:** Add the fuming HNO_3 very slowly at first to avoid sample loss due to the effervescence. Fuming HNO_3 can be hazardous, especially when brought into contact with organics that may still be present in the sample. Exercise extreme care in the following step.

Add fuming HNO_3 dropwise to the precipitate until the effervescence has ceased. If calcium is suspected in large quantities, proceed to step 11.11.8.3.1. If calcium is considered to not be a problem, proceed to step 11.11.8.3.2.

NOTE: If the precipitate is large, consider splitting the sample into two or more centrifuge tubes and fill each with fuming HNO_3.

11.11.8.3.1 Add about 5 mL of fuming HNO_3, followed by 20-30 mL of concentrated HNO_3, then add 15-20 mL of fuming HNO_3. Contact supervision for guidance, if necessary. Centrifuge for at least 5 minutes and decant the supernate to an appropriate waste container.

11.11.8.3.2 Add at least 50 mL of fuming HNO_3 and cool in an ice bath for about 20 minutes. Centrifuge for at least 5 minutes and decant the supernate to an appropriate waste container.

11.11.8.4 Add about 30 mL of concentrated HNO_3 to the precipitate, the volume used depending on sample matrix. Suspend the precipitate using a vortex mixer. Centrifuge and decant the supernate to an appropriate waste container. Repeat the wash one or more times. High calcium content matrices may require several concentrated HNO_3 washes. Record the time

of the last concentrated HNO_3 rinse as the Sr-90/Y-90 separation time on the analytical worksheet.

NOTE: Consult supervision if an unusually large precipitate does not appear to diminish in size after two concentrated HNO_3 washes.

11.11.9 If Sr-85 tracer was added:

11.11.9.1 Dissolve the sample precipitate in reagent water and (depending on the gamma counter to be used) transfer to either a 25 mL volume in a plastic jar or a 20 mL volume in a plastic scintillation vial. Submit the sample with the Sr-85 analytical worksheet to the counting room for a gamma count for Sr-85 recovery. After counting continue with the Sr-90 (by yttrium-90) chemistry as per SOP RICHRC5071.

11.11.10 If the sample has only strontium carrier, with no Sr-85 tracer:

11.11.10.1 Dissolve the precipitate in approximately 10 mL of reagent water, then add approximately 10 mL of concentrated NH_4OH, and vortex. Fill the centrifuge tube nearly to the top with saturated $(NH_4)_2CO_3$ solution. Allow the solution to precipitate for at least 10 minutes. Centrifuge for at least 10 minutes on high speed. Pour the supernate to an appropriate waste container.

11.11.10.2 Wash the precipitate with reagent water. Mix, centrifuge for approximately 5 minutes and decant the supernate to an appropriate waste container.

11.11.10.3 Using a minimum of reagent water and a disposable pipet, transfer the precipitate quantitatively to a previously flamed, tared, and labeled stainless steel 1½" planchet. Place the planchet under a heat lamp until dry.

11.11.10.4 Allow the planchet to cool. Weigh and record the precipitate weight on the analytical worksheet.

NOTE: If the precipitate weight is greater than 105 mg, bake the planchet for approximately 15 minutes by placing it directly on a hot plate set on high heat. Allow the planchet to cool and reweigh. Record the weight on the appropriate analytical worksheet. Consult supervision if the weight remains high.

11.11.10.5 Place the planchets in planchet holders and submit the samples and associated worksheets to the counting room, as directed by supervision, to determine the total Sr-89 plus Sr-90 activity. If necessary several counts (usually three) are made over a two week period to note the Y-90 ingrowth and/or Sr-89 decay. After the Sr counting is completed, store the planchet for the Y-90 chemistry as per SOP RICHRC5071.

12 DATA ANALYSIS AND CALCULATIONS

12.1 For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete computer calculation includes blank subtraction if requested by the customer and complete error propagation.

13 METHOD PERFORMANCE

13.1 The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2 Method Demonstration of Capability documentation is maintained in the quality files.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.
- Aqueous acidic waste pH< 2. Waste is collected in a Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in a Flammable waste container which is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15 REFERENCES

15.1 Sunderman, D.N., Townley, C.W. The Radiochemistry of Barium, Calcium, and Strontium. Subcommittee on Radiochemistry, National Academy of Science-National Research Council, Office of Technical Services, Department of Commerce, Washington, D.C.

15.2 Baratta, E.G., Knowles, F.E., Jr. Association of Official Analytical Chemists. 56: 1,213-218, 1973.

15.3 Krieger, H.L., Whittaker, E.L. "Radioactive strontium in drinking water, Method 905.0" section 9 in Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA 600/4-80-032, August 1980.

15.4 Chieco, N.A., D.C. Bogen, and E.O. Knutson. eds. 1990 EML Procedures Manual, Sr-02, HASL-300, 27th Edition, Volume1. Environmental Measurements Laboratory, US Department of Energy, New York, New York.

15.5 Stevenson, P.C., Nervik, W.E. The Radiochemistry of the Rare Earths: Scandium, Yttrium, and Actinium. Subcommittee on Radiochemistry, National Academy of Science - National Research Council, Office of Technical Services, Department of Commerce, Washington, D.C.

15.6 RadCalc DB, Users Guide, STL Richland.

15.7 STL Quality Management Plan, latest revision.

15.8 STL Richland Laboratory Quality Manual, latest revision.

15.9 STL Richland Quality Assurance Summary, latest revision.

15.10 Associated SOPs

15.10.1 RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

15.10.2 RICHRC5016 - Environmental Sample Preparation.

15.10.3 RICHRC5013 - Soil and Sediment Preparation.

15.10.4 RICHRC5068 – Preparation of Soil, Vegetation and Air Filters by Mixed Strong Acid Leaching.

15.10.5 RICHRC5071 – Yttrium-90 Separation for Strontium-90 Determination in all Matrices.

16 MISCELLANEOUS

16.1 Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review of raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments.

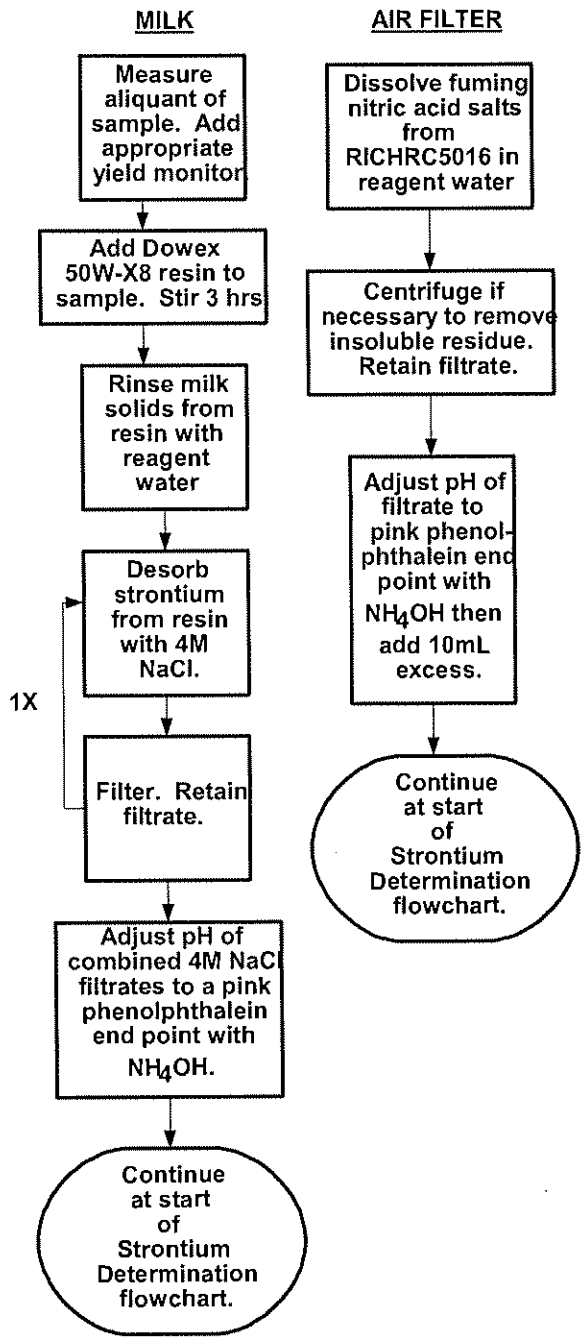
16.2 Records Management/Documentation

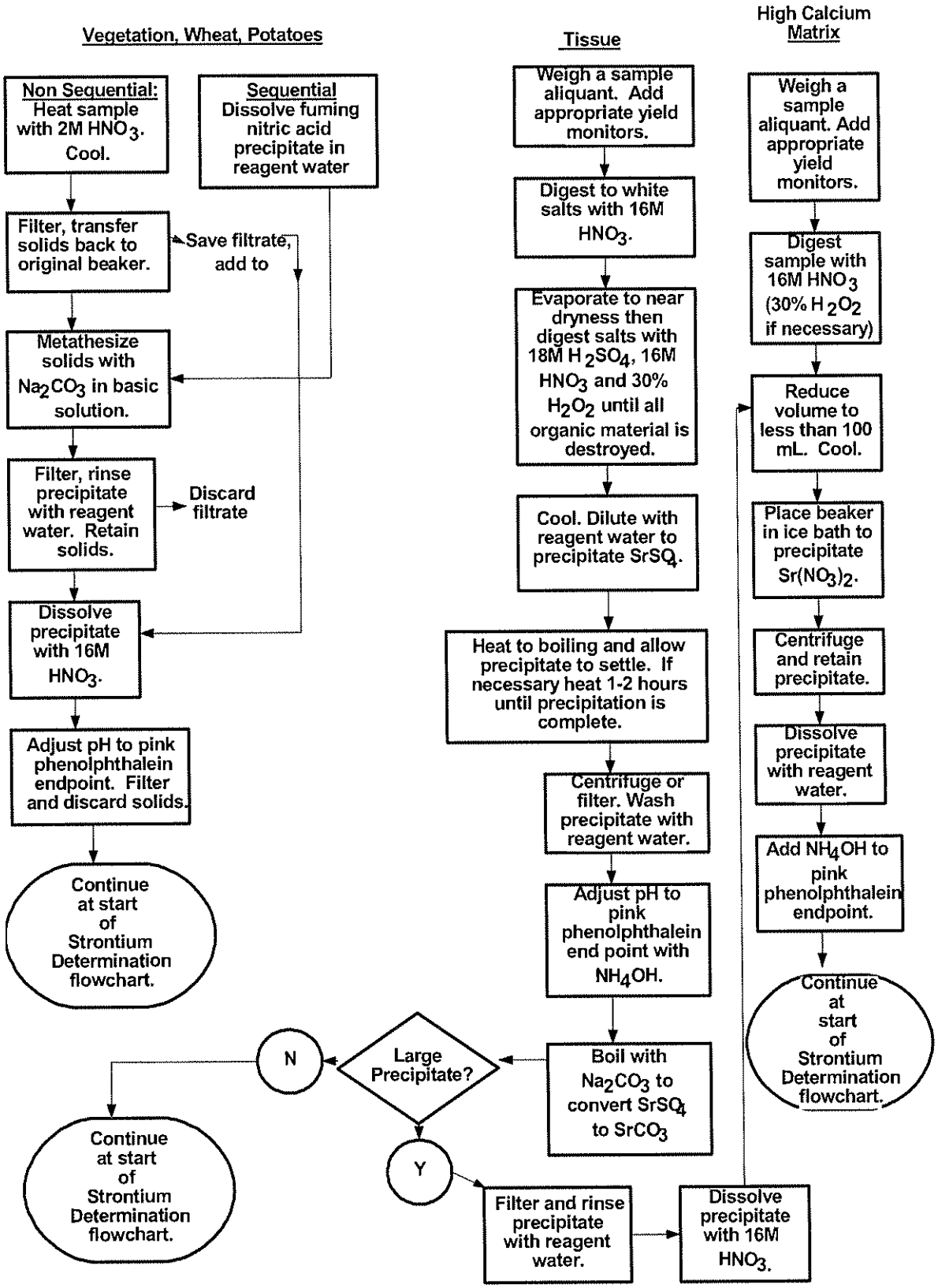
16.2.1 All records generated by this analysis will be filed and kept in accordance with STL Richland policies for records management and maintenance.

16.3 Drinking Water Method Variations

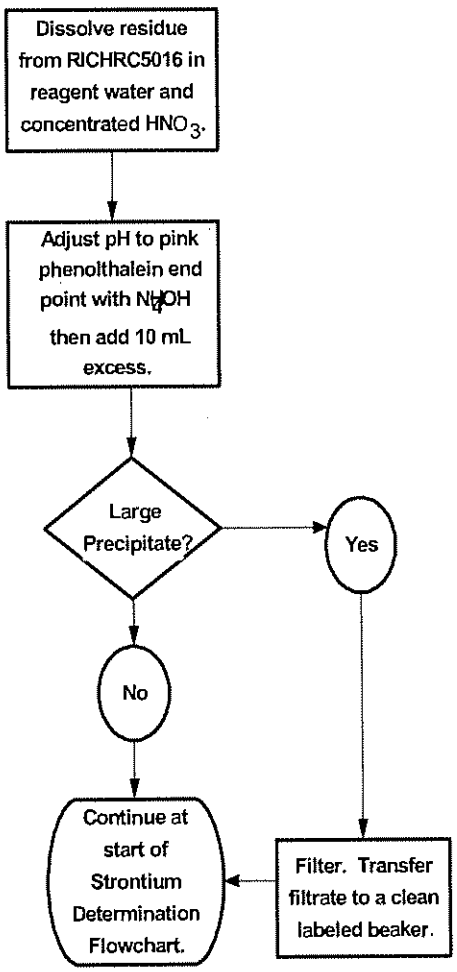
16.3.1 This procedure is compliant with Method 905.0. Ammonium carbonate has been substituted for ammonium oxalate. Also, fuming nitric acid is used in this SOP. These variations were incorporated to accommodate the varying matrices. Drinking water samples show comparable yields and results to method 905.0.

16.3.2 Procedural Flow Chart

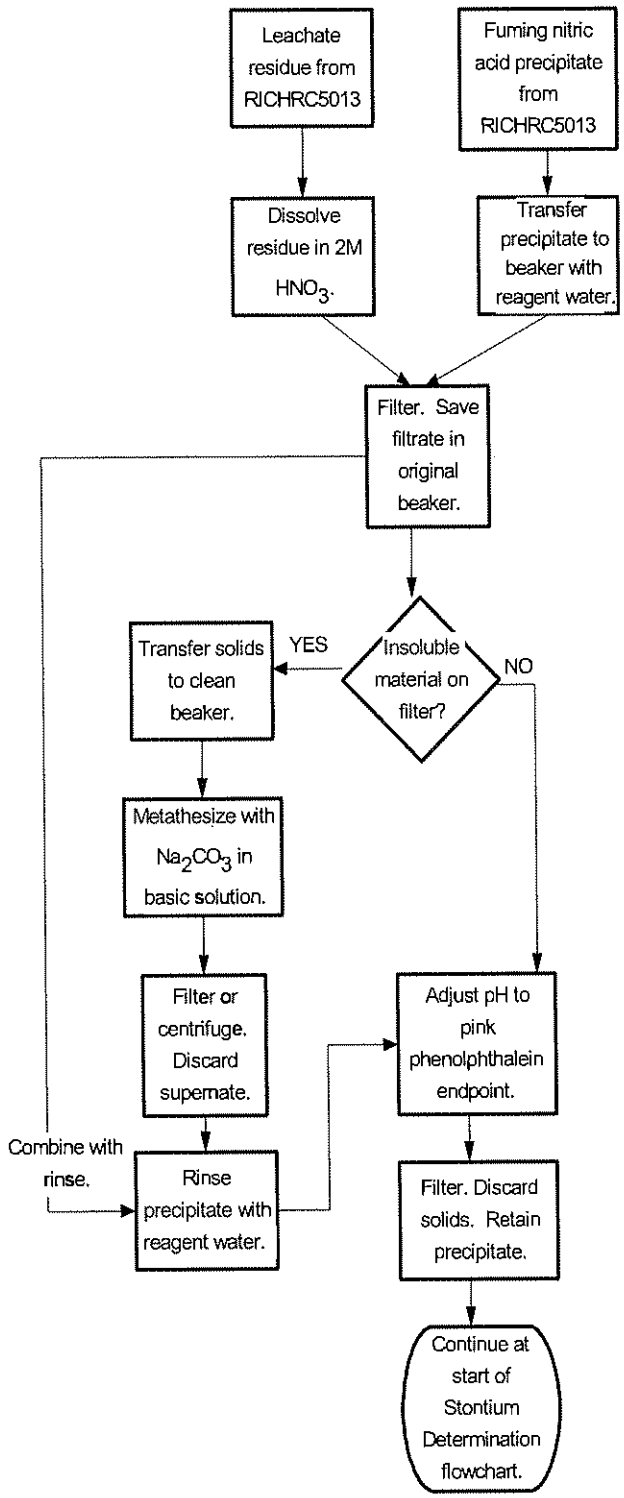



Vegetation, Wheat, Potatoes
Non Sequential: Heat sample with 2M HNO_3. Cool.
Sequential Dissolve fuming nitric acid precipitate in reagent water
Filter, transfer solids back to original beaker.
Save filtrate, add to
Metathesize solids with Na_2CO_3 in basic solution.
Filter, rinse precipitate with reagent water. Retain solids.
Discard filtrate
Dissolve precipitate with 16M HNO_3.
Adjust pH to pink phenolphthalein endpoint. Filter and discard solids.
Continue at start of Strontium Determination flowchart.
Tissue
Weigh a sample aliquant. Add appropriate yield monitors.
Digest to white salts with 16M HNO_3.
Evaporate to near dryness then digest salts with 18M H_2SO_4, 16M HNO_3 and 30% H_2O_2 until all organic material is destroyed.
Cool. Dilute with reagent water to precipitate $SrSO_4$.
Heat to boiling and allow precipitate to settle. If necessary heat 1-2 hours until precipitation is complete.
Centrifuge or filter. Wash precipitate with reagent water.
Adjust pH to pink phenolphthalein end point with NH_4OH.
Boil with Na_2CO_3 to convert $SrSO_4$ to $SrCO_3$
Large Precipitate?
N
Y
Continue at start of Strontium Determination flowchart.
Filter and rinse precipitate with reagent water.
Dissolve precipitate with 16M HNO_3.
High Calcium Matrix
Weigh a sample aliquant. Add appropriate yield monitors.
Digest sample with 16M HNO_3 (30% H_2O_2 if necessary)
Reduce volume to less than 100 mL. Cool.
Place beaker in ice bath to precipitate $Sr(NO_3)_2$.
Centrifuge and retain precipitate.
Dissolve precipitate with reagent water.
Add NH_4OH to pink phenolphthalein endpoint.
Continue at start of Strontium Determination flowchart.

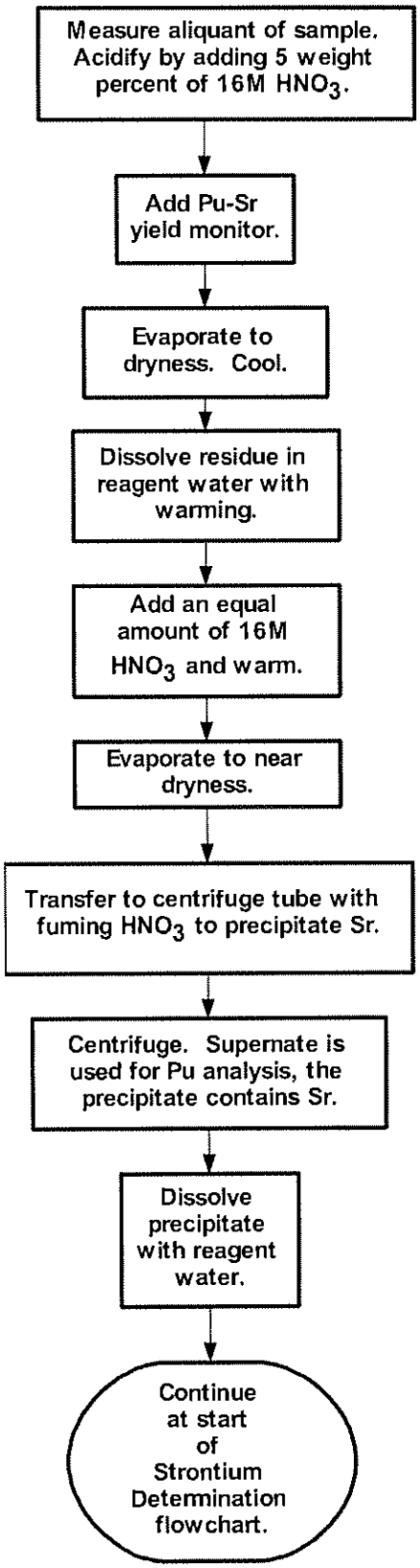
Produce



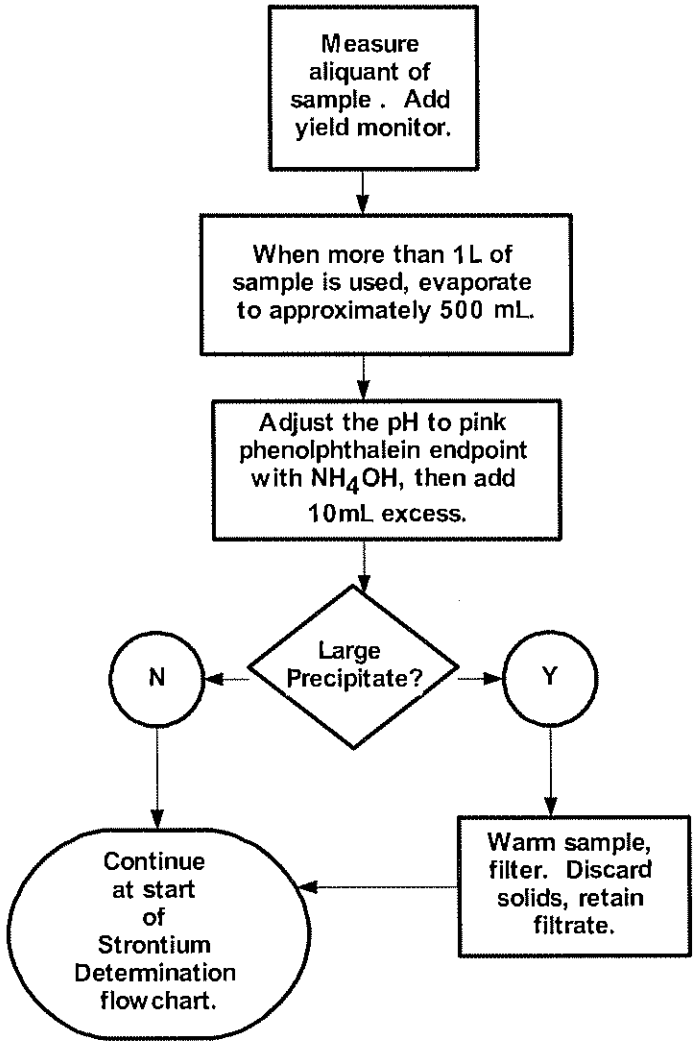
Soil



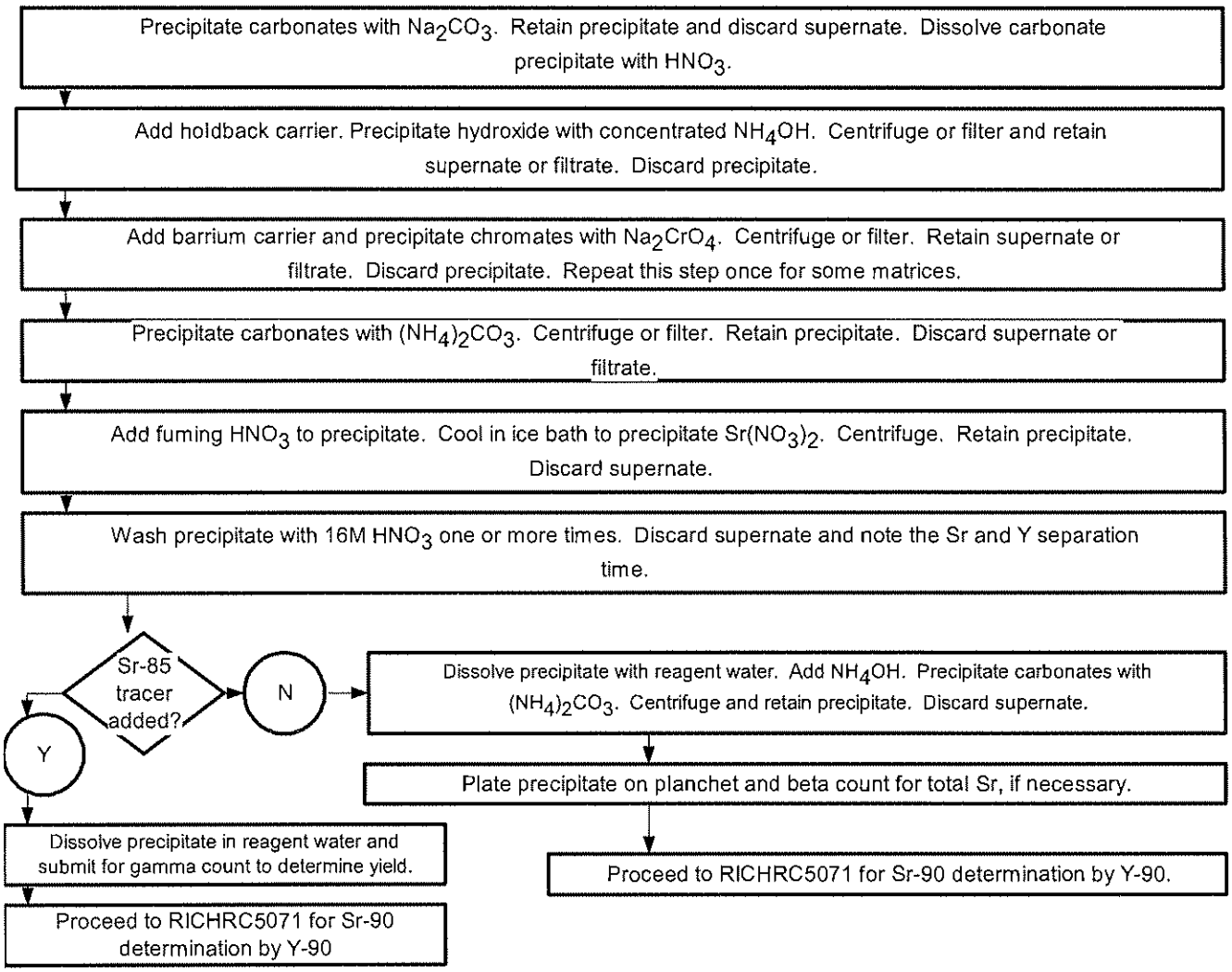
Water - Sequential



Water - Non-Sequential



Strontium Determination



Title: Determination of Uranium by Phosphorescence Analysis

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5058 Rev 4

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1. SCOPE AND APPLICATION

1.1. The purpose of this procedure is to describe the calibration of the kinetic phosphorescence analyzer instrument (KPA) and the analysis of prepared samples for total uranium by laser induced phosphorimetry.

1.2. This procedure is suitable for measurement of uranium concentrations above the minimum detectable concentration (MDC) of 1.0 ng/mL without prior concentration. Lower MDCs are achievable by concentration of the sample.

2. SUMMARY OF METHOD

2.1. A prepared sample is mixed with a complexing agent in the analytical cell. The complexed uranium ions are excited with light from a nitrogen laser and the intensity of emitted light is measured as a function of time with t_0= time of the exciting light pulse. Calibration of the instrument with known standards enables the calculation of a concentration of uranium in the cell. A computer system is used to control the instrument and to perform data calculations. A histogram of the intensity of emitted light as a function of time may also be plotted using the computer system.

3. DEFINITIONS

3.1. Dye Cell - Filled with a solution of Stillbene-420. It absorbs the 337 nm light from the laser and emits light at 420 nm, which is absorbed by the uranium molecules.

3.2. Kinetic Phosphorescence - technique using a pulsed excitation source (laser) and measuring the phosphorescence decay with time-gated detection. This takes advantage of the long emission lifetime of the uranyl ion to discriminate against scattered light and decay of short-lived species.

3.3. Laser Induced Phosphorimetry (LIP) - Phosphorescence involves the absorption of a photon which electronically excites the uranyl complex molecule. Relaxation of the electronic state with the emission of a photon returns the molecule to the ground state. In phosphorescence the relaxation incorporates a triplet electronic state and the relaxation lifetime ranges from microseconds to seconds. A pulsed excitation source is used (20 pulses per second). The pulse of source light (pulsed nitrogen laser at 337 nm that pumps a dye laser, Stillbene-420) is assigned a time of zero. Intensity measurements from each interval are summed for the number of pulses used. Since the number of detected photons at any time are proportional to the number of excited uranium ions, least squares fitting of the logarithm of detected intensity versus time after pulse yields an intercept proportional to the number of excited uranium ions. Stability and optimum conditions are obtained by using a uranium complexing agent. In actual data calculation the instrument plus reagent background is measured and subtracted from the gross sample intensities.

3.4. Photoluminescence - the emission of radiant energy by a molecule, ion or atom that has reached an excited electronic state by absorbing radiant energy.

3.5. Phosphorescence - a special case of photoluminescence in which absorbed incident energy excites a molecule to an electronic triplet state. As the molecule decays back to the ground state, it emits energy in the form of a photon(s) of light. The emitted light is known as phosphorescence. Phosphorescence of organic molecules commonly means emission during a transition from the lowest excited triplet state T_1 to the singlet ground state S_0. For inorganic species any emission involving a change in the spin of the excited electron is, by definition, phosphorescence. Phosphorescence occurs much more slowly than fluorescence because it involves a forbidden transition.

3.6. Reference Cell - Known uranium source assisting in the measurement of background.

4. INTERFERENCES

4.1. Method interferences may be caused by organics, halides, reducing metals and particulate matter if samples were not properly prepared. After a sample is wet ashed and diluted to an appropriate volume with 0.8M nitric acid, caution should be taken not to pipet any solids from the bottom of the vial when taking an aliquot for analysis.

4.2. Inspect the cuvette optical surfaces to assure they are free of scratches. If scratches are found, replace the cuvette. Care should be taken not to touch the optical surfaces of the cuvettes, especially disposable cuvettes, as oils from the fingers will increase the sample background. Quartz cuvettes must be scrupulously cleaned with lint-free wipes between analyses as the cell faces are optical elements and could result in high background if not clean. To clean the cuvettes use the following steps:

4.2.1. Rinse the empty cell with 0.5 M sulfuric acid. Discard the liquid into the appropriate waste container. Repeat the acid rinse at least once more.

4.2.2. Rinse the cell with reagent water. Discard the liquid into the appropriate waste container. Repeat the water rinse at least twice more.

NOTE: Methyl alcohol may be used as a supplemental cleaner for the cell if necessary. When methyl alcohol is used to clean the cell, thorough rinsing of the cell with reagent water is necessary to remove all traces of methyl alcohol before the cell is reused.

4.2.3. Dry the outside of the cuvette with a clean, lint-free tissue.

4.2.4. Visually inspect the cell against a light source to verify the cell optical surfaces are clean and the sample solution is free of particulates.

NOTE: Optionally, the cells when not in use may be soaked in a Hellmann II cleaning solution. The cells should be rinsed well with reagent water and then cleaned as in steps 4.2.1 - 4.2.4 before use after soaking in the cleaning solution.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

CAUTION: Do not look directly at the laser beam. Damage to the eye may occur.

5.1.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methyl Alcohol	Flammable	OSHA 200 ppm (260 mg/m3)	Eye, skin and upper respiratory irritation.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Kinetic phosphorescence analyzer with associated computer system and Instrument Manufacturer's Manual (IMM).

6.2. Pipettors, Eppendorf or equivalent, multiple volume delivery or equivalent.

6.3. Containers, disposable, plastic or leached glass, 15 mL capacity or equivalent.

6.4. Cuvettes, Plastic disposable (optional).

6.5. Cuvettes, Quartz for low detection limits.

6.6. Repipettor, 0-10 mL capacity.

6.7. Tissue, lint free.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: *Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.*

7.2. Hellmann II cleaning solution or equivalent (optional).

7.3. Methyl alcohol (CH_3OH), technical grade or better. **WARNING**: Flammable.

7.4. 16M Nitric Acid (16M HNO_3), concentrated, ultra pure. **WARNING**: Corrosive and oxidizing agent.

7.5. 0.8M Nitric acid (0.8M HNO_3) - Add 5 mL of concentrated, ultra pure nitric acid to approximately 50 mL of reagent water. Dilute to 100 mL with reagent water and mix well.

7.6. Reference Cell solution – 1.0 mL of an appropriate standard (normally standard between 200-300 ng/ml) and approximately 3.0 mL Uraplex.

7.7. Stillbene-420 Solution (Dye Cell solution) - Add 23.9 mg of Stillbene-420 in approximately 20 mL of methyl alcohol. Dilute to 25 mL with methyl alcohol and mix well.

7.8. 18M Sulfuric acid (18M H_2SO_4), concentrated. **WARNING**: Corrosive and oxidizing agent.

7.9. 0.5M Sulfuric Acid (0.5M H_2SO_4). **CAUTION**: Slowly add H_2SO_4 to reagent water with stirring and cooling to avoid splattering.

Add 28 mL of concentrated sulfuric acid to approximately 800 mL of reagent water, mix and allow to cool. Dilute to 1 liter with reagent water and mix well.

7.10. Complexing Agent for uranium, Uraplex (proprietary material from ChemCheck Instruments) or equivalent. Refrigerate concentrated Uraplex until dilution is required. Dilute Uraplex with reagent water as designated on the supplier's container and mix well. Do not store diluted solutions of Uraplex in refrigeration. Use diluted Uraplex solutions at room temperature and within two weeks of dilution.

7.11. Uranium standards are prepared in glassware that has been leached with 4M nitric acid for at least 48 hours. Standards are prepared with 0.8M nitric acid for low range and high range calibration curves, or are obtained from the standard preparation group for the laboratory.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. All samples must be preserved with nitric acid to a pH less than 2. Storage of the sample prior to analysis should not exceed six months.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. A verification standard (see section 7.11) shall be run immediately following calibration and at least once per shift thereafter. Acceptance limits for the verification standard are 90% - 110%. If the results for the verification standard are outside of these limits, stop the analysis, recalibrate and reanalyze samples back to the last valid verification standard. Instrument blanks will be run following each verification standard. If the results for the instrument blank are greater than zero, see supervision for instructions.

9.3. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.4. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.5. Refer to SOP RICH-RC-0002 for QC acceptance criteria and corrective action.

10. CALIBRATION

10.1. Background Determination

10.1.1. Verify that the dye and reference cells have been changed at the interval required in the Laboratory Quality Manual.

10.1.2. A background sample is prepared by mixing 1.0 mL of 0.8M nitric acid with an appropriate volume of complexing agent in a sample cuvette. Cap the cuvette and mix the contents well by inverting the cell multiple times. Wipe the outside of the cuvette with a lint-free tissue and place the cuvette in the instrument.

10.1.3. With the reference and background sample cuvettes in place, determine the background. Run at least five replicate backgrounds to allow the instrument to warm up and become stable.

CAUTION - *Do not open the door of the instrument* while it is in operation as irreversible damage may be caused to the instrument.

CAUTION - Do not look directly at the laser beam. Damage to the eye may occur.

10.2. Instrument Calibration

10.2.1. Starting with the lowest concentration standard, pipet 1.0 mL of standard into the sample cuvette. Add the appropriate amount of complexing agent, cap and mix well by inverting the cuvette multiple times. Wipe the outside of the cuvette with a lint-free tissue. Place the cuvette in the instrument and proceed with the calibration.

10.2.2. Continue with two more standards in the low range to complete the low range calibration.

10.2.3. Repeat steps 10.2.1 and 10.2.2 for three high range standards to produce a high range calibration.

NOTE: If all samples to be analyzed will fall in one concentration range, either low or high, then only that range needs to be calibrated.

10.2.4. The R^2 (linear regression coefficient) for the calibration curve, when applicable, shall be ≥ 0.99.

10.2.5. A calibration check standard shall be analyzed immediately after the calibration is completed and once per shift thereafter (see section 9.2). The calibration check standard shall be within 10% of the known value. For additional calibration verification requirements and frequencies, see specific client requirements.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Samples are prepared by RICHRC5015 or RICHRC5031.

11.2. Add 1.0 mL of the sample prepared in 0.8M HNO_3 to a sample cuvette. Add the appropriate amount of complexing agent, cap, and mix well by inverting the cuvette. Wipe the outside of the cuvette with a lint-free tissue.

NOTE: If the sample appearance or initial results indicate that a dilution is necessary, a smaller amount of sample may be used and an appropriate amount of 0.8M nitric acid added to bring the volume to 1.0 mL.

11.3. Print the report. The plot may also be printed.

11.4. Discard the contents of the cuvette in an appropriate waste container. Clean the cuvette according to section 4.2.

11.5. Record all analytical data on a sample data sheet and run log. Include all samples, method blanks, LCSs, duplicates, etc.

11.6. Repeat steps 11.2 through 11.5 for additional client and/or QC samples.

12. DATA ANALYSIS AND CALCULATIONS

12.1. The KPA instrument calculates the uranium concentration result as well as the uncertainty for the result. The results are reported in units of nanograms of uranium per milliliter (ng/mL) or nanograms per gram (ng/g).

12.2. The samples shall have lifetimes between 150-350 μs and the R^2 for the decay curves shall be ≥ 0.96.

12.3. Minimum Detectable Concentration (MDC) is determined by multiplying 4.65 times the uncertainty of the result for the blank sample prepared with the samples.

12.4. Laboratory Control Sample (LCS) Percent Recovery:

$$\%R = \left(\frac{M_o}{M_s}\right) \times 100$$

Where:

%R= LCS percent recovery.

M_o = Net mass of uranium observed in original prepared solution determined from analysis of the LCS in ng.

M_S = Net mass of expected uranium in original prepared spike solution determined from concentration added to the LCS from $\left(\frac{ng}{ml}\ mL\right)$.

NOTE: If contractually specified, the equation above may substitute mass concentration for mass.

NOTE: When a blank is subtracted, the multiplier in the MDC calculation may be changed to 3.29.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2 Method Demonstration of Capability documentation is maintained in the quality files.

14. POLLUTION PREVENTION

14.1 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents to be disposed.

15. WASTE MANAGEMENT

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container and transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Flammable waste with a pH of < 2. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste

Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

16. REFERENCES

16.1. American Society for Testing and Materials, 1992, "Standard Specification for Reagent Water, D1193-91", Annual Book of ASTM Standards, Volume 11.01, ASTM, Philadelphia, Pennsylvania.

16.2. American Society for Testing and Materials, 1999, "Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry, D5174-97", Annual Book of ASTM Standards, Volume 11.02, ASTM, Philadelphia, Pennsylvania.

16.3. Instrument Manufacturer's Manual for the kinetic phosphorescence analyzer.

16.4. STL Quality Management Plan, latest revision.

16.5. STL Richland Laboratory Quality Manual, latest revision.

16.6. STL Richland Quality Assurance Summary, latest revision.

16.7. Associated SOPs

16.7.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16.7.2. RICHRC0002 - Review of Environmental and Bioassay Data.

16.7.3. RICHRC5015 - Environmental Sample Preparation for Uranium by Laser-Induced Phosphorescence

16.7.4. RICHRC5031 - Separation of Uranium in Urine and Water.

17. MISCELLANEOUS

17.1. Responsibilities

Analyst: Implements SOP as written.

Technical Data Reviewer: Performs first level data review.

Project Manager: Performs final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance programs.

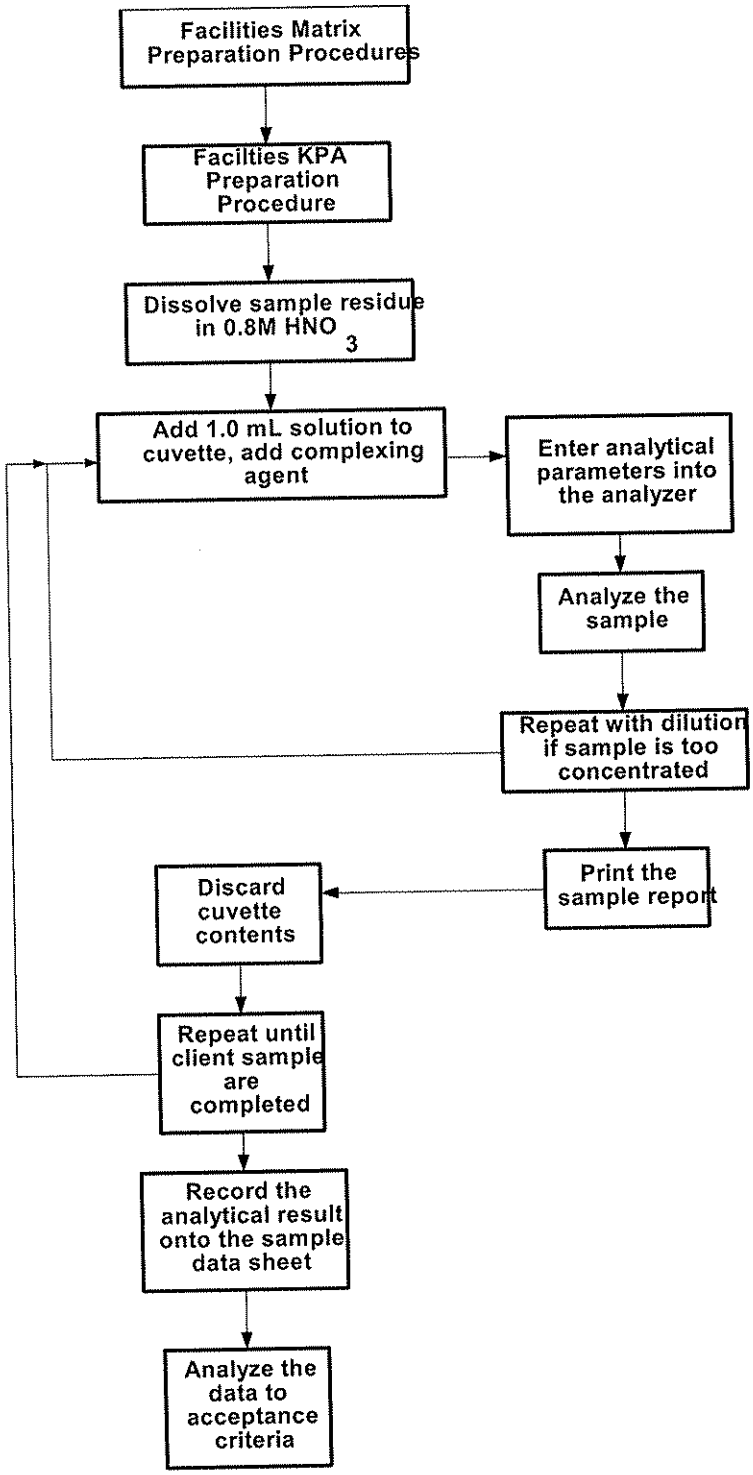
17.2. Records Management/Documentation

17.2.1. All records generated by this analysis will be filed and kept in accordance with STL policies and procedures for records management and maintenance.

17.3 Drinking Water /ASTM Method Variations

17.3.1 This procedure is compliant with ASTM Method D5174.

17.3. Procedural Flow Chart



Title: Separation of Tritium in Water and Aqueous Component of Wine

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5007 Rev 7

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1. SCOPE AND APPLICATION

1.1. Tritium in water or the aqueous component of wine is measured by a direct count of the distilled alkaline sample using a liquid-scintillation counter (LSC). The distillation can be performed using either the traditional distillation apparatus or the Micro Dist™ Method.

1.2. This method is applicable to wine (if the percent alcohol by volume is known) and to ground, surface, drinking, and other types of water samples where enough sample exists to perform a distillation. Additionally, the distillate must be sufficiently free of quenching agents that the quenching will not exceed the range of existing calibration.

1.3. Using 10 mL of distillate and 10 mL of liquid scintillation cocktail, the minimum detectable activity is less than 400 pCi/L with a 75 minute counting time, and the minimum detectable concentration is less than 300 pCi/L with a 150 minute count time. If 5 mL of distillate is generated the minimum detectable activities will be elevated unless longer counting times are used.

2. SUMMARY OF METHOD

2.1. An aliquot of water or wine is made alkaline with sodium hydroxide and distilled. Wine samples are fractionally distilled to separate the water from the other components of wine. A fraction of the distillate is collected for tritium analysis. After distillation, the distillate and scintillation cocktail are pipetted into a vial. The vial is transferred to the refrigerated sample changer of a liquid-scintillation counter and allowed to stabilize before counting. This waiting period allows temperature equilibrium to be reached and the decay of chemiluminescence within the scintillation vials.

3. DEFINITIONS

3.1. Dead water: Water having a very low concentration of tritium, usually found in deep wells that are isolated from surface and shallow ground waters.

3.2. Liquid-scintillation cocktail: A ready-to-use liquid mixture of chemicals that convert the energy of particles emitted by the decay of radioactive atoms into light that can be detected by the phototubes of a LSC.

3.3. Quenching: The term applied to any of several chemical, photochemical, or optical effects which interfere with the scintillation process. Quenching both decreases counting efficiency and distorts the beta-particle spectrum of the radionuclide being counted.

4. INTERFERENCES

4.1. Tritium in reagent water is an interference that cannot be removed. Therefore only dead water or low-tritium-content water shall be used in blanks and spikes.

4.2. For results to be accurate quenching must be compensated for. Alkaline distillation removes many sources of quenching.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.
- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.
- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.

5.1.1 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Ultima Gold	Flammable	None	If swallowed do not induce vomiting except in the presence of, or on the orders of a doctor.

Potassium Perman-ganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Boiling flask - to fit the heating mantle, with built-in side-arm adapter and ground-glass joint; or with two ground-glass joints and separate bent side-arm adapter.

6.2. Clamps and supports - for use with distillation apparatus.

6.3. Condenser - with water supply, drain.

6.4. Dispenser for liquids - automatic, typically one liter capacity, 1-20 mL range.

6.5. Glass stoppers - water sample analysis only.

6.6. Graduated cylinder - 100 mL, glass or plastic.

6.7. Heating mantle - electrically-powered to fit boiling flask, with voltage control, Glas-Col Company or equivalent. It may be a multi-position unit.

6.8. Kimwipes or anit-static wipe.

6.9. pH indicating strip or paper - to include the range of pH 7 to 9.

6.10. Pipettor - 5 mL and 10 mL, critical adjustable, with disposable plastic tips

6.11. Rubber stopper - to fit boiling flask, with hole to hold thermometer.

6.12. Scintillation vial - plastic, approximately 20 mL, with caps, to fit LSC sample changer.

6.13. Spatula.

6.14. Thermometer - range to include 90°C to 110°C.

6.15. Timer - up to about one hour. May be built into the heating mantle controls.

6.16. Micro Dist heating block and the associated Tritium tubes. This apparatus is manufactured by Latchette .

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. Acetic acid, concentrated (glacial CH_3COOH) - Needed only when analyzing wine samples. **WARNING:** Corrosive.

7.3. Acetone - used for equipment cleaning. **WARNING:** Flammable.

7.4. Alcohol (CH_3CH_2OH) - anhydrous, denatured. Needed only when analyzing wine samples. **WARNING:** Flammable.

7.5. Dead water - water which contains little or no tritium.

7.6. Hydrochloric acid wash, (approximately 4M HCl). Add 250 mL concentrated HCl to a 1 liter container. Dilute to 1 L with reagent water and mix well. **WARNING:** Corrosive.

7.7. Liquid Scintillation Cocktail – Ultima Gold LLT from Perkin Elmer, or equivalent. **WARNING:** Flammable.

7.8. Potassium Permanganate ($KmnO_4$) – **WARNING:** Oxidizer

7.9. Sodium hydroxide (NaOH) - pellets. **WARNING:** Corrosive.

7.10. 10M Sodium hydroxide/Potassium Permanganate (10M NaOH)/$KMnO_4$ - Slowly dissolve 4 g of NaOH in 10 mL reagent water. Dissolve a small amount of $KMnO_4$ into the NaOH solution.

7.11. Tritium matrix spike solution - A tritiated water standard is quantitatively diluted with distilled "dead" water to an accurately known concentration. The calibration of the standard is traceable to the National Institute of Standards and Technology.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. Samples must not be preserved with acid or other preservatives. Samples should be analyzed as soon after collection as feasible to reduce the chances of microbial growth. Glass or plastic containers are applicable.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency. One or more instrument blanks should be prepared in a sample batch.

9.4. Refer to SOP RICH-RC-0002 for QC acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A nonconformance shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The nonconformance will be filed in the project file.

11.1. Complete the appropriate sections of the Liquid Scintillation Counting Sheet. Record samples in the distillation logbook.

11.2. For water samples, check the pH with pH paper. If the pH is less than 2, see supervision. Record the pH in the distillation logbook.

CAUTION: Do not fill a boiling flask more than half full.

Transfer an appropriate amount of sample to a boiling flask. Consult supervision or the client specific Quality Assurance Summary (QAS) for volumes.

11.3. Prepare the appropriate quality control (QC) samples as follows:

11.3.1. Water matrix blank.

11.3.1.1. Dead water is distilled in the same manner as the samples.

11.3.2. Water matrix spike.

11.3.2.1. The tritium matrix spike solution is distilled in the same manner as the samples.

11.3.3. Wine matrix blank.

11.3.3.1. 85 mL of dead water, 15 mL of anhydrous alcohol and 0.5 mL of glacial acetic acid distilled in the same manner as the samples.

11.3.4. Wine matrix spike.

11.3.4.1. 85 mL of tritium matrix spike solution, 15 mL of anhydrous alcohol and 0.5 mL of glacial acetic acid distilled in the same manner as the samples.

NOTE: The components of the wine matrix should be measured with graduated cylinders and adjustable pipettors, and mixed together in the distilling flask immediately before distillation.

11.4. Water Preparation using Micro Dist™ Apparatus.

11.4.1. **Note:** In the following portion of the procedure, **D** and **M** refer to the marks on the ends of the collector tube. **D** means 'distillation' or 'discarded' end and **M** means 'measuring' end. See the Latchat manual for further explanation.

11.4.2. Set the controller to 135 degrees C. Allow the heater block to warm up. This will take about 40 minutes.

11.4.3. With the **M** end up; put as many collector tubes as you have samples into the collector tube rack.

11.4.4. Put as many sample tubes into the sample tube rack as you have samples to distill; up to 21 for one block. Place 6.0 mL of water sample (or standard) into each sample tube with a pipetor. If the sample appears to be primarily oil, do not distill. Contact supervision for further directions.

11.4.5. Add 1 to 2 drops of 10 M $NaOH/KMnO_4$ to each sample tube.

11.4.6. Push the **D** end of a Tritium-1 collector tube over the open end of each sample tube to start the seal.

11.4.7. Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

11.4.8. The pressing motion should be smooth constant pressure which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.

11.4.9. Put on heat-resistant gloves. Push the sample tube and the **D** end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

11.4.10. Set the timer for 60 minutes

11.4.11. When 60 minutes are up, put on heat-resistant gloves. Remove the first tube from the block and immediately pull off its sample tube using a downward, twisting motion as opposed to a sideways motion. You must remove the sample tube within 4 minutes of removing it from the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution left in it by dropping it into an appropriate waste container.

11.4.12. Invert each collector tube and place it into the collector tube rack, now with the **D** end up. It should take less than two minutes to pull and separate all 21 tubes

11.4.13. Allow tubes to cool for at least 10 minutes

11.4.14. For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate. Then, slowly return the collector tube to an upright position so that the **D** end is up. Stubborn drops will often fall into the M end when the tube is flicked with your finger.

11.4.15. With the **D** end still up, break the collector tube in half by pulling the **D** end hard towards yourself to break it, then twisting and tearing off the **D** end. Discard the **D** end. Proceed to step 11.6

11.5. Water and Wine Preparation using Traditional Distillation

11.5.1. With a spatula, add 1 or 2 pellets of sodium hydroxide (NaOH) and approximately 0.1g of potassium permanganate ($KMnO_4$) to each sample. Swirl until the pellets are dissolved. Check with pH paper that the pH of the sample is 8 or greater. If not, repeat this step.

11.5.2. The boiling flask and condensers are connected on a heating mantle. Use an appropriate size beaker for the collection vessel under the condenser outlet. For wine samples, the glass stoppers are replaced with rubber stoppers with the thermometers. Adjust the thermometers so that their bulbs are below the surface of the sample but do not touch the flasks. Turn on the cooling water through the condenser.

NOTE: Ensure cold water is running through the condenser column from bottom to top.

11.5.3. **CAUTION**: Attention should be taken to prevent boiling the sample to dryness. Damage to equipment can occur.

Turn on the heating mantle. Adjust the setting so that the sample is boiling lightly.

11.5.3.1.For Water Samples:

11.5.3.1.1. Place a beaker beneath the condenser. When the distillate volume in the beaker is about 10 mL, replace the beaker with a glass scintillation vial. Collect at least 20 mL of distillate in a scintillation vial. Discard the distillate in the beaker to an appropriate waste container.

11.5.3.2.For Wine Samples:

11.5.3.2.1. Place a container under the condenser and collect the distillate while the temperature reaches 100°C. After the temperature has reached 100°C, collect an additional 30 mL of distillate. After the 30 mL has been collected in the waste container, replace the waste container with a plastic scintillation vial. Collect at least 20 mL of distillate in a scintillation vial. Discard the distillate from the waste container to an appropriate waste container.

11.5.4. When the appropriate amount of distillate has been collected, turn the heating mantle off, and allow the glassware to cool. Discard the remaining sample in the distilling flask to an appropriate waste container. Clean the equipment for the next sample by rinsing 2-3 times with 4M HCl wash followed by 2-3 rinses with reagent water. Discard the rinses to the appropriate waste container. Rinse the condensers with reagent water. The distillation flask must appear dry before beginning the next distillation. If it is not dry, either heat the flask with the heating mantle or rinse with acetone. Allow the flask to cool before beginning the next distillation. Discard acetone rinses to the appropriate waste container.

CAUTION: Do not allow the heating mantle to remain on after the flask is dry.

11.6. Preparation of final counting vial

11.6.1. **NOTE**: Gloves must be worn when handling scintillation vials.

NOTE: DO NOT write on the vials, only on the caps.

NOTE: Do not prepare samples in a LSC cassette. Scintillation cocktail can destroy the cassettes.

Write the sample identification number on the cap of the appropriate scintillation vial. Transfer with a pipettor and a clean tip an appropriate volume (as directed by supervision) to a counting vial. Typical sample volumes are 10 mL for low-level samples and 5 mL for high-level samples and MicroDist. Dispense a volume of scintillation cocktail into the counting vial such that the final volume in the vial is 20 mL. Upon the direction of supervision, samples may be diluted to an appropriate volume with dead water.

NOTE: The sample aliquot may be measured by weight in place of a pipettor.

11.6.2. Prepare an appropriate number of instrument blanks, reagent blanks and reagent spikes as determined by supervision or contractual agreement for each batch of samples. Instrument and reagent blanks (for water and wine) are prepared by pipetting the same volume as used in step 11.6.1 of dead water into a scintillation vial and adding a volume of liquid scintillation cocktail such that the final volume is 20 mL. Reagent spikes (for water and wine) are prepared by one of the following ways:

11.6.2.1. Dilute a tritium spike in a scintillation vial to the same volume as in step 11.6.1 with dead water and then add a volume of liquid scintillation cocktail such that the final volume is 20 mL.

11.6.2.2. Pipet the same volume as in step 11.6.1 of tritium matrix spike solution into a scintillation vial and add a volume of liquid scintillation cocktail such that the final volume is 20 mL.

11.6.3. Cap all samples tightly and shake well to mix. Inspect the outside of the vials and remove any dust or smudges with a Kimwipe or anti-static wipe. Place the vials in LSC cassettes, with instrument blanks normally in the first cassette position and the last cassette position. The first position in remaining trays is always a QC blank, spike or instrument blank.

11.6.4. Fill in the remaining required information on the liquid scintillation counting sheet. Take the cassettes with scintillation vials, the completed liquid scintillation counting sheet and the chain of custody to the counting room for liquid scintillation counting.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For computer calculation of the tritium concentrations and the total propagated uncertainty (TPU), consult the RadCalc Users Guide.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2 Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1. Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container and transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste

Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. American Society for Testing and Materials, 1983, Standard Test Method for Tritium in Water in Annual Book, Philadelphia, PA: ASTM D2476-81.

15.2. Krieger, H. L., and Whittaker, E. L, 1980, "Section 10, Tritium in Drinking Water, Method 906.0", Section 5 in Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, U.S, Environmental Protection Agency, Cincinnati.

15.3. RadCalc DB, DB v2.2/DOC v03, Users Guide, STL Richland.

15.4. STL Quality Management Plan, latest revision.

15.5. STL Richland Laboratory Quality Manual, latest revision.

15.6. STL Richland Quality Assurance Summary, latest revision.

15.7. Associated SOPs

15.7.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

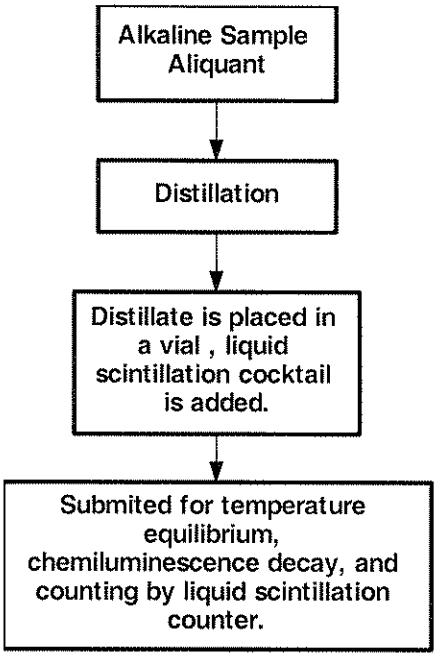
16.2. Records Management/Documentation

16.2.1. All records generated by this analysis will be filed and kept in accordance with STL Richland policies for records management and maintenance.

16.3. Drinking Water Method Variations

16.3.1. This procedure is compliant with Method 906.0.

16.4. Procedural Flow Chart



Title: Carbon-14 by Digestion Method

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5022 Rev 5

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1. SCOPE AND APPLICATION

1.1. This SOP describes the procedure for separating Carbon-14 in water, soil or ash by digestion.

1.2. Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. Carbon carrier, in the form of ammonium oxalate, is added to an unacidified aqueous sample in a closed distillation apparatus. Carbon-free gas (generally pure oxygen) is bubbled slowly through the sample to carry free CO_2 into a gas washing bottle that contains a dilute NH_4OH solution. An oxidizing agent and sulfuric acid are added to the sample to convert carbon compounds to CO_2. Heat is applied and the pure oxygen gas is used to bubble the released CO_2 into the NH_4OH, forming a solution containing salts of carbonic acid, H_2CO_3. Barium chloride solution is added to the collected carbonates, forming a precipitate of $BaCO_3$, which is washed, then dried on a weighed planchet. The dried precipitate is transferred to a plastic vial as a powder and counted via liquid scintillation.

3. DEFINITIONS

3.1. Dead water - Water having a very low concentration of tritium, usually found in deep wells that are isolated from surface and shallow ground waters.

3.2. Double-distilled dead water - Dead water which has been distilled twice.

4. INTERFERENCES

4.1. None.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.
- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.
- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.
- CAUTION: Be careful when disconnecting the Digestion Apparatus, steam may be released.
- Do not use hand to stop centrifuge from spinning.

5.1.1 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Ultima Gold	Flammable	None	If swallowed do not induce vomiting except in the presence of, or on the orders of a doctor.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Silver Nitrate	Poisonous Corrosive Oxidizer		Silver Nitrate should never be mixed with ammonia compounds as it can form azides which are powerful explosives. Never mix with finely particulate metals such as aluminum or zinc. Also avoid contact with organics. Stains skin and can cause burns.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Analytical balance.

6.2. Centrifuge.

6.3. Centrifuge tube, 50 mL, conical bottom, or equivalent with cap.

6.4. Clamps - pinch and spherical various sizes.

6.5. Flask, 500 mL 2-neck boiling or equivalent with stopper.

6.6. Heating mantle for flask size.

6.7. Heat lamp.

6.8. Impinger, midget, modified.

6.9. Gas-washing bottle, 125 mL with fritted cylinder or equivalent.

6.10. Pressurized Oxygen tank with needle valve control.

6.11. Pipet, disposable, plastic.

6.12. Rubber policeman.

6.13. Smog bubbler.

6.14. Stainless steel planchet, 1.5 inch diameter, pre-weighed, with holder.

6.15. Tubing.

6.16. Vial, liquid scintillation, plastic, 20 mL with cap.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. 14.7M Ammonium hydroxide (14.7M NH_4OH) - Concentrated. **CAUTION**: Corrosive.

7.3. Carrier Gas, CO_2 free, commercial preparations of compressed oxygen is preferred. **CAUTION:** Oxidizer. Keep combustibles and ignition sources away from where oxygen is being used or stored. Use in a well ventilated area with appropriate regulator.

7.4. Dead water - water which contains a very low concentration of tritium.

NOTE: Boiled reagent water is adequate for soil or ash samples, unless Tritium is requested.

7.5. Double distilled dead water - dead water which has been distilled twice.

7.6. Liquid Scintillation Cocktail - UltimaGold from Perkin Elmer, or equivalent. **WARNING:** Flammable.

7.7. Potassium persulfate ($K_2S_2O_8$) - reagent grade. **CAUTION**: Oxidizer.

7.8. 5% Silver nitrate (5% $AgNO_3$) -Dissolve 25 g of $AgNO_3$ in 500 mL of reagent water and mix well. Store in a dark bottle, away from light.

7.9. 1.5M Sodium carbonate (1.5M Na_2CO_3) - Add 31.8 g Na_2CO_3 to 100 mL of hot reagent water. Dilute to 200 mL with hot reagent water and mix well.

7.10. 18M Sulfuric acid (18M H_2SO_4) - Concentrated. **CAUTION**: Corrosive.

7.11. The following prepared reagents must be stored in bottles that are sealable. The containers must be closed when not in use and not be allowed to remain open to the air.

7.11.1. 0.1M Ammonium hydroxide (0.1M NH_4OH) - Add 7 mL of concentrated NH_4OH to approximately 900 mL of reagent water. Dilute to 1 L with reagent water and mix well.

7.11.2. 1.5M Barium chloride (1.5M $BaCl_2$) - Add 36.6 g of $BaCl_2 \bullet 2H_2O$ to approximately 80 mL of reagent water. Dilute to 100 mL with reagent water and mix well.

7.11.3. 0.1M Ammonium oxalate carbon carrier (0.1M $(HN_4)_2C_2O_4H_20$) - Add 1.4211 g of ammonium oxalate to exactly 100 mL of reagent water and mix well. Oxalic acid may also be used to prepare the carbon carrier.

NOTE: One mL of carrier yields 39.5 mg of $BaCO_3$.

7.11.4. 0.5M Potassium permanganate (0.5M $KMnO_4$) - Add 7.9 g of potassium permanganate to approximately 80 mL of reagent water. Dilute to 100 mL with reagent water and mix well.

7.11.5. 9M Sulfuric acid (9M H_2SO_4) - Add 50 mL of concentrated sulfuric acid to approximately 80 mL of reagent water. Dilute to 100 mL with reagent water and mix well.

8. SAMPLE COLLECTION, PRESERVATIVES, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Samples must not be preserved. Storage of the sample prior to analysis should not exceed six months.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Assemble the Digestion Apparatus as shown in Figure 1.

11.2. Verify the level of 18M H_2SO_4 in each impinger is between the 20-25 mL mark. If the volume is outside the limit, add or remove 18M H_2SO_4 to bring the volume into range.

11.3. Water Samples:

11.3.1. Add 200 mL of sample for analysis to the 500 mL dual neck flask to be used for each sample.

11.3.2. Add the following to each individual sample flask.

11.3.2.1. 1 mL 0.1M Ammonium oxalate carbon carrier.

11.3.2.2. 1 mL 0.5M $KMnO_4$.

11.3.2.3. 5 mL 9M H_2SO_4.

11.3.3. Add 90 mL of 0.1M NH_4OH to each collection bottle and seal each unit using spring clamps.

11.3.4. Adjust the carrier gas (typically O_2) regulator intake until rapid bubbling occurs in the bottle.

11.3.5. Turn down the regulator until approximately 1 bubble per second is maintained.

11.3.6. Adjust the heat source until the solution in the flask begins to boil. Maintain a slow boil for approximately 30 minutes.

11.3.7. Reduce the heat and continue heating for approximately 30 minutes more.

11.3.8. Turn the heat off.

11.3.9. Proceed to step **11.5**.

11.4. Non-aqueous samples

11.4.1. Add 200 mL of dead water and 5 g of soil or ash sample to the 500 mL dual neck flask to be use for each sample.

11.4.2. Add the following to each individual sample flask:

11.4.3. 0.2 mL 1.5M Na_2CO_3.

11.4.4. 5 g $K_2S_2O_8$.

11.4.5. 5 mL 5% $AgNO_3$.

11.4.6. Add 90 mL of 0.1M NH_4OH to each collection bottle and seal each unit using spring clamps.

11.4.7. Adjust the carrier gas (typically O_2) regulator intake until rapid bubbling occurs in the bottle.

11.4.8. Turn down the regulator until approximately 1 bubble per second is maintained.

11.4.9. Heat the sample until the water boils. Continue heating for 5 minutes.

11.4.10. Turn the heat off.

11.4.11. Proceed to step 11.5.

11.5. **CAUTION**: Be careful when disconnecting the apparatus, steam may be released.

Carefully remove the stopper on the dual flask while being careful not to dislodge the seal that goes from the impinger to the flask connection.

11.6. Break the seal at the flask to the collection bottle and remove the fritted bubbler and allow it to drain. Set the fritted bubbler aside for cleaning.

11.7. Add 2 mL of 1.5M $BaCl_2$ to the collection bottle containing the 0.1M NH_4OH. Allow the sample to precipitate. If the precipitation takes more than 30 minutes, consult supervision.

NOTE: More than 2 mL of 1.5M $BaCl_2$ may be added if unusually large amounts of precipitate forms. This assures all sample collected is precipitated.

11.8. Cover and seal the collection bottle with plastic wrap. Covering will protect the sample from CO_2 contamination from the atmosphere.

11.9. Quantitatively transfer the sample solution from the collection bottle into a 50 mL conical bottle centrifuge tube with reagent water. Place a cap on the tube. Centrifuge for approximately 5 minutes and pour off the supernate to an appropriate waste container.

11.10. Wash the precipitate with approximately 25 ml reagent water, mix well and centrifuge. Discard the supernate to an appropriate waste container.

11.11. Using a disposable pipet, quantitatively transfer the precipitate evenly onto a 1.5 inch tared planchet. Dry the planchet under a heat lamp until the precipitate is dry.

NOTE: 1 ml of 0.1m Ammonium oxalate in a blank sample should yield approximately 39.5 mg.

11.12. Transfer the dried precipitate from the planchet into a 20 mL liquid scintillation vial using a rubber policeman.

NOTE: Gloves must be worn when handling scintillation vials.

NOTE: DO NOT write on the vials, only on the caps.

NOTE: Do not prepare samples in a LSC cassette. Scintillation cocktail can destroy the cassettes.

11.13. Add 5 mL double distilled dead water to the liquid scintillation vial and 15 mL liquid scintillation cocktail. Place a labeled cap on the vial.

11.14. Shake each vial to ensure the solution is mixed, wipe using a lint free tissue and place the vial in a counting tray. Complete the associated paperwork and submit the tray and paperwork to the counting room for analysis.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete computer calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1 Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container and transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. Krieger, HL and Gold, S, Procedure For Radiochemical Analysis Of Nuclear Reactor Aqueous Solutions. EPA-R4-73-014, May 1973, page 38f.

15.2. Rapkin, E, Measurement of $^{14}CO_2$ by Scintillation Techniques, Packard Technical Bulletin #7, January 1962.

15.3. Gold, S, Analysis of Carbon-14 and Tritium in Reactor Stack Gas, EPA-600/4-75-001, October 1975.

15.4. USEPA, Narel, Montana, Ala., Method C-01, September 1, 1991.

15.5. RadCalc DB, Users Guide, STL Richland, latest revision.

15.6. STL Quality Management Plan, latest revision.

15.7. STL Richland Laboratory Quality Manual, latest revision.

15.8. STL Richland Quality Assurance Summary, latest revision.

15.9. Associated SOPs

15.9.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

16. MISCELLANEOUS

16.1. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

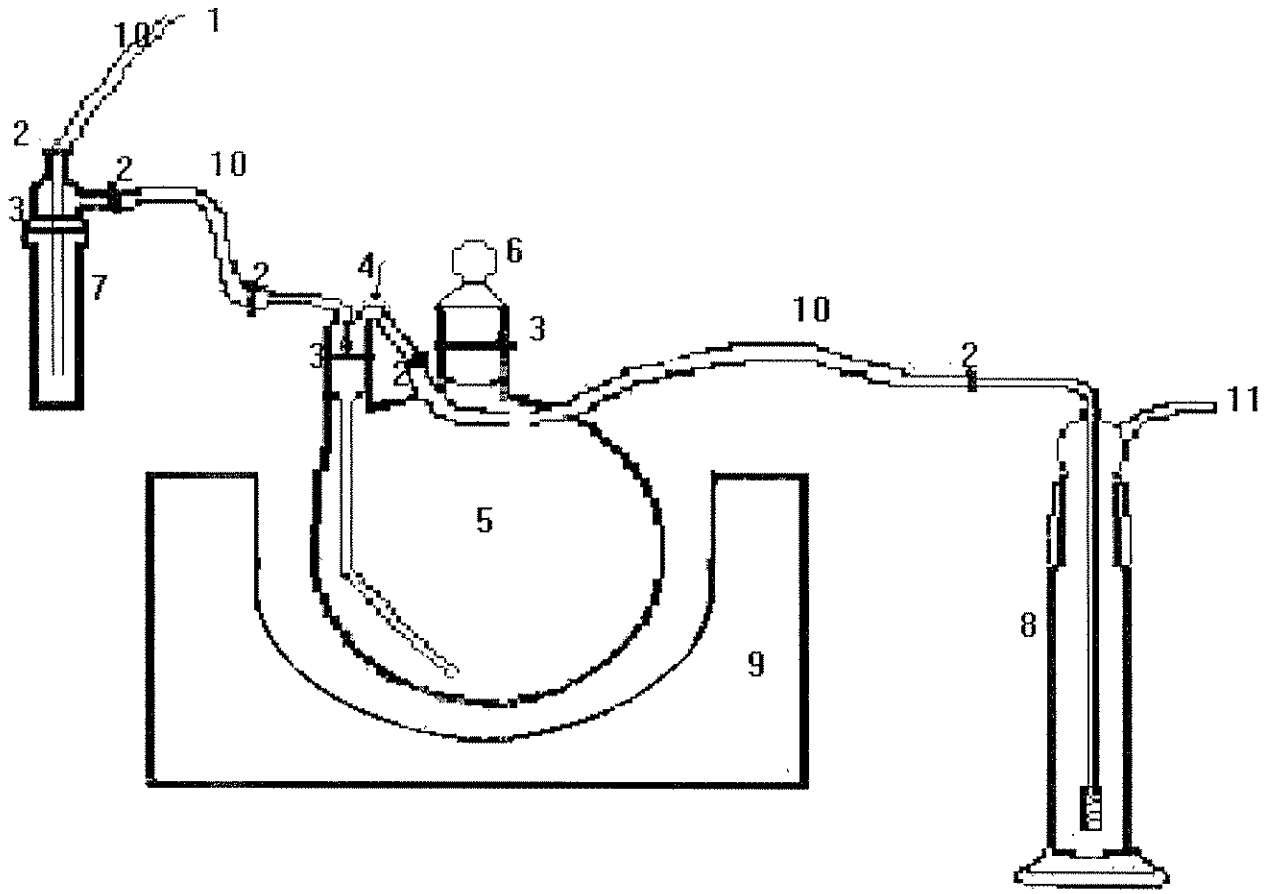
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance policies.

16.2. Records Management/Documentation

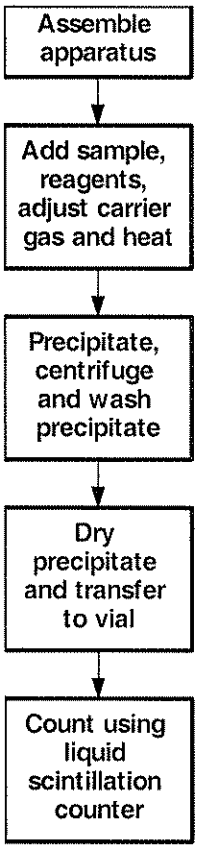
16.2.1. All records generated by this analysis will be filed and kept in accordance with STL QA policies for records management and maintenance.

Figure 1: Digestion Apparatus



1. To O_2 regulator.
2. Pinch clamps.
3. Spherical clamps.
4. Smog bubbler.
5. 2-neck (dual neck) flask.
6. Stopper.
7. Midget impinger modified.
8. Gas collection bottle with fritted cylinder.
9. Heating mantle.
10. Tubing.
11. Gas release to atmosphere.

16.3. Procedural Flow Chart



Title: Separation of Technetium-99 in All Matrices

Approvals (Signature/Date):

Steve Wheland Technical Manager	6/11/08 Date	Dave Harbinson Health & Safety Coordinator	6/11/08 Date
Tim Armstrong Quality Assurance Manager	6/11/08 Date	Jodie Carnes Laboratory Director	6/11/08 Date

This SOP was previously identified as SOP No. RICH-RC-5078 Rev 4

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1. SCOPE AND APPLICATION

1.1 This SOP describes the analysis for technetium-99 in urine, fecal and environmental samples including the destruction of the sample matrix, separation and purification of Tc, and preparation of the sample for counting.

1.2 Refer to Policy P-R-01 for method detection limit information.

2. SUMMARY OF METHOD

2.1. Samples are treated with nitric acid and heat. Technetium is oxidized to Tc(VII) as the pertechnetate ion, TcO_4^-, which is stable in aqueous solutions in the absence of reducing chemical agents. The volume of the liquid is reduced by heating, and the solids are separated from the liquid. The volume is adjusted to approximately 100 mL, and iron, calcium, and barium carriers are added. The sample is made alkaline with ammonium hydroxide, and then sodium carbonate is added. Actinides, lanthanides, alkaline earths, many transition metals, lead, and several anions are precipitated as hydroxides and carbonates away from TcO_4^-. (Ammonium hydroxide is used in place of 6M NaOH as indicated in references, 15.1, 15.2 and 15.3 as it is less hazardous and more convenient to use.) The pH of the supernate is adjusted with nitric acid to approximately pH 1, and the sample is loaded onto an anion-exchange column. Tc is further purified by washing the column with 0.1M nitric acid, then eluted with 6M nitric acid. The eluate is evaporated to approximately 1 mL and transferred to a vial for liquid-scintillation counting.

3. DEFINITIONS

3.1. Dead water is water having a very low concentration of tritium. It usually is obtained from deep wells that are isolated from surface and shallow ground waters.

3.2. Synthetic Urine: Synthetic urine may be prepared according to Procedure RICHRC5028 or Procedure RICHRB5036.

3.3. Synthetic Feces: Synthetic feces may be prepared according to Procedure RICHRC5028 or Procedure RICHRB5036.

NOTE: If artificial blank matrix is not available for spikes or blanks, natural urine or feces may be used in its place.

4. INTERFERENCES

4.1. This procedure will not separate rhenium from technetium. However, a significant quantity of radioactive rhenium is unlikely to be present in all samples.

4.2. If the final extract counted by liquid scintillation is too acidic or is too colored, the quenching of the sample may be below the calibration range of the liquid scintillation counter.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.
- 16M HNO_3 and 30% H_2O_2 when mixed together will liberate large quantities of oxygen. If these are mixed together and the container is sealed, pressure may build up causing a pressure explosion. Always add nitric acid before adding 30% H_2O_2 to avoid possible vigorous reactions. Use extreme caution when wet-ashing samples.
- Do not use hand to stop centrifuge from spinning.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Calcium Carrier (Calcium Nitrate Tetraydrate)	Strong Oxidizer	None listed	May cause respiratory tract irritation. May cause methemglobinemia. May cause eye and skin irritation. May cause digestive tract irritation with nausea, vomiting, and diarrhea. Target organ: blood.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Iron Carrier	Oxidizer	ACGIH 1mg/m^3 TWA NIOSH 1mg/m^3 TWA	May cause severe eye irritation. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. May cause respiratory tract irritation.
Ultima Gold	Flammable	None	If swallowed do not induce vomiting except in the presence of, or on the orders of a doctor.

Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Octanol	Flammable		Liquid may be irritating to skin and eyes. Store in a cool, dry, well-ventilated, flammable liquid storage area or cabinet. Vapors may flow along surfaces to distant ignition sources and flash back.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Beakers: borosilicate glass, various sizes.

6.2. Centrifuge.

6.3. Centrifuge tubes: 90-mL and 250 mL plastic tubes.

6.4. Filter paper: Whatman GF/A or equivalent, 15 cm diameter suggested.

6.5. Filtration apparatus: consisting of Buchner funnel (15-cm diameter. and plastic suggested) with rubber stopper or equivalent on its stem, filter flask (500-mL size suggested), vacuum tubing, and vacuum source.

6.6. Glass wool: borosilicate glass.

6.7. Graduated cylinders: various sizes.

6.8. Hot plate or electric griddle: adjustable heat.

6.9. Ion-exchange column: straight, borosilicate glass, dimensions approximately 10 mm diameter by 18 cm with Teflon stopcock below and reservoir above.

6.10. pH indicator paper or strips: various ranges, to include pH 0.5-1.5 and pH 6.5-8.0, ColorpHast strips from EM Science or equivalent recommended.

6.11. Pipet: transfer, disposable plastic.

6.12. Stirring hot plate: with Teflon stir bars.

6.13. Thermometer: capable of reading 80 to 115°C.

6.14. Vials: liquid scintillation, 20 mL, plastic, with caps.

7. REAGENTS AND STANDARDS

7.1. Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

7.2. 14.7M Ammonium hydroxide (14.7 NH_4OH) - Concentrated. **CAUTION**: Corrosive.

7.3. Anion exchange resin - BioRad AG 1 x 4, 100-200 mesh, chloride form or equivalent.

7.4. Barium carrier, 100 mg Ba/mL (non-standardized): Dissolve 178.0 g $BaCl_2 \cdot 2H_20$ (**WARNING**: toxic) in approximately 700 mL of reagent water. Dilute to 1L final volume with reagent water and mix well.

7.5. Calcium carrier, 100 mg Ca/mL (non-standardized): Dissolve 367 g $CaCl_2 \cdot 2H_20$ (**CAUTION**: Irritant) in approximately 500 mL of reagent water. Dilute to 1L final volume with reagent water and mix well.

7.6. Dead water - water which contains little or no tritium, distilled.

7.7. 30% Hydrogen peroxide (30% H_2O_2). **WARNING**: Corrosive and oxidizing.

7.8. Iron carrier, 50 mg Fe/mL (non-standardized): Dissolve 360 g $Fe(NO_3)_3 \cdot 9H_20$ (**WARNING**: Oxidizer) in approximately 500 mL of reagent water. Dilute to 1L final volume with reagent water and mix well.

7.9. Liquid Scintillation Cocktail - Ultima Gold LLT from Perkin Elmer, or equivalent. **WARNING**: Flammable.

7.10. 16M Nitric acid (16M HNO_3) - Concentrated. **WARNING**: Corrosive and oxidizer.

7.11. 8M Nitric acid (8M HNO_3) - Add 1L of concentrated nitric acid to 1L of reagent water and mix well. **WARNING**: Corrosive and oxidizer.

7.12. 6M Nitric acid (6M HNO_3): add 375 mL of 16M HNO_3 to 600 mL of reagent water. Dilute to 1 liter with reagent water and mix well. **WARNING**: Corrosive and oxidizer.

7.13. 0.1M Nitric acid (0.1M HNO_3) - Add 6.4 mL of concentrated nitric acid to 950 mL of water. Dilute to 1 liter with reagent water and mix well.

7.14. Octanol ($CH_3(CH_2)7OH$) - **WARNING**: Flammable.

7.15. 2M Sodium Carbonate (2M Na_2C0_3): Dissolve 212 g of sodium carbonate in approximately 900 mL of reagent water. Dilute to 1L with reagent water and mix well. This is a nearly saturated solution, and may take quite a while to dissolve.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2. It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to bring it to pH 2.

9. QUALITY CONTROL

9.1. All quality control data shall be maintained and available for easy reference.

9.2. Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3. Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4. Refer to SOP RICH-RC-0002 for sample and QC data acceptance criteria and corrective action.

10. CALIBRATION

10.1. None.

11. PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A Nonconformance Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo will be filed in the project file.

11.1. Sample Preparation

CAUTION: Do not under any circumstances allow the sample to reach dryness. Some Tc compounds are volatile and there may be considerable losses at higher temperatures.

11.1.1. SOIL AND FRESH WATER SEDIMENT

11.1.1.1. The sample is dried and homogenized according to RICHRC5013. Weigh an aliquot of sample, as specified by the client specific QAS, into a labeled beaker (400-mL size suggested). Record the sample weight on the analytical worksheet.

11.1.1.2. Add appropriate tracers and/or spikes as designated in the client specific QAS. Rinse the vials three times with approximately 5 mL of 8M HNO_3, transferring the rinses quantitatively to the appropriate sample beaker. Record the vial information.

11.1.1.3. Add approximately 100 mL of 8M HNO_3 to the sample. Place a magnetic stirring bar in each beaker and cover with a watchglass. Place the beaker on a stirring hot plate. While stirring, digest this mixture for one hour without boiling. Add 8M HNO_3 as needed to keep the sample volume near 100 mL.

11.1.1.4. **NOTE**: Make sure vacuum is applied to the Buchner funnel prior to decanting the samples.

Decant the 8M HNO_3 solution containing the soil residue into a Buchner funnel fitted with a Whatman GF/A filter. Collect the sample leachate under vacuum in a side-arm flask. Rinse the beaker with approximately 20 mL of reagent water and add to the funnel. Continue to apply vacuum until the soil residue is free of visible liquid and liquid ceases to drip from the funnel.

11.1.1.5. Transfer the filtered leachate from the side-arm flask to the original sample beaker. Rinse the flask with small volumes of reagent water and add the rinsate to the beaker. Discard the filter to an appropriate waste container.

11.1.1.6. Place the beakers on a low-temperature hot plate and evaporate to approximately 50 mL. Periodically, add a few milliliters of 30% H_2O_2 to remove as much color as possible from the solution.

11.1.1.7. When the sample volume has been reduced to approximately 50 mL, using reagent water adjust the sample volume to 100 mL.

11.1.1.8. Proceed to section 11.2, Separation and Purification.

11.1.2. ANIMAL MATTER

11.1.2.1. Consult supervision for appropriate sample homogenization step, if necessary. Weigh an aliquot of sample, as specified by the client specific QAS, into a labeled beaker (400-mL size suggested). Record the sample weight on the analytical worksheet.

11.1.2.2. Add appropriate tracers and/or spikes as designated in the client specific QAS. Rinse the vials three times with approximately 5 mL of 8M HNO_3, transferring

the rinses quantitatively to the appropriate sample beaker. Record the vial information.

11.1.2.3. Carefully cover the sample with 16M HNO_3. Place the beakers on a low temperature hot plate and slowly digest the sample to fully ash the sample while minimizing the chance of volatilizing Tc.

11.1.2.4. If necessary, add 16M HNO_3 to keep the sample covered. Add small quantities of 30% H_2O_2 periodically to further the destruction of the matrix to inorganic salts. A clear, colored solution is obtained when the sample has been fully ashed.

NOTE: If residue remains at this point, contact supervision.

NOTE: Addition of some reagent water may be needed to completely dissolve the salts. Use no more water than necessary.

11.1.2.5. Proceed to section 11.2, Separation and Purification.

11.1.3. VEGETATION/PRODUCE/RESIN

11.1.3.1. Samples are dried, chopped and homogenized according to RICHRC5016. Weigh an aliquot of sample, as specified by the client specific QAS, into a labeled beaker (400-mL size suggested). Record the sample weight on the analytical worksheet.

11.1.3.2. Add appropriate tracers and/or spikes as designated in the client specific QAS. Rinse the vials three times with approximately 5 mL of 8M HNO_3, transferring the rinses quantitatively to the appropriate sample beaker. Record the vial information.

11.1.3.3. **NOTE**: Make sure that the vegetation is sufficiently pulverized or compressed so that the acid covers it all.

Add approximately 100 mL of 8M HNO_3 to the sample. Place a magnetic stirring bar in each beaker and cover with a watchglass. Place the beaker on a stirring hot plate. While stirring, digest this mixture without boiling for at least two hours. Add 8M HNO_3 as needed to keep to sample volume near 100 mL. If necessary add more 8M HNO_3 to keep the sample covered.

11.1.3.4. **NOTE**: Make sure vacuum is applied to the Buchner funnel prior to decanting the samples.

Decant the 8M HNO_3 solution containing the sample residue into a Buchner funnel fitted with a Whatman GF/A filter. Collect the sample leachate under vacuum in a side-arm flask. Rinse the beaker with approximately 20 mL of reagent water and add to the funnel. Continue to apply vacuum until the sample residue is free of visible liquid and liquid ceases to drip from the funnel.

11.1.3.5. Transfer the filtered leachate from the side-arm flask to a clean, labeled, beaker (400-mL size suggested). Rinse the flask with small volumes of reagent water and add the rinsate to the beaker. Discard the filter to an appropriate waste container.

11.1.3.6. Place the beakers on a low-temperature hot plate and evaporate to approximately 50 mL. Periodically, add a few milliliters of 30% H_2O_2 to remove as much color as possible from the solution.

11.1.3.7. When the sample volume has been reduced to approximately 50 mL, using reagent water adjust the sample volume to approximately 100 mL.

11.1.3.8. Proceed to section 11.2, Separation and Purification.

11.1.4. AIR FILTER OR "WIPE" SAMPLE

11.1.4.1. If the sample has not been digested and aliquoted according to RICHRC5016, prepare sample and QC samples according to step 11.1.4.2.

11.1.4.2. Place the air filter in a clean labeled beaker (250-mL size suggested). Add 100 mL of 8M HNO_3 to the sample beaker. Digest for at least 2 hours without boiling, adding more 8M HNO_3 as needed. Transfer the sample to one or more labeled centrifuge tubes. Rinse the beaker with reagent water and add the rinses to the tube(s). Centrifuge. Decant the supernate to a clean labeled beaker (400-mL size suggested).

11.1.4.3. Add appropriate tracers and/or spikes as designated in the client specific QAS. Rinse the vials three times with approximately 5 mL of 8M HNO_3, transferring the rinses quantitatively to the appropriate sample beaker. Record the vial information.

11.1.4.4. Proceed to section 11.2, Separation and Purification.

11.1.5. WATER

11.1.5.1. **NOTE**: If Carbon-14, Iodine-129, Iodine-131, or Tritium analyses have been requested and the aliquots are to be taken from the same sample container, remove those aliquot(s) prior to acidification of the sample.

Using a wide range pH paper, measure the pH of the sample and record the pH on the worksheet. If the pH is 2 or less, proceed to 11.1.5.2.

NOTE: Some clients do not want samples analyzed if preservation is incorrect. If the pH is above 2, consult the client specific QAS or supervision to determine if the sample analysis may proceed after acidification.

To acidify the sample, add acid to the sample using approximately 1 mL of concentrated HNO_3 to each liter of sample. Mix the sample and recheck the pH. Continue to add acid in 1 mL increments until the sample pH is below 2. Hold the sample in the original container for a minimum of 16 hours before continuing with this procedure.

11.1.5.2. Measure out an aliquot of sample as specified in the client specific QAS to an appropriately sized and labeled beaker. If significant sediment is present, filter the sample through a Buchner funnel containing a Whatman GF/A filter. Discard the filter to an appropriate waste container. Record the sample size on the appropriate analytical worksheet.

11.1.5.3. Prepare appropriate QC samples. Add the appropriate spike to the QC spike beaker. Record the vial information. Rinse the vial three times with small quantities of 8M HNO_3, adding the rinses to the appropriate beaker. Record the sample size on the analytical worksheet.

11.1.5.4. Place the sample on a low temperature hot plate. Without boiling, evaporate to approximately 100 mL or until salts appear. If salts start forming, slowly add reagent water with stirring until they redissolve. If salt formation begins when the volume is more than approximately 200 mL, consult supervision.

11.1.5.5. Quantitatively transfer the sample to a clean labeled beaker (400-mL recommended). Proceed to section 11.2, Separation and Purification.

11.1.6. URINE

11.1.6.1. Weigh the urine sample by taring a labeled beaker or Erlenmeyer flask on a top-loading balance. Add all the urine from the plastic collection bottles and re-weighing the flask. Record the total sample volume (1g = 1 mL) on the analytical worksheet(s). Verify the sample volume meets contractual requirements. Transfer appropriate amounts of blank urine into both the LCS and the blank flasks. From here on, the LCS, the blank, and the actual samples are treated alike.

NOTE: Samples of insufficient volume are not discarded without instructions from supervisor.

NOTE: Synthetic or raw urine may be used for matrix spikes. Consult the client specific QAS or supervision for further information.

11.1.6.2. Rinse each plastic collection bottle with concentrated HNO_3, unless already acidified, and add the rinses to the flask/beaker using a total volume of acid approximately equivalent to 10% of the sample volume.

11.1.6.3. Aliquot the sample for each analysis requested. Consult the client specific Quality Assurance Summary (QAS) or your supervisor for the appropriate sample size.

11.1.6.4. To the LCS flask only, add the appropriate spike. Rinse the vials 3 times with 2M or 8M HNO_3, transferring the rinses quantitatively to the appropriate sample beaker. Record the vial information.

11.1.6.5. Place the sample on a hot plate. Evaporate the sample to dryness. Wet ash the urine sample with 8M HNO_3 and 30% H_2O_2. Proceed to step 11.2, Separation and Purification.

11.1.7. FECAL

11.1.7.1. Weigh the fecal sample by taring a labeled beaker (1500-mL or appropriate size for fecal analysis) on a top-loading balance, transferring the entire sample from the collection container to the beaker and re-weighing. Record the weight of the total sample on the analytical worksheet(s).

NOTE: Use synthetic feces or a raw fecal sample for matrix spikes. Consult supervision for information and further instructions.

11.1.7.2. Aliquot the sample for each analysis requested. Consult the client specific Quality Assurance Summary (QAS) or your supervisor for the appropriate sample size.

11.1.7.3. To the LCS flask only, add the appropriate spike. Rinse the vials 3 times with 2M or 8M HNO_3, transferring the rinses quantitatively to the appropriate sample beaker. Record the vial information.

11.1.7.4. Add 50 mL 8M HNO_3 to the sample and place on a hot plate. Without boiling, gently digest the sample. If frothing occurs, add approximately 10 mL of Octanol and gently wet ash the sample almost to dryness. Repeat this step twice. Do not bake.

11.1.7.5. Dissolve the sample in a minimum of 8M HNO_3. Filter this mixture through a Buchner funnel using a Whatman GF/A filter paper. Collect the sample leachate under vacuum in a side-arm flask. Rinse the beaker with approximately 20 mL of reagent water and add the rinse to the funnel. Continue to apply vacuum until the sample residue is free of visible liquid and ceases to drip from the funnel.

11.1.7.6. Transfer the filtered leachate from the side-arm flask to a clean labeled beaker (400-mL size suggested). Rinse the flask with small volumes of reagent water and add the rinsate to the beaker. Proceed to step 11.2, Separation and Purification.

11.2. SEPARATION AND PURIFICATION

11.2.1. Add approximately 1 mL of iron carrier (50 mg/mL), approximately 2 mL of calcium carrier (100 mg/mL), and approximately 1 mL of barium carrier (100 mg/mL) to each sample. Add a Teflon-coated stir bar and place the sample on a magnetic stir plate.

11.2.2. While stirring, adjust the pH to alkaline using concentrated NH_4OH. Confirm with pH indicating paper or strip that the pH is greater than 7 before proceeding.

11.2.3. Continue stirring and add 30 to 60 mL of 2M Na_2CO_3.

11.2.4. Filter or centrifuge the sample. Proceed to step 11.2.4.1 for filtration or step 11.2.4.2 for centrifuging.

11.2.4.1. **NOTE**: Make sure vacuum is applied to the Buchner funnel prior to decanting the samples.

Decant the above solution into a Buchner funnel fitted with a Whatman GF/A filter. Collect the sample filtrate under vacuum in a side-arm flask. Rinse the beaker with small amounts of reagent water and add to the funnel. Rinse the sides of the funnel and rinse the precipitate with reagent water. Continue to apply vacuum until liquid ceases to drip from the funnel. Quantitatively transfer the filtrate from the side-arm flask to a clean, labeled, beaker. Discard the filter to an appropriate waste container. Continue with step 11.2.5 .

11.2.4.2. Transfer the sample to a clean labeled 250 mL centrifuge tube. Rinse the beaker with small amounts of reagent water, adding the rinses to the appropriate centrifuge tube. Centrifuge the sample for at least 10 minutes. Decant the supernate to the original sample beaker. Add approximately 50 mL of reagent water to the centrifuge tube. Mix well using a vortex mixer. Centrifuge for at least 10 minutes. Decant the supernate to the appropriate beaker. Continue with step 11.2.5.

11.2.5. **NOTE**: For soil samples, addition of 16M HNO_3 may produce a violent reaction. Acid must be added slowly.

Slowly add 16M HNO_3 until the sample pH is between 2 and 4, checking the pH with indicator paper or strip. Heat gently for 15 minutes or until the effervescence from CO_2 ceases.

11.2.6. Adjust the pH to 1.0-1.3 using 16M HNO_3. Use narrow range pH paper or strip to check the pH. If the sample is over acidified, correct with concentrated NH_4OH, added dropwise. Cool the sample to room temperature before putting on the ion-exchange column.

11.2.7. Prepare a straight ion-exchange column using AG 1 x 4 resin, 100 - 200 mesh, chloride form, with a bed height of approximately 15 cm. Follow the preparation instructions in RICHRC5018 omitting the top glass wool plug.

NOTE: The column flow is at the maximum flow rate.

11.2.8. Place a container under the column to collect the waste. Condition the column with approximately 100 mL of 0.1M HNO_3. Rinse any resin from the side of the column reservoir with 0.1M HNO_3 from a wash bottle.

11.2.9. Pour the sample into the column being careful not to disturb the resin bed as little as possible. Allow the sample to pass through the column. Rinse the beaker with small amounts of 0.1M HNO_3 and add the rinses to the column.

11.2.10. **NOTE**: In this and the remaining column steps, add liquid carefully not to disturb the resin bed as little as possible.

Pass 300 to 500 mL of 0.1M HNO_3 through the column. Discard the waste to an appropriate waste container.

11.2.11. Place a clean, labeled, beaker under the column (150-mL size recommended). Elute the technetium with 50 to 60 mL of 6M HNO_3. Pass an additional 50 to 60 mL of 6M HNO_3, collecting all the 6M HNO_3 in the beaker.

11.2.12. **CAUTION**: Do not let allow the sample to go to complete dryness on the hot plate.

Evaporate the 6M HNO_3 eluate to approximately 1 mL. Add a few drops of 30% H_2O_2 during evaporation to obtain a colorless solution. Cool the sample.

NOTE: It is possible that some samples may require further oxidation requiring a few mL of 30% H_2O_2.

11.3. PREPARATION FOR LIQUID-SCINTILLATION COUNTING

11.3.1. Quantitatively transfer the sample to a liquid-scintillation counting vial. Rinse the beaker using small quantities of dead water and transfer to the vial until a total sample volume as close as possible to 4.5-5.0 mL is obtained.

11.3.2. Add 15 mL of liquid-scintillation cocktail, cap the vial, and mix vigorously. Write the sample identification on the vial cap only. Wipe the vial with a clean tissue. Holding the vial by the cap only, place the vial in an LSC cassette. Fill in the remaining required information on the liquid scintillation counting sheet.

11.3.3. Submit cassettes with the scintillation vials, the completed liquid scintillation counting sheet, and the chain of custody to the counting room for liquid scintillation counting.

11.3.4. The samples are dark-adapted by placing the samples in a refrigerator or the liquid-scintillation counter chamber for at least 30 minutes before initiating counting.

12. DATA ANALYSIS AND CALCULATIONS

For computer calculation of the sample activity and its total propagated uncertainty (TPU), consult the RadCalc Users Guide. The complete calculation includes blank subtraction if requested by the customer and complete error propagation.

13. METHOD PERFORMANCE

13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use.

13.2. Method Demonstration of Capability documentation is maintained in the quality files.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1 Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in a Flammable waste container which is red with a self closing metal lid

Radioactive Waste
Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.

Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

15. REFERENCES

15.1. Chieco, N. A., D. C. Bogan, and E. O. Knutson, eds., 1990, "Technetium-99 in Water and Vegetation", EML Procedures Manual, HASL-300, U.S. Department of Energy, Environmental Measurements Laboratory, New York, New York, pp. 237-242.

15.2. American Society for Testing and Materials, 1991, "Standard Specification for Reagent Water, D1193", Annual Book of Standards, Volume 11.01. ASTM, Philadelphia, Pennsylvania.

15.3. Chu, N. Y., and J. Feldstein, 1984, "Radiochemical Determination of Technetium-99", Talanta, Vol. 31, pp. 809-813.

15.4. Health Physics Society Committee Report HPSR-1, 1980, Upgrading Environmental Radiation Data, EPA 520/1-80-012, U.S. Environmental Protection Agency, Washington, D.C.

15.5. Volchok, H. L., and G. de Planque, eds., 1982, "Radiochemical Determination of Technetium-99", EML Procedures Manual, HASL-300, U.S. Department of Energy, Environmental Measurements Laboratory. New York, New York, procedure E-Tc-01.

15.6. Kotegov, K.V.; Pavlov, O.N.; Shvedov, V.P. Technetium. In: Emeleus, H.J.; Sharp, A.J. Adv. Inorg. Chem. and Radiochem. Vol. II, Academic Press; 1968.

15.7. Lavrukhina. A.K.; Pozdnyokov, A.A. Technetium, Promethium, Astatine and Francium. Ann Arbor: Ann Arbor-Humphrey Science Publishers; 1970.

15.8. Schwochau. K. The Present Status of Technetium Chemistry. Radiochimica Acta 32:139-152; 1983.

15.9. STL Quality Management Program, latest revision.

15.10. STL Richland Laboratory Quality Manual, latest revision.

15.11. STL Richland Site-Specific Quality Assurance Summary, latest revision.

15.12. Associated SOPs

15.12.1. RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

15.12.2. RICHRB5036 - Preparation of Synthetic Urine and Feces Using Recipes from HPS N13.30 Performance Testing.

15.12.3. RICHRC5013 - Preparation of Soil Samples.

15.12.4. RICHRC5016 - Preparation of Environmental Matrices.

15.12.5. RICHRC5018 - Ion-Exchange Preparation.

15.12.6. RICHRC5028 - Preparation of Synthetic Urine and Feces.

16. MISCELLANEOUS

16.1. Method Differences

16.1.1. This SOP follows References 15.1 and 15.5 except that the sample preparation technique for water and vegetation has been slightly modified, and the sample is prepared for liquid-scintillation or beta proportional counting rather than for beta-particle solid-scintillation counting. Sample preparation techniques for soil, air filters and animal matter have been added. In addition, the molarity of nitric acid has been increased to improve the effectiveness of elution. Tc-95m will be used as a tracer when available.

16.2. Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

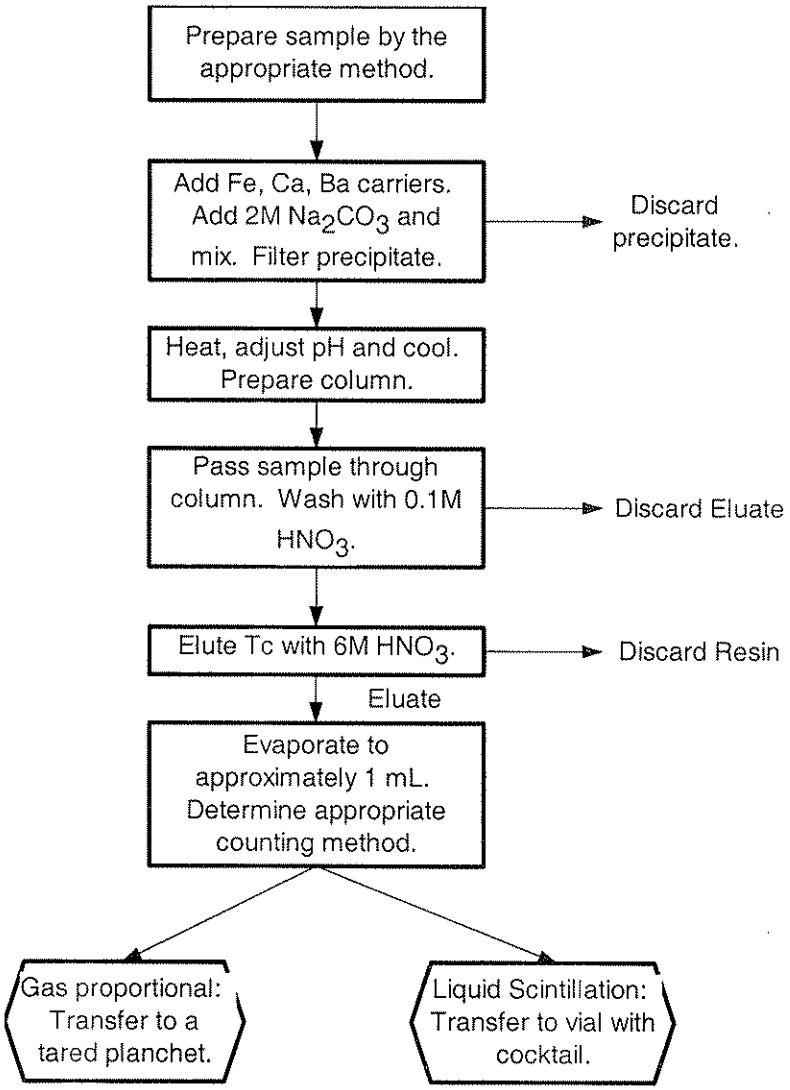
Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the facilities Quality Assurance procedures.

16.3. Records Management/Documentation

16.3.1. All records generated by this analysis will be filed and kept in accordance with STL Richland SOPs for records management and maintenance.

16.4. Procedural Flow Chart



Title: Radium-226 and Radium-228 Separation in Radiochemical Matrices-Adapted from EPA 903.1 and 904.0

Approvals (Signature/Date):

6/11/08	6/11/08
Steve Wheland Technical Manager	Date	Dave Harbinson Health & Safety Coordinator	Date
6/11/08	6/11/08
Tim Armstrong Quality Assurance Manager	Date	Jodie Carnes Laboratory Director	Date

This SOP was previously identified as SOP No. RICH-RC-5005 Rev 6

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RL-RA-001 REVISION 0

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1 SCOPE AND APPLICATION

1.1 This procedure is used to separate Ra-226 and Ra-228, individually or sequentially, in a variety of matrices. Matrices for which this method has been validated include water, soil, bottom sediment, suspended sediment, urine, and feces. However, radium isotopes are usually determined by gamma spectroscopy for soil and bottom sediment.

1.2 Radium is coprecipitated, as a sulfate, with barium and lead carriers. Ra-226 is determined by counting the activity of Rn-222 gas ingrown from the Ra-226 present. This is achieved with a special alpha scintillation system. Ra-228 is allowed to come to secular equilibrium with its daughter, Ac-228, which is then separated from the radium by a yttrium coprecipitation using ammonium oxalate. The resulting oxalate is counted with a beta proportional detector. Throughout this procedure the chemical yield is monitored with a Ba-133 tracer.

1.3 Refer to Policy P-R-01 for method detection limit information.

2 SUMMARY OF METHOD

2.1 The radium in a sample is coprecipitated, as a sulfate, with barium and lead (including calibrated Ba-133 tracer), and the precipitate is dissolved in an alkaline EDTA solution. If Ra-228 is required, Sr-90 is partially removed by repetitive precipitations and dissolutions which manipulate the relative solubilities of Sr, Ba, and Ra sulfates in a buffered EDTA solution. This also serves to remove Ac-228 and start a measured period of Ac-228 ingrowth.

2.2 The radium fraction is gamma counted to determine the Ba-133 tracer yield and then transferred to a radon bubbler for Ra-226. Helium is bubbled through the sample to remove any Rn-222 present, and the bubbler is sealed to begin a measured period of Rn-222 ingrowth. When the Rn-222 has ingrown sufficiently, helium is again bubbled through the sample and, along with the ingrown Rn-222, collected in an alpha scintillation cell. The Rn-222 is allowed to come to secular equilibrium with its first two alpha emitting progeny, and then the activity in the cell is measured in a specially designed counter.

2.3 After sufficient Ac-228 ingrowth, a calibrated yttrium carrier and a lead carrier are then added to the sample. The lead is separated as the sulfide to remove any radioactive lead which may have ingrown from Ra-226 or Ra-228 since the beginning of the ingrowth interval. The Ac-228 is then separated from the Ra-228 by co-precipitation with yttrium as the hydroxide. The precipitate is dissolved, converted to yttrium and actinium oxalates and counted by a beta proportional counter.

2.4 Appropriately prepared fecal salts are suspended/dissolved in small quantities of concentrated nitric acid. Cold fuming nitric acid is used to ensure precipitation of Sr, Ba, and Ra nitrates. Most other ions remain in solution and are discarded. Water dissolves the nitrate precipitates and the radium separation is continued identically to water matrices.

2.5 Soils and sediments are solubilized by microwave bomb digestion or acid digestion. At the end of these procedures the dried sample is dissolved in a small volume of weak nitric acid. This is diluted further and the resulting solution is analyzed as a water sample.

3 DEFINITIONS

3.1 Carrier – Carriers are stable counterparts of the radioactive isotope(s) to be measured. Carriers are added to all samples in an analytical batch such that each sample has a specific measurable QC parameter (yield). From the time of addition, carriers undergo all chemical processing similar to that of the sample. Carriers are not counted; a known form of the carrier is weighed to provide radiochemical yield gravimetrically or is measured by an alternative technique (such as inductively coupled plasma atomic emission spectrometry) to determine radiochemical yield.

3.2 Milking – The separation of the progeny from the parent isotope.

4 INTERFERENCES

4.1 There are no known interferences to the Ra-226 analysis; the other naturally occurring radon isotopes are too short-lived.

4.2 It is well documented that large quantities of Sr-90 and Pb-210 can interfere with the Ra-228 analysis. This procedure is designed to remove ambient levels of Sr-90 and Pb-210. However, higher levels of these nuclides can give a high bias to the Ra-228 result.

4.3 The presence of carbonate in the NaOH solutions lowers the spike yields on Ac-228 in the Ra-228 analysis. Precautions to minimize CO_2 adsorption in these and the solid reagent are discussed under reagents.

5 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.
- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.
- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.
- Do not use hand to stop centrifuge from spinning.
- WARNING: Fuming nitric acid is a severe health hazard if not handled properly. Contact with skin and breathing of vapors must be avoided, and gloves and eye protection must be worn when handling. If fuming nitric acid contacts skin, immediately hold the exposed area under cool running water for fifteen minutes and call for help. Promptly report burns to supervision.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid, Fuming	Corrosive Reactive Oxidizer Poison	ACGIH TLV 2ppm TWA 4ppm STEL	Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat and respiratory track. Symptoms may disappear only to return in a few hours and more severely. Onset of symptoms may be delayed for 4-30 hours.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6 EQUIPMENT AND SUPPLIES

6.1 Alpha scintillation cell counter - calibrated for this procedure only.

6.2 Alpha scintillation cell.

6.3 Analytical balance - capable of reading 0.0001 g.

6.4 Aspirator hose.

6.5 Beakers - glass, various sizes.

6.6 Centrifuge.

6.7 Centrifuge tubes - plastic, 50 mL conical bottom and 90 mL with caps.

6.8 Emanation apparatus for radon (figure 1).

6.9 Drying lamp.

6.10 Filter – 0.45 µm Gelman Membrane, Acrodisc #4497 or equivalent.

6.11 Filter Holder – with Swin-Lok fitting or equivalent.

6.12 Hot plate.

6.13 Filter - nitrocellulose membrane, 47 mm, 0.45m pore size, BA 85.

6.14 pH paper - variable ranges, 1-12 or other suitable range to perform indicated tasks.

6.15 Pipet - transfer, glass or plastic.

6.16 Pipettors - various ranges, 0.1 to 5 mL.

6.17 Plastic wrap.

6.18 Planchets - stainless steel, 2.5 cm (1.0") or 3.8 cm (1.5") diameter, approximately 3 mm (1/8") deep, which have been flamed or muffled overnight at approximately 470°C-500°C.

6.19 Radon bubbler.

6.20 Stir rods - long, glass or plastic.

6.21 Syringe - 20 cc, with Leur-lock fitting, or equivalent.

6.22 Tape - plastic, to seal 50-mL plastic centrifuge tubes.

6.23 Vacuum pump.

6.24 Vortex mixer.

7 REAGENTS AND STANDARDS

7.1 Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nano-pure system. Label all reagents as outlined in procedure RICHQA5002.

NOTE: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

NOTE: Any reagent may be prepared at different volumes so long as the proportions of ingredients remain the same.

7.2 Acetic acid (17.4M $HC_2H_3O_2$) - Concentrated (glacial). **CAUTION:** Corrosive.

7.3 Ammonium hydroxide (15M NH_4OH) - Concentrated. **CAUTION:** Corrosive.

7.4 Ammonium oxalate ($(NH_4)_2C_2O_4$) 4.4% - Dissolve 2.5 g of ammonium oxalate monohydrate ($(NH_4)_2C_2O_4 \bullet H_2O$) in at least 25 mL of reagent water. Heat to dissolve. Dilute to 50 mL. Prepare fresh on each day of use. **CAUTION:** Corrosive.

7.5 Ammonium sulfate ($(NH_4)_2SO_4$) 200 mg/mL - Dissolve 20 g of ammonium sulfate in reagent water and dilute to 100 mL.

7.6 Ammonium sulfide ($(NH_4)_2S$) 2% - Dilute 2 mL of ammonium sulfide, 20%, to 10 mL with reagent water. Prepare fresh on each day of use. This solution slowly decomposes with age. If it is not "straw yellow", discard. **CAUTION:** Flammable and Corrosive.

7.7 Anhydrone™ - Magnesium perchlorate drying reagent. **CAUTION:** Oxidizer.

7.8 Ascarite II™ - Carbon dioxide adsorbent, 8-20 mesh. **CAUTION:** Corrosive.

7.9 Barium carrier and tracer - Prepared by the Standards Laboratory, and issued in individual vials.

7.10 1M Citric acid (1M $COH(CH_2CO_2H)_2CO_2H$) -Dissolve 19.2 g of citric acid monohydrate in reagent water and dilute to 100 mL.

7.11 0.25M Disodium ethylenedinitriloacetate dihydrate, EDTA ($C_{10}H_{14}N_2Na_2O_8 \bullet 2H_2O$) - Dissolve 20 g of NaOH in 750 mL of reagent water, heat and slowly add 93 g of EDTA while stirring. After the EDTA is in solution dilute to 1 L with reagent water.

7.12 Helium gas - High Purity Grade or equivalent.

7.13 30% Hydrogen peroxide (30% H_2O_2). **WARNING**: Corrosive and Oxidizer.

7.14 Lead carrier (15 mg/mL) - Dissolve 2.397 g of lead nitrate in reagent water, add 0.5 mL of nitric acid and dilute to 100 mL with reagent water. **WARNING**: Chronic, acute and reproductive toxin. **CAUTION**: Oxidizer.

7.15 Methyl orange indicator (0.1%) - Dissolve 0.1 g of solid methyl orange in 100 mL of reagent water.

7.16 90% Nitric acid (90% HNO_3) - Fuming. **WARNING**: Corrosive and Oxidizer.

7.17 Nitric acid (Concentrated HNO_3) – **WARNING**: Corrosive and Oxidizer.

7.18 6M Nitric acid (6M HNO_3) - Add 375 mL of concentrated HNO_3 to 625 mL of reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.19 1M Nitric acid (1M HNO_3) - Add 63 mL of concentrated HNO_3 to 500 mL of reagent water then dilute to 1 L final volume. Mix well.

7.20 Sodium hydroxide (NaOH) - Store in a desiccator containing Drierite and soda lime. **WARNING**: Corrosive.

7.21 18M Sodium hydroxide (18M NaOH) - Dissolve 36 g of NaOH to 20 mL of reagent water. Mix the solution in a capped centrifuge tube. Dilute to a final volume of 50 mL. Prepare fresh daily. **WARNING**: Corrosive.

7.22 10M Sodium hydroxide (10M NaOH) - Dissolve 40 g of NaOH in reagent water and dilute to 100 mL. Prepare fresh daily.

7.23 Sodium carbonate (Na_2CO_3) - Saturated aqueous. Add 225 g Na_2CO_3 to 700 mL of reagent water.

7.24 Strontium carrier (10 mg/mL, uncalibrated) - Dissolve 24.16 g of strontium nitrate in reagent water and dilute to 1 L.

7.25 Strontium-yttrium mixed carrier A (20 mg/mL Sr, 18 mg/mL Y, uncalibrated) - Add 22.85 g of yttrium oxide (Y_2O_3) to 20 mL of reagent water. Heat to boiling and slowly add 30 mL of nitric acid while stirring until the yttrium oxide dissolves. Add 400 mL of reagent water to the flask and dissolve 48.32 g of strontium nitrate into the solution. Add 70 mL of concentrated HNO_3 and dilute to 1 L with reagent water. Mix well.

7.26 Strontium-yttrium mixed carrier B - Mix 10 mL of 10 mg/mL strontium carrier and 5 mL of 18 mg/mL yttrium carrier, dilute to 100 mL with reagent water.

7.27 Sulfuric acid (18M H_2SO_4) - Concentrated. **WARNING**: Corrosive.

7.28 Yttrium carrier (18 mg/mL, uncalibrated) - Add 22.85 g of yttrium oxide (Y_2O_3) to 20 mL of reagent water. Heat to boiling and slowly add 30 mL of nitric acid while stirring until the yttrium oxide dissolves. Add 70 mL of concentrated HNO_3 and dilute to 1 L with reagent water.

7.29 Yttrium carrier - Prepared by the Standards Laboratory.

8 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2 It is recommended that water samples be preserved at the time of collection by adding enough 1M HNO_3 to the sample to adjust it to pH 2.

9 QUALITY CONTROL

9.1 All quality control data shall be maintained and available for easy reference.

9.2 Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3 Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4 Refer to SOP RICH-RC-0002 for QC acceptance criteria and corrective action.

10 CALIBRATION

10.1 Each alpha scintillation cell is assigned to a particular counter and must be used only with that counter, because the counting efficiency (cell constant) depends on both the cell and the counter. Each cell is assigned its own unique code.

10.2 Once a cell has had its identification code assigned, its background must be determined. The general protocol for establishing a cell background is as follows:

10.2.1 All cells must be backfilled before their backgrounds are counted. Cells are backfilled as follows:

10.2.1.1 Attach the cell to the helium purge apparatus. Open the stopcock of the cell.

10.2.1.2 Open the vacuum valve. Allow the cell to "pump down" for a minimum of 6 hours.

10.2.1.3 Close the vacuum valve. Fill the cell to atmospheric pressure with helium, and then close the helium supply valve. DO NOT allow the pressure in the cell to exceed atmospheric pressure.

10.2.1.4 Repeat step 10.2.1.2 (without the 6 hour requirement) and 10.2.1.3 twice for a total of three times. Close the stopcock of the cell and remove the cell from the apparatus. Record the "back filled" date on the cell's tag.

10.2.2 The counting time for a cell background should equal or exceed the sample count times.

10.2.3 If a cell gives a background count greater than 1 cpm, it must be backfilled and counted again. When the cell gives less than 1 cpm, it may be used again, except between calibration determinations.

10.3 Once the background of a cell has been determined, its cell constant must be determined before the cell may be used to process samples. Cell constants are determined by following steps 11.5.7 through 11.5.14 of this procedure using special standard bubblers whose Ra-226 concentrations are traceable to NIST.

NOTE: 11.5.5 specifies transferring the solution to a bubbler. This is not necessary for standard bubblers, their solutions will remain in their bubblers at all times.

10.4 Count the sample twice, for fifty minutes each time. Immediately after the second count, the cell should be removed from the counter and steps 10.2.1.1 and 10.2.1.2 of the backfilling procedure above should be performed. This will minimize the buildup of radon daughters in the cell, which would increase the background of the cell. This calibration process is repeated three times for each cell, each time using a different standard bubbler (to minimize any biases due to dilution error in the preparation of the standard bubblers). The cell constant to be used with the cell is the average of the six results so obtained for the three determinations. It should be noted that properly measured cell constants are typically between 1.5 and 2.5 cpm per dpm of Ra-226. This is because the cell counts include not only the alpha particles produced by the decay of Rn-222, but also those produced by decay of Po-218 and Po-214. The half-lives of these two nuclides, and also Pb-214 and Bi-214, are sufficiently short so that all of them can be considered to be in secular equilibrium with the Rn-222 in the cell by the time the first count begins. The true efficiency of most cells is approximately 0.8 counts per disintegration, but it is customary to relate this to the activity of the Ra-226 which produced the Rn-222 because the cells are used to determine (in most cases) not Rn-222 but Ra-226.

10.5 Ra-228

10.5.1 In this procedure, it is not Ra-228 that is directly determined, but Ac-228, the first daughter of Ra-228. It is not practical to calibrate the beta proportional counters with Ac-228 because it has a 6.13 hour half-life. Instead, Sr-89 is used. The E_{max} for Sr-89 is 589 Kev, while the E_{max} of Ac-228 is 404 Kev.

11 PROCEDURE

NOTE: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

NOTE: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A nonconformance shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The nonconformance will be filed in the project file.

11.1 Sample Preparation

11.1.1 Soil and Sediments.

11.1.1.1 Samples are prepared by microwave digestion or acid digestion. If necessary, dissolve the sample residue in 2M HNO_3 if the samples are not received in solution.

11.1.1.2 Transfer the 2M HNO_3 solution to an appropriate size beaker, usually 1-L. Dilute to approximately 500 mL with reagent water.

11.1.1.3 Continue with the Radium Analysis, step 11.2.

11.1.2 Air Filters

11.1.2.1 Samples are prepared according to RICH-RC-5016 in an appropriate sized beaker. Add approximately 500 mL of reagent water to the sample digestate or salts.

11.1.2.2 Continue with the Radium Analysis, step 11.2.

11.1.3 Urine.

11.1.3.1 The sample is acidified with concentrated HNO_3.

11.1.3.2 Measure an appropriate volume of urine as stated in the client specific QAS. Quantitatively transfer the contents of the appropriate QC vial.

11.1.3.3 Continue with the Radium Analysis, step 11.2

11.1.4 Water.

11.1.4.1 Mix the sample and measure an appropriate volume of water as stated in the QAS. Quantitatively transfer the contents of the appropriate QC vial.

11.1.4.2 Continue with the Radium Analysis, step 11.2.

11.2 Radium Analysis.

11.2.1 For each aliquot of water or sample solution, add approximately 5 mL of 1M citric acid, and methyl orange indicator as needed. The solution should be red.

NOTE: Some samples, contain some chemical species that destroy methyl orange upon heating.

11.2.2 Add approximately 10 mL of 15 mg/mL lead carrier to the sample, and, if Ra-228 is required, approximately 1 mL of Strontium-Yttrium mixed carrier A. Stir the sample well with a long stir rod, heat for approximately 30 minutes.

11.2.3 Remove the samples from the hot plate; add 15M ammonium hydroxide until the pH is greater than 5.0, as verified by the methyl orange indicator changing from orange-red to yellow. Allow the samples to cool.

11.2.3.1 For samples in which the methyl orange indicator is destroyed, or the color change is vague, add ammonium hydroxide until the pH of the solution is greater than 5.0, as verified with pH paper.

11.2.4 Carefully add 18M H_2SO_4 dropwise to the sample until the pH is less than 3. The color should change back to red and a precipitate should form.

11.2.5 Add approximately 5 mL of 200 mg/mL ammonium sulfate solution. Return the sample to the hot plate. Stir frequently and keep near boiling for 30 minutes.

11.2.5.1 For routine sample analysis, proceed as follows:

11.2.5.1.1 Remove the sample from the hot plate and allow it to cool slightly. Tightly cover the beaker with plastic wrap. Allow the sample to cool and the precipitate to settle for at least 6 hours.

11.2.5.1.2 Carefully remove as much of the supernate as possible without losing any of the precipitate. Draw off the supernate through a pipet/pipet tip attached to a vacuum hose or decant to an appropriate waste container. After drawing off each supernate, rinse the end of the apparatus with reagent water.

NOTE: Urine samples are wet ashed with HNO_3 and H_2O_2 until the precipitate is white.

Transfer the precipitate to a clean labeled 50-mL conical centrifuge tube with concentrated HNO_3 for urine samples and with reagent water for water samples. Centrifuge and discard the supernate to the appropriate waste container. Proceed to step 11.2.6.

NOTE: If the sample contains large amounts of calcium, as indicated by large amounts of precipitate, perform the "Radium Clean Up" as found in section 16.4.

11.2.5.2 For priority sample analysis, proceed as follows:

11.2.5.2.1 Remove the sample from the hot plate and allow it to cool slightly. Quantitatively transfer the precipitate into a vacuum filter apparatus containing a 47-mm nitrocellulose membrane filter (BA85, 0.45μ pore size). Vacuum filter the precipitate. Discard the supernate to the appropriate waste container.

11.2.5.2.2 Carefully place the filter containing the precipitate in the bottom of a beaker, preferably 250-mL. Add approximately 10 mL of concentrated HNO_3 and heat gently until the filter completely dissolves. Transfer the sample with concentrated HNO_3 into a 50-mL conical bottom centrifuge tube. Centrifuge and discard supernate to the appropriate waste container. Proceed to step 11.2.6.

11.2.6 Add approximately 10 mL of concentrated HNO_3 to the centrifuge tube. Cap the tube and mix on a Vortex mixer. Centrifuge and discard the supernate to the appropriate waste container. Repeat the wash when, determined by experience, there continues to be an excessive amount of precipitate.

11.2.7 Add 25 mL of alkaline EDTA reagent. Cap the tube and mix well using a Vortex mixer. Allow the precipitate to dissolve for 5 to 10 minutes by placing the tube in a hot water bath; remove, and mix well again. Examine the tube for undissolved precipitate. If there is undissolved precipitate, add 1 mL of 10M sodium hydroxide, mix vigorously, and heat again until the precipitate is completely in solution. Add additional 10M sodium hydroxide as needed.

NOTE: Some samples may contain substances that are insoluble in alkaline EDTA reagent. If the pH of the solution is greater than 10, it can be assumed that all barium sulfate is in solution. If this is the case, the sample should be centrifuged and the supernate poured into a clean tube. After confirmation of acceptable Ba-133 tracer yield the precipitate may be discarded to the appropriate waste container. Typical yield is 70%. If the yield is less than 70%, contact supervision.

NOTE: In some cases, further attempts to dissolve white precipitate with later portions of EDTA solution will successfully dissolve the residual precipitate. Contact supervision for direction.

11.2.8 If Ra-228 is requested, proceed to step 11.3.

11.2.9 Allow the sample to cool to room temperature. Seal the centrifuge tube with plastic tape.

11.2.10 Submit the sample for a gamma count to determine the Ba-133 tracer yield. Calculate the Ba-133 tracer yield.

NOTE: The calculated Ba-133 tracer yield is used as a multiplier value. If the value of the multiplier is less than one (yield is greater than 100%), default to 1.0000 and initial and date the analytical worksheet (marked as the default value). If value is greater than 115%, recount the sample.

11.2.10.1 If yields are less than 70% or below the client required yield, and if insoluble material (large amounts of white precipitate) remained in the supernate from step 11.2.7, proceed to the "Radium Clean Up" steps found in section 16.4.

11.2.11 If only Ra-226 is required proceed to step 11.5.

11.3 Ra-228 Analysis

NOTE: Thorough mixing of the samples in the following steps is essential. Use of a Vortex mixer is recommended.

11.3.1 Add 1 mL of strontium-yttrium mixed carrier B to the sample. Add a few drops of 10M sodium hydroxide if any precipitate forms.

11.3.2 Add 1 mL of 200 mg/mL ammonium sulfate to the sample. Add 17.4M acetic acid to the sample until barium sulfate precipitates, then add 2 mL in excess. Cap and mix. Digest in a hot water bath until the precipitate settles. Centrifuge and discard supernate to the waste container.

11.3.3 Repeat step 11.2.7, using 20 mL of alkaline EDTA reagent. Add 1 mL of 10M sodium hydroxide if the precipitate does not dissolve. Add additional 10M sodium hydroxide as needed. Repeat steps 11.3.1 and 11.3.2, then go to step 11.3.4.

11.3.4 Add 10 mL of reagent water and 1 mL of 200 mg/mL ammonium sulfate to the sample. Cap and mix. Centrifuge and discard the supernate into the appropriate waste container. Record on the worksheet the date and time that the supernate was decanted; this is the first Ac-228 separation date and time.

11.3.5 Add 15 mL of alkaline EDTA reagent to the sample. Cap and mix. Heat for 5 to 10 minutes in a hot water bath if needed to assist in dissolving. If the precipitate has not dissolved, mix again. Examine the tube for undissolved precipitate. Add a few drops 10M sodium hydroxide if there is undissolved precipitate. Cap the tube, and then mix until the precipitate dissolves.

11.3.6 **If directed by supervision to perform the Ra-226 analysis first, proceed to step 11.5. Otherwise, allow the Ac-228 to ingrow at this time for at least 36 hours. While it is ingrowing seal the tube with plastic tape and submit the sample for a gamma count to determine the Ba-133 tracer yield.**

NOTE: If the value of the yield is greater than 100%, default to 1.0000 and initial and date the analytical worksheet (marked as the default value).

11.4 Ac-228 Separation

11.4.1 Transfer the contents of the tube to another tube containing yttrium carrier. Rinse the tube with a minimal volume of alkaline EDTA reagent. Add 0.1 mL of lead carrier (15 mg/mL).

NOTE: If precipitate appears gelatinous, contact supervision.

11.4.2 Add 0.3 mL of 2% $(NH_4)_2S$ to the sample. Add 10 drops of 10M NaOH until black lead sulfide precipitates. Cap, vortex, then sit for 10 minutes. Centrifuge and decant the supernate to the original 50-mL centrifuge tube.

CAUTION: Normal precipitate appears black and finely divided. If otherwise, contact supervision.

11.4.3 Add 0.1 mL of lead carrier (15 mg/mL), 0.1 mL of 2% $(NH_4)_2S$ and three drops of 10M NaOH. Cap and vortex, then sit for 10 minutes. Centrifuge and filter the supernate using the 25 mm syringe filter assembly described in the equipment section. The filtrate may be collected in a clean tube.

NOTE: Lead sulfide may precipitate upon the addition of the lead carrier. This is normal, but the $(NH_4)_2S$ and 3 drops of 10M NaOH should be added to insure complete precipitation.

CAUTION: It is very important that no lead sulfide particles remain in the filtrate. If any lead sulfide particles are visible in the filtrate, the sample must be re-filtered.

11.4.4 **CAUTION:** Ac-228 has a half-life of 6.13 hours. Once the yttrium hydroxide has been precipitated, it is important to finish the procedure and submit the samples for counting as quickly as possible.

Add 5 mL of 18M NaOH to the sample in the centrifuge tube. Cap and vortex well. Digest in a hot water bath until yttrium hydroxide coagulates (approximately 5-7 minutes). Centrifuge and decant the supernate into the original 50-mL centrifuge tube. You may thoroughly rinse the PbS waste from the previous tube with reagent water and reuse that tube. Record the time of the yttrium hydroxide precipitation on the worksheet. This is the end of the Ac-228 ingrowth time and the start of the Ac-228 decay time. Save the supernate.

11.4.5 Dissolve the precipitate in 2 mL of 6M HNO_3. Cap and vortex well. Heat in a hot water bath for approximately 30 seconds. If the preicipitate has not dissolved, mix again. Make sure the precipitate is completely dissolved. Add 5 mL of reagent water and 3 mL of 10M NaOH. Cap and vortex. Digest in a hot water bath until yttrium hydroxide coagulates (approximately 5-7 minutes). Centrifuge and discard supernate to the appropriate waste container. Take care not to decant the precipitate.

11.4.6 Dissolve the precipitate with 3 mL of 1M HNO_3. Cap and vortex. Heat in a hot water bath for 30 seconds. Make sure the precipitate is completely dissolved. Dilute to 5 mL with reagent water and add 2 mL of 4.4% ammonium oxalate. Mix the sample well on a vortex mixer for approximately 10 seconds. Centrifuge and discard supernate to the appropriate waste container.

NOTE: More 1M HNO_3 may be required to dissolve the precipitate.

11.4.7 Add 10 mL of reagent water, 0.3 mL of 1M HNO_3 and 0.3 mL of 4.4% ammonium oxalate. Cap and vortex. Centrifuge and discard the supernate to the appropriate waste container.

11.4.8 Repeat steps 11.4.2-11.4.7 once.

11.4.9 **NOTE:** The size of the planchet is determined by which beta counters will be used to count the samples.

To determine the yttrium yield, quantitatively transfer the precipitate to a pre-weighed 2.5 cm (1") or 3.8 cm (1.5") stainless steel planchet with a minimum of reagent water. Dry on a hot plate at a temperature of approximately 250°F for one hour. Weigh the planchet.

11.4.10 Fill in the appropriate information on the worksheet. Submit the planchet and worksheet to the counting room for low beta counting as soon as possible. The sample is counted at least twice to verify the decay of Ac-228.

11.5 Ra-226 Analysis

11.5.1 If Ra-228 analysis was performed first continue with step 11.5.2. Otherwise, proceed to step 11.5.5.

11.5.2 Add 4 mL of concentrated HNO_3 to the Ra-226 supernate from step 11.4.4. Mix well and then add 2 mL of the 200 mg/mL ammonium sulfate solution. Add 17.4M acetic acid to the sample until barium sulfate precipitates, then add 2 mL in excess. Digest in a hot water bath until the precipitate settles. Centrifuge and discard the supernate to an appropriate waste container.

11.5.3 Add 10 mL of reagent water with 1 mL ammonium sulfate to the precipitate. Mix, centrifuge and discard the supernate to an appropriate waste container.

11.5.4 Dissolve the precipitate in 15 mL of alkaline EDTA reagent. Cap, mix, and heat the sample in a hot water bath. Add a few drops of 10M NaOH if the precipitate does not completely dissolve.

11.5.5 Allow the tubes to cool to room temperature. Seal the tube with plastic tape and submit the sample for a gamma count to determine the Ba-133 tracer yield.

NOTE: The calculated Ba-133 tracer yield is used as a multiplier value. If the value of the multiplier is less than one (yield is greater than 100%), default to 1.0000 and initial and date the analytical worksheet (marked as the default value).

11.5.6 Transfer the solution to a radon bubbler. Open both stopcocks and purge the solution by slowly passing helium gas through the bubbler for at least 15 minutes. Close the two stopcocks, and record the date and time on the worksheet. Store the bubbler for at least 3 days. The storage time may vary according to the RDL. Consult supervision or the QAS for possible shorter length of storage.

11.5.7 At the end of the storage period, fill the upper half of an adsorption tube with magnesium perchlorate and the lower half with Ascarite.

NOTE: For minimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing is recommended whenever possible, and the drying tube volume with the Ascarite and magnesium perchlorate must be kept to a minimum. A typical system consists of a drying tube 10 cm x 1.0 cm (I.D.), with each of the drying agents occupying 4 cm and being contained by small glass wool plugs. The column can be reused several times before the chemicals need to be replaced.

11.5.8 **CAUTION:** Do not expose the scintillation cell to fluorescent lighting without blackout cloth covering the window end of the cell.

Attach the tube to the radon bubbler and then attach an evacuated scintillation cell to the tube. Open the stopcock on the cell and check the assembly for leaks. Gradually open the outlet stopcock on the bubbler. When the stopcock is fully open and no further significant bubbling takes place, close the stopcock.

11.5.9 Adjust the helium gas pressure so that the gas flows at slightly above atmospheric pressure (approximately 0.02).

11.5.10 Connect the hose to the bubbler inlet and gradually open the inlet stopcock using the bubbling as a guide. When the stopcock can be fully opened without a significant amount of bubbling, the bubbler is essentially at atmospheric pressure again.

11.5.11 Open the outlet stopcock very slightly and allow bubbling to proceed at a rate, about 0.02, such that 15 to 20 minutes are required to complete the purge.

11.5.12 Toward the end of the helium purge, when the vacuum is no longer effective, gradually increase the helium gas pressure. When the system is at atmospheric pressure, shut off the helium gas, disconnect the tubing from the bubbler inlet; close the inlet and outlet stopcocks of the cell and bubbler, and record the time on the worksheet. This is the beginning of Rn-222 decay and ingrowth of Rn-222 daughters.

11.5.13 Store the scintillation cell for at least 4 hours to ensure equilibrium between radon and radon daughters. Fill in the appropriate information on the worksheet. Count the alpha scintillations from the cell in a radon counter with a light-tight enclosure that protects the photomultiplier tube. Record the counting time on the worksheet for correcting for the decay of Rn-222. See the QAS for appropriate counting protocol.

NOTE: After each analysis, vacuum the cell and allow the cell to pump down for a minimum of 6 hours. Flush the cell three times by evacuation and filling with helium, and store filled with helium at atmospheric pressure. This procedure removes radon from the cell and prevents the build-up of radon daughter products. Before each analysis, the scintillation cell is evacuated, filled with helium and counted to ascertain the cell background.

11.5.14 After the data have been reviewed, return the sample back to a centrifuge tube and store until directed otherwise. If proceeding to a Ra-228 analysis, go to step 11.3.6.

12 DATA ANALYSIS AND CALCULATIONS

12.1 For computer calculation of the Ra-226 concentration, consult the RadCalc Users Guide. If the units selected are dpm per sample, the result given divided by the expected value of the standard bubbler is the cell constant.

12.2 For Ra-226 Lucas cell efficiencies, consult the RadCalc Users Guide. Use the 0RA detector ID and enter 1 as the efficiency. The calculated activity divided by the expected activity is the true efficiency for that Lucas cell.

12.3 For computer calculation of the Ra-228 concentration, consult the RadCalc Users Guide.

12.4 Calculation of Ba-133 tracer yield:

$$\text{Ba-133 yields for Ra-226} = \frac{1}{\left(\frac{observed}{expected}\right)} \qquad \text{Ba-133 yields for Ra-228} = \frac{expected}{observed}$$

13 METHOD PERFORMANCE

13.1 The supervisor has the responsibility to ensure that this procedure is performed by analysts who have been properly trained in its use.

13.2 Method Demonstration of Capability documentation is maintained in the quality files.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1 Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container. Transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap

15 REFERENCES

15.1 Beals, D.M., 1989, "Should the Ra-228 or the Ra-226 Analysis be Performed First?", Internal Technical Memorandum 1989-Ra-02, United States Testing Company, Richland Division.

15.2 Beals, D.M., 1989, "Validation Studies for the Addition of Soil and Sediment Matrices to UST-RD Procedure 20-Ra-01", Internal Technical Report 1989-Ra-03, United States Testing Company, Richland Division.

15.3 Noyce, J.R., February 1981, "Evaluation of Methods for the Assay of Ra-228 in Water". NBS Technical Note 1137, Washington, D.C., U.S. Government Printing Office.

15.4 U.S. Environmental Protection Agency, August 1980, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water", Methods 903.1 and 904.0, EPA-600/40-80-032, National Technical Information Services, Springfield, VA.

15.5 American Society for Testing and Materials, "Standard test method for Ra-226 in Water", Annual Book of ASTM Standards, ASTM D3454-05, Philadelphia, PA .

15.6 RadCalc DB, Users Guide, STL Richland.

15.7 STL Quality Management Plan, latest revision.

15.8 STL Richland Laboratory Quality Manual, latest revision.

15.9 STL Richland Quality Assurance Summary (QAS), latest revision.

15.10 Associated SOPs

15.10.1 RICHQA5002 – Reagent and Non-Radioactive Standard Labeling.

15.10.2 RICHRC5016 - Preparation of Environmental Matrices.

15.10.3 RICHRC0002 – Review of Environmental and Bioassay Data.

16 MISCELLANEOUS

16.1 Method Differences

16.1.1 The principal difference between the EPA procedures and this procedure is the use of a Ba-133 tracer for yield determination for both Ra-226 and Ra-228. The EPA procedure uses a gravimetric barium yield determination for the Ra-228 analysis, and cannot determine the yield as accurately, or at the correct step, in the analysis. The EPA Ra-226 procedure contains no yield determination, i.e. assumes 100% yield, but in performing these analyses sequentially it is very important to determine a tracer yield prior to the Ra-226 analysis. Even when only Ra-226 is to be analyzed, the STL Richland procedure includes a yield determination in case the recovery is not 100%.

16.2 Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

16.3 Records Management/Documentation

16.3.1 All records generated by this analysis will be filed and kept in accordance with STL Richland SOPs for records management and maintenance.

16.4 Radium Clean Up

16.4.1 Rinse precipitate (insoluble material from 11.2.10.1) into a beaker (typically 600-mL).

16.4.2 Add approximately 100 mL of saturated sodium carbonate to the beaker. Boil the sample for at least 30 minutes using a watch glass or equivalent to prevent splattering. This step metathetizes the sulfate to carbonate.

16.4.3 Transfer the mixture to a 90 mL centrifuge tube and centrifuge. Pour the supernate into a container and save until Ba-133 yield is confirmed or until directed by supervision.

16.4.4 Dissolve the remaining precipitate with a minimum of concentrated nitric acid. Fill the tube with a 1:1 (v:v) mixture of fuming nitric acid and concentrated nitric acid. Chill the sample for about 30 minutes in an ice bath to ensure complete precipitation.

16.4.5 Centrifuge the mixture and discard the supernate to the appropriate waste container.

16.4.6 Add 25 mL of concentrated nitric acid to the precipitate. Mix and centrifuge. Discard the supernate to the appropriate waste.

16.4.7 Dissolve the precipitate with reagent water and bring up to a total of 500 mL.

16.4.8 Restart the analysis at step 11.2.1, except do not add a new barium carrier and tracer QC vial. Perform the analysis as normal until Step 11.2.7. At this step use the original 25 mL alkaline EDTA solution containing the previously counted portion of the sample. Doing this recombines the sample that was counted with the portion originally trapped in the precipitate. Upon completion of 11.2.7 continue to 11.2.11.

16.5 Radium Re-Milk

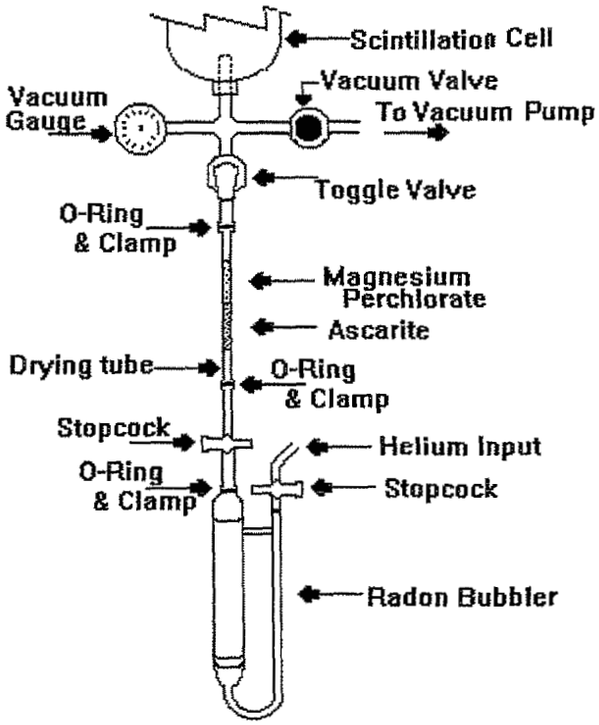
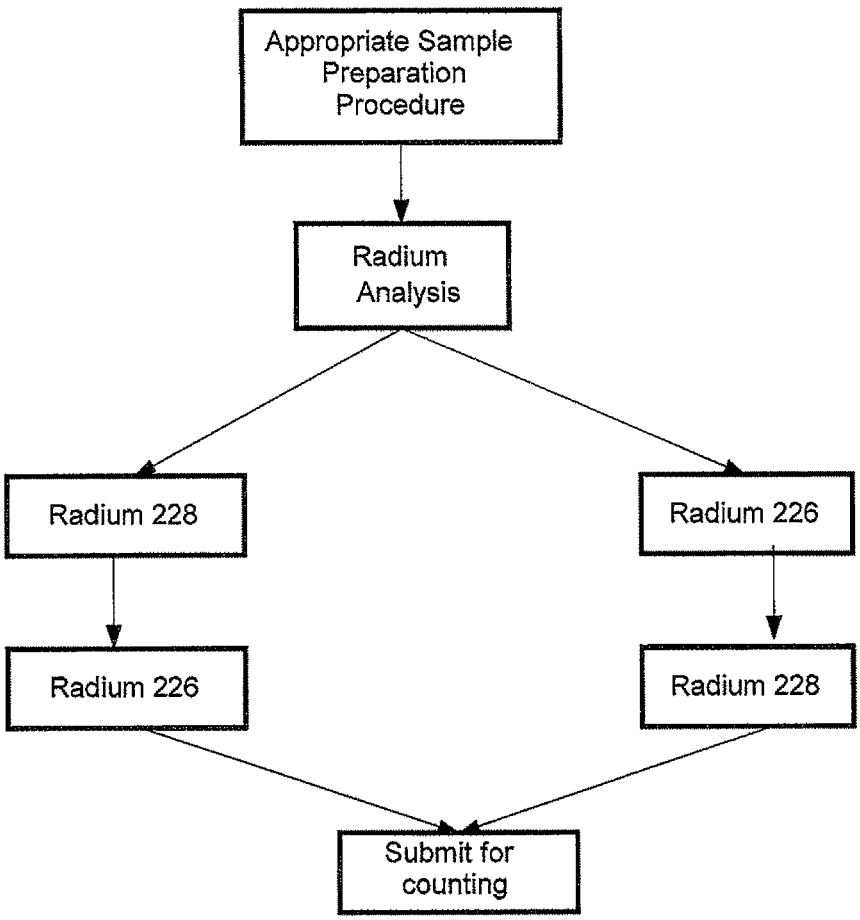
16.5.1 Add approximately 4 mL of concentrated HNO_3 to the reserved supernate from the yttrium hydroxide precipitation from the initial Ac-228 "milking" (step 11.4.4) and mix well.

16.5.2 Add approximately 2 mL of 200 mg/mL ammonium sulfate. Add concentrated glacial acetic acid to the sample until barium sulfate precipitates, then add 2 mL in excess. Cap and mix well. Digest in a hot water bath until the precipitate settles. Centrifuge for approximately 5 minutes and decant the supernate to an appropriate waste container.

16.5.3 Add approximately 10 mL of reagent water and about 1 mL of 200 mg/mL of ammonium sulfate to the sample. Cap and mix well. Centrifuge and decant the supernate to an appropriate waste container. Record the date and time the supernate was decanted on the analytical worksheet. This is the first Ac-228 separation date and time.

16.5.4 Go to step 11.3.5 and continue as normal with the subsequent steps.

16.6 Figure 1. De-emanation Apparatus with Scintillation Cell



16.7 Procedural Flow Chart