

Interim Monitoring Plan

to support:

U.S. Army Corps of Engineers
NWP 14 Permit SPK-2011-00755
Issued: December 6, 2013

and

Utah Division of Water Quality
Utah 401 Water Quality Certification No. SPK 2011-00755
Issued: December 16, 2013

Temporary Closure of the East Culvert, Great Salt Lake Causeway

Submitted by
Union Pacific Railroad
1400 Douglas Street
Omaha, NE 68179-0910

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Acronyms and Abbreviations

°C	degrees Celsius
µg/L	micrograms per liter
µm	micrometers
µmhos	micromhos
µS/cm	microsiemens per centimeter
CaCO₃	calcium carbonate
Corps	U.S. Army Corps of Engineers
CPR	Cardiopulmonary resuscitation
EPA	U.S. Environmental Protection Agency
g/cm³	grams per cubic centimeter
GPS	global positioning system
IMR	Interim Monitoring Report
km	kilometers
L	liters
m	meters
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mL	milliliters
NA	not applicable
ng/g	nanograms per gram
ng/L	nanograms per liter
NGVD	National Geodetic Vertical Datum
NWP	Nationwide Permit
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Program Plan
SM	Standard Methods for the Examination of Water and Wastewater
SOP	standard operating procedures
su	standard units
TBD	to be determined
UDWQ	Utah Division of Water Quality
UPDES	Utah Pollutant Discharge Elimination System
UPRR	Union Pacific Railroad
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey

1.0 Introduction and Background Information

This Interim Monitoring Plan (IMP) is submitted to fulfill a portion of the requirements of the U.S. Army Corps of Engineers' (Corps) Nationwide Permit 14 (USACE NWP 14) verification issued December 6, 2013 (SPK-2011-0075) that authorized the emergency filling and temporary closure of the east culvert. The closure of the culvert was necessary to avoid safety risks to railroad traffic on the causeway associated with the discovery that the culvert was at imminent risk of failure. This IMP is intended to fulfill the monitoring and reporting elements of Special Conditions 2a and 2b of the USACE NWP 14 authorization; the contingency mitigation plan element of the Corps' December 6 authorization will be submitted at a later date.

This IMP is also submitted to fulfill Condition 3 of the Utah 401 Water Quality Certification (No. SPK 2011-00755) issued to the Union Pacific Railroad (UPRR) by the Utah Division of Water Quality (UDWQ) on December 16, 2013. The Utah 401 Water Quality Certification was issued for the UPRR project to authorize temporary closure of the east culvert of the Great Salt Lake causeway. The Utah 401 Water Quality Certification and USACE NWP 14 are included in Appendix A.

Condition 3 of the Utah 401 Water Quality Certification requires UPRR to develop and submit for approval an IMP including a Quality Assurance Program Plan (QAPP). This monitoring plan follows the UDWQ checklist of essential elements for sampling and analysis plans. This QAPP, which is attached as Appendix C, follows the U.S. Environmental Protection Agency's (EPA) requirements for Quality Assurance Program Plans (EPA 2001).

The Utah 401 Water Quality Certification is a requirement of the USACE NWP 14.

1.1 Project and Site History

The rock-filled causeway in the Great Salt Lake was constructed in 1959 to replace a failing open trestle bridge. Two 15-foot-wide concrete culverts (an east culvert at milepost 750.53 and a west culvert at milepost 744.94) were installed in the causeway to allow small boats to navigate through the structure. Over the years, the causeway structure, including the culverts, has been settling into the lake bottom, causing the culverts to become submerged and filled with embankment material. At the request of the Corps in 2003, UPRR agreed to clean the culverts in an effort to facilitate water and salt transfer through the structures and reduce the future accumulation of sediment and debris. Accumulated debris was removed and protective berms were installed in 2004. The culverts were inspected by divers after the cleaning process to verify that the debris and sediment had been removed.

Underwater inspections by divers continued after 2004, revealing significant cracking in both of the culverts. Over the next 6 years, attempts to conduct repairs to the culverts were made; however, the cracks continued to appear and enlarge, jeopardizing the structural integrity of the causeway and increasing the potential to disrupt rail traffic across the causeway.

In 2011, UPRR submitted a preconstruction notification to the Corps requesting authorization to permanently close the east and west culverts and replace the lost aquatic function with the construction of a pile-supported bridge in the causeway at milepost 739.78. Figure 1 below shows the location of the Great Salt Lake causeway, the east and west culverts, and the proposed bridge location.

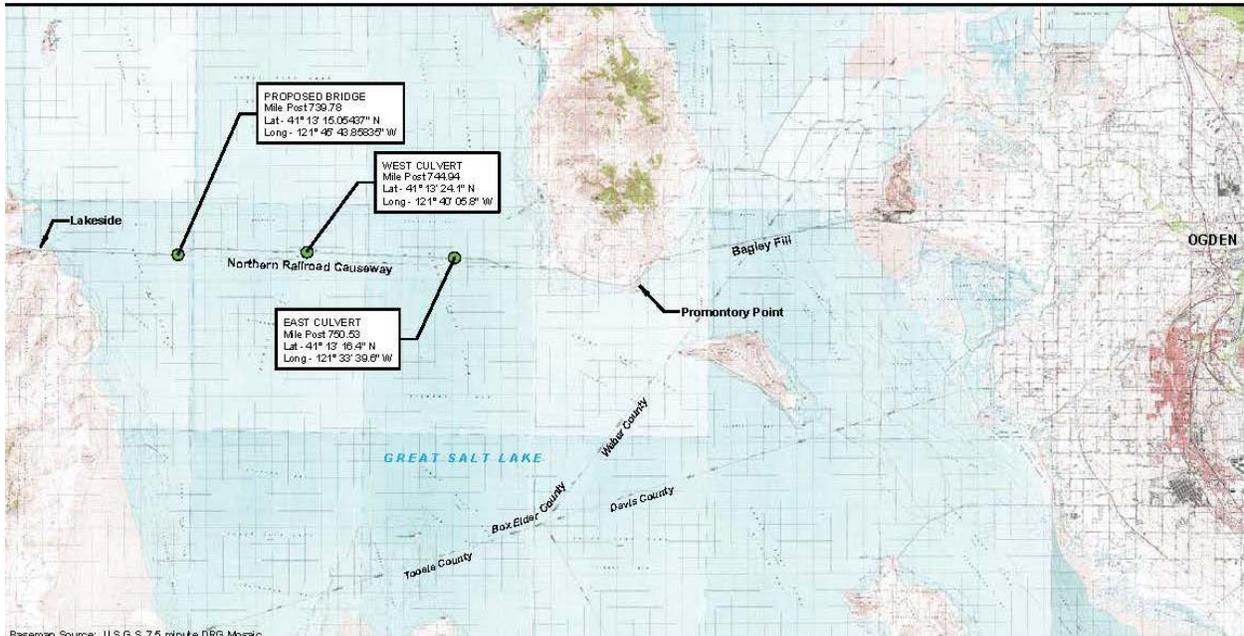


Figure 1. East and West Culverts and Proposed Bridge Vicinity Map

Source: UPRR 2011

The west culvert was closed under emergency authorization from the Corps (SPK-2011-00755, dated August 29, 2012). The east culvert was closed under temporary emergency closure authorization from the Corps (SPK-2011-00755, dated December 6, 2013) and the Utah 401 Water Quality Certification. At the time of closure, the invert of the west and east culverts were about elevation 4,173 feet (National Geodetic Vertical Datum [NGVD]), the top of the causeway was about elevation 4,216 feet (NGVD), and the Great Salt Lake was about 22 feet deep.

The culverts were originally included in the causeway to facilitate small boat traffic; however, as they continued to settle over the years, this use was eliminated because the culverts were sometimes underwater, depending on the lake water level. Since the removal of debris in 2004, the culverts facilitated the exchange of water and salt through the causeway between the lake's North Arm (Gunnison Bay) and South Arm (Gilbert Bay).

With the west culvert permanently closed and the east culvert temporarily closed, the exchange of water and salt through the causeway is reduced. The temporary closure authorizations require submission of a monitoring plan that covers the interim period between closure of the East culvert and implementation of the final mitigation and monitoring plan that will be prepared, reviewed and approved pursuant to a Standard Individual Permit and 401 certification processes. As provided in the Corps and UDWQ temporary closure authorizations, the interim monitoring plan will be superseded by the final mitigation and monitoring plan once approved.

1.2 Regulatory Framework

UPRR requested closure authorization of the east and west culverts from the Corps in 2011. UPRR received emergency authorization in August 2012 to close the west culvert and construct a new bridge to mitigate the loss of both the east and west culverts. That authorization included a requirement to develop a mitigation and a monitoring plan in support of UPRR's proposal to construct a bridge to compensate for loss of water flow and salt transfer that could result from closing the east and west culverts.

In 2013, UPRR and the Corps entered into an informal consultation process on the August 2012 permit pursuant to 33 CFR §330.5(d)(2). On September 25, 2013, Union Pacific submitted a plan to reevaluate the potential impacts of closing the causeway culverts and construct a compensatory mitigation bridge using the 1998 USGS Water and Salt Balance Model. Based on the results of that reevaluation, Union Pacific would revise its bridge proposal and compensatory mitigation and monitoring plans. Union Pacific's plan included coordination of this effort with the UDWQ and other federal and state agencies

During this reevaluation process, UPRR continued inspections of the East Culvert. On October 21, 2013, UPRR notified the Corps that its most recent inspection had identified significant deterioration of the east culvert and that there was an imminent risk of culvert failure. On that basis, UPRR requested emergency authorization to close the east culvert. In response, on December 6, 2013, the Corps authorized the temporary closure of the east culvert (NWP 14, SPK-2011-00755) and a temporary reduction in circulation of flows between the North and South Arms of the Great Salt Lake. The Corps stated that a standard individual permit would be necessary to make the East closure permanent. The December 6, 2013, authorization was subject to a Clean Water Act Section 401 Water Quality Certification by the Utah Division of Water Quality. On December 16, 2013, UPRR received a Utah 401 Water Quality Certification (SPK 2011-00755) for temporary closure of the east culvert.

This IMP is required under the Utah 401 Water Quality Certification to meet Condition 3 and under the USACE NWP 14 authorization to meet the interim monitoring and report requirements of Special Conditions 2a and 2b. By March 6, 2014, UPRR will submit to the Corps and UDWQ a supplemental plan to address additional related requirements of the USACE NWP 14, that is, identification of contingency mitigation measures that could be implemented should the Corps determine, based on interim monitoring results, that adverse effects have resulted from East culvert closure. Therefore, this Plan is referenced as the Interim Monitoring Plan that addresses the sampling, monitoring and reporting requirements of the Corps and UDWQ authorizations, and the supplement will be referred to as the Interim Mitigation Plan. As provided in the UDWQ and Corps authorizations, the IMP will be superseded at the point in the future that a final mitigation and monitoring plan that is approved by the Corps and UDWQ is implemented. That Final Mitigation and Monitoring Plan will be prepared, reviewed and approved pursuant to the standard Corps Individual Permit and UDWQ 401 Certification processes that are now underway.

To address the permanent closure of the east culvert and bridge construction to compensate for closing the east and west culverts, UPRR submitted an application for an individual permit to the Corps and an application for Utah 401 Water Quality Certification to UDWQ on January 7, 2014.

1.3 Summary of Previous Investigations

This section summarizes the previous and ongoing water quality monitoring and sampling efforts performed by federal and state agencies with respect to Great Salt Lake water quality and the culvert closure and bridge construction project. This is not a complete list of all investigations associated with the Great Salt Lake, only those that apply to the project area and the constituents required for sampling by the Utah 401 Water Quality Certification and USACE NWP 14.

1.3.1 U.S. Geological Survey

USGS monitors the surface elevation of the Great Salt Lake in real time at two locations on the lake. The South Arm's elevation is monitored at the Saltair boat harbor on the south end of the lake at USGS site 10010000. The North Arm's elevation is monitored at the Saline site at the southeast corner of the north arm of the lake at USGS site 10010100. These data are available at ut.water.usgs.gov/greatsaltlake/elevations.

USGS has monitored the flows through the two culverts in the UPRR causeway for many years and at the breach (the western end of the causeway near Lakeside) since its construction. The flow through the railroad causeway breach near Lakeside is monitored in real time at USGS site 10010020. In addition, flow through the Antelope Island causeway is monitored in real time at USGS site 410401112134801. Flow data for these two sites are available waterdata.usgs.gov/usa/nwis/uv?10010020 and waterdata.usgs.gov/usa/nwis/uv?410401112134801.

USGS is currently monitoring lake brine flow along the topographic “spillway” between the two parts of the South Arm at three locations. These data are not yet available.

1.3.2 Utah Geological Survey

The Utah Geological Survey has monitored the basic chemistry of Great Salt Lake continually since 1966. Initially, sampling was done frequently at many sites, but now sampling is done about twice per year: once at high water and again at low water. Samples are analyzed for sodium, potassium, magnesium, calcium, sulfate, chloride, total dissolved solids, and specific gravity. During earlier years, the samples were also analyzed for bromine, lithium, and boron, with temperature also taken for each sample.

The sites with the longest period of record (1966 to the present) are three sites in the South Arm (FB-2, AS-2, and AC-3) and two sites in the North Arm (LVG4 and RD2) at the surface, and each successive 5-foot depth to the bottom. These data are summarized in the *Great Salt Lake Brine Chemistry Database, 1996–2011* (UGS 2012).

1.3.3 Utah Division of Water Quality

UDWQ is actively involved in monitoring the water quality in Great Salt Lake in accordance with the 2012 document *A Great Salt Lake Water Quality Strategy* (UDWQ 2012). Information from UDWQ's monitoring efforts will be used to (1) monitor the lake's waters to protect them for their designated uses, (2) prioritize pollutants for the development of

numeric water quality criteria, and (3) determine ambient concentrations for the development of Utah Pollutant Discharge and Elimination System (UPDES) permits.

There are 11 UDWQ monitoring locations throughout the lake, eight in Gilbert Bay, one in Bear River bay, and two in Farmington Bay. Water quality sampling and analysis began in 2011, with two events conducted in 2011 and two events conducted in 2012. Elements of current concern include arsenic, cadmium, copper, lead, mercury (and methyl mercury), selenium, arsenic, and cadmium. UDWQ also conducted sampling in the South Arm associated with creating the selenium egg tissue standard for Gilbert Bay. Sampling associated with the site-specific selenium standard included water quality, benthic macroinvertebrates, brine shrimp, and waterfowl egg tissue monitoring.

Monitoring in 2011 and 2012 also included unfiltered nutrients (ammonia, total phosphorus and total nitrogen), filtered nutrients (ammonia, nitrate + nitrite, nitrite, total phosphorus and total nitrogen), and chlorophyll a.

UDWQ currently samples for a wide array of parameters twice per year: once during the bird nesting season (June) and once during the fall brine shrimp cyst harvest (October). Samples are collected at 11 locations: eight locations in Gilbert Bay, two in Farmington Bay, and one in Bear River Bay (UDWQ 2014). These locations were selected to remain consistent with locations used in routine sample collection and research conducted by the Utah Division of Wildlife Resources' Great Salt Lake Ecosystem Program and USGS's Utah Water Science Center.

The water quality parameters that are monitored include metals (arsenic, cadmium, copper, lead, methyl mercury, selenium, total mercury, thallium, and zinc), unfiltered nutrients (ammonia, total phosphorus, and total nitrogen), filtered nutrients (ammonia, nitrate + nitrite, nitrite, total phosphorus, and total nitrogen), chlorophyll a, temperature, specific conductivity, dissolved oxygen, pH, and orthophosphate. Brine shrimp tissue would be analyzed for metals (arsenic, cadmium, copper, lead, thallium, zinc, total mercury, methyl mercury, and selenium). Total mercury and selenium would also be sampled from shorebird egg tissue and macroinvertebrates.

1.3.4 Utah Division of Wildlife Resources' Great Salt Lake Ecosystem Program

For several years, project staff has monitored the abundance of brine shrimp cysts in the lake. This work is done to support the Division's regulation of the brine shrimp (cyst) harvesting program. When the cyst count per liter of brine drops below a threshold, cyst harvesting is not permitted. This is an ongoing state program. Information about the program is available at wildlife.utah.gov/gsl/harvest/information.php.

The Division also continues to evaluate the effects of nutrients, as well as other factors, on the brine shrimp industry.

1.4 Project Location Map

The project site is located in the portion of the Great Salt Lake in Box Elder County, Utah. The east culvert is about 7 miles west of Promontory Point boat harbor in the UPRR's causeway in the Great Salt Lake. The proposed bridge location is about 5 miles east of the existing 300-foot-long bridge at Lakeside, Utah.

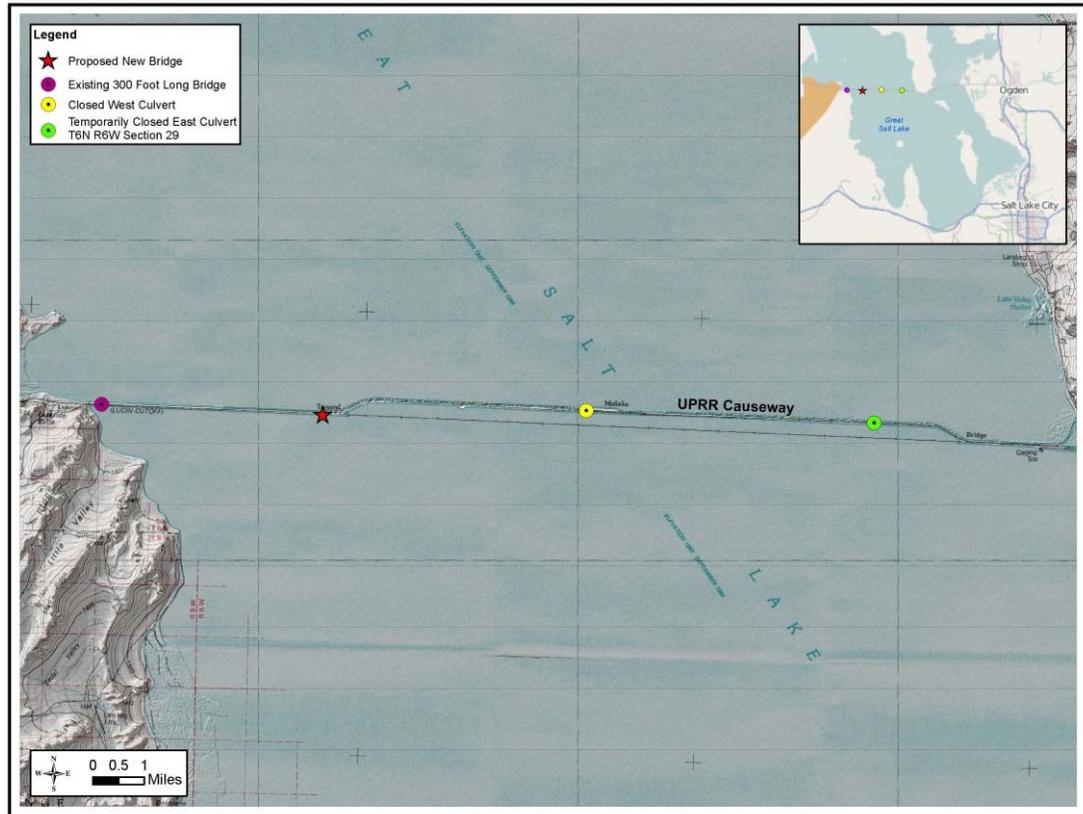


Figure 2. Culvert and Proposed Bridge Location Map

2.0 Objectives and Design

2.1 Objectives

UPRR will conduct interim monitoring to meet the requirements of the USACE NWP 14 authorization and the Utah 401 Water Quality Certification for temporarily closing the east culvert. The interim monitoring consists of three elements: (1) collecting *in-situ* water profiles, (2) collecting grab sample water quality samples for analyses at an off-site laboratory, and (3) collecting brine shrimp samples for analyses at an off-site laboratory and counts. Table 1 lists the goals and objectives of each element of the required interim monitoring. As discussed above, the interim monitoring plan will be superseded by the final Mitigation and Monitoring Plan that will be prepared, reviewed and approved pursuant to standard individual Corps permit and UDWQ certification processes; these processes will be undertaken to authorize permanent closure of the East culvert, and the final compensatory mitigation plan (the current proposal is to construct a 180-ft bridge to compensate for the permanent loss of water and salt transfer through the East and West culverts.

Compiling surface water elevation and collecting salinity gradient data will meet the USACE NWP 14 interim monitoring requirements.

Table 1. Interim Monitoring Goals and Objectives

Element	Goals	Objectives
Surface water elevations	Capture temporary hydrologic impacts resulting from closure of the East Culvert.	Obtain surface water elevations for North Arm and South Arm of the GSL from USGS reporting stations located at Saline and Saltair.
Surface water profiles and conventional water quality	Collect Great Salt Lake total depth, depth to deep brine layer ^a (if present), ambient secchi depth, pH, temperature, and salinity data set.	Collect salinity data consistent with UDWQ and USGS methods and reporting limits.
Surface and bottom water metals, sulfate sampling and dissolved oxygen	Collect Great Salt Lake ambient metals, sulfate, hardness, and dissolved oxygen data set in surface water.	Collect metals, sulfate, and dissolved oxygen water samples at specified locations consistent with UDWQ reporting limits.
Brine shrimp counts and tissue sampling	Collect Great Salt Lake ambient brine shrimp population data and tissue metals and percent moisture data set at co-located South Arm water quality stations.	Collect brine shrimp for taxonomic identification, counts, and tissue analysis at specified locations in accordance with UDWQ-approved reporting limits.

^a *Deep brine layer depth* refers to the vertical zone in a water column in which salinity changes rapidly with depth. For the purpose of this interim monitoring plan, deep brine layer depth, *halocline*, and *chemocline* are synonymous.

2.2 Study Design

The design of the IMP is based on the USACE NWP 14 authorization and Utah 401 Water Quality Certification requirements associated with the temporary closure of the east culvert in the UPRR causeway.

The IMP is focused on characterization of the open waters of Gilbert Bay and Gunnison Bay near the project site. The interim monitoring will be done in compliance with Special Conditions 2a and 2b of the USACE NWP 14 authorization and Condition 3 of the Utah 401 Water Quality Certification to meet the objectives identified therein.

This interim monitoring plan is designed to address the interim monitoring requirements of both the USACE NWP 14 authorization and the Utah 401 Water Quality Certification.

2.3 Representative Sampling Conditions

Field sampling on the Great Salt Lake will occur during conditions that allow safe and reasonably expedient sample collection. Field sampling will be deferred if weather causes hazardous sampling conditions (wind, extreme heat or cold, and/or fog). Field sampling will be deferred if lake levels preclude access from available boat ramps.

Representative sampling conditions will meet the following criteria:

- The open waters of Gilbert and Gunnison Bays are relatively calm, and sampling occurs at least 24 hours after a storm to ensure that the open waters are stable.
- No construction activities are occurring either on the causeway or associated with the Great Salt Lake Minerals Corporation's facilities in Gunnison Bay.
- Sampling and analysis of the open waters are conducted in accordance with this plan.

2.4 Interim Monitoring Parameters

Error! Reference source not found. lists the water quality parameters and constituents and brine shrimp identification and tissue parameters to be measured as required by the Summary Table for Interim Monitoring in the Utah 401 Water Quality Certification and the USACE NWP 14.

Table 2. Water Quality Parameters and Constituents To Be Measured and Methods, with Detection Limits, Reporting Limits, and Laboratory Holding Times for Each

Parameter		Method ^a	Method Detection Limit	Method Reporting Limit	Hold Time
<i>Field Measurements – Surface Water</i>					
Lake elevation ^b	—	USGS automated gage	—	—	—
Total water depth	—	Troll 9500 field measurement	—	0.1 m	Field
Depth to deep brine layer	—	Troll 9500 field measurement	—	0.1 m	Field
Secchi depth	—	—	—	0.1 m	Field
pH	—	SM 4500-H	0.1 su	0.1 su	Field profile
Specific conductivity	—	SM 2510A	0.001 µmhos	0.001 µmhos	Field profile
Temperature	—	SM 2520	0.1 °C	0.1 °C	Field profile
<i>Laboratory Analyses – Surface Water^{d,e}</i>					
Density	—	SM 2710F	—	0.001 g/mL	7 days
Dissolved oxygen	DO	SM 4500-OC	—	0.1 mg/L	8 hours
Hardness	—	SM 2340 C	—	1 mg/L as CaCO ₃	14 days
Sulfate (total)	SO ₄ ²⁻	EPA 300.0	—	1 mg/L	28 days
Total dissolved solids ^f	Salinity ^f	SM 2540C	—	5 mg/L	7 days
Arsenic (total)	As	EPA 1640	0.05 µg/L	0.15 µg/L	180 days
Copper (total)	Cu	EPA 1640	0.04 µg/L	0.12 µg/L	180 days
Lead (total)	Pb	EPA 1640	0.003 µg/L	0.013 µg/L	180 days
Mercury (total)	Hg	EPA 1631E	0.15 ng/L	0.40 ng/L	28 days
Selenium (total)	Se	EPA 1640	0.070 µg/L	0.210 µg/L	180 days
Zinc (total)	Zn	EPA 1640	0.26 µg/L	0.75 µg/L	180 days
<i>Laboratory Analyses – Gilbert Bay Brine Shrimp^e</i>					
Percent moisture	—	SM 2540G	—	1.0%	—
Arsenic (total)	As	EPA 1638	0.014 mg/kg	0.040 mg/kg	180 days
Copper (total)	Cu	EPA 1638	0.03 mg/kg	0.16 mg/kg	180 days
Lead (total)	Pb	EPA 1638	0.004 mg/kg	0.040 mg/kg	180 days
Mercury (total)	Hg	EPA 1631	0.12 ng/g	0.4 ng/g	28 days
Selenium (total)	Se	EPA 1638	0.06 mg/kg	0.15 mg/kg	180 days
Zinc (total)	Zn	EPA 1638	0.20 mg/kg	1.00 mg/kg	180 days

Table 2. Water Quality Parameters and Constituents To Be Measured and Methods, with Detection Limits, Reporting Limits, and Laboratory Holding Times for Each

Parameter	Method ^a	Method Detection Limit	Method Reporting Limit	Hold Time
<i>Laboratory Counts – Gilbert Bay Brine Shrimp</i>				
Brine shrimp (<i>Artemia franciscana</i>)	Dissection microscope	Not applicable	Not applicable	Not applicable

°C = degrees Celsius

µmhos = micromhos

EPA = sampling method from EPA

m = meters

mg/L = milligrams per liter

ng/L = nanograms per liter

SM = Standard Methods for the Examination of Water and Wastewater

^a Laboratory Analytical Method or field equipment

^b Water level data collected from USGS stations at Saltair Beach State Park and Little Valley Boat Harbor will also be compiled from ut.water.usgs.gov/greatsaltlake/elevations.

^c *Brine layer depth* refers to the vertical zone in a water column in which salinity changes rapidly with depth. Determined from conductivity data.

^d Estimated by American West Analytical Laboratories and Brooks Rand Laboratories (metals). Due to the nature of Great Salt Lake water, reporting limits may be elevated for some analyses.

^e Estimated by Brook Rand Laboratories. Due to the nature of brine shrimp tissue, reporting limits may be elevated for some analyses

^f Total dissolved solids will be measured to estimate salinity.

µg/L = micrograms per liter

CaCO₃ = calcium carbonate

g/cm³ = grams per cubic centimeter

mg/kg = micrograms per kilogram

ng/g = nanograms per gram

su = standard units

2.5 Sample Number, Location, and Frequency

Sample number, location, and frequency are based on Utah 401 Water Quality Certification and USACE NWP 14 requirements. The Utah 401 Water Quality Certification stipulated monitoring at three locations in Gilbert Bay south of the UPRR causeway and at two locations in Gunnison Bay north of the UPRR causeway. On January 6, 2014, UDWQ suggested via email that the locations should be 1 kilometer to the north and 1 kilometer to the south of the UPRR causeway, halfway between the proposed bridge and west culvert and halfway between the west and east culverts. In addition, UDWQ suggested that the third Gilbert Bay location could be located 6 kilometers south of the west culvert. These suggested locations are consistent with the locations proposed in this IMP. These locations are to be monitored four times per year for water quality and during the spring, summer, and fall quarters for brine shrimp taxonomic identification, counts, and tissue analysis.

The USACE NWP 14 stipulated interim monitoring quarterly north and south of the UPRR causeway, at locations in the vicinity of the culverts, and on the South Arm spillway. However, during a meeting on January 9, 2014, it was agreed that interim monitoring at the UDWQ proposed sites would satisfy the NWP interim monitoring permit requirements.

Accordingly, the sampling locations and frequencies proposed herein are in satisfaction of the requirements of both authorizations.

The brine shrimp sampling is intended to be conducted at the same time and same South Arm sampling site locations as the water quality sampling; as such the sampling will occur in once in quarters 1 and 2 and twice in quarter 3 at sampling sites 1, 2, and 5. Water quality sampling event schedule, for all locations, of four times per year, to occur within the critical brine shrimp season, is intended to satisfy and substitute for the quarterly sampling requirements in the NWP 14.

Table 3. Interim Monitoring Locations and Frequency

Parameter	Number and Sample Depth	Frequency	Field Duplicate	Field Blank	Equipment Rinsate	Sampling Site				
						1	2	3	4	5
Total water depth	One measurement taken from water surface to bottom of lake.	Four times per year	NA	NA	NA	X	X	X	X	X
Depth to deep brine layer	One location inferred from conductivity profile	Four times per year	NA	NA	NA	X	X	X	X	X
Secchi depth	Measurements taken from water surface and averaged.	Four times per year	NA	NA	NA	X	X	X	X	X
Conductivity, temperature, pH	Vertical profile; measurements taken <i>in situ</i> every 0.5 m. The field conductivity measurements will establish whether there is a deep brine layer present.	Four times per year	NA	NA	NA	X	X	X	X	X
Total dissolved solids, density	Vertical profile; grab samples taken every 1.5 m in upper brine layer; samples taken every 0.5 m in the deep brine layer.	Four times per year	10% of samples	10% of samples	10% of samples	X	X	X	X	X
Total metals (As, Cu, Pb, Se, Hg, Zn), SO ₄ , hardness, and DO	Grab samples taken 0.2 m from the water surface and 0.5 m from the bottom.	Four times per year	10% of samples	10% of samples	10% of samples	X	X	X	X	X
Brine shrimp count	One sample from one vertical tow.	Tri-annually (May, July, and September)	1 per quarter	NA	NA	X	X	NA	NA	X
Brine shrimp tissue, percent moisture	Composite sample from three vertical tows.	Tri-annually (May, July, and September)	1 per quarter	NA	NA	X	X	NA	NA	X

NA = not applicable

2.6 Sample Site Locations

Sampling sites will be located in the open waters of Gunnison and Gilbert Bays at locations specified in the Utah 401 Water Quality Certification and USACE NWP 14, with modifications to the locations of the USACE NWP 14 sites as described herein. Table 4 describes the latitude and longitude of the sampling site locations. Samples will be collected from three locations in Gilbert Bay and two locations in Gunnison Bay, including locations to the south and north of the UPRR Great Salt Lake causeway in the vicinity of the east and west culverts and a location in Gilbert Bay in the basin between the causeway and the rest of Gilbert Bay.

Table 4. Sample Site Locations

Site Name	Latitude	Longitude	Description
<i>Gilbert Bay</i>			
Sampling site 1	41° 12' 49.65" N	112° 43' 4.82" W	Halfway between the proposed bridge and the west culvert; 1 km south of the UPRR causeway
Sampling site 2	41° 12' 47.86" N	112° 36' 52.62" W	Halfway between the west and east culverts; 1 km south of the UPRR causeway
Sampling site 5	41° 10' 9.65" N	112° 39' 25.81" W	6 km south of the west culvert
<i>Gunnison Bay</i>			
Sampling site 3	41° 13' 54.62" N	112° 43' 11.77" W	Halfway between the proposed bridge and the west culvert; 1 km north of the UPRR causeway
Sampling site 4	41° 13' 34.84" N	112° 36' 40.64" W	Halfway between the west and east culverts; 0.5 km north of the UPRR causeway

The Gilbert Bay sample sites will be accessed by boat from the Antelope Island marina about 25 miles southeast of the sample sites.

The Gunnison Bay sample sites will be accessed by boat from the area known as Little Valley Harbor on Promontory Point in unincorporated Box Elder County. Little Valley Harbor is about 60 miles southwest of Brigham City. Access to Little Valley Harbor and the boat launch ramp facility will require private property access agreement(s).

The sampling sites will not be accessed from the UPRR causeway.

2.6.1 Describe Rationale for Site Selection

Interim water quality monitoring sites were selected to meet the requirements of both the Utah 401 Water Quality Certification and the USACE NWP 14. Although the two permits require some of the same sampling parameters, they have slightly different requirements, including different sampling locations. After a meeting on January 9, 2014 with UDWQ and the Corps, the five sampling sites were identified to meet the requirements of both agencies.

Two sampling sites (1 and 3) are located halfway between the proposed bridge and the west culvert south and north, respectively, of the causeway. Each site will be located 1 kilometer into the open waters, away from the causeway. Sampling site 1 is in Gilbert Bay, and sampling site 3 is in Gunnison Bay.

Two sampling sites (2 and 4) are located halfway between the west and east culverts south and north, respectively, of the causeway. Sampling site 2 will be 1 kilometer south of the causeway in Gilbert Bay, and sampling site 4 will be 0.5 kilometer north of the causeway in Gunnison Bay. Sampling site 5 is 6 kilometers south of the west culvert in the open waters of Gilbert Bay.

Sampling sites were also determined based on the depth of the bays. UPRR intends that sampling will occur in the deepest sections of Gilbert and Gunnison Bays to identify whether a deep brine layer is present.

2.6.2 Sampling Location Site Map

Figure 3 shows the interim monitoring sampling locations, which meet the conditions of both the Utah 401 Water Quality Certification and USACE NWP 14 for temporary closure of the east culvert.

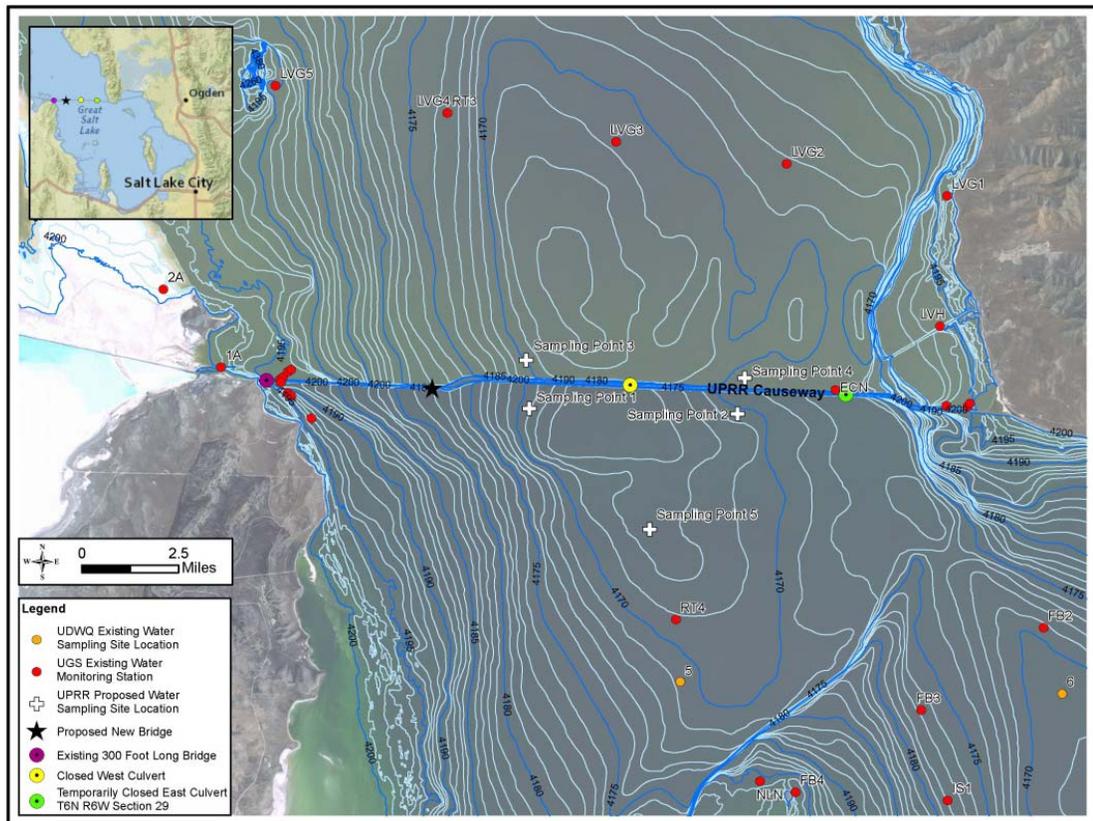


Figure 3. Sampling Site Location Map

3.0 Special Precautions and Safety Plan

3.1 Specific Safety Concerns

A site-specific Health and Safety Plan is included in Appendix B. The safety elements that were identified in the project hazard analysis are driving long distances; slips, trips, and falls; boating safety; heat stress; and cold stress.

3.2 Required Safety training

The boat operator must be proficient at towing, launching, and operating the boat. The boat operator must be aware of navigation constraints and hazards in the Great Salt Lake. At least one person on the interim monitoring field crew must be certified in first aid and CPR (cardiopulmonary resuscitation).

3.3 Invasive Species Plan

Boats, trailers, and equipment will be kept clean and free from aquatic invasive species. Prior to field work, the field crew will be trained on any invasive species issues and best management practices associated with avoiding the spread of invasive species.

4.0 Field Sampling Methods and Documentation

All data will be acquired in accordance with UPRR's *Quality Assurance Program Plan for Great Salt Lake Compliance Monitoring* (QAPP), which was developed to support UPRR's Great Salt Lake Bridge project environmental compliance, including the east culvert closure (provided as Appendix C to this document). Standard operating procedures (SOPs) to be followed during field sample collection are provided in Appendix D. Laboratory QA/QC (quality assurance/quality control), analytical methods, and documentation are provided in Appendix E. Field forms and example Chain of Custody form and other field logistics are provided in Appendix F.

At least two field staff will conduct the field work, along with a boat operator. Sampling equipment, laboratory bottles in coolers, and personal gear will be packed into the boat and checked against a checklist prior to leaving the boat launch. Navigation to the sampling locations will be made with a GPS (global positioning system) device. Once at the sampling location, the boat will be anchored to keep the boat on station. Field staff will note relevant conditions during each sampling event on the field data sheet (such as air temperature, description of location, floating material, evidence of oil and grease, and activities, such as dredging, in the vicinity of sampling site that could cause short- or long-term alterations to water quality).

4.1 Element 1 – *In-Situ* Surface Water Measurements

In-situ water quality measurements include total depth, depth to deep brine layer, secchi depth, and vertical profiles of water temperature, conductivity, and pH. Secchi depth will be measured first, per the SOP in Appendix D. Next, water temperature, conductivity, and pH will be measured every 0.5 meter with a multiprobe water quality meter per SOPs (see Appendix D). Prior to and after each use, the instrument will be calibrated using the manufacturer’s recommended calibration methods. Any variances will be noted on the field data sheet and final report, and the instrument will be recalibrated or repaired as necessary. Calibration checks for pH will be made in between sampling site locations.

The purpose of obtaining the vertical water profiles for conductivity, temperature, pH, dissolved oxygen, total dissolved solids, and density is to characterize the nature of the water column at the sampling location. *In-situ* conductivity profiles will establish whether there is a deep brine layer present. The deep brine layer is defined by an abrupt change in density, salinity, and conductivity. If present, the depth to the deep brine layer will be identified and used to determine the frequency of the grab samples for dissolved oxygen, total dissolved solids and density sample locations. At a minimum, the following will apply:

- If a deep brine layer is present:
 - Collect samples above the deep brine layer every 1.5 meters
 - Collect samples below the deep brine layer every 0.5 meter
- If a deep brine layer is not present:
 - Collect samples every 1.5 meters

4.2 Element 2 – Surface Water Sampling

Each laboratory sample will be collected into laboratory-supplied clean containers. Water samples will be collected at depth with a Kemmerer sampler. Water samples to be analyzed for metals will be taken using “clean hands” methods consistent with EPA’s Method 1669 sampling protocol, (EPA 1996) The UDWQ SOP for “Trace Metals Sample Collection (Clean Hands/ Dirty Hands), Decontamination, and Multiprobe In Situ Monitoring Procedures” (Appendix D) describes filtering samples and decontamination procedures for filtering apparatus. However, since the UPRR interim monitoring does not need to filter samples, those specific parts of the SOP do not apply.

As described in UPRR’s QAPP and field sampling SOP (Appendices C and D) all sample containers will be labeled with an identification label that includes the date and time when the sample is collected and the site where the sample was collected. The sampling site location will be recorded using a GPS unit. All sample containers will be handled in a manner consistent with appropriate chain-of-custody protocols. The sample containers will be preserved (as appropriate), stored, and delivered to the laboratory for analyzing the laboratory parameters listed in **Error! Reference source not found.** in accordance with maximum holding periods for each parameter. A chain-of-custody record will be maintained with the samples at all times. Sampling equipment will be decontaminated between sampling sites.

As part of the field quality assurance program, two field duplicates, field blanks and equipment rinsates will be collected and submitted to the laboratory (approximately one for every 10 analyses).

- A field duplicate is a second sample collected at the same time or immediately after the primary environmental sample. A field duplicate indicates the precision of field sample collection.
- A field blank is a sample of analyte-free water poured into the container in the field and then preserved and shipped to the laboratory with the samples. A field blank indicates whether there was contamination from field conditions during sampling.
- A rinsate is a sample of analyte-free water poured over or through decontaminated field sampling equipment prior to the collection of samples. It indicates the adequacy of the decontamination processes.

4.3 Element 3 – Brine Shrimp Sampling

Standard operating procedures for collecting brine shrimp are in Appendix D. Three vertical plankton tows will be performed at each station and composited into one sample for laboratory analysis. One additional plankton tow will be collected for brine shrimp taxonomic life stage identification and counts. Each tow is from the bottom of the water column to the water surface, using a 165- μ m net with a 20 cm diameter opening. The tow net, with a screened sample bucket attached at the bottom, is lowered to the desired depth, and raised at an approximate rate 0.5 meters per second to collect zooplankton from the water column. After lifting the net from the water it is sprayed with the aid of a battery powered pump assembly to wash the organisms down into the bucket. The sample will be concentrated into the sample bucket and is transferred to a labeled and laboratory-supplied sample jar. The procedure is repeated with a second and third vertical tow, and composited into the same sample jar. The procedure is repeated a fourth time for brine shrimp counts sample jar. The sample jars are then properly stored and the sample collection is recorded on the two chain-of-custody forms (one for the analytical laboratory and one for the taxonomic laboratory).

4.3.1 Sampling Equipment

The sampling equipment that will be used for field work is listed below.

- General
 - Trimble Geo GPS unit with loaded maps and sampling locations
 - Ritein the Rain field notebook
 - Field forms
 - Copy of IMP and SOPs
 - Maps
 - Cell phone
 - Health and safety plan
 - First aid kit
 - Emergency and project phone numbers

- Personal
 - Weather-appropriate clothing
 - Sunscreen
 - Hat
 - Drinking water and food
 - Sunglasses
 - Pens, pencils, sharpies
- Boat (items below)
 - Drift sock and anchor
 - Full tank of gas
- Life jackets
 - Paddle
 - Boat emergency kit
 - Drain plug
 - Boat log (log book in the glove box; note any maintenance and hours used per day)
 - Boat keys
- *In-situ* measurements
 - Secchi Disk with weight and graduated rope
 - Troll 9000 Multiprobe sonde and meter with repair kit and replacement parts
 - De-ionized water and squirt bottles
 - Calibration solutions
- Water chemistry sampling
 - Kemmerer sampler (plus messenger and line)
 - Laboratory-supplied and chain-of-custody forms
 - Fed Ex labels filled out as much as possible
 - Fine-point Sharpie pens
 - Sample bottles, pre-cleaned and of the appropriate material and size
 - “Clean hands” bottles for metals analyses (make sure they are double bagged)
 - Clean bottles for all other analyses
 - Weatherproof bottle labels and spare bottle labels
 - Filters, 0.45 μm
 - Syringes, 60 mL
 - Metal-free sampling pole with sampling cup
 - Alconox
 - De-ionized water
 - Bucket for decontaminating the Kemmerer sampler
 - Gloves, powderless, dye-free
 - Storage bags, zip-type, nonvented, colorless polyethylene (various sizes)
 - Plastic wrap, colorless polyethylene (Saran Wrap or similar)
 - Paper towels

- Cooler, nonmetallic, with white interior for shipping samples; with temperature blanks
- Double-bagged ice packs to keep samples chilled in the cooler during shipment
- Bubble wrap
- Rubber bands
- Duct tape
- satellite phone
- Hard hat and orange safety vest
- Weather-resistant camera
- Brine shrimp sampling
 - Plankton tow net, 165- μ m pore size, 0.5-meter diameter (diameter:length=1:3)
 - Tow net sample bucket with a 165- μ m pore size metal screen
 - Weights, 10–20 pounds
 - Safety line for sample bucket
 - Battery and pump assembly with screened intake
 - Garden hose with spray nozzle
 - Laboratory-supplied sample jars with labels
 - Waterproof notebook
 - Gloves, rubber or vinyl
 - Winch with metering sheave and hydrographic line

4.4 Corrective Actions

As required by the UPRR QAPP, if necessary to obtain a complete dataset, resample within the required interim monitoring window (see Appendix C).

4.5 Field Documentation

Field SOPs, including SOPs for data collection and documentation, are provided in Appendix D. As described in the UPRR QAPP, field forms and field data collection will be recorded.

5.0 Laboratory Sample Handling Procedures

All data will be handled in accordance with UPRR's QAPP, which is provided as Appendix C to this document.

5.1 Sample Containers, Preservatives, and Holding Times

Sample containers, preservatives are provided in Table 5. Reporting limits and holding times were provided above in Table 1.

Table 5. Sample Containers and Preservatives

Constituent	Analytical Method	Minimum Sample Volume	Sample Bottle	Sample Preservation
<i>Physical Property</i>				
Density	TBD	TBD	TBD	TBD
Dissolved oxygen	TBD	TBD	TBD	TBD
Hardness	TBD	TBD	TBD	TBD
<i>Metals</i>				
Mercury, total	EPA 1631	1 x 250 mL	Glass	Chilled <4 °C
Arsenic (total)	EPA 1638	1 x 250 mL	HDPE	Chilled <4 °C
Copper (total)	EPA 1638	1 x 250 mL	HDPE	Chilled <4 °C
Lead (total)	EPA 1638	1 x 250 mL	HDPE	Chilled <4 °C
Selenium (total)	EPA 1638	1 x 250 mL	HDPE	Chilled <4 °C
Zinc (total)	EPA 1638	1 x 250 mL	HDPE	Chilled <4 °C
<i>Inorganic Ions</i>				
Sulfate (total)	EPA 300.0	1 x 500 mL	HDPE	None
Total dissolved solids	SM 2540 C	1 x 1 L	HDPE	None

TBD = to be determined

mL = milliliter

EPA = U.S. Environmental Protection Agency

L = liter

SM = Standard Methods for the Examination of Water and Wastewater

HDPE = high-density polyethylene

5.2 Chain-of-Custody and Sample-Labeling Procedures

Chain of custody and sampling labeling procedures are provided in the QAPP, provided as Appendix C to this document. A chain-of-custody record will be maintained with the laboratory samples at all times. An example Chain of Custody form is provided in Appendix F.

5.3 Sample Transport to Laboratory

Sample transport procedures are provided in the QAPP. Samples will be transported or shipped to the analytical lab in insulated containers within the appropriate holding time (**Error! Reference source not found.**) and will be accompanied by the chain-of-custody form. Samples will be packaged and shipped in accordance with U.S. Department of Transportation standards. The original chain-of-custody will be given to the lab with the samples and UPRR will retain a copy for their records.

For chemical analyses, water quality and brine shrimp samples will be shipped to

Brooks Rand Labs, LLC
3958 6th Avenue NW
Seattle, WA 98107

For taxonomic identification and counts, a sample containing brine shrimp will be shipped to:

EcoAnalysts, Inc.
1420 S. Blaine Suite 14
Moscow, ID 83843

6.0 Analytical Methods and Laboratory Documentation

Analytical methods are described in Table 2. Standard Operating Procedures for these analytical methods are included in Appendix D and in the Brooks Rand Laboratory Quality Assurance Project Plan.

The laboratory will provide a standard Level II deliverable. Level II or Standard deliverables include a brief case narrative or cover letter, sample results summary, QA sample summary, work order receipt report, and chain-of-custody form(s).

7.0 Project Quality Control Requirements

Data will be acquired in accordance with UPRR's QAPP for Interim Monitoring, which was developed in accordance with Utah 401 Water Quality Certification Condition 3 and USACE NWP 14 Special Conditions 2a and 2b. The Utah 401 Water Quality Certification requires the QAPP to be comparable to EPA's requirements for QAPP (EPA 2001) and consistent with the Utah QAPP for the Great Salt Lake Baseline Sampling Program (UDWQ 2014).

The Great Salt Lake Baseline Sampling Program is designed by UDWQ to:

- Establish a public, long-term database of the lake's water quality
- Confirm appropriate sampling and analysis techniques
- Support the development of numeric water quality criteria and assessment of beneficial uses
- Facilitate a collaborative approach with partner agencies

The interim monitoring QAPP is intended to support interim monitoring objectives and permit requirements while complying with the Utah sampling program QAPP.

7.1 Field Instrumentation Limits

The In-Situ Troll 9000 is the only field instrument that will be used. The instrumentation limits are provided in Table 6.

Table 6. Field Instrumentation Limits

Parameter	Range	Accuracy	Resolution
Water temperature	-5 °C to 50 °C	± 0.1 °C	0.01 °C
Conductivity (high range sensor)	70 to 200,000 µS/cm	± 0.8% + 2 µS/cm	Range dependent
pH	0 to 12 pH units	± 0.09 pH units	0.01 pH units

µS/cm = microsiemens per centimeter

7.2 Data Quality Indicators

Data quality indicators are described in the project QAPP (Appendix C).

7.3 Quality Control Limits, Schedule, and Descriptions of Planned Field, Lab Audits, and Assessments

The project quality assurance officer will provide review of field forms and field measurement data quality indicators after every monitoring event. The quality assurance officer will also review laboratory reports and data validation results after each monitoring event.

7.4 Data Quality Assurance Review Procedures

All data will be verified and/or validated as appropriate. In brief, following the field sampling and laboratory analyses, which includes the laboratories' own QA/QC analysis, the UPRR will subject all data to QA/QC procedures including, but not limited to, spot-checks of transcription; review of electronic data submissions for completeness; comparison of results to field blank and duplicate results; and identification of any data that seem inconsistent. If any inconsistencies are found, the UPRR will consult with the laboratory to identify any potential sources of error before concluding that the data are correct.

Monitoring results will consist of all verified chemical detections. Estimated, or "J"-qualified,¹ data will not be used to establish UPRR's regulatory obligations or determine UPRR's compliance. Nevertheless, "J"-qualified data will be provided in the data submittal attached to all reports in the event the data can be used for purposes requiring less accuracy.

¹ Constituent is detected but not quantified, that is, estimated sample concentration is less than the reporting limit but is above the method detection limit and is subject to a high degree of quantitative uncertainty.

8.0 Data Analysis, Record Keeping, and Reporting Requirements

8.1 Data Interpretation Approach

Interim monitoring data will be collected and submitted to UDWQ and USACE. The data are being collected at new sampling locations within the open waters of Gunnison and Gilbert Bays.

The data collected during the interim monitoring are expected to be variable, as previous investigations for water quality of the open waters of the Great Salt Lake have demonstrated with respect to salinity. The variability of the salinity data is expected to fall within historic data ranges.

8.2 Data Record Keeping

Data record keeping is discussed in Section the project QAPP.

8.3 Data Availability

Field and laboratory data will be provided to the USACE and UDWQ in the context of the individual monitoring event reports and annual report required by the USACE NWP 14 and Utah 401 Water Quality Certification, respectively.

8.4 Interim Monitoring Reporting

UPRR will submit interim monitoring reports after each monitoring event for each year per Special Condition 2 of the USACE NWP 14.

UPRR will submit an annual interim monitoring report by January 1 of each year per Condition 3 of the Utah 401 Water Quality Certification. The annual report will include the following sections: (1) Interim monitoring Goals and Objectives, (2) Methods, (3) Results, (4) Discussion, (5) Description of Variances from the IMP (if any), and (6) Consistency Evaluation. The report will include a table that will show for each parameter measured the results of the sampling sorted by sampling location. Data that that are outside of comparable ambient conditions will be highlighted. The report will include in Microsoft Excel format on compact disc (CD) a complete water quality dataset.

The interim monitoring reports and annual reports will be submitted to both UDWQ and USACE.

9.0 Schedule

9.1 Schedule

The schedule provided in Table 7 is directed by Utah 401 Water Quality Certification Condition 3 and USACE NWP 14 Special Conditions 2a and 2b.

Table 7. Schedule

Element	Date
UPRR submits Interim Monitoring Plan to USACE and UDWQ	January 16, 2014
UDWQ issues public notice	March 16, 2014 – April 16, 2014
USACE and UDWQ director approve plan	TBD
UPRR conducts interim monitoring events	May, July, September 2014; January/ February, May, July, September 2015
UPRR submits interim monitoring reports	90 days after event
UPRR submits annual interim monitoring reports	January 2015, January 2016
UPRR stops interim monitoring	2 years or as superseded by implementation of the final approved Mitigation and Monitoring Plan

10.0 Project Team and Responsibilities

10.1 Project Team

The project team members and firms for the interim monitoring plan are:

USACE Project Manager: Ms. Kathleen Anderson

UDWQ Project Manager: Mr. Bill Damery

UPRR Project Manager: Mr. Mark McCune, PE
Director of Structures Design
Union Pacific Railroad
1400 Douglas Street
Omaha, NE 68179-0910

Consultants: Ms. Karen Nichols, Mr. Chad Wiseman, HDR Engineering, Inc.
Mr. Kidd Waddell
Mr. Wally Gwynn

10.2 Sampling Personnel

Sampling team responsibilities are listed in UPRR's QAPP for interim monitoring. Sampling team personnel are:

Monitoring Coordinator: Mr. Chad Wiseman

Field Team: Mr. Chuck Vertucci
Mr. Nathan Nichols
Ms. Alyssa Quinn

10.3 Subcontractors

The following subcontractors will be used:

- Laboratory – Brooks Rand, Seattle, WA
- Boat rental – TBD
- Equipment rental – Enviro-Equipment, Inc.

Appendix A
Regulatory Permits



State of Utah

GARY R. HERBERT
Governor

SPENCER J. COX
Lieutenant Governor

Department of
Environmental Quality

Amanda Smith
Executive Director

DIVISION OF WATER QUALITY
Walter L. Baker, P.E.
Director

December 16, 2013

Mark McCune
Director, Structure Design
Union Pacific Railroad
1400 Douglas Street, Stop 0910
Omaha, Nebraska 68179-0910

Dear Mr. McCune:

Subject: Approval of the 401 Water Quality Certification with Conditions.

Water Quality 401 Certification No.: SPK 2011-00755.

USACE 404 Permit No.: SPK 2011-0755, dated December 6, 2013.

Applicant: Union Pacific Railroad.

Project: Temporary Closure of the East Culvert of Great Salt Lake Causeway.

Purpose: To avoid further safety risks to causeway railroad traffic.

Location: The east culvert is located at Mile Post 750.53, in Section 29, Township 6 North, Range 6 West, Salt Lake Meridian, 41.221 and -112.561, Box Elder County, Utah.

Watercourse: Great Salt Lake, Box Elder County, Utah.

Pursuant to Section 401 of the Federal Water Pollution Control Act, commonly known as the Clean Water Act (CWA), the Division of Water Quality (DWQ) certifies it has reasonable assurances that any discharge associated with the temporary closure of the East Culvert of Great Salt Lake Causeway will not violate surface water quality standards, or cause additional degradation in surface waters not presently meeting water quality standards. In accordance with Section 401(a)(1) of the CWA [33 U.S.C. Sec. 1341(a)(1)], DWQ hereby issues this 401 Water Quality Certification provided the conditions outlined below are met and included in the USACE 404 NWP 14 permit SPK-2011-00755 dated December 6, 2013, and issued to Union Pacific Railroad (UPRR).

The Public Comment period for this action begins Thursday, December 12, 2013 through Wednesday, January, 15, 2014. However, after careful evaluation of information provided by Union Pacific Railroad (UPRR) documenting the imminent threat of failure of the East Culvert, DWQ intends to issue 401 Water Quality Certification to this project after 6:00 p.m. on Monday, December 16, 2013. The Director of the Division of Water Quality (Director) has decided to issue the 401 Certification before the end of the public comment period due to the instability of the east culvert and the need for UPRR to commence its repair work. However, public comments will continue to be accepted until **Wednesday, January 15, 2014 at 6:00 p.m.** The Director will review the comments received, prepare a response, and modify the 401 Water Quality Certification, if appropriate. This certification anticipates that UPRR will pursue an Individual Permit with USACE and the 401 Water Quality Certification will include requirements for monitoring the impacts of the closure of both the East and West Culverts and the restoration of circulation between the North and South Arms of Great Salt Lake.

In 2008 DWQ reclassified the beneficial uses of Great Salt Lake (Class 5) into five subclasses to more accurately reflect different salinity and hydrologic regimes and the unique ecosystems associated with each of the four major bays and adjacent wetlands. Great Salt Lake has the following beneficial use classifications: Classes 5A - Gilbert Bay; 5B - Gunnison Bay; 5C - Bear River Bay; 5D - Farmington Bay; and 5E - Transitional waters along the shoreline. With limited water quality criteria defined for Great Salt Lake, DWQ relied on its anti-degradation policy and procedures to protect existing uses and ensure water quality of Great Salt Lake is maintained.

Therefore, as a condition of 401 Water Quality Certification for this UPRR project, DWQ has requested that the USACE include the following conditions in the USACE 404 NWP 14 permit SPK-2011-00755, dated December 6, 2013:

1. The conditions in this certification may be modified by the Director in response to information received during the 30-day public notice period ending January 15, 2014 at 6:00 p.m. or any time thereafter in order to meet state water quality standards. The Director will notify UPRR of any changes and provide an opportunity to confer regarding any necessary modifications.
2. Approval is given to temporarily reduce the circulation between Gilbert and Gunnison Bays, previously provided by the East Culvert, with authorization to do so ending March 21, 2014. UPRR agrees that before March 21, 2014 it will provide the Director with sufficient information to allow a determination to be made as to whether the impacts of the closure of the East Culvert are temporary and limited resulting in no Level II anti-degradation review being required, in accordance with UAC R317-2-3, or that the impacts are not temporary and limited resulting in a Level II anti-degradation review being required. The Director will make this determination on or before March 21, 2014. The Director's determination will provide for a public notice and comment period.
3. Within 30 days of the Director's signing of this Certification, UPRR will submit an Interim Monitoring Plan including a Quality Assurance Project Plan for interim monitoring. Interim monitoring will be conducted until superseded by the approved Mitigation and Monitoring Plan required by Condition 5.

The interim plan will include the requirements identified in the "Summary Table for Interim Monitoring Plan," below. A minimum of three locations in Gilbert Bay and two locations in Gunnison Bay will be monitored. The locations will be on each side of the Causeway in the vicinity of the East and West Culverts and a location in Gilbert Bay in the basin located between the Causeway and the rest of the Gilbert Bay.

Completeness of the interim plan will be determined by comparison with the EPA Requirements for Quality Assurance Project Plans (EPA/240/B-001/003 March 2001). Within 90 days of this Certification, the Director will hold a 30-day public comment period on the Interim Monitoring Plan. After the public comment period, the Director will approve the Interim Monitoring Plan or notify UPRR in writing of the deficiencies. The interim monitoring will be conducted in accordance with the approved Monitoring Plan and will begin no later than May 2014. In the event that UPRR is unable to commence monitoring by May 2014 DWQ will conduct the monitoring and UPRR will reimburse DWQ for all associated costs.

Results from the interim monitoring will be submitted to the Director for approval within 90 days of monitoring. UPRR will submit an annual report, by January 1 of each year, which summarizes the monitoring results including all laboratory and field supporting quality control data for the previous calendar year of all data collected.

Summary Table for Interim Monitoring			
Matrix	Field Parameters	Laboratory Analytes	Frequency
Water	secchi depth, total water depth, depth of chemocline (if present), surface to bottom profile at a frequency of no greater than 0.5 meters: salinity, dissolved oxygen, pH, temperature	total arsenic, total copper, total lead, total selenium, total mercury, total zinc, and total sulfate	May, July, September, and January or February 4 events/year
Gilbert Bay Brine Shrimp	Brine shrimp counts per liter of water from at least 3 tow samples	total arsenic, total copper, total lead, total selenium, total mercury, and total zinc	May, July, September 3 events/year

4. UPRR will continue to model and report the potential water quality impacts of closing the East Culvert as compared to the water quality as of November 9, 2012 and the potential water quality impacts of the compensatory opening(s) in the Causeway. UPRR is currently proposing a 180' bridge to compensate for the closure of the East and West Culverts. UPRR must acquire all necessary easements to ensure they are able to build the bridge.
 - a. The modeling will include the following elements:
 - 1) Update, recalibrate, and run the 1998 USGS Water and Salt Balance Model *Water-Resources Investigations Report 00-4221, Water and Salt Balance of Great Salt Lake, Utah, and Simulation of Water and Salt Movement through the Causeway, 1987 – 98* (Loving, Waddell and Miller, 2000) to evaluate the potential impacts of culvert closure and bridge construction on the water and salt balance between the North (Gunnison Bay) and South (Gilbert Bay) Arms of Great Salt Lake. The modeling effort shall include consultation with a representative appointed by the Director to review modeling progress at a frequency determined by the Director. The Director's review will include the development of baseline conditions, model input parameters, output sensitivity to parameters, quantitative or semi- quantitative evaluation of variability and uncertainty, model code modifications, simulations, model calibration, and any other information relevant to the model, as determined by the Director.
 - 2) UPRR will provide a report prepared by the United States Geological Society (USGS) documenting its review of the model. The USGS Scope of Work must be approved by the Director.
 - b. UPRR will submit the following to the Director for review: construction plans, specifications, and the schedule for construction of the bridge or other changes to the Causeway that could affect the circulation between Gunnison and Gilbert Bays. The Director will approve or disapprove the schedule for bridge construction.

5. UPRR will submit to the DWQ for approval a Mitigation and Monitoring Plan. The Mitigation and Monitoring Plan shall be submitted to the Director for approval. The Director may take action on the Mitigation and Monitoring Plan after a minimum 30-day public comment period. Within 60 days of the close of the public comment period, the Director will either approve or disapprove the plan. The Director will notify UPRR in writing of deficiencies in the plan if the plan is not approved. UPRR will correct the deficiencies to the Director's satisfaction, revise the plan, and resubmit it to the Director for approval within 30 days of the written notification unless the deadline is extended by the Director. Director will approve or disapprove changes to the Mitigation and Monitoring Plan and may hold additional public comment periods at the Director's discretion.

If an Environmental Assessment, Environmental Impact Statement, or other analyses of potential impacts are submitted to the United States Army Corps of Engineers to support the Clean Water Act Section 404 individual permit, this information will also be submitted to DWQ to be considered for the Mitigation and Monitoring Plan. The Mitigation and Monitoring Plan will include the relevant components described by the *EPA Requirements for Quality Assurance Project Plans* (EPA/240/B-001/003 March 2001) including the parameters to be monitored, the frequency of monitoring, and any proposed triggers for changing the monitoring plan or circulation conditions between Gunnison and Gilbert Bays shall be included in the plan. The plan will describe the mitigation options that could be implemented in response to findings of the monitoring. The options will at minimum specifically address options for either increasing or decreasing the circulation between Gilbert and Gunnison Bays if the Director concludes that the monitoring indicates degradation is occurring. After a minimum of 5 years of monitoring including the interim monitoring, UPRR shall submit a report documenting the results of the monitoring during the 5-year period which describes any long-term changes in flow and salt transfer associated with the project in relation to the beneficial uses of Great Salt Lake, Anti-degradation policy, numeric criteria and narrative standards. The report shall describe UPRR's justification for cessation of monitoring in light of these findings. If the Director approves the report, the monitoring program may cease. If the Director disapproves, the report, UPRR, and DWQ shall meet and consider which aspects of the monitoring program should continue and additional term of monitoring.

6. The applicant shall not use any fill material which may leach organic chemicals (e.g., discarded asphalt) or nutrients (e.g., phosphate rock) immediately adjacent to or into Great Salt Lake.
7. The applicant shall obtain the following permits from the DWQ prior to the construction phase of the project:
 - a. Dewatering activities, if necessary during the construction, may require coverage under the UPDES General Permit for Construction Dewatering, Permit No. UTG070000. A fact sheet describing the permit application procedures are located on our web site at: <https://secure.utah.gov/stormwater/main.html>. The permit requires water quality monitoring every two weeks to ensure that the pumped water is meeting permit effluent limitations, unless the water is managed on the construction site.
 - b. Construction activities that disturb one acre or more are required to obtain coverage under the Utah Pollutant Discharge Elimination System (UPDES) Storm Water General Permit for Construction Activities, Permit No. UTR300000. The permit requires the development of a storm water pollution prevention plan (SWPPP) to be implemented and updated from the commencement of any soil disturbing activities at the site until final stabilization of the project. A fact sheet describing the permit application procedures are located on our web site at: <https://secure.utah.gov/stormwater/main.html>

Page 5

Please contact Mr. Bill Damery at (801) 536-4354, wdamery@utah.gov with any questions you may have concerning this 401 Water Quality Certification with Conditions.

Sincerely,



Walter L. Baker, P.E.
Director

WLB:wd:mc

cc: Jason Gipson, USACE
Julia McCarthy, U.S. EPA Region VIII

File: SPK 2011-00755
wdamery\wp\RDCC\401 Certs New\Causeway UPR GSL\WQ Cert for NWP-14



REPLY TO
ATTENTION OF

DEPARTMENT OF THE ARMY
U.S. ARMY ENGINEER DISTRICT, SACRAMENTO
CORPS OF ENGINEERS
1325 J STREET
SACRAMENTO CA 95814-2922

December 6, 2013

Regulatory Division (SPK-2011-00755)

Mr. Mark L. McCune, P.E.
Director of Structures Design
Union Pacific Railroad
1440 Douglas Street, Stop 0910
Omaha, Nebraska 68179-0910

Dear Mr. McCune:

We are responding to your October 21, 2013 letter request for a Department of the Army permit for the Great Salt Lake Union Pacific Railroad (UPRR) Causeway East Culvert Closure project. This project involves discharging clean rock fill material into the Great Salt Lake, a water of the United States, to temporarily close the East Culvert which is in danger of failure. Filling the culvert is needed to prevent closure of the UPRR Causeway track across the Great Salt Lake. The East Culvert is located at Mile Post 750.53, in Section 23, Township 6 North, Range 6 West, Salt Lake Meridian, Latitude 41.22128°, Longitude -112.56051°, Box Elder County, Utah.

Based on the information you provided, the proposed activity, resulting in the temporary loss of approximately 0.17-acre of waters of the United States and a temporary reduction of the circulation of flows between the North and South Arms of the Great Salt Lake, is authorized by Nationwide Permit Number 14, *Linear Transportation Projects*. However, until Section 401 Water Quality Certification for the activity has been issued or waived, our authorization is denied without prejudice. Once you have provided us evidence of water quality certification, the activity the work may proceed subject to the conditions of the 401 certification and this Nationwide Permit 14 verification.

Your work must comply with the general terms and conditions listed on the enclosed Nationwide Permit 14 information sheets, the Utah Nationwide Permit Program Regional Conditions and the following special conditions:

Special Conditions

1. All equipment must work from existing causeway fill.
2. Within 90 days of the date of this verification, you shall submit to the Corps and the Utah Division of Water Quality an interim mitigation and monitoring plan to include identification of contingency measures to restore or mitigate for the loss of North Arm brine movement into the South Arm of the Great Salt Lake due to the closure of the East Culvert. Contingency measures are necessary due to the potential for adverse effects to the beneficial uses of the Great Salt Lake as a result of closure of East Culvert. The interim mitigation and monitoring plan may be superseded upon implementation of a final mitigation and monitoring plan approved by the Corps and Utah Division of Water Quality.

a. The interim mitigation and monitoring plan must address the collection and definition of 2012 baseline conditions, including defined and repeatable monitoring points for lake elevation levels and salinity gradients. Data collection is to capture temporary hydrologic impacts such as changes in salinity or water elevation gradients resulting from closure of the East Culvert. Monitoring sites will, at a minimum, be located on each side of the lake in the vicinity of the culverts as well as on the South Arm spillway to monitor changes to the deep brine layer.

b. Quarterly data collection and monitoring reports following closure of the East Culvert will be submitted to the Corps and the Utah Division of Water Quality. The first report is due three months following submission of the interim mitigation and monitoring plan. The quarterly monitoring shall continue until the Corps determines, for two consecutive years, that no adverse environmental effects have occurred as a result of closure of the East Culvert, or until the monitoring is superseded by implementation of a Corps-approved final mitigation and monitoring plan.

c. If, as determined by the Corps, quarterly monitoring data indicates adverse effects have resulted from closure of the East Culvert, the Corps may require UPRR to implement the interim measure(s).

3. You shall implement and maintain appropriate construction best management practices to safeguard water quality to prevent grout or other pollutants from entering the open waters of the Great Salt Lake during closure of the culvert.

4. You are responsible for all work authorized herein and ensuring that all contractors and workers are made aware and adhere to the terms and conditions of this verification.

5. You shall submit an after-action report to include photographs documenting the East Culvert closure work in progress, BMPs implemented, and of the completion of culvert closure. This report shall be submitted within 30 days of completion of the authorized work.

6. Within 60 days of receipt of this permit, you shall provide the Corps a firm schedule for completion of the 3-step plan for the modeling update, recalibration and simulations analysis, identification of appropriate monitoring parameters with a cause-and-effect relationship to the overall UPRR culvert closure and bridge construction project, and the projected date for submission of your final mitigation and monitoring plan for Corps approval.

After completion of the authorized work, you must sign the enclosed Compliance Certification and return it to this office within 30 days.

This verification is valid until March 18, 2017, when the existing Nationwide Permits are scheduled to be modified, reissued, or revoked. Furthermore, if you commence or are under contract to commence this activity before the date that the relevant NWP is modified, reissued or revoked, you will have twelve (12) months from the date of the modification, reissuance or revocation of the NWP to complete the activity under the present terms and conditions. Failure to comply with the General and Regional Conditions of this NWP, or the project-specific Special Conditions of this authorization, may result in the suspension or revocation of your authorization.

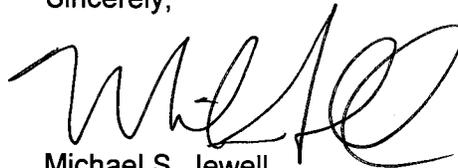
This NWP verification does not obviate the need to obtain other federal, state, or local permits, approvals, or authorizations required by law; do not grant any property rights or exclusive privileges, and do not authorize any injury to the property or rights of others.

This NWP 14 verification is only for the temporary filling of the East Culvert due to the potential for failure and does not address the permanent solution for maintaining train operations across the UPRR Causeway. Activities in waters of the United States proposed for a permanent solution, including whether to leave the East Culvert fill material in-place, will be evaluated under our standard individual permit procedures. A public notice describing your proposal for a permanent solution will be issued next week. With regard to the August 2012 NWP permit verification for the West Culvert, we will continue to informally consult with you to determine the final disposition of that verification during the standard individual permit process for the permanent project.

We would appreciate your feedback. At your earliest convenience, please tell us how we are doing by completing the customer survey from the lower link on our District website.

Please refer to identification number SPK-2011-00755 in any correspondence concerning this project. If you have any questions, please contact Kathleen Anderson at our Utah-Nevada Regulatory Branch, 533 West 2600 South, Suite 150, Bountiful, Utah 84010-7744, by email at Kathleen.Anderson@usace.army.mil, or telephone at 801-295-8380 extension 10. For more information regarding our program, please visit our District website at www.spk.usace.army.mil/Missions/Regulatory.aspx.

Sincerely,



Michael S. Jewell
Chief, Regulatory Division
Sacramento District

Enclosures

cc: (w/o encls)

Ms. Debra Schafer, General Director, Maintenance of Way-Environmental, Union Pacific Railroad, debralschafer@up.com

Mr. Stephen Cheney, Project Manager, Union Pacific Railroad, scheney@up.com

Mr. Robert Blysmas, Counsel, Union Pacific Railroad, rblysmas@up.com

Mr. Wayne Whitlock, Pillsbury Winthrop Shaw Pittman LLP, wayne.whitlock@pillsburylaw.com

Mr. William Damery, Utah Division of Water Quality, wdamery@utah.gov

Mr. Walt Baker, Utah Division of Environmental Quality, wbaker@utah.gov

Ms. Laura Ault, Utah Division of Forestry, Fire and State Lands, lauraault@utah.gov

Appendix B
Health and Safety Plan

Health and Safety Plan

to support:

Utah Division of Water Quality
Water Quality 401 Certification No. SPK 2011-00755
Issued: December 16, 2013

and

U.S. Army Corps of Engineers
NWP 14 Permit SPK-2011-00755
Issued: December 6, 2013

Temporary Closure of the East Culvert, Great Salt Lake Causeway

Submitted by
Union Pacific Railroad
1400 Douglas Street
Omaha, NE 68179-0910

January 15, 2014

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1.0 Project Manager Signature Page

In order for this Project Safety Plan to be effective, HDR is requiring that the Project Manager conduct a safety briefing prior to the beginning of field work. The safety briefing will include overview of this plan and verification that each project team member has received all hazard specific training required for their project activities.

To confirm that team members have completed the necessary training, a training database may be accessed through the HDR H&S Intranet Portal using the following link:

<http://enterprise/sites/hr/safety/Pages/training-tracker.aspx>

By signing below, I attest that the briefing was conducted, all training has been completed and all Personal Protective Equipment (PPE) provided.

Signature of Project Manager*

Printed Name of Project Manager

Date Signed

*Once this page has been signed and dated, please put a copy in the project file to fulfill the QC process.

2.0 Introduction

2.1 Purpose

HDR has developed this project-specific Health and Safety Plan (HASP) to identify hazards that may adversely affect HDR employees conducting project assignments throughout the duration of the INTERIM MONITORING PLAN: TEMPORARY CLOSURE OF THE EAST CULVERT OF GREAT SALT LAKE CAUSEWAY project.

The reader of this Plan should understand the following:

- It is written to promote the safest working environment possible for the Project;
- It is intended to supplement and clarify HDR's Corporate Safety Policies;
- This Plan sets minimum expectations for safe work; it does not alter or supplant any OSHA standards, Federal or State Law or Regulation.

This project-specific HASP applies to HDR employees and HDR subcontractors who work on the INTERIM MONITORING PLAN: TEMPORARY CLOSURE OF THE EAST CULVERT OF GREAT SALT LAKE CAUSEWAY project, and especially to those employees conducting on-site work on a part-time or full-time basis.

Note: This HASP must be amended whenever the project scope changes, new activities arise that have not been included previously, or when new information surfaces. Project employees will be notified of any changes through email communication, verbal communication, and/or through training.

2.2 Statement of HDR Health and Safety Policy

At all times and on all sites, it is HDR's policy, practice, and responsibility to provide a place of employment where HDR employees can conduct project-related activities in a safe and healthy environment. HDR strives to ensure the health and safety of its employees by identifying and mitigating recognized hazards to avoid or eliminate potential for injury or illness. However and at the same time, HDR employees shall not instruct other on-site contractors and/or HDR subcontractors on safety best practices, safety enhancements, or advise how to do something safer. This is a contract requirement and a liability issue. Alternatively, observed unsafe practices should be reported immediately to the controlling employer who is responsible for overall project site safety and to the HDR project manager, Karen Nichols. An exception to this rule is that if HDR staff witness an unsafe act that they deem to be immediately dangerous to the life or health of any site personnel, the HDR employee should warn any exposed personnel, regardless of company affiliation, to stop their unsafe exposure or activity, and then report the situation as described above.

HDR employees need to be conscious for the safety of other project personnel and are expected to promote safe work habits. Personal safety will take priority over all project deadlines, demands, and any other considerations. "When in doubt, do what's safe." HDR employees are encouraged and empowered by HDR to maintain a safe workplace and only work when the hazards have been removed, controlled, or mitigated. No one will be required to participate in a job related task if his or her safety is at risk.

2.3 Roles and Responsibilities of HDR Employees

HDR employees are required to be continually conscious of safety hazards and are expected to actively participate in all safety training programs relevant to the work which they are performing. Everyone assigned to the Project Team has responsibilities to:

- Plan, organize, and perform each facet of work in the safest manner possible;
- Be constantly alert for unsafe acts and conditions and report them immediately;
- Report unsafe acts or conditions regardless of their level of employment, and
- Attend and actively participate in HDR trainings, meetings, and briefings, including those specified in this HASP.

2.4 Subcontractors

To verify compliance with HDR's H&S program, HDR shall provide HDR subconsultants with this HDR HASP. The subconsultant(s) shall confirm in writing that their H&S plan meets or exceeds the requirements presented herein. When there is a difference or question of H&S policy between HDR and the HDR subcontractor, the matter shall be discussed with the HDR Project Manager, OSC, or HDR Corporate H&S representative to gain resolution, prior to the start of project exposure. In general, the most stringent H&S rules (HDR or subconsultant) shall apply.

2.5 Project Description, Location, and Activities

Water quality monitoring and brine shrimp sample collection for laboratory analysis.

3.0 Emergency Action Plan (EAP)

3.1 Overview

The information contained in this section serves as the Emergency Action Plan (EAP) for the INTERIM MONITORING PLAN: TEMPORARY CLOSURE OF THE EAST CULVERT OF GREAT SALT LAKE CAUSEWAY project. In addition, HDR H&S Procedure #24 - *Emergency Action Plan*, may also be referred to as a reference. This EAP should be transmitted to project employees via verbal discussion at the initial project kick-off meeting or initial site tailgate briefing, and (a) posted at the jobsite in any office space, and/or (b) maintained in project vehicles. Since project conditions may change, update this EAP as necessary.

3.2 Required Information

3.2.1 Emergency Contact Numbers

Insert the following emergency contact numbers prior to leaving for the field.

	Name if Known	
Fire		911
Police		911
Emergency Rescue Services		911
UPRR Project Manager	Mark McCune	(402) 544-5194
HDR Project Manager	Karen Nichols	(801)743-7843
Office or Project Safety Coordinator	Nathan Nichols	801-918-2695 (cell)
Director of Safety	Jim Woolcott	402-399-4823 402-216-8187 (cell)

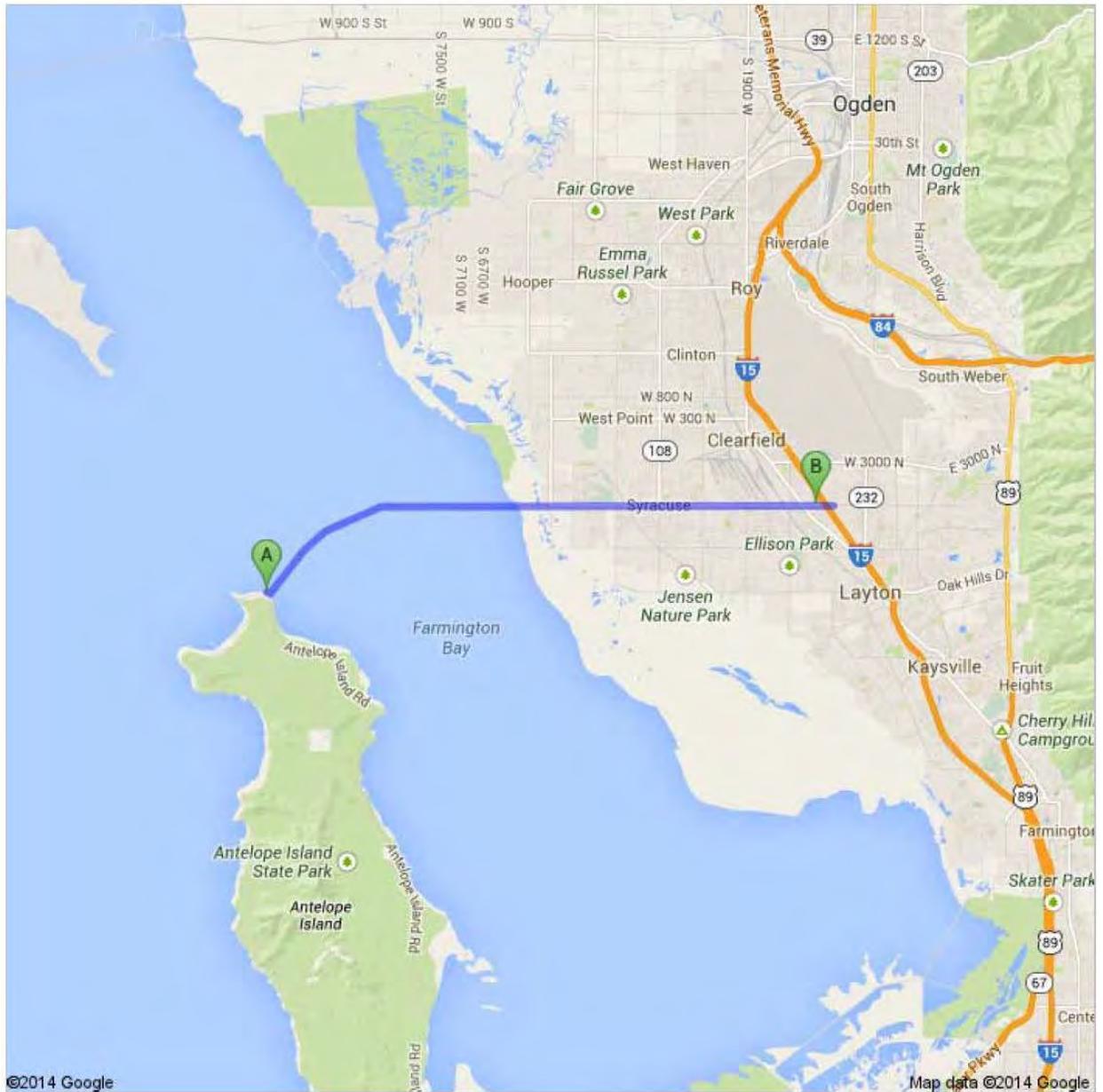
Caution the emergency number "911" is not applicable in all areas. If this is the case, the above numbers should be replaced with appropriate emergency contact numbers.

3.2.2 Medical Facilities

The nearest medical facility to the project location is identified below:

Project name and location	INTERIM MONITORING PLAN: TEMPORARY CLOSURE OF THE EAST CULVERT OF GREAT SALT LAKE CAUSEWAY
Name of nearest medical facility	Davis Hospital and Medical Center
Address	1600 West Antelope Drive, Layton Ut
Phone number	801-807-1000
Hours of operation	24 Hours Emergency

A map to the medical facility is shown below.



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3.3 First Aid/CPR Capability

If the planned project work will be remote (e.g., more than 15 minutes away from the nearest medical facility listed in Section 2.0), then at least one person currently trained in first aid/CPR must be present when project staff are onsite. On multi-employer worksites, this may be a contractor or client employee, as long as they agree to provide coverage. At initial project kick-off meeting, identify all First aid responders, so workers know who to go to if the need arises.

1 For this project, the following individuals have been trained to provide first aid.

First Aid Responder	Training Expiration Date
Chad D. Wiseman (First Aid, CPR, AED)	1/17/15

2 **3.4 Project “Office” Setup (applicable if the project**
 3 **requires an office; otherwise delete)**

4 All office space must be set up with the following:

- 5 • Trailers, once sited, must be securely tied down and grounded;
- 6 • A 20 lb ABC dry powder fire extinguisher must be placed in the space, upright and
 7 fully charged, in an easily accessible location;
- 8 • An OSHA, “Employee Right to Know” Poster should be prominently posted
- 9 • Access to the HDR Health and Safety Program Manual, either in electronic or hard
 10 copy form.
- 11 • A first aid kit of sufficient size for the anticipated number of project staff should be
 12 maintained in the trailer (reference HDR Health and Safety Procedure #30 - *First aid*
 13 *and CPR* [for specific kit requirements]).
- 14 • If project will be of extended duration, a weather radio is strongly recommended.

15 **3.5 Project Vehicles**

16 If the project will provide leased or company vehicles, the question of whether they should be
 17 equipped with fire extinguishers arises. Typically, we want to extinguish electrical harness
 18 fires and save the vehicle, and in these cases, we will locate a 10 lb ABC Fire Extinguisher
 19 under the seat, or in the cab. These are of small capacity and will fully discharge/empty in a
 20 few seconds, so they can only be used to extinguish very small fires. The operator must have
 21 received training on the use and limitations of fire extinguishers, and they should be visually
 22 inspected monthly to ascertain they remain fully charged and operable. They should also be
 23 shaken every month or so, as the normal vibrations generated by the vehicle will tend to
 24 compact the powder extinguishing media.

25 A copy of the project EAP must also reside in each project vehicle – place in glove
 26 compartment or equivalent place to keep from being destroyed by normal activity.

27 **3.6 Fire Emergency**

28 Structural or wild fire emergencies may occur in the project area. Therefore, it is critical that
 29 a fire emergency plan be determined for the project. If a fire of any size is detected by an
 30 employee, the following initial steps shall be followed:

- 1 1. The work shall be stopped and employees shall leave the area as soon as possible.
2 The employees shall gather at the designated Rally Point or an alternative location if
3 the Rally Point is no longer deemed safe.
- 4 2. The appropriate agency shall be notified of the fire; refer to Section 2.0, Required
5 Information.
- 6 3. If the fire is in an incipient stage, authorized fire fighters may attempt to extinguish
7 the fire using fire extinguishers provided in the area.
- 8 4. The on-site HDR safety representative or PM, is to be notified of the situation
9 immediately.
- 10 5. If a fire-related evacuation is ordered, no employee shall be allowed to re-enter the
11 project area until the fire department has declared it safe to do so.

12 **3.7 Inclement Weather**

13 Inclement weather may occur while on the project site or during travel to and from the
14 project. The project team should address any anticipated inclement weather conditions that
15 may impact the team. Weather conditions vary by geographical region and season, and may
16 include lightning, thunderstorm activity, hurricanes, earthquakes, avalanches, high winds,
17 and/or tornadoes. A short discussion on the proper actions of project staff if facing these
18 conditions should be held prior to site arrival. This discussion should include stop work and
19 communication procedures, evacuation routes and shelter locations, in the case of remote
20 project work, as appropriate.

21 **3.8 Incident Reporting**

22 If, despite prevention efforts, a workplace injury should occur, it should be reported to
23 Corporate Health and Safety using the HDR online Accident/Incident Report Form ([LINK](#)),
24 hosted on the H&S portal. A written form may be submitted if online access is unavailable.

25 If the injury requires medical treatment and/or time away from work, make sure to notify
26 your local HR representative AND corporate safety. Corporate H&S should be contacted
27 immediately following any incident that requires emergency medical treatment.

28 **3.9 Regulatory Requirements/References**

- 29 • HDR H&S Procedure #24 - Emergency Action Plan (EAP)
- 30 • HDR H&S Procedure #27 - Portable Fire Extinguishers
- 31 • HDR H&S Procedure #30 - First Aid/CPR

4.0 Defensive Driving

It is imperative that HDR employees use safe driving habits and be continually aware of the hazards associated with operating a vehicle, both within the project area and while commuting to and from the project area. Traffic-related work deaths are eight times the total number of workplace deaths not related to traffic. Of these traffic deaths, approximately 80% are due to human operator error. The four most prevalent operator error factors are driving while impaired, tired, distracted, and/or frustrated (“Road Rage”). Many accidents can be avoided by eliminating or controlling these factors and by driving defensively.

The HDR Vehicle Policy must be reviewed and followed by all HDR employees prior to the use of company vehicles and use of other vehicles while in the course of HDR business.

4.1 Hazard Control

4.1.1 Safe Driving Requirements

While operating any licensed motor vehicle during work-related business, all HDR employees shall conform to the following:

- All HDR employees using a vehicle on company business shall hold a valid driver’s license. This license must be in the vehicle that is being driven.
- Drivers shall not be under the influence of alcohol.
- Drivers shall not be under the influence of, or use any controlled drug or substance, including any amphetamines, narcotic drugs, or any other substance that renders the driver incapable of safely operating a motor vehicle. This does not apply to any substance administered by a physician (medication, medicine) who has advised the driver that the substance will not affect the driver’s ability to safely operate a motor vehicle.
- Excessive speed is a leading cause of automobile crashes, and there is no work function that is so urgent that speeding is necessary. Drivers shall not drive at speeds greater than those prescribed or posted-plan trips to allow adequate drive time.
- Drivers shall obey all traffic signs and signals.
- Drivers and passengers shall wear seat restraint systems during vehicle movement.
- Drivers shall never let anyone ride in the back of pick-up trucks or on their running boards. Passengers may only sit in permanent interior seats designed for passenger occupancy.
- Do not exceed vehicle maximum load capacity, and never load vehicles so that visibility in any window is obstructed.
- All drivers shall not operate a motor vehicle while the driver’s ability or alertness is so impaired, or so likely to become impaired through fatigue, illness, or any other cause as to make it unsafe for him/her to begin or continue to operate the motor vehicle.

- In case of an accident with another vehicle, move to a place of safety (if able to do so) and obtain name, address and telephone numbers of other drivers involved. Contact the local police and do not attempt to move the involved vehicles unless instructed to do so by the police. For any type of accident, always obtain a copy of the police report of the accident. Notify your supervisor as soon as possible.
- HDR employees should avoid all activities which distract or impair the driver's concentration. HDR employees should avoid eating, reading, or operating the vehicle's radio/stereo in such a way that it would cause a distraction while operating the vehicle. **Texting while driving is strictly prohibited.** To keep these distractions from impairing the driver's concentration, drive to a safe location, stop, and perform the necessary activity.
- All HDR employees must comply with the current HDR company policy regarding cellular phones, pagers, and two-way radios as outlined in the HDR Vehicle Policy. Additionally, HDR employees must also follow state and local laws which regulate cell phone usage. Cell phone usage by *Required Driver's* is **prohibited** while driving or operating an HDR owned, leased or rented vehicle, or while driving a personal vehicle in the performance of their job duties.

4.1.2 Safe Driving Tips

- Conduct a pre-trip inspection of your vehicle. Check tire pressure and tread, fluid levels, wiper blades, lights and flashers. Never mix radial tires with other tire types.
- Before operating, get comfortable in the vehicle, lock your seat restraint belt into place, adjust mirrors, and locate and test all controls (lights, windshield wipers, emergency flashers, defroster, etc.). This is especially critical when operating a rental vehicle for the first time. Resist the impulse to immediately drive off the rental lot: take a couple of minutes to adjust mirrors and find the location and operation of the critical accessory controls. Merging into rush hour local traffic is not the time to do this!
- Never warm up a vehicle in an enclosed area, such as a garage. The buildup of carbon monoxide can be fatal.
- Take it slow and think ahead. Keep your eyes on the road. Observe all parts of the environment, not just straight-ahead. Maintain proper following distance (three to four seconds on dry pavement, eight to ten seconds on wet or slippery/icy surfaces) and side space. Identify alternate paths of travel – escape routes in case of emergency.
- In deer prone areas, slow down and scan ahead on both sides for likely spots where deer might suddenly emerge. If one suddenly appears, begin slowing if possible (given traffic conditions) until the danger of collision is past.
- Avoid driving while fatigued. Methods for fighting fatigue include pulling to the side of the road and closing eyes/resting, getting out and moving around at a rest area, rolling down the windows and turning up the radio.

- When pulling into parking lots, park to avoid having to back out if at all possible. Backing a vehicle is a very dangerous activity – visibility is restricted. Take extra care while backing. Use a spotter to help you back up safely if necessary. Do not rely just on mirrors.
- If you lose control of the vehicle due to icy conditions or hydroplaning, take your foot off the accelerator to slow down and regain control. If equipped with traditional brakes, do not apply the brakes while the vehicle is out of control. However, if your car is equipped with anti-lock brakes (ABS) you should immediately apply the brakes to regain control of the vehicle.
- If you experience a tire blow out, your first reaction should be to remove your foot from the accelerator and gain control of the vehicle; do not initially apply the brake, as doing so will increase the sideways momentum. Once you have regained control, pull over to a safe location to change the tire.
- Ensure that the vehicle receives the proper regular maintenance recommended by the manufacturer.
- Ensure that the vehicle has a mechanical jack and spare tire. In addition, depending upon the remoteness of the area you will be traveling, you may consider packing any or all of the following emergency equipment: flashlight, first aid kit, fire extinguisher, flares, and/or tools.

4.2 Training Recommended/Required

All HDR employees who may be using a motor vehicle for HDR company business should read and become familiar with HDR H&S Procedure #32, *Defensive Driving*, the HDR Vehicle Policy, and attend any defensive driving training offered in your area by HDR. Defensive Driving courses are also offered through most state motor vehicle departments.

4.3 Regulatory Requirements/References

- HDR H&S Procedure #32, Defensive Driving
- HDR Vehicle Policy

4.4 Applicable Form(s)

An [Auto Claim Reporting Form](#) can be found on the Legal site. Please complete if an employee is involved in an accident while driving a vehicle owned by HDR or rented for purposes of conducting HDR business.

5.0 Slip, Trip, and Fall Prevention

Each year, physical injuries due to common slips, trips, and falls (S/T/F) while walking account for a significant percentage of all reportable accidents nationwide. Most of these accidents are preventable through proper housekeeping, correct walking surfaces/footwear, and simple precautions. It is the objective of HDR to prevent injuries or “near misses” occurring from same-surface slip, trip, or fall hazards by the identification, elimination, and/or control of these hazardous conditions.

There is a difference between slips, trips, and falls.

- Slips occur when a foot contacts an unexpected slippery surface and slides suddenly forward, resulting in the body falling backwards; head impact and concussions are the likely result.
- Trips occur when the foot unexpectedly contacts something of resistance – a sidewalk crack, higher surface, etc. – that retards planned stride movement, and the body’s momentum causes the person to pitch forward, landing on their front side. Chest, arm, and facial injuries are often the result; very dangerous if holding sharp objects.
- Falls from the same elevation occur when the person’s balance is disrupted for any reason – turned ankle, step into a hole, uneven terrain. The ankle and knee ligaments/tendons are susceptible to injury, as is any body part striking any object during the fall.

So the root cause of all of these remains the same – encountering an unexpected change in the walking surface (change in frictional resistance or level) resulting in a loss of balance.

Common project site sources of S/T/F hazards are:

- Stepping out of vehicles onto uneven terrain/loose gravel/ice – realize you are shifting your weight from a sitting to a standing posture, and transferring this weight onto the new surface. Do this carefully, especially in winter in a parking lot. Initially reduce stride and assess.
- Carrying items while walking. This has several dangers – holding any items reduces your ability to use your hands/arms to recover from a momentary loss of balance, and carrying a large item, such as a box, impedes your view of the walking path in front of you.
- Embarking/disembarking from boats. Very common source of injury. Docks are stationary and at a higher elevation, while boat floors are rocking with wave action, and have clutter/seats, etc. in them, reducing the targeted landing spot for feet. Shifting your weight to leave a dock and embark into a small boat is especially dangerous. Performing a one minute stretch (hamstrings, hips, knee bends, low back) for increased flexibility (aids in balance) is a very good idea before embarking.
- Climbing ladders and walking on elevated grating-type (expanded metal) surfaces. These freeze easily and hide the presence of ice.

5.1 Hazard Control

Most S/T/F accidents can be avoided through:

- **Awareness** – recognize trouble spots/uneven terrain and avoid where possible. Watch your pathway while you walk.
- **Housekeeping** – do not stack materials/cords in walkways, close file drawers, apply de-icer, or manually remove on walking and climbing surfaces – don't create a S/T/F hazard!
- **Wear proper footwear** – many serious injuries result from ankle turns. Wear over-the-ankle boots, laced up snugly. Select soles that offer good traction (lugged, not smooth) and are made from high frictional resistance materials (rubber-like compounds). These two characteristics will prevent many falls and injuries, due to uneven terrain.
- **Stride dynamics** – Slips generally happen when an employee walks across one surface with a higher frictional resistance (e.g., carpet), which sets his/her stride at a fast pace, and then steps with that same stride onto a new surface with a lower resistance (marble, wet floor). Reduce the distance of your stride (space between steps) and slow your pace when first encountering a new walking surface – almost walk gingerly, until you have ascertained what pace the surface friction will support. Keep toes pointed a little outwards to enhance stability; make wide turns around corners. The ultimate stride goal in slick conditions is to keep your center of gravity directly between your legs, and your legs as close to vertical under your trunk!
- Avoid jumping or running on project sites – both actions increase both the likelihood of, and the extent of injury suffered as a result of, a S/T/F.
- **Flexibility** – Strive to increase your flexibility through wellness initiatives. S/T/F hazards are ubiquitous – we cannot escape exposure, whether on the project site or at home. Personal flexibility increases your ability to recover momentary loss of balance, and prevents or minimizes strain/tear damage to tendons and ligaments when a S/T/F does occur.

Notes: Fall hazards of six feet or more (falls from elevation) should be evaluated separately to determine what fall preventive steps might be implemented – fall protection is required at heights of six feet or greater. This six foot rule also applies if walking/stepping across a >6 ft. excavation.

5.2 Personal Protective Equipment (PPE)

PPE of hard hat and protective-toed boots is required on any HDR construction field site.

5.3 Training Recommended/Required

A Slip, Trip and Fall PowerPoint presentation is available through the HDR portal site.

1 **5.4 Regulatory Requirements/References**

- 2 • HDR H&S Procedure #3, Slip, Trip, and Fall Prevention
- 3 • HDR H&S Procedure #12, Fall Protection (fall from elevation)
- 4

6.0 Water and Boating Safety

This project will include activities performed on, over, or near bodies of water. HDR employees must recognize the inherent hazards associated with working in and around water, whether directly exposed through wading/swimming, or potentially exposed while present on surface watercraft or near water bodies.

6.1 Hazard Control

Generally any body of water with a depth of two feet or greater is considered a drowning hazard; however, other factors need to be considered such as flow velocities, water temperature, the ability to rescue injured employees, and the existence of other hazards such as unseen submerged jagged objects, and biological hazards.

At navigation locks, docks, wharves, or other shoreline installations, the wave movement of docked vessels may contribute to struck-by and caught-between hazards. Work within cofferdams may present a severe water hazard, as a sudden rupture can result in engulfment.

6.2 Personal Protective Equipment (PPE)

6.2.1 Personal Floatation Device

HDR employees working (a) out of any boat, (b) over or adjacent to water with a depth of two feet or more, or (c) wherever the danger of drowning exists, must wear a United States Coast Guard (USCG) approved Personal Flotation Device (PFD), also called “life preservers.” If worn properly, these are designed to keep your head above water and prevent drowning. Specifications for various PFDs are presented below. Exception: Employees protected from falling into water by using fall arrest systems, and those conducting inspections that involve climbing structures above or below the bridge deck. In the latter case, a life ring with rope and a skiff must be available.

The USCG divides all PFDs into five current classifications. Two classes are approved for general HDR use as PFDs – Class III and V. These are designed to be worn as apparel around the body during all times of water exposure. Type IV is a circular life ring designed to be thrown to personnel who are in the water, as a rescue measure. Types I and II are full body float suits suitable for off-shore or open ocean use.

Personal Flotation Devices

Classification	Design	OSHA / Comments
Type I – Offshore Life Jacket	Designed to turn an <u>unconscious</u> person in water to vertical position. Open ocean apparel. <i>Designed with minimum 35 lbs. buoyancy</i>	While acceptable, they are very bulky and will limit mobility. Emergency use only. Not for everyday use.

<p>Type II – Near shore Buoyant Vest</p>	<p>Designed to turn an <u>unconscious</u> person to a vertical position. Coastlines, Great Lakes, etc. <i>>15½ lbs. buoyancy.</i></p>	<p>While acceptable, they are very bulky and will limit mobility. Not for everyday use.</p>
<p>Type III – Flotation Aid</p>	<p>Designed to keep a <u>conscious</u> person in a vertical position. Designed for everyday water activities (e.g., boating, skiing) <i>Minimum 15½ lbs. buoyancy.</i></p>	<p>Acceptable for all HDR activities. (New Type III <u>inflatable</u> PFDs are approved <u>only</u> if rated for commercial or industrial use).</p>
<p>Type IV – Throwable Device (Life Ring)</p>	<p>Throw rings designed to be thrown into the water for rescue. Not worn on body. <i>Minimum 16½ lbs. buoyancy.</i></p>	<p>Required in boats, on wharfs and in certain shore situations.</p>
<p>Type V – Special Use Device</p>	<p>Catchall category - various designs for specific water activities – includes deck suits, work vests, hybrid PFDs, etc. <i>Minimum 15½ lbs. buoyancy.</i></p>	<p>Acceptable for HDR activities as long as mfg. label does not exclude from use in planned work activity. (See note below)</p>

1 **NOTE:** There are now many Type V PFDs marketed that are inflatables. OSHA specifies
 2 that only Type V PFDs approved for “commercial” or industrial” use are allowed to be worn
 3 during employment activities. This prohibits the use by HDR personnel of commonly
 4 marketed inflatable PFDs advertised or rated for “recreational” use.

5 **NOTE:** For cold weather work on boats, or on floating docks where the risk of falling into
 6 the water is present, if the water plus air temperature is less than 110° Fahrenheit a float coat
 7 or a float suit must be worn in lieu of a vest-type PFD. Simply stated:

- 8 • Water temperature + air temperature < 110 °F = float coat or suit required.
- 9 • Water temperature + air temperature ≥ 110 °F = vest-type PFD allowed.

10 **6.2.2 Waders**

11 If staff are planning to wade into shallow water, waders (in addition to the PFD) are required.
 12 Waders come in in two styles – either as a single large pants unit, or as individual leg
 13 protectors. While waders protect from water contact, if allowed to fill with water during a slip
 14 or fall, can become an anchor in rapid currents, pulling the wearer downstream and under the
 15 surface. The critical safety factors in wader selection are that the wader be appropriate both
 16 seasonally (provide insulation), environmentally appropriate (good traction, material allowed
 17 by local regulation), and sized appropriately for the wearer. Some project work may
 18 necessitate that two sets of waders be acquired – e.g., rubber and either neoprene or
 19 breathable – for use depending on temperature of water and climate changes.

20 **6.3 Training Recommended/Required**

21 HDR employees subject to water hazards are required to complete training on HDR H&S
 22 Procedure #18, *Water and Boating Safety*. Training shall be provided by the OSC or other
 23 designated provider who, through experience and/or past training, has the necessary water
 24 safety knowledge and skills. This training must include a demonstration of the correct way to
 25 don a life vest, and the importance of pre-use inspection.

6.4 Regulatory Requirements/References

- 29 CFR 1926.106, Working Over or Near Water
- 29 CFR 1926.605, Marine Operations and Equipment
- 23 CFR 1926.802, Cofferdams
- HDR H&S Procedure #18, Water and Boating Safety

6.5 Applicable Form(s)

The checklist on the next page is based on the HDR H&S Procedure #18, *Water and Boating Safety* and information obtained from the U.S. Coast Guard website (<http://www.uscg.mil/>), *Use, Wear and Care of PFDs for Commercial Applications*. It is not to be construed as complete.

7.0 Water and Boating Safety Attachment

Water Safety Checklist

Prior to Conducting Activities on or Near Water

Life Rings or Buoys

- Life rings or ring buoys are readily available.
- Life rings have lights when used after dark.

Safety Blocks

- Safety blocks are available for employees working on shoreline installations.

Life Vests

- All HDR employees are wearing CGSB approved life vests (PFDs).
- All PFDs have been inspected for defects prior to the start of work:
 - Original float material is present
 - Buoyant material is securely held in position
 - Webbing or straps are not ripped, torn, or separated from an attachment point on the PFD
 - No structural components fail when tugged
 - There are no rips, tears, or holes
 - All seams in fabric or coatings are sealed and securely stitched
 - Metal or plastic hardware, including buckles and straps, are whole, properly formed, and not corroded
 - No signs of water logging, mildew odor, or shrinkage of the buoyant materials
 - No air leaks (for kapok PFDs check by gently squeezing the bag)

Following work on or near water

- PFDs are drip-dried thoroughly before they are put away.
- PFDs are stowed in a well-ventilated place.

Safety Skiffs

- At least one skiff is immediately available for use in rescue.
- Personnel that are trained in launching and operating the skiff are readily available.
- Skiffs either are kept afloat or ready for instant launching.
- Skiffs are fully equipped:
 - Four oars (Two if the skiff is motor powered);
 - Oarlocks attached to gunwales or the oars;
 - One ball-pointed boat hook;
 - One ring buoy with 27 meters feet of solid braid polypropylene or equivalent line attached, and
 - PFDs in number equaling the skiff rating for the maximum number of personnel allowed onboard.
- Navigation lights are available and used for night operations.

1 **Cofferdams**

- 2 If overtopping of the cofferdams by high water is possible, provisions for controlled flooding of the
3 work area have been designed into the system.
- 4 If personnel or equipment are required or permitted on cofferdams, standard railings or equivalent,
5 protection are provided.
- 6 At least two means of rapid exit are provided for personnel and equipment working on cofferdam
7 walkways, bridges, or ramps.
- 8 A plan (including warning signals) for evacuation of personnel and equipment in case of emergency
9 and for controlled flooding has been developed and posted in the immediate project area.
- 10 Cofferdams located close to navigable shipping channels shall be protected from vessels in transit.

11 **Floating Barges**

- 12 Ramps for access of vehicles to or between barges are:
- 13 Of adequate strength
- 14 Provided with sideboards
- 15 Well maintained
- 16 Properly secured
- 17 Unless employees can step safely to or from the wharf, float, barge, or river towboat, either a ramp or
18 a safe walkway has been provided.
- 19 Jacob's ladders are of the double rung or flat tread type.
- 20 They are securely fastened at the top
- 21 The rungs are well maintained
- 22 The rungs have no visible cracks or defects
- 23 Either a Jacob's ladder hangs without slack, or it is pulled up entirely.
- 24

8.0 Cold Stress

HDR employees conducting extended fieldwork during periods of low temperatures or in cold, wet conditions are subject to cold-related disorders. This section describes the hazards associated with exposure to cold temperatures, and the proper responses to prevent or minimize adverse health effects. Since there is no specific OSHA regulatory standard addressing cold stress, the guidelines presented here are in conformance with the recommendations presented in the publication, *Threshold Limit Values for Chemical Substances and Physical Agents* (latest year), published by the American Conference of Governmental Industrial Hygienists (ACGIH).

8.1 Hazard Control

Cold-induced injuries include immersion (trench) foot, frostbite, hypothermia, and Raynaud's Phenomenon, all or most of which can result in loss of a limb or death if not properly treated. These cold-induced illnesses and the preventative methods available for implementation should be discussed with the project staff prior to going to the field. Project management must make sure that field staff are provided with adequately insulated personal protective clothing, fluids, and warm up shelters as needed prior to cold weather project initiation. Team leaders should remind staff to drink adequate fluids, change wet clothing, and take warm up breaks as necessary during project execution.

8.1.1 Prevention Methods

Maximum **severe shivering** indicates that there is a significant decrease in the body's core temperature. Therefore, exposure to cold should be immediately terminated for any HDR employee when observable shivering occurs – get the employee into a warm area for recovery.

Pain in the extremities is commonly the first early warning sign of the onset of cold stress. Don additional warm, dry clothing, especially on the affected body part (hands, feet, head).

Wear adequate insulating dry clothing if work is to be performed in air temperatures below 40 °F (4 °C).

Wind is an enemy in cold weather, as it rapidly strips the body of heat. Wear wind resistant outer clothing and cover the head, where much heat loss occurs.

At air temperatures below 36 °F (2 °C), it is imperative that **workers who become immersed in water or whose clothing becomes wet** (from external sources, not incidental sweat) be immediately provided a complete change of clothing and remain in a warm area while being observed for symptoms of hypothermia.

Workers who are **suffering from diseases or taking medication that interferes with normal body temperature regulation**, or which reduces tolerance to cold environments, should be excluded from prolonged work in cold below 30°F (-1 °C).

For **exposed** skin, continuous exposure should not be permitted when the wind chill reaches -25 °F (-32 °C). Refer to local weather reports or the wind chill chart in this section to determine current equivalent chill temperature. If outside work must be conducted in this

1 extreme cold, cover all exposed skin with clothing, layering as necessary. Take frequent
2 breaks in a warm shelter, and loosen clothing to allow sweat to evaporate.

3 Cold temperatures greatly increase the susceptibility to **vibration-induced injury**. When
4 working in cold environments limit exposure time to vibrating tools and mechanical
5 processes – incorporate job rotation among available staff to minimize duration of exposure.

6 **Dehydration** occurs insidiously in cold environments, and may increase the susceptibility of
7 the worker to cold injury due to a significant change in blood flow to the extremities. Warm
8 sweet drinks and soups should be provided at the work site to replenish caloric intake and
9 fluid volume. The intake of coffee, however, should be limited because of the diuretic and
10 circulatory effects. The same applies to alcohol consumption, which increases blood
11 circulation to the skin, and interferes with mental acuity, which can lead to risk taking.

12 These recommendations apply to healthy employees in fair to good physical condition. Older
13 employees or those with circulatory problems may need to avoid extremely cold
14 environments, or wear extra clothing; if in doubt, the employee should consult a physician
15 familiar with cold stress factors and their medical condition.

16 8.2 Care for Cold-Related Illnesses

17 There are four types of cold-induced injury resulting from prolonged cold exposure:
18 hypothermia, frostbite, immersion foot, and Raynaud’s phenomenon. **All cold-related**
19 **injuries require immediate removal from the cold environment and proper medical**
20 **treatment.** The supportive first aid measures included here are to be used only until proper
21 medical treatment by a qualified physician can begin.

22 8.2.1 Hypothermia

23 Hypothermia results when the body core temperature falls below 95 °F (35 °C), a critical
24 body threshold. Below this point, the victim cannot produce enough body heat by himself or
25 herself to recover. At this point, a true medical emergency exists. **True hypothermia always**
26 **requires immediate attention**, since untreated hypothermia can lead to ventricular
27 fibrillation (heart attack) and death. Visual warning signs are a possible reduction in
28 shivering, slurred speech, inactivity, and/or disorientation.

29 Remove the victim to a warm area out of any wind. Remove all cold wet clothing and wrap
30 the victim in warm blankets. The victim may be disoriented and unable to talk clearly or
31 understand simple questions. If conscious and able to converse, they may be given warm
32 (non-caffeinated, non-alcoholic) liquids to drink, and sweetened foods high in carbohydrates.
33 Keep victim awake until medical assistance arrives.

34 8.2.2 Frostbite

35 Frostbite is the actual freezing of body tissue. The extremities are most commonly affected,
36 and therefore frostbite generally first appears in toes, fingers, nose, and ears. Regardless of
37 the wind chill, frostbite does not occur until the absolute ambient temperature falls below
38 freezing, 32 °F (0 °C), or when bare skin is in contact with some object below this
39 temperature. **The first warning of frostbite is often a sharp prickling sensation.**
40 Frostbitten skin is characterized initially by turning red, then blue/red, and finally by loss of

1 color and feeling in the affected tissue. The skin may become waxy pale in appearance
2 because of a lack of oxygen. **Frostbite damage may be reversible if properly treated in**
3 **the first 12 to 24 hours.** If not treated, frostbitten areas may become gangrenous. Workers
4 who have suffered frostbite are susceptible to future recurrences and subsequent injury.

5 The affected area should be gradually warmed (immediate or sudden heating of affected areas
6 must be avoided, to minimize further tissue damage). Superficial frostbitten areas
7 (characterized by a sudden blanching or whitening of the skin, firm to the touch, resilient
8 tissue beneath) are best warmed by placing them next to warm skin. A good guideline when
9 rewarming frostbitten areas is to not raise the temperature much above that of the body. The
10 abdomen and the armpit are body areas that can be used to rewarm frostbitten areas. Deep
11 frostbitten tissue is characterized by cold, pale, or darkened tissue that is solid to the touch.
12 **Do not rub the frostbitten part, and do not break any blisters.** Wrap the affected part
13 lightly, protect from further injury, and do not allow the victim to use the affected limb or
14 area until cleared by a physician.

15 8.2.3 Immersion Foot (Trench Foot)

16 Immersion foot, aka “trench foot,” is caused by chronic cooling for prolonged periods, and is
17 most commonly seen in workers who stand in cold water for long continuous periods. Injury
18 is thought to be due to persistent local tissue anoxia, resulting in damage to the blood
19 capillary walls. This condition may be aggravated by tight footwear. It is characterized by
20 intense pain, tingling, itching, and discoloration of the foot.

21 When possible, air-dry and elevate your feet, and exchange wet shoes and socks for dry ones
22 to help prevent the development of trench foot.

23 Treatment for trench foot is similar to the treatment for frostbite. Take the following steps:

- 24 • Thoroughly clean and dry your feet.
- 25 • Put on clean, dry socks daily.
- 26 • Treat the affected part by applying warm packs or soaking in warm water (102 °F to
27 110 °F) for approximately five minutes.
- 28 • When sleeping or resting, do not wear socks.
- 29 • Obtain medical assistance as soon as possible.
- 30 • If you have a foot wound, your foot may be more prone to infection. Check your feet
31 at least once a day for infections or worsening of symptoms.

32 8.2.4 Raynaud’s Phenomenon

33 Raynaud’s phenomenon, also called “white fingers,” is used to describe a vascular hand
34 abnormality characterized by a loss of circulation associated with exposure to cold, and/or
35 vibration. The onset of Raynaud’s phenomenon is gradual, and is characterized by several
36 stages. The initial stage is manifested by occasional pain, and a slight loss of hand sensitivity.
37 If removed from cold and vibration, it is usually reversible at this stage. As the condition
38 worsens, pain and numbness increases, and finger sensitivity decreases. As the blood vessels
39 are damaged, blood flow slows and the skin temperature decreases. In the pronounced stages,

1 fingers become white and the hands feel cold and moist. At this point, the condition is
2 irreversible. Employees who routinely work in cold environments should limit the duration
3 that they use rotating or vibrating tools.

4 **8.3 Personal Protective Equipment (PPE)**

5 The primary protection against cold-related injuries is the use of thermal protective clothing.
6 In general, employees should wear adequate insulating dry clothing in air temperatures below
7 40 °F (4 °C) or when wind chill reaches –25 °F (–32 °C). If subjected to the extreme cold,
8 cover all exposed skin with clothing, layering as necessary. Wear mittens or gloves, an outer
9 layer of clothing impermeable to water, when the possibility of becoming wet through
10 splashing is present, and a light windbreaker-type jacket to protect against the wind.

11 If steel-toed safety shoes transmit cold and become uncomfortable, substitute alternative
12 protective footwear, such as, high impact plastic/rubber footwear.

13 In brief, many layers of light clothing are better than one or two heavy layers. The outer layer
14 should be wind-resistant, and the layers should be capable of being vented at the wrist, neck,
15 and waist to reduce wetting by perspiration. Moisture (sweat) reduces the ability of the
16 clothing to trap air, as well as removing heat from the skin surface as sweat evaporates. It is
17 important the employees bring additional clothing to replace any clothing that becomes wet
18 from external water sources or from perspiration.

19 Also, eye protection for out-of-doors work in snow and/or ice covered terrain should be worn.
20 Safety glasses/ goggles with ultraviolet/glare protection should be worn when snow could
21 cause blowing ice crystals or reflective radiation.

22 **8.4 Training Recommended/Required**

23 All HDR employees who work on project sites in cold weather should be provided awareness
24 training on cold stress, including proper clothing practices, proper eating and drinking habits,
25 recognition of impending frostbite, signs/symptoms of hypothermia, and cold injury
26 avoidance work practices. HDR's *Cold Stress* PowerPoint presentation, available through the
27 H&S Department, fulfills this requirement.

28 **8.5 Regulatory Requirements/References**

- 29 • ACGIH, Threshold Limit Values for Chemical Substances and Physical Agents
- 30 • HDR H&S Procedure #29, Cold Stress

31 **8.6 Applicable Form(s)**

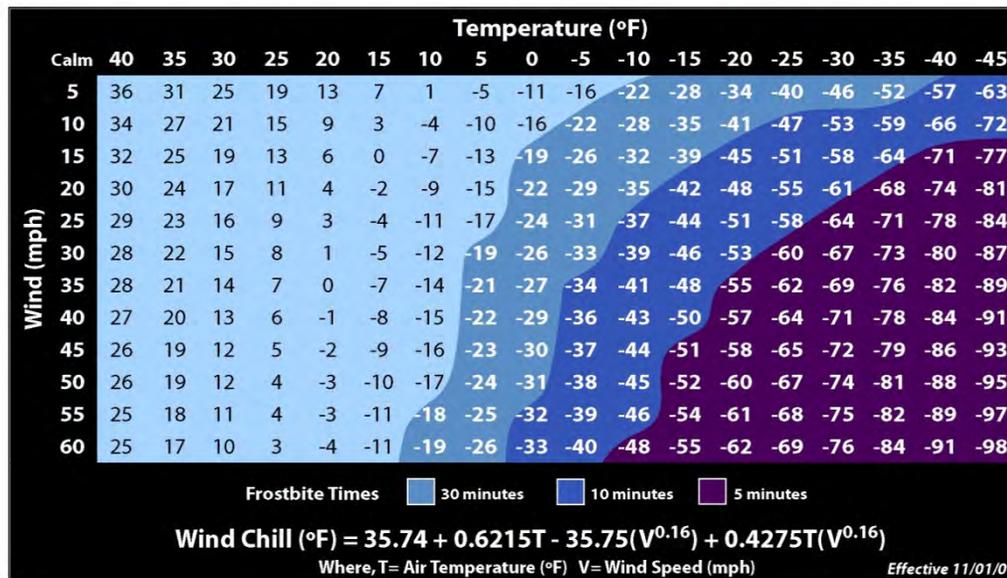
- 32 • Threshold Limit Values Work/Warm-Up Schedule for Four Hour Shift (attached)
- 33 • Wind Chill Chart (attached)

9.0 Cold Stress Attachment

THRESHOLD LIMIT VALUES WORK/WARM-UP SCHEDULE FOR FOUR-HOUR SHIFT*											
Air Temperature Sunny Sky		No Noticeable Wind		5 mph Wind		10 mph Wind		15 mph Wind		20 mph Wind	
°C (approx)	°F (approx)	Max. Work Period	No. of Breaks								
-26° to -28°	-15° to -19°	(Norm breaks) 1		(Norm breaks) 1		75 min.	2	55 min.	3	40 min.	4
-29° to -31°	-20° to -24°	(Norm breaks) 1		75 min.	2	55 min.	3	40 min.	4	30 min.	5
-32° to -34°	-25° to -29°	75 min.	2	55 min.	3	40 min.	4	30 min.	5	Non-emergency work should cease	
-35° to -37°	-30° to -34°	55 min.	3	40 min.	4	30 min.	5	Non-emergency work should cease			
-38° to -39°	-35° to -39°	40 min.	4	30 min.	5	Non-emergency work should cease		Non-emergency work should cease			
-40° to -42°	-40° to -44°	30 min.	5	Non-emergency work should cease		Non-emergency work should cease		Non-emergency work should cease			
-43° to below	-45° & below	Non-emergency work should cease									



Wind Chill Chart



*Source: Adapted from *Threshold Limit Values (TLV) and Biological Exposure Indices (BEI)* booklet: published by ACGIH, Cincinnati, Ohio, 2008.

10.0 Heat Stress

Extended Fieldwork conducted during periods of high temperatures and/or humidity can result in heat-related disorders. This section describes the hazards associated with exposure to high temperatures and the proper responses to prevent or minimize adverse health effects. While there is no specific OSHA standard addressing heat stress, these guidelines are in conformance with the recommendations presented in the publication, *Threshold Limit Values for Chemical Substances and Physical Agents* (latest year), published by the American Conference of Governmental Industrial Hygienists (ACGIH).

10.1 Hazard Control

Prolonged exposure to heat can result in heat rash (prickly heat), heat cramps, heat exhaustion, or heat stroke. Heat stroke is life threatening and requires immediate professional medical attention. Expanded descriptions of each of these ailments can be found in HDR's H&S Procedure #28, *Heat Stress*. An overview of these heat-induced illnesses and proper preventative actions should be discussed with the project staff prior to going to the field.

10.1.1 Prevention Methods

Begin Work Hydrated – It is critical that all field staff arrive daily at the project location fully hydrated. The importance of this cannot be overstated – beginning work in a hot environment dehydrated will result in further dehydration. Continue drinking non-alcoholic fluids after work each day, to replenish fluids prior to work the next day.

Provision for Water (or other drinking fluids) – One quart per hour per employee of non-alcoholic, decaffeinated, cool (50 to 60° F) drinking fluids needs to be readily available to exposed HDR employees. Smaller volumes are acceptable if fluids can easily be replenished. When working in the heat, drinking fluids should be consumed at a target rate of one cup (eight ounces) every 20 minutes at a minimum. During plan development, project planning must consider the weight, volume, and transportation of cooled fluids that are necessary for field staff use at the field site – this may be the most important safety element of hot fieldwork. Team leaders should encourage all heat-exposed staff to drink frequently!

Self Monitor Hydration – urine should be pale yellow in color. If dark yellow, increase fluid consumption!

Access to Shade (rest area) – Generally, ambient temperatures over 85°F require access to shade. Employees exhibiting symptoms of heat illness, or believing a preventative recovery period is needed, should be provided access to a shaded rest area that is either open to the air or provided with ventilation or cooling for a period of no less than five minutes. Access to this shaded resting area shall be permitted at all times. If none is available, use your vehicles air conditioning unit to cool down.

Additional Prevention Methods – Consider employee factors such as acclimatization, fitness, previous exposure to heat illness, age, and individual abilities to handle the heat. Carefully oversee the field efforts of new employees, frequently reminding them to drink, and take shade breaks until they become acclimated to the heat.

1 Inform female workers of the possible adverse consequences of hot work while pregnant due
2 to elevated core body temperatures.

3 Avoid the use of alcohol and caffeinated beverages which contributes to dehydration and
4 reduced heat tolerance.

5 10.2 Care for Heat-Related Illness

6 In case a heat-induced illness occurs during field activities, make sure project teams are
7 knowledgeable about how to contact and direct emergency medical assistance to the field
8 site.

9 10.2.1 Heat Rash (Prickly Heat)

10 Heat rash, which is commonly observed in tropical climates, is a painful temporary condition
11 caused by clogged sweat pores, typically from sleeping in hot, humid quarters. Heat rash
12 appears as tiny red bumps on the skin, and can impair sweating, resulting in diminished heat
13 tolerance. Heat rash can usually be cured by providing cool sleeping quarters; body powder
14 may also help absorb moisture.

15 10.2.2 Heat Cramps

16 Heat cramps are characterized by painful intermittent spasms of the voluntary muscles
17 following hard physical work in a hot environment. Heat cramps usually occur after heavy
18 sweating, and often begin towards the end of the workday. The cramps are caused by a loss of
19 electrolytes, principally salt. This results in fluids leaving the blood and collecting in muscle
20 tissue, resulting in painful spasms. Treatment consists of increased ingestion of commercially
21 available electrolytic “sports” drinks (because of individual sensitivity, it is best to dilute by
22 doubling the amount of water required by package directions, or add water to the liquid
23 form).

24 10.2.3 Heat Exhaustion

25 This condition is characterized by profuse sweating, **weakness**, low blood pressure, rapid
26 pulse, dizziness, and frequently nausea and/or headache. The skin is cool and clammy, and
27 appears pale. The body core temperature is normal or depressed. Victim may faint and/or
28 vomit. **This is the most common work-related heat illness**, and usually occurs after an
29 extended period of work – look for signs of onset after lunch – employee may suddenly need
30 to sit down, feel faint, weak, or nauseated.

31 First aid consists of placing the victim in a cool area, loosening clothing, placing in a head-
32 low (shock prevention) position, and providing rest and plenty of fluids. **Any worker who is**
33 **a victim of heat exhaustion may not be exposed to a hot working environment for an**
34 **absolute minimum of 24 hours, and if fainting has occurred, the victim should not**
35 **return to any work until authorized by a physician.**

10.2.4 Heat Stroke

This is the most serious heat disorder, and is life threatening.

Heat stroke is a true medical emergency. This results when the body's heat dissipating system is overwhelmed and shuts down (thermoregulatory failure). Heat stroke results in a continual rise in the victim's deep core body temperature, which is fatal if not checked. The symptoms are hot, dry, flushed skin, elevated body core temperature, convulsions, delirium, unconsciousness, and possibly, death.

First aid consists of immediately moving victim to a cool area; cool the body rapidly by immersion in cool (not cold) water or sponging the body with cool water; treat for shock and obtain immediate medical assistance. Treatment response time is critical when assisting a victim of heat stroke! Do not give coffee, tea, or alcoholic beverages.

10.3 Personal Protective Equipment (PPE)

Unfortunately, there is no known PPE to prevent heat-related illnesses. It is recommended, however, that clothing be light, loose fitting, and breathable. The use of impermeable PPE clothing such as those made of Tyvek®, is discouraged, as the risks of heat-related illness are significantly elevated. If protective clothing is required, special precautions must be taken to address the elevated heat stress risk.

10.4 Training Recommended/Required

All HDR employees who will be conducting field activities on this project should receive awareness training on heat stress. HDR's University website offers a PowerPoint presentation, Module E2A, *Outdoor Settings, Part 1*, which includes a component on heat stress.

10.5 Regulatory Requirements/References

- American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values for Chemical Substances and Physical Agents
- HDR H&S Procedure #28, Heat Stress

10.6 Applicable Form(s)

The project or designated Health and Safety Officer shall record all monitoring results on the [HDR Heat Stress Log](#).

Appendix C
Quality Assurance Project Plan

Quality Assurance Project Plan

to support:
Utah Division of Water Quality
Utah 401 Water Quality Certification No. SPK 2011-00755
Issued: December 16, 2013

and

U.S. Army Corps of Engineers
NWP 14 Permit SPK-2011-00755
Issued: December 6, 2013

Temporary Closure of the East Culvert, Great Salt Lake Causeway

Submitted by
Union Pacific Railroad
1400 Douglas Street
Omaha, NE 68179-0910

January 16, 2014
Revised March 10, 2014

Group A Elements: Project Management

1.0 Title and Approval Sheet

This Quality Assurance Project Plan (QAPP) is to be used by HDR, Inc. when collecting water quality monitoring data in support of Union Pacific Railroad's (UPRR) Culvert Closure and Bridge Construction Project, Great Salt Lake Causeway (project), located in Box Elder County, Utah. This QAPP was designed to be consistent with State of Utah's *Draft Quality Assurance Project Plan for the Great Salt Lake Baseline Sampling Program*, which is incorporated into this QAPP by reference (UDWQ 2013).

APPROVAL SIGNATURES

Union Pacific and Consultant Team

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
Project Manager			
QA Officer			
Monitoring Coordinator			
Technical Advisor			

Utah Division of Water Quality

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
Permit Manager			
QA Officer			

** This is a contractual document. The signature dates indicate the earliest date when monitoring for the project can start.*

Notes:

UPRR = Union Pacific Railroad

QA = Quality Assurance

HDR = HDR Engineering, Inc.

UDWQ = Utah Division of Water Quality

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2.3 List of Acronyms

°C	degrees Celsius
µg/L	micrograms per liter
ASTM	American Society for Testing and Materials
CCV	continuing calibration verification
COC	chain of custody
DO	dissolved oxygen
DQO	data quality objective
DQR	Data Quality Report
EPA	U.S. Environmental Protection Agency
FSP	Field Sampling Plan
GPS	global positioning system
HCl	hydrochloric acid
HDPE	high-density polyethylene
HNO ₃	nitric acid
ICS	interference check samples
ICV	initial calibration verification
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LCL	lower control limit
MB	method blank
MDL	method detection limit
mg/kg	milligrams per kilogram
mL	milliliters
MS	matrix spike
MSD	matrix spike duplicate
NELAC	National Environmental Laboratory Accreditation Conference
PARCC	precision, accuracy, representativeness, completeness, and comparability
PARCCS	precision, accuracy, representativeness, comparability, completeness, and sensitivity
PE	performance evaluation
QA	quality assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	quality control
%R	percent recovery
RF	response factor
RL	reporting limit
RPD	relative percent difference
RSD	relative standard deviation
RT	retention time
SOP	standard operating procedure
UAC	Utah Administrative Code
UPRR	Union Pacific Railroad

3.0 Distribution List

This document will be distributed to the key personnel listed in Table 3-1 and will be provided as an attachment to relevant reports and upon request.

Table 3-1. Personnel Responsibilities

Name	Affiliation	Title	Contact Information
Mark McCune	UPRR	Project Manager	
Karen Nichols	HDR	HDR Project Manager	
Chad Wiseman	HDR	Monitoring Coordinator	
Carin Loy	HDR	QA Officer	
TBD	HDR	Data Manager	
TBD	TBD	Laboratory Project Manager	
TBD	EcoAnalyts	Taxonomic Laboratory Project Manager	

QA = Quality Assurance

TBD = to be determined

UPRR = Union Pacific Railroad

4.0 Project/Task Organization

4.1 Involved Parties and Roles

This QAPP has been prepared to support water quality monitoring component(s) of UPRR's Culvert Closure and Bridge Construction Project, Great Salt Lake Causeway. Within this QAPP are descriptions of methods, procedures, and practices that will be used to assure and control the quality of chemical data.

Key personnel who will be involved in the project are listed above in Table 3-1. Under contract to UPRR, HDR will be responsible for all aspects of the water quality monitoring including the organization of field staff, scheduling of sampling days, field quality assurance/quality control (QA/QC), coordination with the off-site laboratory, and reporting.

The Monitoring Coordinator is responsible for monitoring and verifying implementation of the QA/QC procedures found in this QAPP. Key personnel assigned to the project will have reviewed the QAPP and will be instructed by Monitoring Coordinator regarding the requirements of the QA/QC program. The Monitoring Coordinator will work directly with the field staff and Laboratory Project Managers to ensure that QAPP objectives are being met. All members of the team will continually assess the effectiveness of the QA/QC program and recommend modifications, as needed.

4.2 Quality Assurance Officer Role

The QA Officer is familiar with the study, but not involved in day-to-day implementation. The QA officer is versed in HDR policies, water quality field sampling, and laboratory procedures. The QA officer will review the study's intermediate and final products, and work with the Monitoring Coordinator to ensure they are of high quality when complete.

The QA Officer is responsible for monitoring and verifying implementation of the QA/QC procedures found in this QAPP and its referenced Standard Operating Procedures (SOPs). Key personnel assigned to the project will have reviewed the QAPP and monitoring plan, and will be instructed by the QA Officer regarding the requirements of the QA/QC program. The QA Officer will work directly with the Monitoring Coordinator or other designee and Project Manager to ensure that QAPP objectives are being met. Laboratory analytical services will be provided by a nationally-certified laboratory.

4.3 Persons Responsible for QAPP Update and Maintenance

The Monitoring Coordinator is responsible for keeping the QAPP up-to-date. The project team will continually assess the effectiveness of the QA/QC program and recommend modifications, as needed. Modifications may be instigated by any member of the study team—the Monitoring Coordinator, field staff, the QA Officer, the laboratory project manager, or others. Revisions to the content of this document will be formalized in the table following the title page. New versions of the QAPP will be available to project personnel and attached to subsequent reports. If there are any variances or non-conformances with the QAPP, they will be documented in applicable monitoring report.

4.4 Organizational Chart and Responsibilities

The organizational chart for implementation of the water quality investigation component of the project is presented in Figure 1.

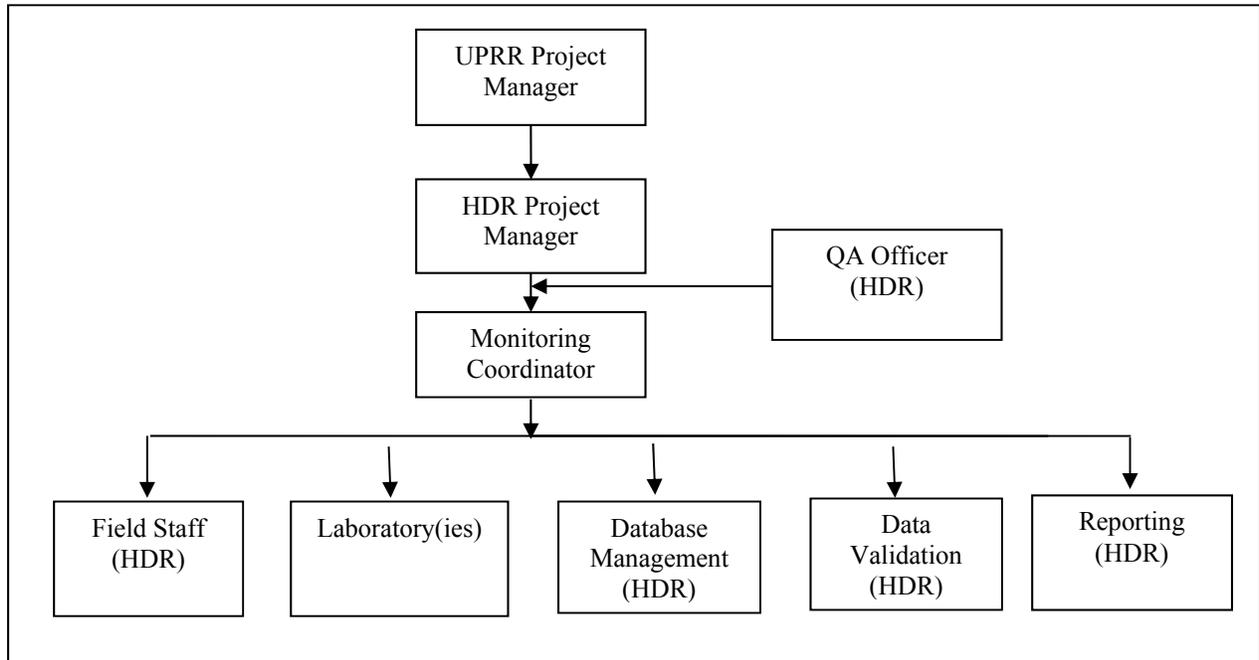


Figure 1. Organizational Chart

5.0 Problem Definition/Background

5.1 Problem Statement

UPRR's Culvert Closure and Bridge Construction Project will be implemented through phases or "tasks," the first of which is the temporary causeway east culvert closure. Water quality monitoring is required or is anticipated to be required by the environmental permits (for example, Utah 401 Water Quality Certification, Clean Water Act Section 404 permit) associated with each task. This QAPP has been developed to provide guidance and quality assurance for water quality sampling and analyses conducted to implement the monitoring requirements. Task-specific information, such as sample locations, can be found within each task's monitoring plan. As practicable, each monitoring plan developed to support the culvert closure and bridge construction will be consistent with "sampling and analyses plan" requirements described in the Utah Division of Water Quality's *Checklist of Essential Elements for Sampling and Analysis Plans* (UDWQ, no date).

5.2 Decisions or Outcomes

The collected data will provide one or more “snap-shots” of the physical and/or chemical state of surface water in the study area, as required in the permit(s) and defined in the task monitoring plan. The data will be filed with the requesting agency. The data may be integrated with other information or data and used for trend analyses or for modeling. Additional information and detail can be found in the project monitoring plan.

5.3 Water Quality Regulatory Criteria

Great Salt Lake’s beneficial uses include of primary and secondary contact recreation, which consists of activities such as swimming, wading, boating, and fishing (Utah Administrative Code [UAC] R317-2-6.5). Waterfowl, shorebirds, and other water-oriented wildlife including the aquatic organisms in their necessary food chain are the components of the wildlife beneficial use for Great Salt Lake (UAC R317-2-6.5).

Great Salt Lake has only a single numeric criterion to protect beneficial uses. It describes the maximum selenium concentration in bird eggs necessary to protect the lake’s aquatic wildlife (12.5 mg/kg dry-weight) (UAC R317-2-14). The State of Utah’s narrative anti-degradation standard applies to all other constituents (UAC R317-2-3).

6.0 Project/Task Description

6.1 General Work Statement

Each monitoring plan details the scope of the water quality monitoring to be undertaken. Chemical constituents and characteristics of surface water will be measured both in the field and through collection of water quality samples for off-site laboratory analyses by a nationally certified laboratory. Examples of in situ water field measurements that may be performed include pH, specific conductivity, instantaneous water temperature, dissolved oxygen (DO), DO percent saturation, turbidity, and Secchi disk. Examples of analyses that may be performed on samples sent to an off-site laboratory are trace metals, and nutrients. Chemical constituents and characteristics of tissue will be determined through collection of biota for off-site laboratory analyses

Refer to the “Group B Element: Data Generation and Acquisition” section of this QAPP for quality assurance practices associated with sample collection, instrument calibration, and so forth.

6.2 Project Schedule

Each task’s schedule is specified in its associated monitoring plan.

6.3 Geographical Setting

The Great Salt Lake is a dynamic terminal lake located in Northern Utah. It is the sixth largest lake in the United States and the world’s fourth largest terminal lake. Great Salt Lake’s salt concentrations range from freshwater conditions to conditions seven times greater

than the ocean. UPRR's causeway bisects the major bays of the Great Salt Lake, Gilbert and Gunnison bays and distinct water quality conditions exist in each bay. Gilbert Bay receives the bulk of the freshwater inflow into the lake and supports brine shrimp. Gunnison Bay salinities and mineral concentrations are higher than Gilbert Bay salinities and minerals.

6.4 Constraints

Water quality sample collection may occur over a wide range of weather conditions (rain, snow, sun, wind, high heat, and cold weather). Windy conditions may temporarily preclude sampling on the lake. Sampling in both Gilbert and Gunnison bays will require the use of a boat with different launch sites. There is no public boat access to Gunnison Bay, and therefore monitoring in Gunnison Bay is contingent on identifying a suitable boat launch. A suitable boat launch must have road access with a ramp suitable for boat launching at low lake levels, and must have deep enough water between the launch and monitoring stations to operate an outboard motor. Private landowner permission will be required to regularly access the Gunnison Bay launch. Due to the long distances to launch sites and long distances between sampling sites in the lake, only 2–3 sampling locations will be completed per day in order to meet the laboratory's hours of operation or shipping deadlines. In addition, because separate launch sites are required to Gilbert and Gunnison bays, monitoring will at both bays on the same day is not possible. Finally, a local boat rental must be procured for use in both Gilbert and Gunnison bays. The boat must have enough deck space to accommodate several sample coolers, sampling equipment, personal equipment, and at least three people (including the boat operator). Surface water and brine shrimp samples are highly susceptible to contamination during sampling and handling activities by both the field personnel and the analytical laboratory. Therefore, sampling logistics must allow the use of proper equipment to minimize contamination.

7.0 Quality Objectives and Criteria for Measurement Data

Data quality objectives (DQOs) are a set of performance or acceptance criteria that the collected data should achieve in order to minimize the possibility of either making a decision error or failing to keep uncertainty in estimates to within acceptable levels. DQOs are defined in terms of five parameters: precision, accuracy, representativeness, completeness, and comparability (PARCC) and differ with different measurement techniques.

DQOs for the project are presented in Table 7-1.

Table 7-1. Data Quality Objectives, by Measurement Type

Precision	Accuracy	Representativeness	Completeness	Comparability
<i>Field Measurements Surface Water (for example, pH, specific conductivity, temperature, dissolved oxygen)</i>				
Not applicable	Instrument calibration meets manufacturers' requirements	Sample locations, sampling frequency and analytical methods follow monitoring plan.	90%	Meets target reporting limits
<i>Analytical Laboratory Analyses Surface Water and Brine Shrimp (for example, metals, nutrients)</i>				
Field duplicates within 10%; Laboratory QA/QC meet method requirements.	Laboratory QA/QC meets method requirements.	Sample locations, sampling frequency and analytical methods follow monitoring plan.	90%	Meets target reporting limits

Precision is a measure of the reproducibility of analyses under a given set of conditions. In other words, precision describes how well repeated measurements agree. Precision is typically evaluated by comparing analytical results from duplicate samples and calculating the relative percent difference (RPD), where RPD is defined as:

$$RPD = \left(\frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2} \right)} \right) \times 100$$

, where C_1 and C_2 are the analyte's concentrations in each duplicate

Precision will be determined through the use of field duplicates, laboratory matrix spike/matrix spike duplicates (MS/MSD) and laboratory control samples/laboratory control sample duplicate samples (LCS/LCSD).

Accuracy is a measure of the bias that exists in a measurement system. In other words, accuracy describes how close an analytical measurement is to its "true" value. For analytical samples, accuracy is typically measured by analyzing a sample of known concentration (prepared using analytical-grade standards) and comparing the analytical result with the known concentration. Accuracy will be evaluated in terms of percent recoveries determined from results of MS/MSD and LCS/LCSD analyses.

Representativeness is the degree sampling data accurately and precisely depict selected characteristics. The representativeness of the data is mainly dependent on the sample design, such as locations (spatial), sampling frequency (temporal), and sample collection procedures, as well as analytical constituents and methods. Each monitoring plan will present the study design.

Completeness, which is expressed as a percentage, is calculated by subtracting the number of rejected and unreported results from the total planned results and dividing by the total number

of planned results. Estimated results do not count against completeness because they are considered usable as long as any limitations are identified. Results rejected because of out-of-control analytical conditions, severe matrix effects, broken or spilled samples, or samples that could not be analyzed for any other reason are subtracted from the total planned number of results to calculate completeness. Though regulations currently do not require a specific percentage of data completeness, it is expected that the measurement techniques selected for use in this project are capable of generating data that is of 90% or more completeness for field and laboratory analyses.

Comparability is the degree of confidence with which one data set can be compared to another. A broad spectrum of analytical constituents has been selected to characterize water quality and the use of approved/documented analytical methods will ensure that analytical results adequately represent the true concentrations of constituents within these samples. In addition, target reporting limits have been selected for each analyte, where appropriate, to ensure that the analytical methods used are of adequate sensitivity to generate useful data for the purposes of this project. Presented in the monitoring plan, whenever practicable, target reporting limits will be selected to be consistent with State of Utah's *Draft Quality Assurance Project Plan for the Great Salt Lake Baseline Sampling Program* (UDQW 2013).

8.0 Special Training Needs/Certification

Proper training of field and laboratory personnel represents a critical aspect of quality control.

All field personnel that participate in water quality monitoring will have reviewed this QAPP. Field personnel will have also been trained in water quality sample collection (including QA/QC, grab sampling techniques, flow measurement techniques, completing laboratory chain-of-custody forms, ordering correct laboratory analyses, and proper handling of water samples), field analysis (including instrument calibration, data recording procedures, and interpretation of collected data), and GPS use. All samplers will be provided hands-on training in the "clean hands-dirty hands" technique by the QA Officer or his designee when trace metals are constituents of interest (EPA 1996; see Section 11). The QA Officer or his designee will provide training to field personnel. Documentation of training will be maintained in the project file.

All laboratories utilized to perform analytical services will be nationally certified. The certification includes requirements that laboratory personnel will be certified and trained. Certification and training is documented in the laboratory's own QAPP and verified by the accreditation entity's audit.

9.0 Documents and Records

9.1 Project Documents, Records, and Electronic Files

The documents and records that will be used or generated during this project include the following:

Monitoring Plan. The monitoring plan contains information regarding sampling locations, frequencies, sample collection methods, analytical methods, target reporting limits, and water quality objectives. The monitoring plan is, as much as practicable, consistent with the

guidance provided in the Utah Division of Water Quality's *Checklist of Essential Elements for Sampling and Analysis Plans* (UDWQ, no date). The Health and Safety Plan, QAPP, and field and laboratory Standard Operating Procedures (SOPs) are provided as appendices to the monitoring plan.

Quality Assurance Project Plan. The QAPP (this document) contains details on the quality assurance and quality control procedures that will be implemented throughout the water quality monitoring task(s). The QAPP is an appendix to the monitoring plan.

Standard Operating Procedures. Standard Operating Procedures (SOPs) contain details on the specific actions that will be implemented throughout the water quality monitoring task(s). The SOPs are provided in an appendix to the monitoring plan.

Field records. The Monitoring Coordinator or designee will maintain all field records, including field data sheets documenting results of field analyses and QC samples, equipment maintenance and calibration documentation, and sample collection and handling documentation (copies of chain-of-custody forms, shipping receipts, etc.).

Laboratory records. The analytical laboratory will generate records for sample receipt and storage, instrument calibration, analytical QC, and reporting. Lab reports summarizing analytical results and QC results will be provided to HDR both in hard-copy and electronic formats. The information contained within and the format of the data report package will include at a minimum the sample identification number (ID), sampling date/time, test method, extraction date/time, analysis date/time, analytical result, QA sample results, instrument and equipment calibration information, and a description of any corrective action taken to resolve data quality issues.

Data verification records. Field data sheets, field QC results, chain-of-custody forms, and lab reports from each sampling event will be reviewed by the QA Officer or designee and documented for the project file.

Project database. Microsoft Excel spreadsheets will be used to store all water quality data gathered during this project.

9.2 Retention of Project Documentation

The original field notebooks and forms, equipment maintenance and calibration documentation, chain-of-custody forms, laboratory reports, and data verification records will be stored at the HDR office at 3949 South 700 East, suite 500, Salt Lake City, UT 84107. Records will be transferred to UPRR upon completion of the project or earlier, at UPRR's discretion.

9.3 Electronic File Back-up

All electronic files will be stored on HDR network servers and will be backed-up on a regular basis by the HDR information technology staff

9.4 Distribution of QAPP Revisions

Revisions that occur after the original QAPP is approved will be indicated on the QAPP title page and will be distributed in subsequent deliverables and upon request.

Group B Elements: Data Generation and Acquisition

10.0 Sampling Process Design

For each phase of the project, the monitoring plan presents the study design, including sample locations, frequency of sample collection, analytical parameters, and laboratory methods.

11.0 Sampling Methods

Data will be obtained in the field and in the laboratory.

The field sampler will maintain a field notebook and will note relevant conditions during each sampling event on the field data sheet. At a minimum, the following information pertaining to each sample will be recorded: date, time, weather conditions, name(s) of people collecting samples, units of measurements, depth, GPS coordinates for sample site, and lakewater level.

Gloves and other appropriate personal protective equipment will be worn during sample and data collection activities. Observations of any field conditions that could affect sample results will be recorded in the field form. Digital photo documentation of sampling conditions may also be performed. All field notes will be clearly written in a format that can be reproduced (that is, scanned [PDF]) and entered into electronic format (Microsoft Word or Excel).

11.1 Field Data Collection

The field measurement equipment that may be used during this project includes the following:

- Handheld multi-parameter meter (In-Situ Troll 9000) or equivalent. A sonde will be used to measure water temperature (± 0.1 °C), pH (± 0.2 standard unit, or su), specific conductance (range dependent resolution), and depth.

Prior to each use, the instrument will be calibrated using manufacturer's recommended calibration methods (see Section 16). Any variances will be noted on the field data sheet and final report. If necessary to obtain a complete dataset, re-sampling within required monitoring window will be performed. Non-disposable sampling equipment will be thoroughly cleaned between sampling sites.

Any field collected data that are not already in electronic format (Microsoft Excel) will be hand entered into an electronic format and checked by a second-party.

11.2 Analytical Sample Collection

Surface samples will be collected using a grab sampling technique. Samples will be collected at depth using a Kemmerer bottle or equivalent. Each laboratory sample will be collected using laboratory-supplied clean containers, certified to meet the reporting limits specified in the study plan. Water samples to be analyzed for metals will be collected using "clean hands-

dirty hands” method¹ consistent with the EPA Method 1669 sampling protocol as described in *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA 1996; Attachment A).

As part of the field quality assurance program, field blanks and equipment rinsates will also be collected and submitted to the laboratory for analysis (see Section 14). Laboratory grade media will be provided by the laboratory will be used for quality assurance samples. While still in the field, full sample containers will be labeled, placed in re-sealable plastic bags (for example, Ziploc), and stored in a cooler on ice to maintain a temperature of approximately 4 °C.

12.0 Sample Handling and Custody

A chain-of-custody record will be maintained with the laboratory samples at all times.

A chain-of-custody form that identifies the sample bottles, date and time of sample collection, and analyses requested will be initiated at the time of sample collection and prior to sample shipment or release. Identification information for each sample will be consistent with the information entered in the field notebook. The samples will be transported or shipped to the analytical lab in insulated containers within the appropriate holding time and will be accompanied by the chain-of-custody form. If shipment is needed, the samples will be packaged and shipped in accordance with U.S. Department of Transportation standards. The original chain-of-custody will be given to the lab with the samples and HDR will retain a copy for their records.

Once received by the laboratory, a sample receipt and storage record will be generated. The laboratory will perform all analyses within the constituent- or method- specific holding times.

After analyses, all samples will be disposed of in accordance with federal, state, and local requirements.

13.0 Analytical Methods

The monitoring plan presents the laboratory methods that will be employed. Containers, preservatives, holding times, and QA/QC requirements are specified in the analytical methods and/or in the laboratory’s own standard operating procedures. Analytical methods are preferentially U.S. Environmental Protection Agency (EPA) or American Society for Testing and Materials (ASTM) methods and are detailed in the laboratory’s own quality assurance manual.

For each analyte, the laboratory must be able to achieve target reporting limits and method detection limits that are consistent with those presented in the State of Utah’s *Draft Quality Assurance Project Plan for the Great Salt Lake Baseline Sampling Program* (UDWQ 2013). Estimated, that is, “J-flagged,” data will be provided in report attachments, but only the most certain informing will be used to inform monitoring decisions.

¹ One member of a two-person sampling team is designated as “dirty hands”; the second member is designated as “clean hands.” All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as “clean hands.” “Dirty hands” is all other activities that do not involve direct contact with the sample.

14.0 Quality Control

14.1 In-Situ Data Collection

Projects that require pH sampling also require a method of back-up or corrective action for inconsistent or questionable measurements collected in the field. For example, if pH is measured at less than 6 or greater than 8.5 in the field, a second measurement must be taken to verify the value. The second measurement could consist of ensuring that pH is included in the analyses of grab samples or recalibrating the probe and re-measuring in the field. This information must be recorded in the field notes as well with explanations for the activity.

14.2 Sample Collection

QA/QC activities for sampling processes include the collection of field duplicates for chemical testing, and the preparation of field blanks and/or equipment blanks as necessary. The number of duplicates should be one per every ten stations sampled or one per field visit.

Blanks will be prepared by pouring water known to be free of the substance of interest, that is, reagent-free deionized water, into a sample collection container then subsampling into the appropriate number of replicate sample containers. Ultrapure certified metals-free water will be used for hardness and metals.

14.3 Analytical Laboratory

All laboratories providing analytical support for this project will have the appropriate facilities to store, prepare, and process samples and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. The nationally certified laboratory will have a quality assurance plan in place and will adhere to standard protocols for accuracy, precision, instrument bias, and analytical bias.

The laboratory's deliverable (that is, data package) will include information documenting their ability to conduct the analyses with the required level of data quality. Such information may include results from inter-laboratory calibration studies, control charts, and summary data from internal QA/QC checks, and results from analyses of certified reference materials. Additionally, the laboratory will report any inconsistencies or problems associated with any sample run(s) to HDR, who will document the situation as a variance or non-conformance, as appropriate (for example, contaminated reagents, equipment malfunction, lost or broken sample bottles upon receipt, etc.).

15.0 Instrument/Equipment Testing, Inspection, and Maintenance

15.1 Field Equipment

The field measurement equipment that may be used during this project includes the following:

- Handheld multi-parameter meter (In Situ Troll 9000 or equivalent. This sonde will be used to measure temperature, pH, and conductivity in the field.

Prior to each field visit, the sonde will be rented from and calibrated by the manufacturer. Upon receipt of the Troll 9000 and prior to leaving for the field, the Field Lead or his designee will confirm the probe is working. Written documentation of calibration will be maintained in the project file, attached to relevant reports, and provided upon request.

In the event that the sonde shows signs of malfunction or drift in readings during fieldwork, basic diagnostics will be performed. At a minimum, the following will be checked: batteries, computer connection, and software. The probes will be examined for obstructions, such as algae, or physical damage. The user manual will be taken into the field that includes some basic trouble shooting. If basic trouble shooting is not successful, the sampling team will order a replacement rental unit and return to sample the site in a few days and within the sample period specified in the monitoring plan.

15.2 Laboratory Equipment

All laboratories utilized to perform analytical services will be nationally certified. The certification includes requirements that the laboratory maintain their analytical equipment in accordance with manufactures instructions and analytical method requirements. Instrument testing, inspection and maintenance procedures are documented in the laboratory's quality assurance manual. Records will be kept at the laboratory and available upon request.

16.0 Instrument/Equipment Calibration and Frequency

Field instruments will be calibrated according to manufacturer's instructions immediately before use in the field. Sondes will be rented from and calibrated by the manufacturer immediately before use in the field. Documentation of calibration prior to each field visit will be maintained in the project file.

Table 16-1. Field Instrument Calibration and Frequency

Parameter	Calibration Frequency	Standard or Calibration Instrument Used
Temperature	Four times per year	Certified thermometer
Conductivity	Every sampling day	Conductivity standard (concentrations TBD)
pH	Every sampling day	pH 7.0, 4.0, and 10.0 buffers

17.0 Inspection/Acceptance of Supplies and Consumables

Project supplies and consumables that may directly or indirectly affect the quality of results include filters, samplers, gloves, bottles and more. To avoid contaminating samples through supplies, supply selection will be made to meet the needs of the monitoring plan. Supplies will be examined for damage as they are received and consumables will be replaced no later than the date recommended in the manufacturer's instructions.

The nationally certified laboratory will provide all bottles used for sample collection and cleanliness certification will be provided. Specifically, all equipment used for trace metals sample collection will be certified clean and double-bagged, allowing for the measurement at the concentrations required for the study plan using the clean-hands-dirty-hands technique described in EPA Method 1669 (EPA 1996).

A small inventory of critical spare parts for field equipment (DO membranes, o-rings, and temperature and conductivity probes) will be kept by HDR and brought in the field if needed; however, perishable supplies or expensive parts may not be kept on hand, and will need to be ordered when needed. All spare parts and supplies will be obtained through the equipment manufacturer or other reputable sources.

18.0 Non-direct Measurements (Existing Data)

Water quality data has been previously collected in the study area. Though it is unknown at this time what existing data may be incorporated into monitoring documents, if any, the known level of review of all incorporated existing data will be disclosed.

19.0 Data Management

Field and laboratory data will be entered and maintained in Excel spreadsheets. The contract laboratory will provide an electronic data deliverable and an electronic narrative that includes, at a minimum, Level II documentation.

Throughout the relicensing, the original field notebooks and forms, equipment maintenance and calibration documentation, chain-of-custody forms, laboratory reports, and data verification records will be stored at the HDR office at 3949 South 700 East, Suite 500, Salt Lake City, UT 84107. Records will be transferred to UPRR upon project completion or earlier, at UPRR's discretion.

Group C Elements: Assessment and Oversight

20.0 Assessments and Response Actions

Periodic assessments will be conducted to ensure that data collection is conducted according to requirements presented in this QAPP. The Monitoring Coordinator will have the primary responsibility for assessing compliance with the QAPP requirements pertaining to sample collection and handling procedures, field analytical procedures, laboratory analytical procedures, and communicating project status to the QA Officer and Project Manager. The QA Officer or his designee will conduct reviews of field sampling and analysis procedures at the beginning of each field season. The reviews may be performed at a demonstration site or involve accompanying sampling personnel to determine whether sampling activities are being conducted in accordance with the QAPP and monitoring plan. Laboratory analyses will be assessed through evaluating results of QC samples and compliance with DQOs.

If a non-conformance is identified, the QA Officer and/or Monitoring Coordinator will notify the Project Manager immediately. The Project Manager, QA Office, and Monitoring Coordinator will discuss the observed discrepancy with the appropriate person responsible for the activity to determine whether the information collected can still be considered accurate, what the cause(s) were leading to the deviation, how the deviation might impact data quality, and what corrective actions might be considered. The QA Officer and Monitoring Coordinator will then follow up to ensure that corrective actions have been implemented.

21.0 Reports to Management

The study schedule is specified in each monitoring plan. As described in the each monitoring plan, the primary deliverables will consist of a cover letter with tables, transmitting the monitoring data collected to the permitting agency.

Group D Elements: Data Validation and Usability

22.0 Data Review, Verification, and Validation Requirements

Data review, verification and validation are steps in the transition between data collection via sampling and analysis and data use and interpretation. Although data review, verification and data validation are commonly used terms, they are defined and applied differently in various organizations and quality systems. For the purposes of monitoring, the terms will be generally defined as follows:

- Data review ensures the data have been recorded, transmitted, and processed correctly. That includes, ensuring the data are sensible and checking for data entry, transcription, calculation, reduction, and transformation errors.
- Data verification is the process for evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual specifications (EPA 2002).
- Data validation is an analyte and sample specific process that extends the evaluation of data beyond method, procedure, or contractual compliance to determine the quality of a specific data set relative to the end use (EPA 2002). Data validation begins with the output from data verification.

23.0 Verification and Validation Methods

Documentation of review, verification, and/or validation will be maintained in the project file (Figure 2) Follow each monitoring event, all data will be reviewed and verified. In brief, following the field sampling and laboratory analyses, which includes the laboratories' own QA/QC analyses, HDR will subject all data to QA/QC procedures including, but not limited to: spot-checks of transcription; review of electronic data submissions for completeness; comparison of results to field blank and rinsate results; and, identification of any data that seem inconsistent. If any inconsistencies are found, HDR will consult with the laboratory to identify any potential sources of error before concluding that the data is correct.

Monitoring results will consist of all verified chemical detections. Estimated, or “J”-qualified,² data will not be used to establish UPRR’s regulatory obligations or determine UPRR’s compliance. Nevertheless, “J”-qualified data will be provided in the data submittal attached to all reports in the event the data can be used for purposes requiring less accuracy. If the laboratory needs to re-extract samples and re-run the sample under different calibration conditions, the data identified by the laboratory, as the most certain, will be used. If field-sampling conditions, as measured by the field blank and the rinsate sample results, indicate that samples have been corrupted, HDR will identify the data accordingly.

² Constituent is detected but not quantified, that is, estimated sample concentration is less than the reporting limit but is above the method detection limit and is subject to a high degree of quantitative uncertainty.

Figure 2. Data Review and Verification Checklist

Group E Elements: Data Review and Verification Checklist	
<p>This checklist should be used to document data review verification of data generated through implementation of the monitoring plan.</p>	
24.0	General
<input type="checkbox"/>	For each sample event, samples have been collected and analyzed at all locations and for all analyses specified in the monitoring plan.
<input type="checkbox"/>	For each sample and analyses, the project file contains records field notes, chain-of-custody, and analytical results, including quality assurance documentation (hardcopy and electronic)
25.0	Field Data
<input type="checkbox"/>	Field notes and/or data sheets include date, time of sample collection, field sampling staff, time arrived at site, time left site, site identification, description of site conditions (weather), field parameters, lake level, sample collection procedures, and call-out quality assurance samples collected. If mistakes are found on the field data sheet, changes can be made by crossing out the mistake and marking the change with a date of change, initials, and reason for change.
<input type="checkbox"/>	Documentation of field equipment calibration is in the field notes and/or project records.
<input type="checkbox"/>	Field data entered into Excel, have been checked by a second-party.
26.0	Laboratory Report
<input type="checkbox"/>	Field duplicates, blanks, and rinsates were submitted to the laboratory at the frequency specified in the monitoring plan.
<input type="checkbox"/>	Any constituents found in blanks or rinsates are discussed in the report.
<input type="checkbox"/>	Any duplicate concentrations that differ by more than 10% are discussed in the report.
<input type="checkbox"/>	Samples were received by the laboratory intact and analyzed within method and/or study specified holding times.
<input type="checkbox"/>	On laboratory reports, sample IDs, analyses, reporting/detection limits, units, column labels, footnotes, and titles are accurate. Have lab re-issue report with corrections if there are inconsistencies.
<input type="checkbox"/>	Check that non-detects are always reported in the same manner using consistent notation. For example, either “ND” or “<.” Have lab re-issue report with corrections if there are inconsistencies.
<input type="checkbox"/>	If observed, elevated detection limits are discussed in the report.

27.0 Reconciliation with User Requirements

To fulfill UPRR's data needs, it is important that the data collected during this project are accurate, precise, representative, and complete, and can therefore be used to document water quality. These data requirements will be assessed by ensuring that DQOs are met throughout the project.

After each discrete monitoring event, the Monitoring Coordinator will evaluate if the DQOs of Table 7-1 have been met. Results of the evaluation will be documented on the Data Review and Verification Form provided in Figure 23-1. If the impact of the QC failure on data quality is minimal, the data will be flagged and included with in the database. If a greater impact is found, the Monitoring Coordinator will work with the QA Officer to determine the next steps. Data that does not meet the DQOs listed in Section 7 will be evaluated to (1) determine the cause of the problem; (2) determine whether corrective actions can be implemented so that DQOs are met in the future; and/or (3) determine if re-sampling is necessary to meet completeness or other PARCC objectives.

At the end of the monitoring program, the data generated under this project will be given to UPRR.

28.0 References

[EPA] U.S. Environmental Protection Agency

1996 EPA Method 1669.

2002 United States Environmental Protection Agency. 2002. Guidance on Environmental Data Verification and Data Validation (EPA QA/G-8), November.

[UDQW] Utah Division of Water Quality

No date Checklist of Essential Elements for Sampling and Analysis Plans.

2013 *Draft Quality Assurance Project Plan for the Great Salt Lake Baseline Sampling Program.*

Appendix D
Field Standard Operating Procedures and Forms

Appendix D
Field Standard Operating Procedures

Table of Contents

1. Secchi Depth Measurement
2. Water Sample Collection
3. Brine Shrimp Sample Collection

Secchi Depth Measurement

Clarity for ponds, lakes, bays, estuaries, and oceans is measured with a Secchi Disk. The measurement is referred to as a Secchi Disk Transparency.

Equipment

Disks: For freshwater lakes the black and white Secchi Disc should be used. Normally a Secchi Disk 20 cm in diameter is used. For large, deep, oligotrophic freshwater lakes it may be more suitable to use an all white oceanographic disc. For salt-water bodies of water, such as oceans, bays, or estuaries, use an oceanographic Secchi Disc (all white) with a standard diameter of 51cm.

Marked line: A number of programs use a marked line (1/4 to 1 foot or portions of meters). Periodically check for shrinkage by comparing the marked line against a measuring tape.

Measuring Secchi Depth

1. To prevent glare from affecting the normal vision of the disk, position yourself with the sun at your back, on the shaded side of a vessel, bridge or dock. Do not wear sunglasses.
2. Lower Secchi Disk into water until it just disappears (extinction depth).
3. Read depth from the calibrated line. For an unmarked line use a clothespin to mark the line.
4. Raise Secchi Disk until it just appears. Read depth from calibrated line or for an unmarked line mark with another clothespin.
5. Add readings from Steps 1 and 2. Divide by 2. With the unmarked line and clothespins, measure from the disk to the halfway mark between the two clothespins.
6. Records as Secchi Disk Transparency.

When making Secchi disk readings, be aware that the resolution of the data is dependent on the increments of measurement on the calibrated line. Report the results as being on one of those marks, or halfway between. For example, if your line is marked in increments of whole meters and if the reading is between 2 and 3 meters, then call it 2.5 meters. In other words report the results in terms of either whole or half increments.

In some cases Secchi readings may be made from a small vessel where the observer is very close to the water surface. When the observer is close to the water surface a clothespin or similar device may be attached to the line at the water surface to mark the extinction depth. The line may then be brought out of the water and a ruler or measuring tape may be used to determine the exact extinction depth.

If the Secchi disk reaches the bottom and is still visible, then an extinction depth is not able to be determined at that location. Instead just record the fact that the disk was seen on the bottom and record the depth to the bottom at that location.

Whenever making Secchi readings use the same type of disk and procedure for all readings. Always record the location, date, time, weather conditions, name of the observer(s), tide (if applicable), and the size and type of disk.

Tips: It is best to make Secchi depth measurements between 10:00 am and 2:00 pm.

If time trend data is being collected it is important to use the same disk if possible or an identical disk at the least. As disks age please keep them clean, free of scratches and good operable condition.

Total and Dissolved Water Sampling

Introduction

Water samples will be collected to measure total selenium, total mercury, dissolved methylmercury, total trace metals (arsenic, cadmium, copper, silver, zinc), nutrients (total nitrogen, total phosphorus, ammonia), and Chlorophyll-a.

This SOP was adapted and updated from the original SOP (Naftz, 2006) prepared as part of the Utah Division of Water Quality's project, Development of a Selenium Standard for the Open Waters of Great Salt Lake (CH2M HILL, 2008).

Pre-sampling Checklist

The pre-sampling checklist of materials needed during water sampling includes the following:

- A GPS unit
- Multi-parameter probe for field water quality measurements
- A map showing sampling sites with coordinates
- Bound field log book
- Cleaning supplies - deionized water, hydrochloric acid (HCl), Liquinox solution
- Waders or wading boots, as required
- Up to 1-L/min delivery rate portable peristaltic pump (Refer to EPA method 1630/1631 for pump specification)
- Teflon® or Masterflex® tubing suitable for the pump
- 0.45µm mesh capsule filters
- 500-mL to 1-L glass bottles (fluoropolymer glass) with fluoropolymer or fluoropolymer-lined cap with labels
- Discrete depth sampler, e.g. Kemmerer bottles
- Ziploc® Bags
- Digital camera
- Disposable powderless nitrile gloves/elbow gloves
- Labels
- Marker pens and pencils
- Cell phones in case of emergency
- Cooler filled with ice
- Disposable paper towels
- First-aid kit
- Distilled water

Cleaning Procedures

Verify that tubing, processing chamber, and sampling bottles and equipment are clean. If equipments and sample bottles are supplied by the laboratory that will perform analysis, it should be the laboratory's responsibility to generate acceptable blanks to demonstrate that the equipments and containers are free of contamination before they are shipped to the field sampling team. If not clean or for field cleaning, the follow procedures will be used:

Sample Tubing Cleaning Procedure

Laboratory Cleaning

1. Soak in 0.2% Liquinox solution for 30 minutes. Scrub with brush.
2. Change gloves.
3. Rinse 3 times with tap water*.
4. Change gloves.
5. Soak in 5% HCl solution for 2-3 hours. (skip this step if your equipment has ANY non-removable metal)
6. Change gloves.
7. Rinse 3 times thoroughly with deionized water (DIW)*.
8. Double bag equipment.

**To facilitate flow of solutions thru the tubing, use a peristaltic pump or large syringe.*

Field Cleaning

1. Pump 1-L of DIW through tubing and rinse tubing ends just before sampling.
2. Inspect tubing
 - o If tubing is visibly dirty or sampling site is contaminated continue to step 3.
 - o If dirt is not visible continue to step 5.
3. Pump 1 L of 0.1% Liquinox solution through tubing and on ends.
4. Pump 1 L of tap water or DIW
5. Carefully pump 1 L of 5% HCl solution through tubing and on ends. Capture and dispose of HCl.
6. Pump 2 L of DIW through tubing and on ends.
7. Double bag equipment.
8. Discard neutralized solutions appropriately.
9. Clean stainless steel connections or metal tubing using detergent wash and tap water/DIW rinse procedures.

Sampling Equipment Cleaning Procedure

1. Clean equipment using NFM protocols (See TWRI book 9, Chapter A3.2.1)
2. Soak in 0.2% Liquinox solution for 30 minutes. Scrub with brush.
3. Change gloves.
4. Rinse 3 times with tap water.
5. Change gloves.

6. Soak in 5% HCl solution for 2-3 hours. (skip this step if your equipment has ANY non-removable metal)
7. Change gloves.
8. Rinse 3 times with DIW.
9. Double bag equipment.

Capsule Filter Cleaning Procedure

1. Attach pump tubing to inlet connector of capsule filter. **Make sure direction of flow through capsule filter matches the direction-of-flow arrow on the side of capsule.**
2. Select a short length of clean tubing onto capsule filter outlet extending into a drain.
3. Pump 1 L (large-capacity >600cm² filter) or 100 mL (small-capacity 19.6 cm² filter) through capsule filter.
4. Remove tubing from DIW reservoir and continue operating pump in forward at mid-range speed to drain remainder of DIW in capsule filter.
5. Detach capsule filter from tubing.
6. Put in clean, Ziploc® bag until ready for use.

Sample and Collection Bottles Cleaning Procedure

1. Heat bottles to 65°C in 4N HCl for 2-3 hours.
2. When bottles cool down, rinse them 3-4 times thoroughly with deionized water.
3. Fill bottles with deionized water containing 0.4% (v/v) HCl and cap tight.
4. Place the bottles overnight in a clean oven at 60°C.
5. When bottles cool down, rinse 3-4 times thoroughly with deionized water.
6. Refill bottles with deionized water containing 0.4% (v/v) HCl and cap tight.
7. Store bottles in a clean bench until the outside of the bottles are dry.
8. Tighten bottle caps and double-bag the bottles in new Ziploc® bags.
9. Store in wooden or plastic boxes until used.

Pre-Rinse Sample Bottles

(For glass, and acid-rinsed bottles - this step can be done in the laboratory prior to going into the field)

1. Put on powderless nitrile gloves.
2. Fill each bottle about ¼ full of DIW and cap.
3. Shake vigorously and decant DIW.
4. Repeat steps 2 and 3 two more times.
5. Following final rinse, fill each bottle half full with DIW and cap.
6. Rinse exterior of bottle with DIW and dry with lint-free laboratory tissue.
7. Store bottles in doubled Ziploc® bags when transported to field.

Label bottles with site id, date, time, and sample designation code (FA for filtered samples and RA for unfiltered samples).

Clean Hands/Dirty Hands Technique

Clean Hands/Dirty Hands technique will be used for all sample collection and sample processing. Before field work begins, the clean hands (CH) person and dirty hands (DH) person should be designated. Table 1 designates the duties of CH/DH. In summary of Table 1, the CH person has the only contact with the sample bottle; transfers sample from sampler to splitter; filters, extracts, and preserves sample. The DH person operates sampling equipment and manages any contact with sources of contamination (for example, the pumps). CH works inside processing chamber while DH works outside the processing chamber.

Table 1 – Clean Hands/Dirty Hands Techniques for Water Quality Sampling

<ul style="list-style-type: none">• Clean Hands/Dirty Hands techniques require two or more people working together.• At the field site, one person is designated as Clean Hands (<i>CH</i>) and a second person as Dirty Hands (<i>DH</i>). Although specific tasks are assigned at the start to <i>CH</i> or <i>DH</i>, some tasks overlap and can be handled by either, as long as the prescribed care is taken to prevent contaminating the sample.• <i>CH</i> and <i>DH</i> wear appropriate disposable, powderless gloves during the entire sampling operation and change gloves frequently, usually with each change in task. (Wearing multiple layers of gloves allows rapid glove changes.) Gloves must be appropriate to withstand any acid, solvent, or other chemical substance that will be used or contacted.• <i>CH</i> takes care of all operations involving equipment that contacts the sample; for example, <i>CH</i><ul style="list-style-type: none">- Handles the surface-water sampler bottle- Handles the discharge end of the surface-water or ground-water sample tubing- Handles the inner protective bag on the churn splitter- Transfers sample to churn or cone splitter- Prepares a clean work space (inside vehicle)- Sets up processing and preservation chambers- Places equipment inside chambers (for example, sample bottles, filtration and preservation equipment)- Works exclusively inside chambers during collection/processing and preservation- Changes chamber covers, as needed- Sets up field-cleaning equipment and cleans equipment• <i>DH</i> takes care of all operations involving contact with potential sources of contamination; for example, <i>DH</i><ul style="list-style-type: none">- Works exclusively exterior to processing and preservation chambers- Prepares and operates sampling equipment, including pumps and discrete samplers, peristaltic pump switch, pump controller, manifold system- Operates cranes, tripods, drill rigs, vehicles, or other support equipment- Handles the compressor or other power supply for samplers- Handles tools such as hammers, wrenches, keys, locks, and sample-flow manifolds- Handles single or multiparameter instruments for field measurements- Handles the churn carrier, including outer protective bags- Handles stream-gaging or water-level equipment- Sets up and calibrates field-measurement instruments- Measures and records water levels and field measurements

Sample Collection

Unfiltered Samples

1. *CH/DH*: Put on gloves.
2. *CH*: Prepare a clean processing area and surface. The processing area will be a plastic surface that is protected from wind.
3. *DH*: Assemble processing chamber.
4. *CH*: Insert processing chamber bag.
5. *CH/DH*: Change gloves.
6. *DH*: Remove capped sample bottle from transport bag and insert in processing chamber.
7. *CH*: Field rinse sampler bottles with small amount well mixed raw sample (*raw sample must be well mixed by slowly inverting the capped sample bottle 3-5 times. Do not aerate the sample by shaking vigorously*). This is applicable only to samples that are not preserved.
 - a. If bottles were previously rinsed and half-filled with DIW, discard DIW and rinse once with well mixed sample.
 - b. If bottles were not pre-rinsed with DIW, rinse twice with DIW, followed by one rinse with well mixed sample.
8. *CH*: Transfer well mixed sample from sampler bottle into appropriate sample bottle and cap.
9. *CH*: If sample bottles do not contain preservatives, preserve sample using preservative if needed,
10. Remove sticker from preservative vial and stick it on the field sheet for lot tracking.
11. Dispose of empty preservative vial in waste container.

Filtered Samples

1. *CH/DH*: Put on one or several layers of powder-free gloves.
2. *CH*: Assemble clean processing chamber, attach chamber cover, and change gloves.
3. *CH*: Place capsule filter, sample bottles, and discharge end of peristaltic pump into chamber.
4. *CH*: Open DIW container and cover with plastic bag.
5. *CH*: Insert intake end of peristaltic pump tubing through the plastic covering and into a 1-L container of DIW.
6. *DH*: Attach tubing to peristaltic pump head and pump DIW to fill tubing.
7. Discharge waste rinse water through a sink funnel or a toss bottle.
8. Discard DIW stored in DIW-pre-rinsed sample bottles. If not pre-rinsed, rinse twice with DIW.

Filtering a sample

1. Field rinse peristaltic pump tubing with the water to be sampled
 - a. *CH*: Rinse the outside of each end of the pump tubing.
 - b. *CH*: Transfer intake end of pump tubing into composite sample.
 - c. *DH*: Start pump to slowly pump sufficient sample to completely fill tubing.
 - d. *CH*: Discard rinse water through appropriate receptacle. Prevent water from ponding in processing chamber.
 - e. *DH*: Stop pump after tubing is field rinsed.
2. Field rinse capsule filter:

- a. *CH*: Remove cleaned capsule filter from plastic bag and attach discharge end of pump tubing to filter inlet connector.
 - b. *DH*: At low speed, pump sample through the tubing to capsule filter.
 - c. *CH*: Turn capsule filter so outlet is point up and flow of the sample forces trapped air out of capsule filter. **Do not let sample spray onto chamber cover. Chamber cover must be changed if sample has sprayed on to it.**
 - d. *DH*: Stop pump as soon as filter is full of sample.
3. Collect Sample Filtrate.
- a. *CH*: Check that there is a tight connection between the pump tubing and the capsule filter.
 - b. *DH*: Check the intake tube is properly inserted in the sample and start pump.
 - c. *CH*: Collect a maximum of 25 mL of the water to be sampled. **Do not exceed 25 mL.**
 - d. *CH*: Field rinse a pre-cleaned FA sample bottle.
 - e. *DH*: Stop pump in time to prevent losing filtrate.
 - f. *CH*: Cap bottle, shake, and discard rinse water.
 - g. *DH*: Start pump and resume flow.
 - h. *DH*: Stop pump after bottle is filled.
 - i. *CH*: Field rinse any remaining sample bottles. **Use no more that a total of 100 mL of filtrate per capsule filter to field rinse any remaining bottles for filtered samples.**

Sample Preservation if Required

All *CH* person.

1. Change gloves.
2. Move samples requiring chemical treatment to preservation chamber.
3. Place first preservative and its waste container insider chamber.
4. Change gloves.
5. Add preservative to FA bottles.
6. Change gloves.
7. Disassemble and clean chamber frame.

For filtered samples that do not require preservation.

1. *CH*: Set samples outside processing chamber
2. *DH*: Check that information on bottle is correct and complete.
3. *DH*: Pack samples for shipping or in ice if cooling is required.
4. *CH*: Rinse all reusable equipment with DIW immediately-before equipment dries.
5. Discard the capsule filter after filtering each sample-do not reuse.

Field Measurements

All field water quality parameters (temperature, pH, dissolved oxygen, conductivity) will be simultaneously measured with water sample collection using Multi-parameter probe.

Multi-probe Calibration

1. Check the display logger to determine the battery level to see if recharging or new batteries are necessary.
2. Prior to calibration, all instrument probes on the multi-probe must be cleaned according to the manufacturer's instructions. Failure to perform this step can lead to erratic measurements. The probes must also be cleaned by rinsing with deionized water before and after immersing the probe in a calibration solution.
3. For each of the calibration, solutions used should provide just enough volume so that the probe and the temperature sensor are sufficiently covered. When done with the calibration solutions, do not return it to the original bottle. Save solution in separate container or dispose properly.
4. All calibration should be done using manufacturer's instruction and using manufacturer recommended calibration solution before every sampling event.

All calibration should be done in the following order: temperature, conductivity, pH, dissolved oxygen.

Field Measurement Procedure

Field measurements commonly are monitored within a cross section of the surface-water body to (a) help determine how well mixed the stream is, and consequently the sampling method to be used (NFM 4.1), and (b) determine the field-property values of the water body at the selected site. In situ use of a multi-parameter instrument is the most efficient means of obtaining such data

1. Wait a minimum of 60 seconds for the sensors to reach thermal equilibrium with the water temperature at each new location. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
2. At each measuring point, allow the field-measurement values on the instrument display to stabilize within an established criterion as specified in the QAPP before recording final field measurements. Field-measurement values will be considered stable if the variability among three or more consecutive readings, spaced some number of minutes apart, conforms to the designated criteria specified in QAPP.

Field Logbook

Field activities will be documented through journal entries in a bound field logbook, which is dedicated to this project. The field logbook will be water-resistant, the pages will be sequentially numbered, and all entries will be made in indelible ink. Each page of the field logbook will be dated and signed by the person making the entry. The field logbook will contain all pertinent information about sampling activities, site conditions, field methods used, general observations, and other pertinent technical information. Examples of typical field logbook entries include the following:

- Date and time of sample collection
- Name of personnel present
- Referenced sampling location description (in relation to a stationary landmark), GPS coordinates, and maps
- Daily temperature and other climatic conditions

- Field measurements, activities, and observations (e.g., depth of water, condition of water, other relevant conditions)
- Media sampled
- Sample collection methods and equipment
- Types of sample containers used
- Sample identification and cross-referencing
- Types of analyses to be performed
- Site sketches
- Visitors to the site
- Color photographs taken during sampling activities will be numbered to correspond to photo log entries. The name of the photographer, date, time, site location, and photograph description will be entered sequentially in the photo log as photographs are taken.

Additional information will be recorded in the field notebook as required by DWQ.

Reference

Naftz, D. Total and Dissolved Water Sample. Program Manual for Development of Selenium Standard for Open Waters of Great Salt Lake. Utah Department of Environmental Quality, Division of Water Quality. May 1, 2006.

CH2M HILL. 2008. Development of Selenium Standard for Open Waters of Great Salt Lake. Utah Department of Environmental Quality, Division of Water Quality, Salt Lake City, Utah.

Brine Shrimp Sampling

Introduction

Sampling of brine shrimp in GSL can help assess the impacts on critical biota as related to variations in selenium, mercury and other trace metals concentrations in the lake and also help evaluate the transfer of these contaminants through trophic compartments of the GSL food web.

This Standard Operating Procedure (SOP) was adapted and updated from the procedure of Marden, 2008, prepared as part of the Utah Division of Water Quality's (DWQ's) project, Development of a Selenium Standard for the Open Waters of Great Salt Lake (CH2M HILL, 2008). The objective of this SOP is to collect composite brine shrimp samples from the GSL for the analysis of selenium, mercury and trace metals in whole-body tissues.

Pre-sampling Checklist

The pre-sampling checklist of materials needed during macro-invertebrate sampling will include the following:

- A Global Positioning System (GPS) unit
- A map showing sampling sites with coordinates
- Bound field log book
- Digital camera
- Waders and boots as needed
- 50-cm-diameter, 165 micron mesh size plankton net with removable collection cup that has screen less than 125 micron mesh size
- 1-L Nalgene® Bottle
- Filters and filtration system
- Gloves
- Spray bottle and garden hose with attached water source (i.e., lake water)
- Weights and lines as needed for plankton net
- Safety line for collection cup
- Labels
- Marker pens and pencils
- Cell phone in case of emergency
- Cooler filled with ice
- First-aid kit
- Weather appropriate clothing
- Distilled water
- White plastic or enamel sorting tray
- Forceps

Procedures

Summary of Method

Composite brine shrimp samples will be collected by means of a plankton tow net lowered to a predetermined depth from the back of a boat and raised vertically through the water column to collect the required sample mass. Once the net is free from the water, the net is rinsed from the outside using lake water to free any organisms/debris from the side of the net and to concentrate them into the sample cup at the bottom of the net (see Figure 1, courtesy Brad Marden). The samples are then transferred in Nalgene® bottles by rinsing the cup with filtered lake water and sent to the laboratory for further cleaning/separation and analysis.

Preparation

Prior to use, the net should be carefully inspected for holes or tears. The net and collection cup should be carefully cleaned and thoroughly rinsed using distilled water to remove any visible dirt or contaminant. Ensure that the collected cup is firmly attached to the net. Ensure that sample bottles are prepared and appropriately labeled.

Sampling Procedure

Once the boat is on station, the total depth of water will be measured. If the deep brine layer is present at this station, the depth to the top of the deep brine layer will also be measured. Both total depth of water and the depth to the top of deep brine layer will be documented.



The goal of this sampling effort is to collect brine shrimps from the entire depth of water above the bottom of the lake or above any deep brine layer if present. Samples will generally be collected from the water column beginning 3 feet above the bottom of the lake. If a deep brine layer is observed, hauls should begin approximately 1-foot above the top of the deep brine layer. If the lake depth is less than 6 feet in depth, the boat should be used to tow the plankton net obliquely through the water column to collect the required sample. Care should be taken to keep the net above the bottom of lake to prevent collection of sediment.

Note that a calibrated flow meter will be required if an objective is to measure the density of brine shrimp in the water column. This is not a stated objective for this SOP, thus is not required.

The net will slowly be lowered in a constant upright position to the desired depth. The zero point for the depth is when the rim of the plankton net is at the water surface. Make sure that the tow line is vertical as the net is lowered.

Raise the net at a constant speed until the rim of the plankton net is above the water. Net hauls will be conducted to obtain sufficient mass of brine shrimp for analysis (target 5

grams wet weight) and additional mass whenever feasible should be collected. Do not interrupt the tow by stopping and starting while the net is being towed to the surface.

Once the net is raised above the water surface, rinse it gently from the outside with lake water using a garden hose (as shown in the Figure) to rinse all organisms and debris off of the net and into the sample cup at the bottom. Carefully detach the cup.

Rinse the screening and sides of the collection cup gently with filtered lake water using a spray bottle. At those sites where the water is less saline, other zooplankton may be mixed in with the brine shrimp. Also, the lake water column may contain brine fly larvae during certain times of the year. If so, visible zooplankton will be separated out using forceps and a visual estimation will be made of the relative abundance (by mass) of families of macro-invertebrates within each sample. This will be documented in the field logbook. All other visible detritus, such as algae, sticks etc. will also be removed before storing samples. Further separation of brine shrimp from other zooplankton, if present, will be done in the laboratory. Then transfer the samples from the collection cup to appropriately labeled 1-L Nalgene® bottles using filtered lake water. Store the bottles on ice. Samples will be shipped on wet ice to the laboratory for further separation and analysis. All bottle labels will be double checked before sample storage.

Record the date, station, number of net hauls, depth of tow, angle of tow, and other required information in field log book.

On arrival to the laboratory, the brine shrimp samples will be rinsed with distilled water on a 125µm screen to rinse excess salt from the brine shrimp. This may be repeated up to three times to ensure as much salt is rinsed off as possible. Brine shrimp should then be placed into a large petridish where brine fly larvae or remaining detritus may be removed. The brine shrimp will then be stored in appropriately labeled Nalgene® bottles with as little distilled water as possible. Samples may be frozen for up to one year.

Lack of sufficient organisms for testing requirements at any location will be noted in the field log book. Field notes of all field activity will be recorded in a bound field logbook. Field notes will include date and time, names of personnel conducting the survey, the work performed, any problems identified as well as corrective actions taken, and other appropriate general comments or observations.

Field Logbook

Field activities will be documented through journal entries in a bound field logbook, which is dedicated to this project. The field logbook will be water-resistant, the pages will be sequentially numbered, and all entries will be made in indelible ink. Each page of the field logbook will be dated and signed by the person making the entry. The field logbook will contain all pertinent information about sampling activities, site conditions, field methods used, general observations, and other pertinent technical information. Examples of typical field logbook entries include the following:

- Date and time of sample collection
- Name of personnel present
- Referenced sampling location description (in relation to a stationary landmark), GPS coordinates, and maps
- Daily temperature and other climatic conditions

- Field measurements, activities, and observations (e.g., depth of water, condition of water, other relevant conditions)
- Media sampled
- Sample collection methods and equipment
- Types of sample containers used
- Sample identification and cross-referencing
- Types of analyses to be performed
- Color photographs taken during sampling activities will be numbered to correspond to photo log entries. The name of the photographer, date, time, site location, and photograph description will be entered sequentially in the photo log as photographs are taken.

Additional information will be recorded in the field notebook as required by DWQ.

References

Marden, B. 2006. Synoptic Survey of the Pelagic Zone: Selenium in Water, Seston and *Artemia*; Program Manual for Development of Selenium Standard for Open Waters of Great Salt Lake. Utah Department of Environmental Quality, Division of Water Quality, Salt Lake City, Utah. May 11, 2006.

CH2M HILL. 2008. Development of Selenium Standard for Open Waters of Great Salt Lake. Utah Department of Environmental Quality, Division of Water Quality, Salt Lake City, Utah.

Appendix E
Laboratory QA/QC (Quality Assurance/Quality Control), Analytical
Methods, and Documentation

Appendix E
Laboratory QA/QC, analytical methods, and documentation

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3. National Environmental Laboratory Accreditation Program (NELAP) Accreditation
4. SOP #BR-0066: Metals in Brackish and Seawater
5. SOP #BR-0060 : Metals in Water, Total Dissolved Solids <1000 mg/L
6. SOP #BR-0006 : Mercury in Water
7. Brooks Rand Labs Memorandum: Blank Correction of Trace Metals Data
8. SOP #BR-XXXX: Metals in Tissue [Reserved]
9. SOP #BR-0002: Mercury in Tissue

**COMPREHENSIVE
QUALITY ASSURANCE PLAN**

for the

ANALYTICAL SERVICES DIVISION

of

BROOKS RAND LABS
3958 6th Avenue NW
Seattle, Washington 98107 U.S.A.
206.632.6206
206.632.6017 (fax)
www.brooksrand.com
brl@brooksrand.com

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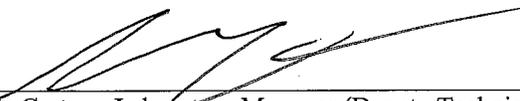
LABORATORY'S APPROVED SIGNATORIES



Michelle Briscoe – VP Analytical Services (Technical Director)
(effective upon sign-off Lead technical Director)

2/3/12

Date



Annie Carter – Laboratory Manager (Deputy Technical Director)
(to sign-off upon return from leave)

2-6-12

Date



Frank McFarland – Quality Assurance Manager

2/3/12

Date

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2.0 Statement of Policy

The Brooks Rand Labs' (BRL) Analytical Services Division is committed to sound and useful quality assurance/quality control (QA/QC) management practices resulting in the production of accurate analytical data. The principal focus of the analytical laboratory is to provide specialized analytical services for trace metals analysis in environmental samples with an emphasis on ultra-low detection limits, metals speciation, and unusual or non-routine matrices.

Obtaining accurate data is dependent upon an effective and consistent quality assurance program. To meet this need, National Environmental Laboratory Accreditation Conference (NELAC) and Department of Defense Quality Systems Manual (DoD QSM) standards have been incorporated into BRL's quality assurance program. Internal audits are conducted by BRL, and external audits of BRL's facilities are conducted by the Florida Department of Health (DOH) Environmental Laboratory Accreditation Program every two years to ensure that BRL meets the requirements of NELAC standards and by ANSI-ASQ National Accreditation Board/ACLASS every two years to ensure that BRL meets the requirements of the DoD QSM. Reciprocity NELAC accreditation is granted by Oregon Environmental Laboratory Accreditation Program, New York State DOH, New Jersey Department of Environmental Protection, State of Maine Department of Health and Human Services, and State of Louisiana Department of Environmental Quality. BRL is also accredited by the Washington State Department of Ecology and reciprocity accreditation is granted by the California State Department of Health Services. The Washington State Department of Ecology routinely conducts audits of BRL's facilities every 3 years to ensure that BRL's quality assurance program meets the agency's specific requirements. Additionally, periodic external audits initiated by clients serve to ensure that Brooks Rand Labs continually meets the specific requirements of our client.

Brooks Rand Labs management is committed to continually improving the quality assurance program. The BRL quality assurance program is implemented through a team effort across the entire laboratory group. All personnel concerned with environmental testing activities within Brooks Rand Labs must familiarize themselves with the quality system documentation [Comprehensive Quality Assurance Plan (CQAP) and all relevant standard operating procedures (SOP)] and implement the documented policies and procedures in their work. A listing of the general considerations and objectives of the overall program are as follows:

- *Maintenance of sample integrity.* Integrity is maintained by following documented and accepted sample handling procedures for the preservation, custody, storage, labeling, and record keeping associated with samples received by the laboratory.
- *Use of approved analytical methods.* Analytical methods and related procedures approved by the EPA are readily available. These are read and followed by all analysts. In addition, BRL is on the cutting edge of method development for the analyses of trace metals. All BRL-developed methods undergo rigorous testing and validation before they are approved by BRL scientists for use in the analysis of customer samples.

- *Regular evaluation of analytical results.* The results from quality control tests and from sample analyses are continually evaluated to identify method weaknesses and/or to detect a need for further analyst training.
- *Instrumentation performance and maintenance.* Determination of instrument performance level by frequent calibration and the analyses of performance evaluation samples, and through scheduled preventive maintenance, is documented on a real-time basis. Instrument calibration is performed as part of each analytical procedure.
- *Data reduction and report formatting.* Various levels of data review from acquisition to the final report are incorporated to minimize any potential errors in the final data. The report format is variable from a standard format to a customized data package, with or without electronic data deliverables (EDD).
- *Method performance (precision and bias) documentation.* Data from analyses are monitored using control charts to assess performance and to detect trends.
- *Regular evaluation of the quality system.* Brooks Rand Labs management is committed to continually improve the quality system. Annual reviews of all standard operating procedures and the CQAP, as well as routine audits of the laboratory and management reviews are some of the procedures used to find and correct deficiencies in the quality system.

Brooks Rand Labs management is committed to professional laboratory practices and to the quality of our environmental testing in providing services to our clients. The above considerations are documented to ensure the quality of the data generated by BRL. Subsequent sections of this manual will detail the various elements of the QA program developed and practiced by the laboratory.

The QA program is structured such that the CQAP is the primary reference for quality policies and procedures. As long as the CQAP contains all of the necessary requirements of the quality system, then no additional SOP is necessary. If there is a discrepancy between the CQAP and any SOP, the policy or procedure contained in the CQAP takes precedence and the discrepancy must be resolved as quickly as feasible. Any written directions that disagree with the CQAP and SOPs is considered a departure from the approved QA plan and may not be followed unless it has been approved by the QA Officer and the Vice President of Analytical Services. Refer to Section 8.5 for details on how any exceptional departure from BRL procedure is handled.

3.0 Organization and Responsibility

3.1 Duties and Responsibilities of Personnel

The laboratory staff is organized in such a way that all analytical personnel are trained in a variety of laboratory duties. Individuals are specialized in their area of primary responsibility, but training overlaps so that there are always secondary personnel trained to perform the primary functions of staff that may be absent. Specific responsibilities have different minimum qualification requirements. The descriptions of responsibilities and their minimum qualifications are listed in Table 3.1.

TABLE 3.1 RESPONSIBILITIES AND MINIMUM QUALIFICATIONS

Title	Responsibilities	Minimum Qualifications
VP of Analytical Services	Oversees operations of the laboratory, including: management of personnel and analytical services, contracting, client services, sales & marketing, QA/QC, R&D, budgeting, and financial controls	Bachelors degree in physical sciences (advanced degree or equivalent experience preferred) and 15 years experience in the environmental analytical lab business, with 10 years in management positions
Laboratory Manager	Oversees operations of the laboratory, including: management of all lab personnel and all analytical services, R&D, method development, facilities improvements, and scheduling	Bachelors degree in physical sciences and 6 years experience in the environmental lab business, with 5 years in management positions
Technical Directors	Oversees operations of the laboratory, including: maintaining instrumentation and equipment, technical oversight, method development, validation, and approval, R&D, responsible for ensuring laboratory compliance with the NELAC, DoD, and all other accrediting authority standards	Bachelors degree in physical sciences (advanced degree or equivalent experience preferred) with 24 hours of college chemistry credits, and 3 years experience in the environmental trace metals analytical lab business, with 1 year in a supervisory position
Project Management Group Lead	Oversees the project management group and manages client projects, including: internal communication of client requirements, reporting to client	Bachelors degree in physical sciences or equivalent and 3 years experience in the environmental lab business
Project Manager	Manages client projects including: internal communication of client requirements, reporting to client	Bachelors degree in physical sciences or equivalent and 1 year experience in the environmental lab business

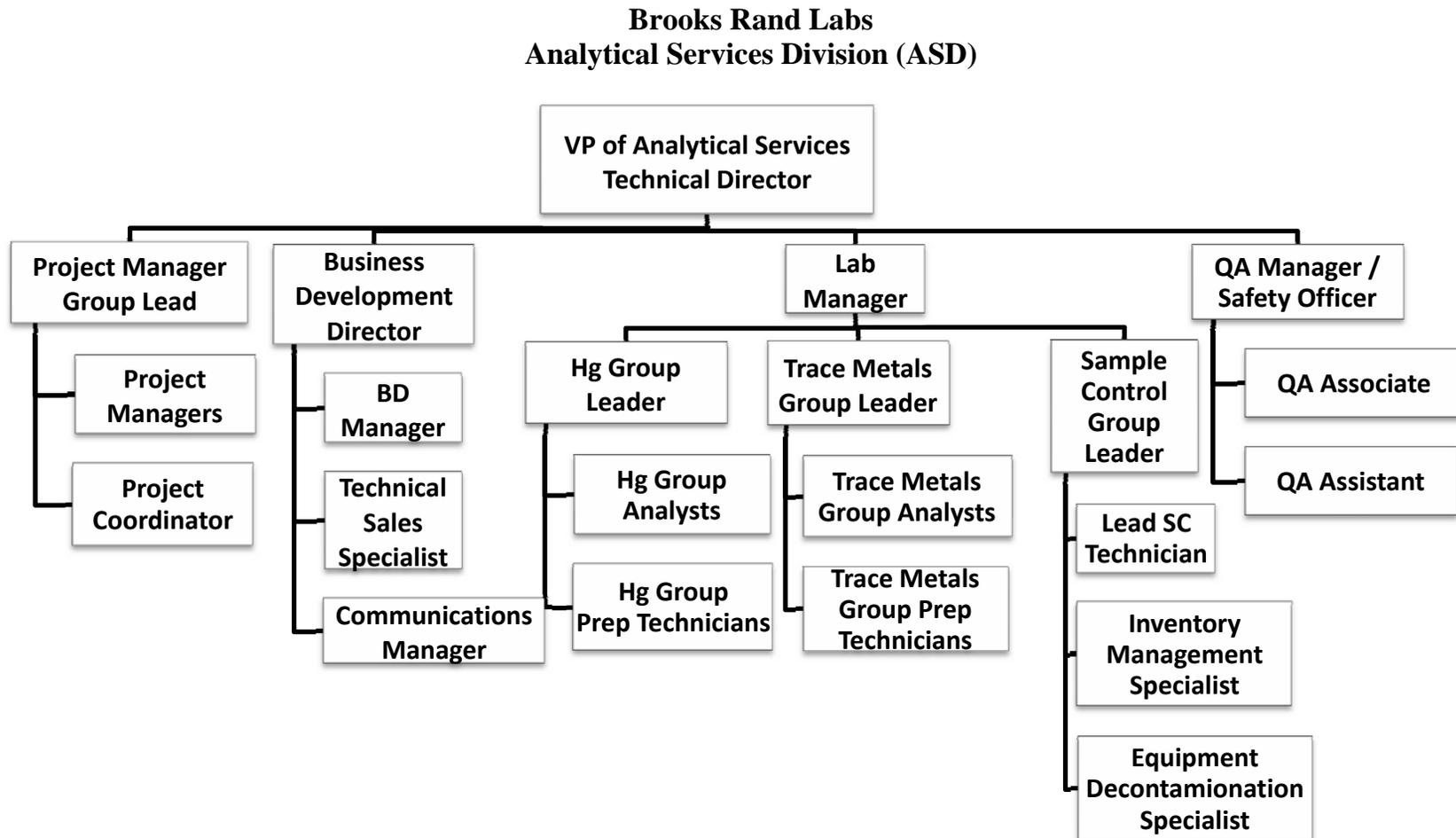
TABLE 3.1 RESPONSIBILITIES AND MINIMUM QUALIFICATIONS (CONTINUED)

Title	Responsibilities	Minimum Qualifications
QA Manager	Oversees QA group; has the authority and is responsible for implementing, maintaining, and improving the QA program, ensuring that all personnel understand their contribution to the QA program, ensure that communication takes place at all levels regarding the effectiveness of the QA program, evaluating the effectiveness of training, using all available tools to monitor trends and continually improve the QA program, and ensuring laboratory compliance with the TNI, DoD, and all other accrediting authority standards	Bachelors degree in physical sciences (advanced degree preferred) and 3 years lab experience with 1 year of applied QA principles
QA Associate	Assist QA Manager in duties	Bachelors degree in physical sciences and 6 months experience in the environmental lab business or Associates degree and 1 year of analytical lab experience with 6 months of applied QA principles.
QA Assistant (as necessary)	Assist QA Manager in duties	Bachelors degree in physical sciences or Associates degree and 6 months experience in the environmental lab business
Mercury Lab Group Leader	Oversees the mercury analytical group including: training records, sample preparation, analysis, and scheduling within the group. Overseas classical chemistry methods for percent total solids and total volatile solids performed by the mercury group.	Bachelors Degree in physical sciences and 1 year of analytical lab experience as an analyst, or 5 years experience in the environmental lab business
Trace Metals Group Leader	Oversees the trace metals analytical group including: training records, sample preparation, analysis, and scheduling within the group. Overseas classical chemistry methods for percent total solids and total volatile solids performed by the trace metals group.	Bachelors Degree in physical sciences and 1 year of analytical lab experience as an analyst, or 5 years experience in the environmental lab business
Analyst	Perform and document sample preparations and analyses following SOPs, instrument calibration and reagent/standard preparation	Bachelors Degree in physical sciences or equivalent and 1 year of analytical lab experience or Associates degree with 2 years analytical lab experience.
Sample Control Group Leader	Oversees sample control group including: training, custody of samples, and scheduling within the group. Overseas classical chemistry method for total suspended solids performed by the sample control group.	Associates Degree and 1 year of analytical lab experience
Lab Technicians	Individual Lab Technicians will perform some or all of the following: Receive, log-in, and store samples; decontaminate lab ware; prepare bottle and reagent testing; prepare bottle orders/sampling kits; dispose of samples.	Associates degree or equivalent college education or High School Graduate with 6 months experience in the environmental lab business

3.2 BRL Organization

There is a defined chain of responsibility along which the laboratory staff is organized. The organization of the laboratory personnel is shown in Figure 3.2.

FIGURE 3.2 – ORGANIZATIONAL CHART



3.3 Managerial Responsibilities for the Detection of Improper, Unethical, and Illegal Actions

Brooks Rand Labs holds management responsible for ensuring that all client data is properly and accurately reported. To this end, management works diligently to ensure that all employees of BRL are free from undue commercial, financial, and any other pressures that may adversely affect the quality of their work. In addition, the management of BRL works proactively to detect any improper, unethical, or illegal actions that might arise due to such pressures before such actions can adversely affect client data.

All information relevant to client results, from sample receipt to the analysis and reporting of data, goes through several levels of review. Management keeps track of all work that appears sloppy or contains mistakes and all changes made to the LIMS are electronically tracked and stamped with the date/time of the change and who instigated it. All employees routinely meet with senior management at which time work-related problems are discussed so that any undue pressures can be brought out into the open. Immediate supervisors speak daily with all employees and strive to keep aware of the activities and general attitudes of those employees for which they are responsible. Employee work is additionally reviewed during monthly audits.

All employees receive training to ensure that each is fully aware as to what constitutes improper, unethical, and illegal behavior and what the consequences are for such behavior (refer to BRL SOP BR-1101) and must sign the “Brooks Rand Labs Ethical and Legal Responsibilities Agreement” form stating that they agree to adhere to all aspects of the ethics program at BRL prior to working with client samples. Any employee who becomes aware of unethical behavior is encouraged to report the behavior to BRL management. Any employee should feel free to report such behavior to any manager, on up to the President of BRL. Brooks Rand Labs management assures that any reporting of improper, unethical, or illegal behavior will remain strictly confidential. If such behavior is detected, the responsible employee is immediately brought before senior management. If the behavior is unintentional and appears to be caused by undue pressures, every effort is made by management to eradicate the pressures. If the behavior is deemed willful, then senior management is responsible for determining the best course of action for BRL and its clients. Under no circumstances is any behavior that might adversely affect the quality of the data produced by BRL tolerated.

4.0 Training

4.1 Technical Training

Brooks Rand Labs personnel are trained in every aspect of their duties prior to the analysis of client samples. An experienced technician who has previously demonstrated their capability to perform the procedures for which a new employee is being trained directly supervises all training.

Brooks Rand Labs is also on the cutting edge in the development of new techniques for the analysis of trace metals. In such situations where a scientist is developing a new technique, they must train themselves in the new procedures. The lead scientist is expected to develop the training protocol by which future technicians will be trained in the method.

Regardless of how training takes place, an initial demonstration of capability (IDOC) for each method must be successfully completed as per NELAC and DoD QSM standards prior to any analysis of client samples. The DOC serves as an indicator of the successful completion of training. From then on, the consistent meeting of quality control criteria serves as the ongoing DOC. The QA Manager reviews the ongoing DOC annually to ensure the continued proficiency of each technician. The conclusions of these reviews are recorded in each employee's training records.

4.2 Safety Training

All BRL employees receive training in laboratory safety that they are required to review on an annual basis. Safety training includes "Right-to-Know" training as to the potential chemical and physical hazards of working in an environmental laboratory and how best to reduce these hazards. Training also includes what procedures to take in the case of a laboratory accident and the locations of all safety and first aid equipment.

4.3 Training in Legal and Ethical Rights and Responsibilities

All BRL employees receive annual training in their legal and ethical rights and responsibilities. This training includes the following topics: Non-discriminatory workplace; drug free workplace; data manipulation; and workplace ethics. This training also specifies the potential punishments and penalties for improper, unethical, or illegal actions performed by BRL employees. The Brooks Rand Labs data integrity plan (SOP BR-1101) discusses in detail the specific legal and ethical rights and responsibilities of employees at BRL. Training on this SOP is required for all personnel in the Analytical Services department.

In conjunction with this training, each employee must attest that they are free from any commercial, financial, and other undue pressures, which might adversely affect the quality of their work prior to working with client samples.

4.4 Documentation of Training

Each employee is responsible for documenting all training in their personal training records and each Group Lead must review the training records for all employees within their group to ensure

completeness. At a minimum, the Quality Assurance Manager audits the training records quarterly and reports any deficiencies to the Group Leads and the Laboratory Manager so that they can be corrected. Training records are updated annually to ensure that all personnel continue to be proficient in their assigned tasks. Records for each type of training (i.e. Technical, safety, and legal and ethical) are maintained and stored for a minimum of five years, regardless of the employment status of the individual.

4.5 Additional Training

The Quality Assurance Manager reviews each employee's training records quarterly. Any deficiencies found are recorded in the monthly QA audits. In addition, the technical abilities of each employee are constantly monitored through the analysis of quality control samples. If quality control criteria are not consistently met, additional training is required under the supervision of the Laboratory Manager. Any additional training is fully documented and a new DOC must be successfully completed before the technician may restart analyzing client samples.

5.0 Capabilities and Quality Assurance Objectives

5.1 Acceptance of New Work

The VP of Analytical Services (along with any necessary assistance from the [Project Management Group Lead](#), project managers, QA Manager, and individual group leaders) carefully reviews the specific requirements of every contract before any new work is accepted by Brooks Rand Labs. BRL will accept a project only after the VP of Analytical Services has ensured that BRL possesses the appropriate facilities and resources to carry out the work as specified by the client.

5.2 Capabilities of Organization

BRL is an analytical laboratory primarily focused on providing analytical services for the determination of low-level trace metals and metals speciation in environmental samples. Brooks Rand Labs specialties are threefold: 1) providing the lowest detection limits commercially available, 2) speciation of oxidation state and organometallic forms; and 3) analysis of non-routine matrices.

Each sample preparation method followed at Brooks Rand Labs is dependent upon the analyte of interest and the type of matrix being analyzed. Refer to the specific analytical method or standard operating procedure (SOP) for a description of each particular preparation method utilized at BRL. Other sample preparation methods may be used upon request for specific enforcement or compliance-based contracts.

5.3 Quality Assurance Objectives

Brooks Rand Labs is dedicated to providing the finest services to its clients. To meet this objective, every position at BRL is staffed with trained personnel and competent managers who possess the authority and resources to produce meaningful metals data and meet the needs of our clients.

The primary purpose of the Quality Assurance Program at BRL is to ensure that all data reported to our clients are accurate and reproducible. To this end, BRL implements procedures to ensure that all staff are qualified and fully trained to perform their specific laboratory duties, that laboratory instrumentation is properly maintained and calibrated, and that materials are adequately stocked and tested prior to use in the laboratory. All data reported by the laboratory undergoes several levels of review before being approved for release by the Quality Assurance Department.

5.4 Subcontracted Work

Occasionally, a client may wish to work directly through Brooks Rand Labs even for analyses that BRL does not currently perform. Under these conditions, BRL will subcontract work to other laboratories with the client's approval. The subcontracted laboratories must meet all project specific requirements before samples may be delivered.

[Subcontract laboratories are selected by Brooks Rand Labs based a culmination of many factors. These include but are not limited to laboratory capabilities, past work experience, data quality \(including data presentation\), accreditation / certification, price, turnaround time, customer service,](#)

and electronic data deliverable (EDD) capabilities. Example reports can be requested from a potential subcontract laboratory.

Once subcontracted work has been contracted between Brooks Rand Labs and the client, a purchase order agreement is issued by Brooks Rand Labs to the subcontract laboratory.

All samples are logged into Brooks Rand Labs' Laboratory Information Management System and a subcontract order is created. When samples are submitted to the subcontract laboratory, they are accompanied with the original chain-of-custody form and the subcontract order.

The subcontract laboratory will email the appropriate Brooks Rand Labs Project Manager with the final report and EDD (if requested). The Project Manager will then forward the report to the Quality Assurance Manager. Data is reviewed and notes will be written regarding the data set. If there are outstanding issues, the Project Manager will contact the subcontract laboratory and work to resolve the issue/gain clarification. Depending on the reporting level, Brooks Rand Labs may supply a cover letter to the client regarding the data set provided by the subcontract laboratory. Final reports (and EDDs) will be emailed by the Project Manager to the client.

6.0 Sampling Procedures and Requirements

6.1 Sampling Capabilities

BRL conducts field sampling on a very infrequent basis. Therefore, the following sampling procedure topics are only briefly addressed:

Sampling Equipment - All sampling equipment is decontaminated [and/or tested](#) prior to and following every sampling event and stored in a secure designated area. Any equipment requiring calibration or maintenance, as specified by the manufacturer’s instructions, is placed on a routine calibration/maintenance schedule.

Field Sample Documentation - During site visits, minimal notes regarding specific field parameter measurements, general observations, hydrologic conditions, and overall suitability are documented, if applicable. These notes are entered as Work Order Comments in BRL’s LIMS for the related project(s).

Sample Dispatch - Field samples are relinquished by the sample collection team to BRL’s Sample Control Group following a strict chain-of-custody process. Time, date, and samplers signatures are documented.

Field Reagent and Waste Disposal - All field reagents and wastes generated or used during field sampling activities should be collected and disposed of in accordance with all state and federal regulations.

6.2 List of Equipment Provided by BRL for Sampling

TABLE 6.2 - CONTENTS OF BRL SAMPLING KITS

<u>Equipment</u>	<u>Construction</u>	<u>Use</u>	<u>Parameter Groups</u>
Sample Container(s)	Teflon [®] – FEP, PFA Fluorinated – FLPE Glass – I-Chem 200 series HDPE (for solids only) Ziploc [®] bags (some biota)	Sampling/Storage	Mercury and monomethyl mercury in water/soil/biota
	HDPE bottles LDPE, HDPE, or PP jars Ziploc [®] bags	Sampling/Storage	Trace Metals, except Hg, in water/soil/biota
	Iodated carbon (IC) Traps or Gold Coated Media in Ziploc [®] bags	Sampling/Storage	Mercury in air
Shipping Containers	Plastic cooler or cardboard box	Sample Transport	All parameter groups
Gloves, Clean Room	Vinyl, non-powdered	Sampling	All parameter groups

6.3 Decontamination Procedures

Client Equipment

BRL supplies sample containers for all analyses. Clients may provide their own sample containers at their discretion, but Brooks Rand Labs cannot guarantee the cleanliness of containers that have not been cleaned and/or tested by Brooks Rand Labs.

Cooler/shipping containers

All coolers are cleaned prior to use for shipping samples or sample containers. Appropriate sample containers are placed in the coolers to make a sampling kit. Sampling kits are sent via freight carrier (UPS or FedEx) to the sampling team.

Sample Containers

Due to the possible occurrence of false positive results due to trace metals contamination, it is extremely important that all water samples are collected in rigorously acid-cleaned or pretested containers that are double-bagged in poly bags and suitable to the analyses to be performed.

6.4 Sampling Protocol

BRL recommends that all samples to be analyzed for trace metals are collected following the guidelines laid out in EPA Method 1669 (7/96): Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.

6.5 Sample Preservation, Holding Times, Container Types, and Required Volumes

All preservation reagents used by BRL are analytical grade or better. For mercury analysis, samples not being filtered in the lab may be sent to BRL at ambient temperature via ground shipment where they will be preserved with pretested ultra-trace BrCl. For **most** other parameters, the field sampling crew can add the appropriate preservative (See Table 6.5) or they should send the samples on ice via overnight shipping to be preserved at BRL.

TABLE 6.5 - SUMMARY OF SAMPLE CONTAINERS & PRESERVATIVES

Parameter	Method	Minimum Volume	Container	Means of Preservation	Holding Time
A. Water¹					
As and Se (for HGAAS analysis ONLY)	BR-0020	500 mL	HDPE ²	0.4% (v/v) 12 M HCl; pH < 2 within 28 days of collection	6 months
Arsenic (As) Speciation	EPA 1632	125 mL		0.4% (v/v) 6 M HCl at time of collection; Store in Dark at 0-4 °C ³	28 days
Selenium (Se) Speciation	BR-0061	250 mL		Field-filtration recommended, especially for samples with high levels of solids; unpreserved; zero headspace; keep dark; maintain collection temperature as best possible	Dependant on sample matrix
MeHg (Freshwater)	EPA 1630	250 mL	Fluoropolymer, FLPE, or Glass with Fluoropolymer lined lids	0.4% (v/v) 12 M HCl; Store in Dark at 0-4° C	6 months
MeHg (Salt Water ≥ 10 ppt salinity)	EPA 1630	250 mL		0.2% (v/v) 18 M H ₂ SO ₄ ; In Dark at 0-4 °C	6 months
Total Hg	EPA 1631E	250 mL		Preserve to pH < 2 in original sampling container within 28 days	90 days
Acid-labile Hg	BR-0003	250 mL		0.8% 12 M HCl within 24 hrs of collection; Store in Dark at 0-4 °C	Analyze 21 days (± 3 days) after preserv. (being investigated)
Total Volatile Hg	BR-0005	1-L	Glass with Fluoropolymer lined lids	No head space; Store in Dark at 0-4 °C	24 hours
Reactive Hg	In-House	250 mL	Gold traps stored in plastic bags	Field collect reactive Hg onto gold traps and mail overnight	Gold traps stable for 5 days from collection
Fe (II)	SM3500B	40 mL	Glass with Teflon-lined lid w/preservation	0-4 °C, dark, 1% (v/v) 12 M HCl at collection (pre-preserved vial)	48 hours
ICP-MS Metals (Freshwater)	EPA 1638, Mod.	125 mL	HDPE	1% (v/v) HNO ₃ ; pH < 2 in lab, should be acidified within 14 days of collection ⁴	6 months
ICP-MS Metals (Brackish or Seawater)	EPA 1640, Mod.	1 L	HDPE	0.1% (v/v) HNO ₃ (APDC Prep) or 0.2% (v/v) HNO ₃ (RP prep) or 1% (v/v) HNO ₃ (chelating column procedure) in lab, should be acidified within 14 days of collection	6 months
Cr (VI)	SW 7196A	125 mL	HDPE	Store at 0-4 °C	24 hours
	SW 7196A, Mod.			16 mL/L of 25% NaOH (pre-preserved bottle); store at 0-4 °C	30 days
TSS	EPA 160.2	500 mL	HDPE	Store at 0-4 °C	7 days
Lab pH, hydrogen ion	EPA 150.1	25 mL	Glass or HDPE	0-4 °C	Analyze immediately

¹ Samples to be analyzed for dissolved analytes must be filtered prior to preservation. This should preferably be done on site in the field. If this is not possible, the sample must be chilled (0-4 °C) and filtered within 48 hours of collection (24 hours for mercury samples).

² High Density Polyethylene

³ All temperature ranges of 0-4 °C assume an acceptable measured temperature of ± 2 °C from either extreme as long as the samples do not freeze.

⁴ While Brooks Rand Labs suggests that samples be acidified within 14 days of collection, there is no good scientific evidence to indicate that not doing so will impact data quality as long as samples are acidified in the original collection container for a minimum of 24 hours prior to analysis.

TABLE 6.5 - SUMMARY OF SAMPLE CONTAINERS & PRESERVATIVES (CONTINUED)

Parameter	Method	Minimum Volume	Container	Means of Preservation	Holding Time
B. Wet Sediments and Soils					
Total Metals	Various	Fill 4 oz jar	FLPE, Glass or HDPE	0-4 °C during shipping, ≤ 4 °C and in dark in lab	1 year ⁵
Metal Species (other than As species and Reactive Hg)	Various	Fill 4 oz jar	FLPE, Glass or HDPE	0-4 °C during shipping, -15 to -30 °C and in dark in lab	1 year
As Species	EPA 1632	Fill 4 oz jar	FLPE, Glass or HDPE	0-4 °C during shipping, < -18 °C in lab	2 years
Reactive Hg	In-House	Fill 4 oz jar	FLPE or HDPE	Immediately chill to ≤ 4 °C and freeze within 48 hours of collection, store < -18 °C in lab	90 days
Cr (VI)	SW 3060a/ 7196a	Fill 4 oz jar	FLPE, Glass or HDPE	0-4 °C during shipping; ≤ 4 °C in lab	280 days
% Solids	EPA 160.3	100 mL	FLPE, Glass or HDPE	0-4 °C	7 Days ⁶
C. Dry Sediments and Soils					
Total Metals	Various	Fill 4 oz jar	FLPE, Glass or HDPE	N/A (Room Temperature is OK)	1 year
Metal Species	Various	Fill 4 oz jar	FLPE, Glass or HDPE	Room Temp OK (recommended 0-4 °C during shipment; ≤ -15 °C in lab)	1 year
Cr (VI)	SW 3060a/ 7196a	Fill 4 oz jar	FLPE, Glass or HDPE	0-4 °C during shipment; ≤ 4 °C in lab	28 days
D. Wet Tissues					
Total Metals or Species (other than As)	Various	Fill 4 oz jar	FLPE, Glass, HDPE or Ziploc bags	0-4 °C during shipping, -15 to -30 °C, Dark in lab	1 year
As Species	Various	Fill 4 oz jar	FLPE, Glass, HDPE, or Ziploc bags	0-4 °C during shipping, < -18 °C in lab	2 years
E. Tissues (freeze dried)					
Total Metals	Various	Fill 4 oz jar	FLPE, Glass or HDPE	N/A (Room Temperature is OK)	1 year
Metal Species (other than As Species)	Various	Fill 4 oz jar	FLPE, Glass, HDPE, or Ziploc bags	Room Temp OK (recommended 0-4 °C during shipment; ≤ -18 °C in lab)	1 year
As Species	EPA 1632	Fill 4 oz jar	FLPE, Glass, HDPE, or Ziploc bags	N/A (Room Temperature is OK)	2 years
F. Air					
Total Hg	EPA 324 / IO-5	NA	Iodated Carbon Trap or Gold Coated media	Ends plugged, store in Ziploc® Bag	6 weeks
MeHg	BR-0011	10 L	Tenax trap	1 °C, Dark	48 hours
G. Biomonitoring					
Total Metals (including Hg) for Urine	Various	90 mL	Polyethylene Urine Specimen Container (transfer to FPE for Hg analysis)	0-4 °C during shipment; 0-4 °C in lab (or ≤ -15 °C to -30 °C in lab)	28 days (1 year if frozen – being investigated)
Total Metals and Metals Speciation in Whole Blood	Various	7 mL	7 mL royal blue top EDTA tube	0-4 °C during shipment; ≤ -15 °C to -30 °C in lab	1 year
Total Metals and Metals Speciation in Hair	Various	100 mg	Ziploc® bag	Dark, room temperature	1 year

⁵ There are no established holding time limitations for solid samples.

⁶ Although the standard temperature / holding time requirements for % solids are 0-4 °C for 7 days, many solid samples are frozen and held for much longer periods prior to analysis for other parameters. Ideally, sample aliquots for each parameter should be removed prior to freezing. If this has not been done and % solids analysis is required for the samples, then the aliquots for % solids should be removed at the same time as the aliquots for the other parameters to ensure similar sample characteristics between aliquots.

6.6 BRL's Policy on Accepting Samples

Brooks Rand Labs will only accept samples for analysis from parties with whom a written contract has been jointly signed or from long-time clients in good standing with BRL's accounts receivable department. If a signed contract is not in place, samples are still received and placed on "hold." Any time-sensitive work, such as preservation or filtering, is still performed and the samples are stored appropriately. Once the Project Manager establishes the contracting paperwork, the samples are taken off hold status and the samples may be batched for further analysis. The terms under which BRL would enter into a contract are explained in section 5.1 of this document.

Once a legal contract is in place, BRL will accept client samples even if the samples have not been preserved or handled properly, but all evidence of improper preservation and/or handling will be fully documented by BRL at the time of receipt. Examples of improperly handled samples include those with holding time violations, temperature violations, pH violations, evidence of improper sampling technique, improper handling (i.e. broken custody seal), improper documentation of samples on the chain of custody (COC) form, etc.

In the case of samples that have been collected or preserved improperly, the Project Manager immediately contacts the client to determine whether the client desires to continue with the analysis of samples. At the request of the client, BRL will perform analyses of samples even if they have non-conformance issues, but all such samples shall have their results qualified to indicate the non-conformance.

In the case of improperly documented samples, the Project Manager or her agent will contact the Field Sampler to clarify any questions concerning the COC before samples are batched.

At all times, BRL reserves the right to not accept samples that are deemed to be a threat to the health or safety of BRL personnel beyond what might reasonably be expected while working within an environmental laboratory.

Refer to the sample receiving SOP (BR-0300) for specific information pertaining to BRL's sample acceptance policy.

7.0 Sample Custody

7.1 Field Custody

Formal custody requirements begin at BRL with the shipment of sample containers to the field. Every shipment must be documented by BRL. With the exception of HDPE bottles sent for the collection of hydride, [Se speciation, and all solid](#) samples, a minimum of 10% of the bottles from 10% of the cases for each manufacturer lot # are tested for all applicable analytes prior to shipment. BRL provides Chain-of-Custody (COC) forms and two custody seals with each container shipment. Sample collection dates and times should be provided on the COC by the organization conducting the field sampling. If provided, the COC is used as documentation for sample collection dates and times. In addition, all sample container shipments are documented to track container information such as bottle cleaning batch numbers, quantity of containers shipped and their date of shipment.

While BRL does not typically provide field services, we do recommend that certain precautions be taken when collecting samples. Special consideration should be given to the procurement, transportation, preservation, and storage of samples to be analyzed. These procedures are intended to ensure that any analyte originally present in the sample matrix has not degraded and that contamination has not been introduced. For example, for mercury work, only rigorously acid-cleaned FEP, or pre-tested FLPE and glass containers with fluoropolymer lined lids may be used for water samples. Water samples to be analyzed only for total mercury by EPA Method 1631E may be shipped via ground service unpreserved as long as the samples are to be oxidized in their original sampling containers. Otherwise, water samples should either be shipped to BRL at the method-required temperature within 48 hours of collection and preserved upon receipt, or samples may be preserved in the field with the appropriate preservative as per specific method instructions. See section 6.5 of this document for container, preservation, and holding time requirements for other analyses. Tissues and other solid matrices may be stored in FLPE containers, HDPE containers, glass containers with fluoropolymer lined lids, or [plastic bags/wrap](#). Solid samples are preserved by shipping on ice, followed by storage in a freezer at [-15](#) to [-30 °C](#) (solids to be analyzed for arsenic speciation must be stored ≤ -18 °C).

The courier is responsible for documenting the custody of the samples while the samples are in transit from the field to BRL.

7.2 Laboratory Custody

7.2.1 BRL Definition of Laboratory Custody

A sample is considered to be "in custody" in the laboratory if it meets one of the following criteria:

- It is in the Lead Sample Control Technician's (or designated alternate's) possession
- It is in the analyst's possession
- It was in a Lead Sample Control Technician's, designated alternate's, or analyst's possession and then locked or sealed to prevent tampering.
- It is in a secure area (i.e., storage)

7.2.2 Sample Receipt

All samples delivered to BRL are received by the Lead Sample Control Technician or designated alternate in the laboratory receiving area. Upon delivery of samples the Lead Sample Control Technician or designated alternative signs and dates the receipt and the COC form (refer to SOP BR-0301 for example of form).

Immediately after opening the cooler or other container, the Lead Sample Control Technician confirms the presence of ice, measures sample temperatures (if required), and documents the condition of the samples (intact, broken, leaking, etc.). The Lead Sample Control Technician also verifies that each container is properly labeled and sealed and compares the sample ID or field ID number against the COC form. The temperature of the samples at the time of receipt is determined by aiming a calibrated IR thermometer directly into a sample.

<Reference to temperature blanks removed>

The Lead Sample Control Technician is also responsible for ensuring that all samples are properly preserved. If any filtration or analysis of volatile mercury species is required, this should be performed before the preservation of samples. All samples must be preserved in accordance with the preservation instructions in each appropriate analytical methodology. Water samples for certain analytes do not require acidification and are stored in the refrigerator at 4 °C. If water samples that do require acidification are preserved in the field, the Lead Sample Control Technician checks the pH and documents that it is less than 2. If it is not less than 2, the measured pH is documented on the Sample Receiving Log, additional preservation reagent is added to the sample(s), and this addition is documented.

If the sample ID and the COC do not match, the seals on any of the containers are broken, the temperature of the samples is above the method specified storage limit, or the samples are not properly preserved, the Sample Control Technician notes the problem [directly in the LIMS “Project Notes” for the affected work order](#) and notifies the Project Manager. The project manager then immediately notifies the client of any concerns.

If sample containers arrive with too little sample for analysis and this is noticed at receipt, then the Sample Control Technician goes ahead and logs the sample in for all analyses requested on the COC, sets the status for the analyses on the affected sample to “cancelled”, and writes “insufficient sample for analysis” in the container comments field.

All of the above information is documented at the time of receipt on the BRL Sample Receiving Checklist. This form also includes a section for describing any non-conformance issues and their resolutions. Detailed instructions for the filling out of this form, as well as an example of the form are found in SOP BR-0300. Refer to SOP BR-0300 for a detailed description of BRL’s sample acceptance policy.

7.2.3 Sample Log In

When logging in samples, the Lead Sample Control Technician must check the [LIMS “Project” information](#) against the samples received to ensure that the work has been authorized. If any discrepancies exist, the Project Manager is immediately notified and the discrepancy is noted on the BRL Sample Receiving Checklist.

All samples are given a unique sample identification number at the time of sample log in. This number consists of a work order number that is unique to each sample shipment received and a

sample number for each sample within that particular shipment. Work order numbers consist of a 7-digit code (yyww####) where the first two numbers are associated with the year, the next two are associated with the week of the year, and the final three are associated with the number of shipments received in that week (e.g., the eleventh sample shipment received in the 45th week of 2012 is given the work order number 1245011). The samples within a shipment are then each identified by sequential numbering. For example, if three samples were received in the 1245011 shipment they would be given the sample numbers 1245011-01, 1245011-02, and 1245011-03. The client's sample ID and the BRL ID numbers are both entered into the LIMS. The BRL work order numbers (in addition to the client's ID numbers) are referenced during all laboratory preparations and analyses.

When a bottle is removed from the Ziploc[®] bags in which it was sent, the bottle should be rinsed with clean DIW (for low-level samples) and/or wiped with a clean cloth. Bottles are then labeled with the BRL sample number, customer project number, client sample ID, matrix, date of sample receipt, preservation, storage location, and list of analytes to be analyzed for. An example of a BRL sample label is as follows:

1245011-01	CWP-MM008
Client ID: Effluent A	
Matrix: Water	11/03/2012
Preservation: 5% HNO3	
Home Location: Cabinet #7	
As, TR Cd, TR Co, TR Fe, TR	

After all of the log-in information is recorded in the LIMS, the BRL Work Order Receipt form (refer to SOP BR-0300) is generated from the LIMS and is signed and dated by the Lead Sample Control Technician.

Custody of the original samples is tracked in the LIMS by updating the storage location of the samples in the bench sheet every time that they are moved.

7.2.4 Sample Storage

All samples are stored in a secure area. A secure area is defined as a locked area within the premises of BRL with restricted access. To satisfy these custody provisions, the laboratory implements the following procedures:

- Access doors to the laboratory are kept locked, except during normal working hours
- Visitors must sign in and are escorted while in the laboratory
- Samples remain in the secure area until they are removed for sample preparation or analysis

After the samples are logged in, the Lead Sample Control Technician stores them, according to their specific holding requirements, in either the refrigerator, freezer, or on shelf space in the secure sample storage cabinets

Samples requiring refrigeration or freezing are stored in facilities dedicated to secure sample storage in a sample storage room located in the northwest corner of the facilities. The samples are removed from the shipping cooler and stored in their original containers, unless damaged. Samples not requiring refrigeration are stored on shelves in the secure sample storage cabinets, which helps to protect samples from UV radiation. All standards and other chemicals used at BRL are stored separately from samples.

After the samples are stored, all sample information is placed in a folder. This information includes the client's COC form(s), a copy of the BRL Work Order Receipt form, [the shipping way bill](#), and any other documents included with the shipment. The folder is labeled with the work order, project reference number, [received date](#), and due date. The folder is given to the Project Manager who then reviews the information, signs and dates the BRL Work Order Receipt form, and files the folder in the "Active Customer" file located in the Project Manager's office. The "Active Customer" files are sorted alphabetically by the project reference number. Each BRL Sample Receiving Checklist is stored in sample control.

To ensure that sample holding times are met, samples for all projects are assigned a due date. Each analytical Group Lead is responsible for ensuring that all due dates (or sample turn-around times) are met. This is done by checking the LIMS to see what deliverables are approaching the due dates. In addition, all Sample Processing Forms (SPF) have due dates recorded on them for each project, which correlates to the date that the sample preparation, analysis, data review and report need to be completed. This date is generally [four](#) days prior to the final report due date in order to allow sufficient time for final report generation, review and submittal. If samples are on a rush turn-around schedule, then the final due date will be adjusted to give less time between the date on the SPF and the date that the final report must be sent to the client. When this is the case, the Project Manager is responsible to inform all laboratory personnel that the data is on a quick turn-around schedule.

The duration of original sample storage at BRL is set at two months following the submittal of the final report, unless contractual requirements indicate a longer period of storage.

7.2.5 Sample Distribution and Tracking

The system for tracking samples through preparation and analysis consists of the LIMS, laboratory worksheets, laboratory notebooks, instrument operation logbooks, instrument printouts (raw data), and final analytical reports.

7.2.5.1 Sample Batching - After samples are received and logged-in, the samples are then batched by the analytical Group Leads. Batches are sequentially numbered starting with the letter B, then the last two digits of the year, followed by a four digit sequential number (e.g. the 805th batch in 2011 is numbered B110805. Samples are assigned to each batch in the LIMS. Sample custody is tracked electronically in the LIMS through the bench sheet.

Original samples are batched according to the method by which they are to be prepared and analyzed. At the time of batching the SPF is printed from the LIMS. Any special QA requirements and/or pertinent information provided by the client concerning the sample

preparation/analysis should be noted on the SPF. This information should be added to the project comments in the LIMS so that it will automatically appear on any SPF including samples for that project. **If the project comments field is not large enough, additional notes can be made in the project notes field with instructions in the project comments field to “see project notes.”** Once batched, the status of the samples is changed from “available” to “batched” in the LIMS.

7.2.5.2 Sample Preparation - The SPF is given to the scientist responsible for sample preparation. From the time the scientist removes samples from the storage area the SPF must remain with the sample batch. All sample preparation details must be documented on a form or in a logbook. Copies of all preparation documentation, once complete, must accompany the SPF. In order to track both original samples and sample preparations the preparation technician documents the removal of original samples from their primary storage location to the preparation location and back to their storage location in real time in the LIMS at the LIMS prep bench sheet. After the original samples are logged in as being returned to storage, the preparation technician changes the samples in the prep bench sheet to “extracts.” These extract samples can now be tracked separately from the original samples. The location of the extracts is entered as the preparation location. When sample preparation is finished and the extracts are moved to the lab or other storage location, this information is entered into the LIMS prep bench sheet. From then on, every time the extracts are moved, up to and including disposal, this information is updated in real time.

During sample preparation, any comments on unusual observances or deviations from the analytical method or SOP must be documented. (Note: Senior management must approve any deviations from the analytical method or SOP prior to the preparation of the samples.) Following sample preparation, the prepared samples, along with the SPF and all preparation documentation, are stored in a secure laboratory area. Once prepared, the status of the samples is changed from “batched” to “prepared” in the LIMS.

Note: If during sample preparation the technician notices that there is insufficient sample for preparation, the technician should send an email informing their Group Lead of this information and write the information on both the SPF and the benchsheet. The Group Leader should set the analysis for the affected sample to “cancelled”, write “insufficient sample for analysis” in the container comments field, and send an email to the affected Project Manager and the other Group Leaders if any other analyses are affected. It is up to the Group Leaders to coordinate who will set any other affected test code’s analytical status to “cancelled.”

If the sample is exhausted following preparation, then the technician should make a note on the benchsheet and send an email to the Group Leader, affected Project Manager, and the QA Group. The PM then adds a note to the container comments field for all affected samples. Should the sample be inadvertently rebatched, this note will show up on any subsequent SPFs making it clear that the sample is already exhausted and cannot be reanalyzed.

7.2.5.3 Sample Analysis – When analyzing the samples, the analyst builds a sequence that contains the calibration and other sequence specific QC (ICVs, CCVs, CCBs) as well as all

samples, including batch QC, from all of the batches analyzed as part of the sequence. When a batch is analyzed, the analyst must sign and date the SPF and update the LIMS. Any comments on unusual observances or deviations from the analytical SOP must be documented and must be referenced on the SPF. As previously mentioned, movement of the batch throughout the lab is documented in the LIMS at the prep bench sheet. The analyst then uploads the data into the LIMS and signs and dates the SPF with when this action was performed. During the upload of the data, the status of all samples is changed from “prepared” to “analyzed” in the LIMS. The analyst then performs the primary review of the data.

7.2.5.4 Primary Data Review - When the data is reviewed, the reviewer must sign and date the SPF, update LIMS, and comment on any unusual observances or deviations from appropriate. Primary data review includes checking all LIMS entries in the prep bench sheet and the data upload for accuracy, determining whether criteria is met, and preparing analyst notes about the quality of the data. The analyst then puts together the data package, which includes a printout of the Analysis Sequence form, any sequence lab bench sheets, all SPFs, all sample preparation documentation, and any analyst notes. Instrument raw data is saved electronically as a PDF file. Once the data has been primary reviewed, the status of the samples is changed from “analyzed” to “reviewed – primary” in the LIMS and the SPF is signed and dated.

7.2.5.5 Final Review - The QA Manager, or his designee, reviews the final data. After the final review, either the QA Manager or his designee must sign and date the SPF and include comments on any unusual observations and/or deviations from the analytical method or SOP. The QA Manager or his designee also updates the batch status LIMS from “reviewed – primary” to “reviewed – final.” If any samples require rebatching, this is performed by QA prior to changing the status of the samples in the analyzed batch to “reviewed – final.” (Refer to section 12 of this document for additional discussion of the data reduction, validation, storage, and reporting process.)

7.2.5.6 Deviation Traceability - All documents are used to track any deviations from generally accepted handling of the samples. The main form for tracking deviation is the SPF. This form should contain any mention of unusual events or occurrences or deviations from SOPs and should list where this information can be found if relevant. Examples of possible entries on the SPF include, but are not limited to the following:

- Samples not cold when removed from refrigeration-see instrument log book.
- Samples over distilled-see distillation prep sheet.
- Samples prepared differently from SOP-see preparation notes.
- Out-of-Control calibration curve - see analyst’s notes.

Each person is responsible for filling-out the appropriate information for the task performed. The next responsible person will not accept the data and SPF unless the data package is complete for what has been performed so far. In this way all necessary information concerning samples and all sample handling steps can be traced and noted in the report to the customer.

7.2.5.7 Subcontracting - Only in extremely rare occasions will BRL subcontract samples for analysis. This is done only with the prior consent of the client and the subcontractor laboratory must have an established and documented laboratory quality system that

complies with all of the requirements of the original contract. For example, if a project has been contracted under Department of Defense (DoD) Quality Systems Manual (QSM) requirements, then the subcontracted laboratory would have to meet the same requirements and also have DoD accreditation for all of the subcontracted analyses prior to analyzing any of the samples. In such a case, the documentation to transfer samples includes collection date and time (if available from the field samplers), the Field ID#, the BRL Lab ID #, the date of preparation (if extracts are transferred), and the requested analyses. [Refer to section 5.4 for further discussion.](#)

7.2.6 Sample Disposal

7.2.6.1 Sample Preparations – Unless otherwise specified in the contract, sample preparations may be disposed of once the preparations have been analyzed and the data has been reviewed and reported to the client. Additionally, sample preparations may be disposed of if the Laboratory Manager has determined that there is no further value in analyzing the preparations, such as [water](#) preparations for methyl mercury that are only stable for a maximum of [two](#) days. The disposal of each batch must be documented in the LIMS.

7.2.6.2 Original Samples – It is BRL policy to maintain all samples (aqueous and solid) for a minimum of two months after reporting results unless previous arrangements have been made with the client. At least once a year, all refrigerators and freezers should be cleared of any samples for which results have been reported more than two months ago. Samples that require longer storage should be separated from those that may be disposed after the two month period. The Sample Receiving Log in the LIMS must be updated to indicate that the samples have been disposed.

7.2.6.3 Disposal Guidelines – The concentration of all elements of interest in each sample preparation and each original sample is calculated to determine the proper disposal method for each sample (Refer to BRL SOP BR-0303 for disposal limits for specific elements). The method of disposal (routine verses high-level disposal) must be indicated on the appropriate form.

7.2.6.3.1 Routine Disposal

7.2.6.3.1.1 Water Samples and Acid Digestions - All water samples (including preparations) and acid digested solid samples that are not designated as being hazardous may be disposed down the drain. All acidic samples must be neutralized with Soda-Ash prior to disposal.

7.2.6.3.1.2 Native Solid Samples and Dry Weights - All native solid samples (not sample preparations) that are not designated as hazardous may be discarded directly into the garbage.

7.2.6.3.2 High Level Disposal - All High Level metal sample waste (as well as other waste that is considered to be hazardous) must be recorded in the Sample Receiving Log (original samples) or on the SPF (sample preparations). The total volume added to the High Level Waste containers must be logged in the “Waste Disposal Log.”

7.2.6.3.2.1 Water Samples and Acid Digestions - All water samples (including preparations) and acid digested solid samples that are designated as hazardous are placed directly into the high level metals/corrosives waste storage container.

7.2.6.3.2.2 Native Solid Samples and Dry Weights - All native solid samples (not sample preparations) that are designated as hazardous are disposed of directly into the hazardous waste container.

7.2.6.3.2.3 All Solvent Extracts - All solvent extracts must be treated as hazardous waste. Solvent extracts may be consolidated in clearly marked containers near the hazardous waste fume hood, and then disposed of as hazardous waste.

7.2.6.3.3 Non-Routine Disposal - Samples that are designated by the client to be high level in an analyte not performed by BRL shall be considered hazardous and treated as hazardous waste upon release for disposal. In certain cases, BRL may contract with a client to analyze samples that are known to be hazardous beyond the scope of our analysis (such as samples containing a high level of organic contaminants or dioxins), these samples will be flagged as requiring special disposal (as per the Laboratory Director's instruction) and disposed of through a licensed hazardous waste acceptance facility. BRL may also arrange with the client to return the leftover samples after analysis.

7.2.6.3.4 High-Level Metals Waste Transport and Ultimate Disposal - Once a sufficient volume of waste is generated, warranting proper disposal, a waste disposal company should be contacted, and the waste scheduled for pick-up. It shall be the responsibility of the waste handling company to transport and dispose of the high level metal waste in a manner consistent with local and federal environmental laws and regulations.

7.2.6.3.5 Low-level Radioactive Waste - All samples required to be disposed as low-level radioactive waste need to be in accordance with all local, state, and federal regulations regardless of the concentrations of other constituents. [Current licensing at Brook Rand Labs does not allow for the storage or disposal of any waste above two times the background levels measured at Brooks Rand Labs.](#)

7.2.6.4 Documentation – [The LIMS is updated](#) when necessary to both document disposal of samples (and sample preparations) and to initiate disposal or transfer of samples.

[<Removed example Incident Report page – Refer to BRL SOP BR-1204 for discussion of incident reports>](#)

8.0 Analytical Procedures

8.1 Method References

Refer to the tables in section 6.0 for method number references and to Appendix A for a list of BRL analytical Standard Operating Procedures (SOPs).

8.2 Field Methods

Not Applicable. BRL is not currently involved in the analysis of samples directly in the field.

8.3 Analytical Method Modifications

Methods BR-0006 and BR-0002 (Modifications of EPA Method 1631, Revision E and EPA Method 1631, appendix to) - EPA Method 1631.E describes the determination of mercury in ambient water while the Appendix to EPA Method 1631 describes the determination of mercury in solids. Any modifications that Brooks Rand Labs has made to these methods are fully documented in the appropriate SOP. All solid (biological, sediments and soils) matrices are prepared in accordance with SOP BR-0002, *BRL Procedure for EPA Method 1631, Appendix to (1/01): Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)*. All aqueous matrices are prepared in accordance with SOP BR-0006, *BRL Procedure for EPA Method 1631, Revision E (8/02): Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS)*. Please refer to the method validation package for SOPs BR-0002 and BR-0006 in Appendix C (available upon request).

Method BR-0011 (Modification to EPA Draft Method 1630) – BRL has developed a method for the determination of methyl mercury at the ultra-trace level in various matrices. The SOP for this method, BR-0011: *Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation and CVAFS Detection*, is included in Appendix B (available upon request). By this method waters are distilled to remove methyl mercury from the matrix. Alternatively, water samples may be extracted to remove methyl mercury from the matrix or analyzed by direct ethylation. Biological samples (i.e. animal and plant tissue) are digested in a KOH/Methanol solution. Sediment samples are extracted using dichloromethane. After sample preparation all samples are ethylated with tetraethyl borate which forms ethyl derivatives of the mercury species. The ethylated mercury species are collected on a Tenax[®] trap that is then introduced into the GC oven, pyrolytic column, and AFS detector. Under the flow of an inert carrier gas, the Tenax[®] trap is gently heated to release the mercury species, which are then separated chromatographically prior to being decomposed to elemental mercury (Hg⁰), in the pyrolytic column. The AFS detector then detects Hg⁰. Please refer to the method validation package for SOP BR-0011 in Appendix C (available upon request).

Method BR-0021 (Modification to EPA Draft Method 1632, Revision A) – BRL has developed a method for the determination of inorganic arsenic, trivalent arsenic,

monomethyl arsinic acid, and dimethyl arsinic acid at the trace level in various matrices. The SOP for this method, BR-0021: *BRL Procedure for EPA Method 1632, Revision A (1/01): Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry*, is included in Appendix C (available upon request).

Method BR-0060 (Modification to EPA Methods 200.8, 1638, and 6020) –The SOP for this method, BR-0060: *Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using a Perkin-Elmer ELAN DRC II*, is included in Appendix C (available upon request). Any modifications that Brooks Rand Labs has made to this method are fully documented in the SOP.

Methods BR-0063, BR-0066, and BR-0069 (Modification to EPA Method 1640) – The SOPs for these methods, BR-0063: *Determination of Trace Elements in Seawaters and Low Level Waters by Online Column Chelation Preconcentration – Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II*, BR-0066: *Reductive Precipitation of Total recoverable and Dissolved Metals from Brackish and Seawater Samples* and BR-0069: *Extraction Using Co-APDC for Nickel, Copper, Silver, Cadmium, and Lead in Water*, are included in Appendix C (available upon request). Any modifications that Brooks Rand Labs has made to this method are fully documented in the SOPs. Modifications to the analysis of samples are documented in BR-0060: *Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using a Perkin-Elmer ELAN DRC II*.

Method BR-0080 (Modification to SM 3500 – Fe B) – The SOP for this method, BR-0080: *Determination of Iron Speciation in Water Samples by Colorimetric Detection*, is included in Appendix C (available upon request).

Method BR-0085 (Modification to EPA Methods SW 3060A and SW 7196A) – The SOP for this method, BR-0085: *Determination of Hexavalent Chromium (Cr^{6+}) in Sediment and Aqueous Samples* is included in Appendix C (available upon request).

8.4 Laboratory Operations

8.4.1 Laboratory Glassware

All glassware for ultra-trace metals analysis must be rigorously cleaned, in order to minimize possible contamination. Glassware is initially cleaned using Alconox[®] and DIW and scrubbing with a brush. After thorough rinsing with DIW, the glassware is immersed into either a large rectangular vat containing 50% HCl or one containing 50% HNO₃, depending on how great the concentration of analyte in the glassware was prior to cleaning. Each of these acid vats is equipped with an immersion heater and a calibrated voltage regulator, or Variac). After filling the vat with glassware, the Variac and heater are turned on to heat the vat to 75°C and the samples are soaked for a period of 48 hours. Glassware to be used for ICP-MS analyses is stored in the cold 30% nitric acid vats.

Glassware for certain parameters other than ultra-trace metals need only be cleaned with Alconox and DIW followed by copious rinsing with DIW. A detailed account of the decontamination procedures for laboratory glassware is described in SOP BR-0402.

8.4.2 Reagent Storage

All supplies (i.e., glassware, chemicals, and reagents) are of the highest possible quality to ensure quality assurance and to avoid contamination. Reagents purchased from commercial vendors are labeled with the date received, the date opened, and the expiration date. Reagents used for stock and working standards are prepared from analytical reagent grade chemicals or higher purity grades, unless such purity is not available. Reagent water is prepared by deionization of city water using reverse osmosis. Each prepared reagent is clearly labeled with the composition, concentration, date prepared, initials of preparer, expiration date, BRL lot # and special storage requirements, if any.

Reagent water used in the laboratory is produced by reverse osmosis. The level of mercury in the reagent water is less than 0.2 ng/L and is checked during mercury analyses. Reagent water is tested monthly for ICP-MS metals at each sink used to clean bottles, prepare samples/reagents, or analyze samples. The reagent water is at metal concentrations below the method reporting limits (MRL) for each metal. If reagent water fails to meet the criteria for any metal, then the water may not be used for analysis of the metal until reagent water blanks have met the criteria.

Reagent solutions are stored in appropriate glass or plastic containers under conditions designed to maintain their integrity (refrigerated, dark, etc.). Shelf life is listed on the label, and the reagent is discarded after it has expired. Acids used are either glass-distilled or analytical reagent grade for trace metal analysis. Reagent solutions are checked for contamination by testing reagent blanks before use.

Refer to BRL's Chemical Hygiene Plan for a list of all chemicals used at BRL. The aforementioned document also describes where and how these chemicals are stored at BRL. Material Safety and Data Sheets (MSDS) are stored on the server as PDF files and should be consulted for detail concerning potential hazards associated with specific chemicals. MSDSs are organized on the server by both chemical name and by CAS number. BRL SOP BR-0500 describes the documentation of standards and reagents in the LIMS and the testing of standards and reagents.

8.4.3 Waste Disposal

Handling, storage, and disposal of laboratory-related hazardous wastes are subject to the regulations contained in the Resource Conservation and Recovery Act. BRL shall store, package, label, ship, and dispose of hazardous wastes in a manner which ensures compliance with all federal, state, and local laws. Potentially hazardous wastes include all standards, reagent solutions, process wastes, solvents, native samples, sample extracts, and digestates.

A waste is considered hazardous if:

1. The waste material is listed as hazardous in 40 CFR Part 261.30-261.33.
2. The material exhibits any of the characteristics of hazardous waste: ignitability, corrosiveness, reactivity, or EP toxicity.
3. The waste is listed in 1 or 2 above and is not excluded by any provisions under the Resource Conservation and Recovery Act.

A waste is considered an acute hazardous waste if it is identified in 40 CFR Part 261.31, 261.32, 261.33 (e) as an acute hazardous waste.

BRL is categorized as a Large Quantity Generator. This category is defined as: A generator who generates at least 1000 kilograms of hazardous waste or 1 kilogram of acute hazardous waste in a calendar month and stores all generated waste for no more than 90 days (40 CFR Part 261.5).

BRL shall ensure delivery of hazardous waste to a treatment, storage, or disposal facility, which is:

1. Permitted under 40 CFR Part 270
2. In the interim status under 40 CFR Parts 270 and 265
3. Authorized to manage hazardous waste by a state with a hazardous waste management program approved under Part 271; or
4. Permitted, licensed, or registered by a state to manage municipal or industrial solid waste (subject to local regulations).

Hazardous waste solvents as identified in the 40 CFR Part 261 may not be evaporated off in a fume hood. Solvents evaporated off during the extraction/testing process are exempt. Acidic and basic wastes may be neutralized and disposed of via the sanitary sewer if they are not hazardous due to the presence of other constituents (as subject to local regulations). Heavy metals may be precipitated from the liquid portion and disposed via the sanitary sewer (subject to local regulations).

Hazardous waste storage is limited to quantity and/or accumulation time and must comply with RCRA regulations as specified in the 40 CFR. These wastes should be packaged and separated according to the compatible groups (e.g. solvents, acids etc.).

Samples submitted to BRL for analysis are excluded from regulation as hazardous waste under 40 CFR Part 261.4(d) provided the samples are being transported to or from the laboratory, are being analyzed, are being held for analysis or are being maintained in custody for legal reasons. However, once a decision is made to dispose of the laboratory samples, the exclusion provisions of 40 CFR Part 261.4(d) no longer apply. Samples that have been identified as hazardous may be either: 1) returned to the generator; or, 2) disposed of according to applicable Resource Conservation and Recovery Act (RCRA) regulations. Samples, which are determined to be non-hazardous, may be subject to local environmental regulations. A sample collector shipping sample to a laboratory and a laboratory returning samples to a sample collector must comply with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements.

Native samples and sample preparations must be disposed of in accordance with local, state, and federal regulations. Residual native samples must be separated by matrix (water, sediment/soil, and biota) and placed in the appropriate containers for disposal. Remaining sample preparation solutions must be separated by digestion type (acid, base, solvent extract) and placed in the appropriately labeled disposal containers.

8.4.4 Laboratory Procedures

BRL currently has one clean room for ultra-trace mercury analysis and a semi-clean room for other trace metal analyses.

The mercury laboratory, prep laboratory, receiving laboratory, bottle washing and sample storage areas are monitored monthly for atmospheric mercury levels to ensure that levels are suitably low for ultra-trace level mercury analysis. A warning level has been established at 15 ng/m³ with a shutdown control level at 25 ng/m³. Reagent water is tested for mercury each day prior to beginning analysis by testing bubbler blanks. The average bubbler blank must contain less than 20 pg Hg. Clean room sticky mats are located at the entrance to minimize tracking in particles.

The AA / ICP-MS lab is where other metals analyses are conducted. This lab contains two laminar flow hoods with HEPA filters. Incoming air is pre-filtered. The laminar flow hood is at one end of the room with the air intake at the other to facilitate efficient circulation through the HEPA-filter. In addition, the entrance to this lab has an enclosed gowning area to reduce direct flow from outside air. Reagent water is tested by ICP-MS at least once a month. Clean room sticky mats are located at the entrance to minimize tracking in particles.

8.5 Exceptional Departures from Standard Operating Procedures (SOPs)

The QA Officer, Lab Manager, and/or the Vice President of Analytical Services must approve of any departure from BRL standard operating procedures. Under no circumstances is the Sample Preparation Technician or the Analyst authorized to alter any standard procedure without managerial approval. Such approval and the actual departure from BRL procedure must be fully documented and conveyed to the affected client. All quality control criteria must still be met for all reported data.

9.0 Calibration Procedures

9.1 Instrumentation List

TABLE 9.1 - INSTRUMENTATION LIST

<u>Description</u>	<u>Manufacturer</u>	<u>Model #</u>	<u>Unique ID#</u>	<u>In Service Date</u>
<u>Analyzers</u>				
CVAFS Hg Detector	BRL	III	BR-05	03/12/02
CVAFS Hg Detector	BRL	III	BR-06	03/07/02
CVAFS Hg Detector	BRL	III	BR-09	08/06/03
CVAFS Hg Detector	BRL	III	BR-10	05/10/04
CVAFS THg Auto Analyzer	BRL	Merx-T	Merx-T	05/10
CVAFS MeHg Auto Analyzer (GC Unit)	BRL	Merx	Beta	06/07
CVAFS MeHg Auto Analyzer (Purge & Trap Unit)	BRL	Merx	Merx-1	06/09
ICP-MS	Perkin Elmer	ELAN DRC II	Ellie Z1300410	01/04/05
ICP-MS	Perkin Elmer	ELAN DRC II	Darcy AI13200711	11/08
Auto Sampler	ESI	SC-4 w/FAST	Jack Rack'em FST04-080606	05/08
Auto Sampler	ESI	SC-4 w/FAST	FST04-081012	11/08
<u>HPLC</u> Auto Sampler Thermal Compartment	DIONEX	ICS Series	11010036 10120774	01/11 01/11
Flame AAS	Buck Scientific	Buck 205	112	10/03/05
ICP-MS Chiller	Polyscience	3370	108400314	10/08
Colorimetric Spectrophotometer	Thermo - Scientific	Evolution 60S	2R1P203001	05/11
<u>Digestion Equipment</u>				
Microwave oven	BERGHOF	SPEEDWAVE	000262	04/11
Sonicator	Branson	1510R-MT	RKA090407117D	04/11
Distillation Blocks (total = 5)	BRL	DI-02	NA	Latest 09/10
Hot Block Digester	BRL	LINX	GFD 1009102	01/11
Hot Block Digester	Environmental Express	SC100	2932CEC1445	09/04
Hot Block Digester	Environmental Express	SC154	4667CEC2213	09/04
Water Bath	Blue M	MW-1120A-1	M5-8717	Prior to 2000
Centrifuge	Eppendorf	5810	0012951	04/08

TABLE 9.1 INSTRUMENT LIST (CONTINUED)

<u>Description</u>	<u>Manufacturer</u>	<u>Model #</u>	<u>Unique ID#</u>	<u>In Service Date</u>
Hot Plates (total = 4)	Various	NA	NA	09/04
<u>Balances</u>				
Top Loading (to 0.1 mg)	Mettler Toledo	AL54	1226280324	06/06
Top Loading (to 1 mg)	Sartorius	E1200	39010004	Prior to 2000
Top Loading (to 1 mg)	Ohaus	AR1530	H171 12031 20715 P	01/04
Top Loading (to 10 mg)	Ohaus	SP602	7126020087	10/04
Top Loading (to 10 mg)	Ohaus	SP402	7123210873	10/04
<u>Ovens</u>				
Scientific Oven	Blue M	OV-490A-2	JT-1800 (BR-01)	06/10/02
Scientific Oven	Fisher Scientific	630F	BR-02	Prior to 2000
Scientific Oven	Blue M	SW-17TA-1	SW-1881 (BR-03)	10/04
Scientific Oven	Fisher Scientific	650G	502N0046 (BR-04)	03/05
Scientific Oven	Thermo Prec.	6567	602428	03/08
Muffle Furnace	Isotemp	550-58	1510060889906	2006
<u>Refrigerators/Freezers</u>				
Walk-In Refrigerator/ Freezer Unit	Easton Refrigeration	Various Units Combined	Walk-In	12/08
Chest Freezer	General Electric	CB22DL	RA180154	Prior to 2000
Chest Freezer	General Electric	FCM7SUAWW	GR274463	07/08
Chest Freezer	Frigidaire	FFC15C4CW0	WB40945673	01/05
Chest Freezer	Frigidaire	GLFC2027FW5	WB81135168	07/08
<u>DIW System</u>				
Reverse Osmosis Deionized Water System	US Filter (Serviced by Siemens)	ROSLW1003	9001-756	Updated to 500 gallon capacity 08/15/05
<u>Conductivity/pH Meters</u>				
pH/Conductivity/TDS/ Temperature Meter	Oakton	pH/CON 510 series	162259	01/27/05
Salinity Meter	Oakton	SALT 6, Acorn series	328917	03/08

9.2 Standard Receipt and Traceability

All stock standard solutions are received by the analytical laboratory and are documented in the LIMS. Information documented in the LIMS includes source, type of standard, date of receipt, lot number (if applicable), and expiration date. PDF copies of stock standard certificates are attached to the LIMS standard page for the standard. Original certifications for all stock standards are maintained in a designated binder located in the main office area.

All standard solutions are stored in a manner that is consistent with the manufacturers' recommendations.

Standards traceability is achieved by documenting all standard solution information in the LIMS. In addition to the previously mentioned documentation for stock standards, documentation for intermediate standard solutions must include: identification of primary (stock) standard used, the preparation date, method of preparation (specifically dilution information), the preparer's name, the concentration prepared, BRL lot #, and the expiration date. Documentation for working standards must include: identification of the stock and intermediate standards used, the preparation date, method of preparation (specifically dilution information), the preparer's name, the concentration prepared, BRL lot #, and the expiration date.

9.3 Standard Sources, Preparation, and Testing

All working standards are documented for traceability as discussed in section 9.2. All intermediate and working standards are made in accordance with the protocols of the specific procedure for which the standards shall be used. Refer to Table 9.3 and/or the analytical method or SOP for the specific procedures followed for the preparation of any intermediate or working standard.

Any new standard must be tested prior to use. The acceptance criterion is that the average recovery of the new standard is within $\pm 5\%$ of the average recovery of the previous standard. A minimum of three replicates of the old and the new standard must be analyzed for comparison. The RSD of the measurements of each standard may not exceed 5.0%. **Standards that are made daily are not tested against the old standard prior to use. Instead, they are verified against the second source standard.**

Quality control reference materials are currently acquired from the National Resource Council of Canada (NRCC), the National Institute of Standards and Technology (NIST), the International Atomic Energy Agency (IAEA), or Community Bureau of Reference (BCR).

TABLE 9.3 - STANDARD SOURCES AND PREPARATION

Instrument Group	Standard Source(s)	How Received	Storage	Preparation from Source	Lab Storage	Preparation Frequency
Atomic Fluorescence	Total Hg – High Purity Standards (calibration) NIST 1641d (independent check)	Solutions of 1000 µg/mL CRM Solution of 1601 µg/mL	Room temp. 2% HNO ₃ 4 °C; 2% HNO ₃	Intermediate standards are prepared from Stock standard	10000 ng/mL, 2% BrCl at 4 °C	annually
				Intermediate standards are prepared from Stock standard	1000 ng/mL, 2% BrCl at 4 °C	annually
				Working standards are prepared from intermediate	10ng/mL & 1 ng/mL, 1% BrCl at room temperature	monthly
				Verification standards are prepared from a source other than the calibration standards	1.601 ng/mL, 1% BrCl at room temperature	monthly
Atomic Fluorescence	Methyl Hg – Strem Chemicals, Alfa Aesar, or Environmental Resource Associates DORM-3 (Fish Homogenate)	Solutions of ~ 2000 ppm MeHg Solid CRM 355 ng/g	Room temp. in the dark Room temp. in desiccator	Intermediate standards are prepared from stock standard	1000 ng/mL, 0.2% HCl 0.5% HOAc in dark at 4 °C	annually
				Working standards are prepared from intermediate	1 ng/mL & 10 ng/mL, 0.2% HCl 0.5% HOAc in dark	monthly
				~90-100 mg of CRM into 10 mL of KOH/methanol and diluted to 40 mL with methanol; final concentration of 0.8-0.9 ng/mL	Room temp. in the dark	monthly

TABLE 9.3 - STANDARD SOURCES AND PREPARATION (CONTINUED)

Instrument Group	Standard Source(s)	How Received	Storage	Preparation from Source	Lab Storage	Preparation Frequency
ICP-MS	<u>Single-Element</u> High Purity Standards	Solutions of 1000 or 10000 ppm	Room temp. in the dark	Intermediate standards are prepared from Stock standards	Plastic cabinet under TM clean hood, 2% nitric	semi-annually
				Working standards are prepared from intermediate	Plastic cabinet under TM clean hood, 2% nitric	daily/ as needed
	<u>Multi-Element</u> CPI International (independent check)	Various conc. Depending on element	Room temp. in the dark	1000x dilution working standard	Clean hood of ICP-MS room, 2% nitric	semi-annually / as needed
				4x dilution prepared from intermediate	Clean hood of ICP-MS room, 2% nitric	monthly / as needed
	<u>NIST 1643e</u> National Institute of Standards and Technology	Various conc. Depending on element	Room temp. in the dark	5x dilution at the instrument	Not stored	made daily

TABLE 9.3 - STANDARD SOURCES AND PREPARATION (CONTINUED)

Instrument Group	Standard Source(s)	How Received	Storage	Preparation from Source	Lab Storage	Preparation Frequency
HPLC-DRC- ICP-MS	<u>Se(IV)</u> Spex Certi Prep	Solutions of 1000 ppm	Fridge 0-4 °C	Intermediate standards are prepared from Stock standards	Not stored	made daily
	<u>Se(VI)</u> High Purity Standards	Solutions of 1000 ppm	Fridge 0-4 °C	Intermediate standards are prepared from Stock standards	Not stored	made daily
	<u>Se (species)</u> Inorganic Ventures (independent check)	Solutions of 1000 ppm	Fridge 0-4 °C	Intermediate standards are prepared from Stock standards	Not stored	made daily
Atomic Absorption	<u>As (species)</u> High Purity Standards	Solutions of 1000 ppm	Fridge 0-4 °C	Working Standard are prepared from stock standards	Fridge 0-4 °C	monthly
	<u>As (species)</u> Lab Chem (independent check)	Solutions of 1000 ppm	Fridge 0-4 °C	Working Standard are prepared from stock standards	Fridge 0-4 °C	monthly
pH Meters	Scientific Products	pH 4, 7, 10	Room temp.	NA	NA	NA
Conductivity Meters	Fisher Scientific	Solutions of 9.77 µmhos 96 µmhos and 974 µmhos	Room temp.	NA	NA	NA

9.4 Instrument Calibration

The analytical methods or the SOP for the specific method specifies all calibration protocols, frequency and acceptance criteria. Full documentation for calibration is included in the sample data. In addition, each instrument has a log book in which summarized information is documented. This summarized documentation includes date, analyst, batch #, calibration coefficient (or response factor), correlation coefficient (r), average blank level, and instrument noise level [or other relevant instrument information](#). In addition, any instrument maintenance is documented in the instrument log books.

9.4.1 CVAFS, HGAAS, and ICP-MS Instrument and Method Calibration

Instrument abbreviations are as follows: Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS), Hydride Generation Atomic Absorption (HGAAS), and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Each instrument used to analyze samples must pass the calibration criteria established in the appropriate method or operating procedure. The instrument calibration consists of analyzing a minimum of three standards (HGAAS and ICP-MS) covering at least one order of magnitude (one at the low end, one in the middle and one high standard below the upper limits of linearity within the calibration curve) and a calibration blank (Note: A minimum of five standards must be used in the calibration for all CVAFS work). These standards should span the linear range of the instrument. The correlation coefficient (r) of the initial calibration for ICP-MS must be ≥ 0.995 . If the squared correlation coefficient (r^2) is calculated for the ICP-MS calibration, then r^2 must be ≥ 0.990 . For CVAFS the RSD of the calibration coefficients must be $\leq 15\%$ and for HGAAS the RSD of the calibration coefficients must be $\leq 20\%$. The initial calibration check, consisting of one standard at the mid-point of the calibration curve and one calibration blank, is performed immediately following this calibration. Continuing calibration verification standards are analyzed at the end of each batch or sequence and, depending on the analytical method, at a frequency of 10% during the course of the analytical sequence. Initial and continuing calibration checks are used to establish whether ongoing instrument calibration is acceptable. The calibration is verified with a standard prepared from a source independent of the calibration standards.

When calibrating the instrument, the low calibration standard must be equal to or less than the method reporting limit (MRL). Standards may be removed from the bottom end or top end of the calibration when they do not meet acceptance criteria as long as at least three consecutive standards remain, however, this will result in a reduced range of quantitation. It is never permissible to drop a mid-level point from the calibration without also dropping either all of the points below or all of the points above it as well. Results should not be reported if the instrument result for the sample is above the result for the high calibration standard. It is standard practice to dilute the high-level sample and reanalyze it such that the result at the instrument falls within the calibration. A result that is outside of the calibration range would not be reported without appropriate qualification or explanation.

It is standard procedure at Brooks Rand Labs to calibrate analytical instruments daily prior to analyzing any client samples. Under certain circumstances further analysis of samples may be

reinitiated without recalibrating the instrument. If this is to be done for any reason, the following procedures must take place prior to the analysis of any blanks or client samples:

- 1) Less than 12 hours must have passed since the calibration was last verified
- 2) The Laboratory Manager, the QA Manager, or specific Group Lead must approve of the deviation from standard BRL procedure and document the approval on the SPF
- 3) Both an ICV and a CCV must be run to verify the calibration
- 4) Either the QA Manager or the Group Lead must approve of the calibration verification results prior to beginning to analyze samples

All standards used to prepare the calibration standard solution are obtained from chemical suppliers and are of high purity and concentration. The standards are routinely checked by the laboratory for traceability to National Research Council of Canada (NRCC) or National Institute of Standards and Technology (NIST) Standard Reference materials. These commercial standards are used as stock standards. Working standards are made from the stock standards at appropriate concentrations to cover the linear range of the calibration curve as outlined in the individual procedures. Preparation of all standards is recorded in the LIMS (as described in SOP BR-0500). All solutions are labeled as follows: name of solution, concentration of solution, date prepared, LIMS ID number, expiration date, and analyst's initials. All laboratory analysis (including instrument calibration) is documented by the analyst on the analytical bench sheets. All information concerning the calibration must be stored such that the calibration can be recreated if need be.

9.4.2 Periodic Calibration Procedures for other Laboratory Equipment

Periodic calibration checks are performed for associated equipment such as balances, thermometers, ovens, and refrigerators that are required in analytical methods but that are not routinely calibrated as part of the analytical procedure. All the calibration measurements are recorded in a laboratory log book as outlined in SOP BR-1200.

BALANCES

Balances are calibrated annually by a contracted, certified professional. Balances are also checked with Class S weights on a daily or as-used basis. [At the beginning of each day that the balance is used](#), the analyst is required to perform at least one calibration check in the range of the material to be weighed. All calibration checks are documented in a laboratory log book. All weights used to calibrate balances on a daily basis are themselves calibrated at a minimum every 5 years against NIST traceable weights.

TABLE 9.4 - CRITERIA FOR BALANCE CALIBRATION CHECKS
4-POINT BALANCE

Class S / 1 Weight (g)	Warning Level (g)	Control Level (g)
0.0100	0.0099 - 0.0101	0.0098 - 0.0102
0.1000	0.0997 - 0.1003	0.0995 - 0.1005
1.0000	0.9995 - 1.0005	0.9990 - 1.0010
10.0000	9.9950 - 10.0050	9.9900 - 10.0100
100.0000	99.9500 - 100.0500	99.9000 - 100.1000

3-POINT BALANCE

Class S / 1 Weight (g)	Warning Level (g)	Control Level (g)
0.100	0.099 - 0.101	0.098 - 0.102
1.000	0.995 - 1.005	0.990 - 1.010
10.000	9.950 - 10.050	9.900 - 10.100
100.000	99.750 - 100.250	99.500 - 100.500

TOP LOADING BALANCES

Class S / 1 Weight (g)	Warning Level (g)	Control Level (g)
1.00	0.99 - 1.01	0.98 - 1.02
10.00	9.95 - 10.05	9.90 - 10.10
100.00	99.5 - 100.50	99.00 - 101.00
200.00	199.00 - 201.00	198.00 - 202.00

PIPETTES

All pipettes are calibrated weekly. Pipettes performance is monitored by gravimetrically measuring the volume of DIW dispensed by each pipette over the range of its use prior to calibration with the assumption that the density of the water in the laboratory is 1.000 g/mL (± 0.003 g/mL). The volume dispensed by each pipette is then re-measured after calibration and both measurements are maintained in a laboratory log book. Bias and precision are measured for all new pipettes prior to being put into service and then monthly thereafter. Bias and precision are based on 10 measurements. The criteria are that the average measurement must be within $\pm 2\%$ of the measured volume and the RSD of the measurements must be $\leq 1\%$.

OVENS, HOTPLATES, SAND BATHS, WATER BATHS, REFRIGERATORS, AND FREEZERS

Temperatures are checked with calibrated thermometers and necessary adjustments to the temperature settings are made as required. Refrigerators and freezers are checked on a daily basis and all ovens, hotplates, sand baths, and water baths are checked at least once during each use. Refrigerator and freezer temperatures are recorded in laboratory logs that are maintained by the Sample Control Group Lead. Oven, hotplate, sand bath, and water bath temperature are recorded in the sample preparation logs.

THERMOMETERS

The performance of each thermometer is compared annually to a certified NIST-grade thermometer and correction factors are posted for each thermometer in the area where it is used.

10.0 Preventative Maintenance

10.1 Routine Maintenance Measures

Refer to SOP BR-1205 (Preventative Maintenance) for greater detail of specific procedures.

TABLE 10.1 - PREVENTATIVE MAINTENANCE

<u>Instrument</u>	<u>Activity</u>	<u>Frequency</u>
ICP-MS	Inspect and/or change all tubing	Daily
	Clean sampler and skimmer cones	Daily
	Inspect torch and injector	Daily
	Check gas and coolant levels	Daily
	Change roughing pump oil	Monthly*
	Update mass calibration (tuning)	Monthly
	Replace quartz torch and injector	Semi-Annually*
	Replace sampler and skimmer cones	Semi-Annually*
	Replace RF coil	Semi-Annually*
	Replace chiller air filter	Annually*
	Replace ion lens	Annually*
	Schedule annual maintenance with Perkin-Elmer	Annually
HPLC	Change eluents	Daily
	Inspect lines for leaks and obstructions	Daily
	Monitor suppressor flow	Daily
	Clean and regenerate suppressor	Monthly*
	Clean and test analytical column	Monthly*
CVAFS (Total Hg)	Prepare new soda lime pre-traps	Daily
	Condition bubblers and blank traps	Daily
	Check all fittings	Daily
	Soak bubblers for 15 minutes in 1% KOH and then over the weekend with 10% HCl	Weekly*
	Inspect and/or change all tubing	Monthly*
	Make, test, and change out traps	Quarterly*
	Change lamp	Semi-Annually*
	Blank traps on incoming gas lines	Semi-Annually*
	Clean/change quartz cell	Annually*
Check Electronics	Annually	

* or as needed

TABLE 10.1 - PREVENTATIVE MAINTENANCE (CONTINUED)

<u>Instrument</u>	<u>Activity</u>	<u>Frequency</u>
CVAFS (MERX-T)	Prepare new soda lime pre-traps	Daily
	Check all tubing and clear any liquid in tubing	Daily
	Inspect and/or change all tubing	Monthly*
	Change Traps	Semi-Annually*
	Change lamp	Semi-Annually*
	Change traps on incoming gas lines	Semi-Annually*
	Clean/change quartz cell	Annually*
CVAFS (MeHg)	Inspect and/or change all tubing	Monthly*
	Condition GC column at 80 °C overnight	Quarterly*
	Change lamp	Semi-Annually*
	Check and change out traps	Semi-Annually*
	Blank traps on incoming gas lines	Semi-Annually*
	Clean/change quartz cell	Annually*
	Replace GC column	Annually
AA - Flame	Check tubing, pump and lamps	Daily
	Rinse water removal trap with DIW	Daily*
	Clean spectrophotometer windows	Weekly
	Soak bubblers over weekend in 30% nitric acid	Monthly*
	Inspect and/or change all tubing	Monthly*
	Clean nebulizer	Semi-Annually
	Fine tune the instrument wavelength	Annually*
	Check instrument optics	Annually*
Colorimetric / Spectrophotometer	Clean sample compartment	Daily
	Windows cleaned	Monthly
	Check Electronics and lamp alignment	Annually
pH Meter	Clean; 2 pt. Calibration	After each use
Balances	Clean pans and compartment	Before and after every use
	3 to 4 pt. Calibration check	Before every use
	Certified Calibration	Annually
Pipettes	Full calibration over entire range of pipette	Weekly*
Conductivity Meter	Check batteries and probe cables	Weekly*
Refrigerator / Freezers	Check temperature	Daily
	Clean interior	Monthly*
	Check temperature against NIST certified thermometer	Annually

* or as needed

10.1.1 Air Testing

The mercury lab, the sample preparation lab, the receiving laboratory, bottle washing, and the trace metals lab are monitored monthly for atmospheric mercury levels to ensure that these levels are sufficiently low for ultra-trace level mercury analysis. Air from each lab is pumped through a soda lime pre-trap and onto either a gold wire or gold-coated sand trap at a flow rate of 1 L/min until at least 20 L of air have been collected per trap. A warning level has been established at 15 ng Hg/m³ with a shutdown control level at 25 ng Hg/m³. Results from the monthly air tests are electronically on the server.

10.1.2 Water Testing

Reagent water is monitored for Hg on a daily basis when calibration blanks are analyzed. A minimum of four 100 mL aliquot of fresh reagent water, each with 0.5 mL NH₂OH·HCl and 0.5 mL of SnCl₂, are analyzed at the beginning of the run sequence. The average results must be < 25 pg Hg with a standard deviation < 10 pg Hg. A high level of mercury detected in the reagent water analysis may also be attributed to the bubbler itself, the SnCl₂, or the soda lime pre-traps. Regardless of the source, all analysis is stopped until the source of contamination is determined and the problem is corrected. The results are stored with each batch.

Reagent water is tested for trace metals by ICP-MS at a minimum of once per month when instrument water blanks collected from every sink used to clean equipment, prepare reagents/samples, or analyze samples are analyzed. Specific elements are tested for with each batch. Currently, water blanks must be less than the element specific MRL or client specific requirements. Results for water testing are stored on the server in Excel[®] spreadsheets.

10.1.3 Equipment and Reagent Testing

All reagents (acids, standards, etc.) and equipment (bottles, vials, etc.) are tested prior to use. The acceptance criteria for specific reagents and equipment are specified in the individual SOPs describing the use of the reagents or the decontamination of equipment. In all cases, contract specified requirements take precedence over BRL acceptance criteria.

10.2 Documentation

Instrument logbooks are maintained for all equipment. These logbooks contain a complete history of past performance and maintenance. For each CVAFS and AA instrument, a logbook is kept to document instrument usage, routine maintenance, and non-routine repairs.

10.3 Contingency Plans

10.3.1 Major Equipment Failure

For major equipment failure of CVAFS instruments, the laboratory has backup instrumentation. BRL is an instrument manufacturer specializing in ultra-trace level mercury analyzers; therefore, a stock of replacement parts and complete analyzers exist and expert service personnel are readily available.

For flame AA's, rental equipment is locally available in the case of a major equipment failure while instrumentation is being repaired.

For the ICP-MS, BRL has two Perkin Elmer ICP-MS instruments. Perkin Elmer's service record is excellent, and none of our ICP-MS instruments has ever been out of service for more than 1 week.

BRL currently has an excess of balances and refrigerators/freezers. If any of this equipment fails backup equipment is immediately available. Other equipment such as the conductivity meter and the pH meter are relatively inexpensive and will be purchased immediately if major equipment failure is determined.

10.3.2 Invalidation of work

Results for all sample analyses affected by equipment failure may be ruled invalid depending upon the circumstances. When QC criteria are not met during analysis, all instrumentation is thoroughly checked and appropriate maintenance action is taken. Subsequent reanalysis of the affected samples is then initiated after the instrumentation is proven to be functioning properly. The QA Manager and the Lab Manager have the authority to stop work whenever there is evidence of non-conforming work. Once work is stopped, corrective action must take place and be documented. Permission to restart work must be granted by the QA Manager or the Lab Manager.

11.0 Quality Control Checks and Routines to Assess Precision and Accuracy and the Calculation of Method Detection Limits

The laboratory uses quality control samples to assist in assessing the validity of the analytical results of field samples. The use of quality control samples helps to assess analytical accuracy and precision in the laboratory. Quality control samples are analyzed in the same manner as field samples at a frequency described either in the individual procedures or in the contract with the client. If the quality control sample results fall within acceptable criteria (also detailed in the method), then the field sample data are considered to be valid or acceptable as is. However, it is important to keep in mind that errors made during sample collection can seriously affect the analytical results of field samples. In other words, the quality or validity of the field sample data is only partially supported by the laboratory quality control sample results. Field quality control samples are the other necessary component for the validity of field sample results.

Laboratory quality control (QC) samples include method blanks, calibration checks, replicates, spiked samples, and certified reference materials (CRM). The specific frequency and type of QC samples analyzed are described in the individual analytical method, SOP, or client-specific Statement of Work (SOW). In some cases, contracts may specify additional or more stringent QC requirements beyond what the method requires. In these cases the contract specific QC requirements are followed. In addition to these routine QC samples, performance evaluation samples required for state certification are analyzed semi-annually.

11.1 Quality Control Checks

11.1.1 Field QC Checks

Brooks Rand Labs is rarely involved in field sampling. The client is typically responsible for field sampling activities and therefore mandates the requirements for field QC checks. However, BRL suggests that the following field QC be collected.

11.1.1.1 Trip Blanks

Trip blanks are used to demonstrate that sampling equipment and collected samples have not been contaminated during transit. Trip blanks consist of laboratory reagent water collected into a sampling container at the laboratory. The trip blank is then double bagged (as per sampling containers for use in the field) and affixed with a custody seal to indicate if it has been tampered with. The trip blank is then shipped with the sampling kit to and from the field. The trip blank must not be opened again until it has returned to the laboratory.

When collected and analyzed, the level of the analyte of interest in the trip blank should be less than the reporting limits or less than 10% of any affected sample results. If criteria are not met, then the client must be notified and every effort should be made to determine the source of the contamination and to eliminate it if possible.

11.1.1.2 Field Blanks

Field blanks are used to demonstrate that the samples were not contaminated during the collection procedure or while in transit (Note: The analysis of trip blanks in conjunction

with field blanks can better pinpoint the source of contamination). Field blanks are collected in the field, typically using lab-supplied reagent water, and simulating the collection of actual samples as well as can be done. Once collected, the field blank is treated in every way as an actual sample.

When collected and analyzed, the level of the analyte of interest in the field blank should be less than the reporting limits or less than 10% of any affected sample results. If criteria are not met, then the client must be notified and every effort should be made to determine the source of the contamination and to eliminate it if possible.

Many methods require that field blanks be collected and analyzed if results are to be reported for regulatory purposes. While Brooks Rand Labs does not require that clients provide field blanks for analysis, BRL does inform clients of this regulatory requirement in the quote signed by the client prior to any work performed as well as in any case narrative that includes relevant results.

11.1.1.3 Field Duplicates

Field duplicates are used to assess precision in the collection procedures. When collected, the field duplicate relative percent difference (RPD) should be no greater than that allowed for method duplicates by the specific analytical method, the SOP, or the SOW. If the RPD is greater than the acceptance criterion, then the sampling team should be notified. When analyzed in conjunction with method duplicates (Section 11.1.2.7), field duplicates will aid in determining the source of any imprecision.

11.1.2 Lab QC Checks

11.1.2.1 Method Blanks

A method blank is a sample of reagent water treated as a sample such that it **is prepared in conjunction with and** undergoes the same analytical processes (**i.e. same reagents added in equivalent amounts, digested in the same type container at the same temperatures/times, etc.**) as the corresponding field samples. Method blanks are used to monitor laboratory performance and contamination introduced during sample preparation and analysis. The method blank minimum frequency and acceptance criteria are method specific (Refer to specific SOP). Also refer to the specific analytical method, the SOP, or the contractual requirements.

In cases where a sufficient number of method blanks (minimum of four) have been prepared and analyzed with the batch to characterize the nature of the blanks and the potential for any reagent or spot contamination, one blank may be rejected as a Grubb's Outlier if it meets the criteria for doing so at the 5% or less risk of false rejection level (refer to Section 11.2.2 for further discussion on how the Grubb's Test for Outliers is applied to data). If a method blank is rejected as a Grubb's Outlier, then its value is not used to calculate the mean or the standard deviation of the method blanks used to blank-correct the batch data. If no spot contamination is evident in the batch (e.g. elevated trip or field blanks, random dissolved results significantly greater than total results), then the rejected method blank is not considered when evaluating the rest of the data. However, if there is evidence of additional spot contamination, then the data is evaluated against the method blank considered to be a

Grubb's Outlier such that any data point not ≥ 10 times the rejected method blank would require reanalysis or appropriate qualification.

Note: Some projects do not allow for the rejection of any method blank, such as those under the DoD QSM 4.2. For such projects the Grubb's Outlier method blank is still not used to correct the results, but all results are judged against the Grubb's Outlier as described above regardless of whether there is any further evidence of spot contamination in the batch or not.

The discarding of any data point as a Grubb's Outlier and the potential affect on overall data quality must be narrated to the client. Current LIMS limitations do not allow method blanks rejected as Grubb's Outliers to appear on the "Method Blanks & Reporting Limits" page of the report. Therefore, the value of any rejected method blank must be reported in the case narrative section of the data report. Grubb's Outliers may never be discarded for non-method blank corrected data. Refer to Section 12.6 (Data Reporting) for specific instructions on how method blanks are evaluated and reported for non-method blank corrected results.

11.1.2.2 Matrix Spikes

Matrix spikes are routinely included in the analytical batch as they are required for most methods utilized at BRL. Method-specific or client-specific frequency and recovery requirements are variable and available in the method, the SOP, or the SOW, whichever is applicable. Matrix spikes are typically analyzed at a frequency of one per every ten client samples. Although not a requirement, if a batch contains samples of different submatrices, matrix spikes should be prepared and analyzed for each submatrix type to ensure that there is no matrix-specific interference. It is up to the client to request additional matrix spikes on their samples if they suspect matrix issues.

The target spiking level of the matrix spikes is 2-5 times the native sample concentration or 5 times the MRL, whichever is greater. However, it is not always possible to know the concentration of the native sample before preparing the matrix spikes. Historical data should always be consulted prior to spiking in-house samples if this data is available. If historical data is available, no further action is required as long as the spiking level is still within 1-20 times the native concentration. If the native result agrees with the historical data and the sample is spiked incorrectly, then the native and its associated matrix spikes should be reprepared and reanalyzed. Lacking historical data for the samples, most methods have default spiking levels. If these levels end up being outside of the acceptable spiking concentration limits (1-20x), then if at all possible a post-digestion spike should be prepared at the target spiking level (2-5 times the native concentration) and analyzed for the sample.

11.1.2.3 Blank Spikes

When spike blanks are employed at the request of a client as an additional QC check to monitor the efficiency of the method, a minimum frequency of one per sample batch must be prepared and analyzed.

The policy at BRL is to analyze one BS at approximately 10 – 20 times the MRL with default acceptance criteria of 75-125% if an appropriate CRM is not available.

11.1.2.4 Performance Evaluation (PE) Samples

Performance Evaluation samples are analyzed as blind samples and are analyzed at a minimum of semi-annually. BRL purchases PE samples from Environmental Resource Associates (ERA) semi-annually. All PE studies utilize samples that are blind not only to the analyst but also the entire laboratory staff until after the results have been submitted to the appropriate agency and the final report for the study is issued. ERA PE results are forwarded directly to BRL, the Washington State Dept. of Ecology, State of Florida Dept. of Health, Oregon State Environmental Laboratory Accreditation Program, State of Louisiana Dept. of Environmental Quality, State of New Jersey Dept. of Environmental Protection, New York State Dept. of Health, California Dept. of Health Services, and the Maine Dept. of Health and Human Services for accreditation purposes.

Additionally, BRL routinely participates in laboratory intercomparison studies offered by such institutes as the International Atomic Energy Agency (IAEA), the United States Geological Survey (USGS), Florida Department of Environmental Protection, etc. Laboratory intercomparison studies such as these allow BRL the opportunity to evaluate our performance on more non-traditional matrices not typically available from PE providers.

11.1.2.5 Calibration Verification

Independent Calibration Verification (ICV) standards are standards that are from a different source than the working standards. The ICV is analyzed once immediately following the calibration or at the beginning of an analytical batch. Verification standards made directly from the working standards are also used throughout the analysis to check the continuing accuracy of the calibration. They are often referred to as Continuing Calibration Verification (CCV) standards or Ongoing Precision Recovery (OPR) samples. For most methods utilized at BRL, the CCV/OPR samples must be analyzed at the beginning and the end of an analytical batch and at a frequency of at least 10% throughout the analysis. **For most analyses,** Continuing Check Blanks (CCB) are analyzed after each CCV/OPR sample to ensure that there is no carry-over of analyte to the field sample analysis. Additional requirements may be specified in the specific analytical method, SOP, or contractual requirements.

11.1.2.6 Quality Control Samples

Quality control (QC) samples are additional QC checks for evaluating the accuracy of the analysis. These samples may be prepared by BRL (as with Laboratory Fortified Blanks) or purchased from an outside source (as with CRMs) depending upon their availability. QC samples range from Laboratory Certified Standards (LCS) to matrix specific CRMs. Regardless of their source, QC samples are always prepared from a different source than the working standards. Frequency and recovery criteria for QC samples are method specific. Refer to the specific analytical method, the SOP, or the SOW for specific frequency and recovery requirements.

11.1.2.7 Duplicates (Method Duplicates or Matrix Spike Duplicates)

Duplicate samples or matrix spike duplicates must be analyzed at a minimum frequency of 10% per analytical batch for all analytical methods employed at BRL. If a batch contains samples with different matrices, then duplicates should be analyzed for each matrix. Refer

to the specific analytical method, the SOP, or the SOW for specific frequency and precision requirements.

11.1.2.8 Reagents and Standards Purity Checks

All reagents used in the preservation, preparation or analysis of samples must be checked for the appropriate parameters prior to use. All reagent testing results are stored electronically on the server and the reagents are then labeled with the BRL assigned lot number, the date of testing and the measured concentrations of the analytes of interest.

Likewise, all standards are tested against previously tested, non-expired standards prior to use to ensure that they are acceptable for use as calibration, calibration verification, or spiking standards.

11.2 Routine Methods Used to Assess Precision and Accuracy

11.2.1 Accuracy and Precision

11.2.1.1 Precision

Precision from two or more replicates is expressed as % Relative Percent Difference (% RPD) or % Relative Standard Deviation (or % RED) and shall be calculated from the following formulae:

$$\text{RPD} = \left(\frac{|a - b|}{\bar{x}} \right) \times 100$$

Where: a = result a from native sample, or for matrix spike samples, result from the matrix spike (native + spike concentration) sample
b = result b from native sample duplicate, or for matrix spike samples, result from the matrix spike duplicate (native + spike duplicate concentration) sample
 \bar{x} = Mean (average) of the two results

$$\% \text{RSD} = \left(\frac{s}{\bar{x}} \right) \times 100$$

Where: \bar{x} = Mean (average) of the data points
s = Standard deviation calculated as:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

Where: x_i = the individual data point for each n
n = the total number of data points

11.2.1.2 Accuracy from Spiked Samples

The accuracy of a measurement shall be determined by the recovery of a known amount of analyte in a real sample as:

$$\% R = \left(\frac{C_s - C_u}{S} \right) \times 100$$

Where: C_s = concentration of spiked sample
 C_u = concentration in non-spiked sample (can be 0 for results < MDL)
 S = expected concentration (spiking level)
 $\%R$ = percent recovery

11.2.1.3 Accuracy from Known Concentrations

The accuracy of a measurement based on known concentrations shall be calculated as:

$$\% R = \left(\frac{\text{Sample concentration}}{\text{Reported True Value}} \right) \times 100$$

11.2.1.4 Upper and Lower Warning and Control Limits for Acceptance Criteria
Upper and Lower Warning Limits (WL) and Control Limits (CL) for determining acceptance criteria shall be calculated as follows:

$$CL = P_{av} \pm 3s$$

where: CL = Control Limit (upper and/or lower)
 P_{av} = Mean of P (percent recovery or RPD)
 s = standard deviation of the mean of P

and

$$WL = P_{av} \pm 2s$$

where: WL = Warning Limit (upper and/or lower)

11.2.2 Quality Control Charts

Quality Control charts are used to [determine acceptance criteria for in-house developed methods and review the relevance of QA criteria parameters used in each analytical method](#). Separate quality control charts should be established for each analytical method, for each parameter or analyte, and for each matrix type, both for precision and for accuracy. Control charts are automatically updated for all test codes in the LIMS as data is uploaded.

Control charts are constructed and used to monitor laboratory certified standards and SRMs/CRMs performances, spike recoveries, duplicate analyses, calibration verification standard recoveries, and blank analyses. Control charts use both the mean and standard deviation in order to identify out-of-control events as per Standard Methods, 21st Edition, Section 1020 B.

The LIMS automatically generates control charts, where the mean and the standard deviation, warning limits, and control limits are automatically calculated and updated. Control charts can be determined by method, who prepared the samples, who analyzed the samples, which instrument was used to analyze the samples, and over what dates the samples were analyzed. The individual data points are plotted against the mean and the ± 2 (warning limit), ± 3 (control limit), and ± 4 standard deviations.

It takes a minimum of 10 data points from at least 3 non-consecutive calendar days of analysis to "define" a control chart. The use of "real time" control charts is instrumental in indicating when an analysis is out-of-control. Out-of-control events may be indicated by the following occurrences.

- 1) QC sample result that exceeds the control limit even after reanalysis
- 2) Three out of four consecutive QC sample results that exceed the warning limit
- 3) Five out of six consecutive QC sample results exceed \pm one standard deviation from the mean
- 4) Five consecutive QC sample results in decreasing or increasing order [in the same calibration](#)
- 5) Seven consecutive QC sample results are on the same side of the mean (Only applies to QC samples used to measure accuracy and not those used to measure precision)

An outlier is an extreme value, high or low, that has questionable validity as a member of the measurement set with which it is associated. Outliers are **not** used in assembling the quality control charts for purposes of setting acceptance limits. Outliers may be rejected from the data set for the following reasons:

- A known experimental aberration occurred, such as instrument failure or inconsistency in the procedure or technique
- The T value for the data is larger than the tabulated values using the Grubb's test for outliers (Table 12.1). Outliers at BRL are determined with a 95% confidence level (or 5% risk of false rejection). The T value is calculated using the following equation:

$$T = \frac{|X_0 - \bar{X}|}{SD}$$

where: X_0 is the extreme value being measured

\bar{X} is the mean of the measurement set for n observations including X_0

SD is the standard deviation associated with X including X_0

If a value is rejected, the mean and standard deviation are recalculated using the remaining data. This procedure can be reiterated using the next extreme value until no outliers remain.

TABLE 11.2 - GRUBB'S TEST FOR OUTLIERS

Number of Data Points	Risk of False Rejection				
	0.1%	0.5%	1%	5%	10%
3	1.155	1.155	1.155	1.153	1.148
4	1.496	1.496	1.492	1.463	1.425
5	1.780	1.764	1.749	1.672	1.602
6	2.011	1.973	1.944	1.822	1.729
7	2.201	2.139	2.097	1.938	1.828
8	2.358	2.274	2.221	2.032	1.909
9	2.492	2.387	2.323	2.110	1.977
10	2.606	2.482	2.410	2.176	2.036
15	2.997	2.806	2.705	2.409	2.247
20	3.230	3.001	2.884	2.557	2.385
25	3.389	3.135	3.009	2.663	2.486
50	3.789	3.483	3.336	2.956	2.768
100	4.084	3.754	3.600	3.207	3.017

Tabulated values obtained from Quality Assurance of Chemical Measurements by John Keenan Taylor, 1987.

11.3 Method Detection Limits

The method detection limit (MDL) is the minimum concentration of an analyte of interest that can be measured and reported with 95 percent confidence that the value is above zero. MDLs are determined by replicate analysis of a sample that is one to five times the estimated detection limit for the analyte of concern **or up to 10 times the level for multi-element tests**. The sample aliquots to be used may be from a native sample or a representative matrix that has sufficient analyte (present or spiked) to make the concentration one to five times the estimated MDL. If a sample low enough in the analyte of interest is not available, then method blanks may be spiked at the appropriate level for the MDL study. A minimum of seven sample aliquots (BRL routinely prepares and analyzes eight MDL samples) must be analyzed for the determination of the MDL. As long as seven sample aliquots remain, one MDL sample may be discarded, but only if there is a defensible reason for doing so (e.g. the auto sampler did not sample the cup, sample was not spiked, etc.). The reason for the abnormal result must be known and it must be shown that no other sample results could have been affected. The MDL is then calculated as the standard deviation of the replicate analysis multiplied by the "student's t" value for the number of replicates analyzed (3.143 for seven replicates; 2.998 for eight replicates). When evaluating a MDL, the sample aliquots must be carried through the entire method as per client samples. If, for a particular method of analysis, the concentration in the sample aliquots is below the MDL, then they cannot be used to calculate the MDL. In such a case, the MDL study is repeated with appropriately spiked MDL samples. More specific information on the MDL procedure and calculation are found in the EPA in "Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11", 40 CFR 136, Appendix B.

MDLs are determined for each method used at BRL prior to the analysis of client samples by that particular method. **For research methods or methods that BRL is not accredited for use, MDLs may be estimated from the standard deviation of the method blanks.** New MDL studies are performed

annually for aqueous samples and biennially for solids methods. More frequent MDL studies may be required by accrediting bodies or at the discretion of BRL management. Additionally, the MDL must be re-determined any time major changes in a procedure are made. Major changes include changes in personnel, instrumentation, procedural changes to either the preparation or the analysis of samples, etc. The MDL study is intended to represent the capabilities of BRL and; therefore, should only be performed by experienced analysts.

As part of the MDL study, a **Limit of Detection (LOD) validation check** must be performed either during or immediately following the study (within one week and prior to analyzing any samples using the new MDL) on all instruments that might be used for the analysis. The **LOD validation check** consists of an appropriate sample prepared at 2 – 3 times the determined MDL for single analyte tests and 1 – 4 times the MDL for multi-analyte tests. The response produced during the analysis of the **LOD validation check** sample must be greater than 3 times above the instrument's noise level to be acceptable. If the **LOD validation** sample analysis fails to meet the acceptance criterion, then additional **LOD validation** checks must be performed at a higher level to set a higher MDL or the MDL study must be re-conducted. The MDL verification check sample must be analyzed quarterly on each instrument used to analyze samples. As a rule, the MDL verification sample is prepared and analyzed at levels of 1, 2, and 3 times the MDL **when first establishing the MDL/LOD and then at 2 to 3 times the MDL quarterly. It is BRL policy to always set the LOD at a level of at least 2 times the MDL and no more than 3 times the MDL.**

Brooks Rand Labs currently defines the different units for the MDL validation test as such.

- **Background Noise:** The average response of the instrument or calibration blanks during a single analytical run (sequence).
- **Instrument Noise:** The variation of the individual instrument or calibration blanks around the background noise during the sequence. To be as conservative as possible, this is measured for any single sequence as the absolute difference between the response of the lowest and the highest instrument blanks.
- **MDL Verification Sample Response:** This is measured as the instrument response for the analysis of the MDL verification sample corrected for the background noise.

For example, instrument response for total mercury analysis is measured in units of peak area (PA). If four calibration blanks were analyzed and gave responses of 59 PA, 98 PA, 81 PA, and 69 PA, then the background noise would be the average (76.75 PA or 77 PA) and the instrument noise would be 98 PA – 59 PA = 39 PA. For this example, the instrument response for the MDL validation sample would need to be greater than 77 PA + (3 x 39 PA) or greater than 194 PA in order for the MDL validation criteria to be met.

NOTE: The requirement of the MDL verification check may be met through the analysis of client samples prepared with a batch that happen to be approximately 2 times the determined MDL. That is, a specific MDL verification sample need not be prepared if another sample prepared with the batch meets the requirements of the MDL verification sample. However, the initial MDL verification immediately following a new MDL study must be performed prior to any sample analysis.

Some additional clarification is required between how NELAC and the DoD QSM use the MDL verification sample to establish the Limit of Detection (LOD). NELAC treats the LOD as BRL treats the MDL; namely, the LOD is the detection limit (DL) for the method of interest

and is verified by analyzing an **LOD validation** check sample. The DoD QSM defines the DL for the method in the same way that BRL defines the MDL. However, by the DoD QSM, the LOD is set by the level of the **LOD validation** check sample and it will always be greater than the DL. What this **means** is that for work covered by the NELAC standard and any work not requiring accreditation, BRL will report down to the MDL unless otherwise specified in the contract. Whereas, for work covered by the DoD QSM, BRL will report down to the level of the lowest **LOD validation** sample that meets the acceptance criteria, but not below the MDL.

All MDL studies are documented and the Quality Assurance Manager keeps the documentation on file. Documentation includes the date of the study, the name of the analyst conducting the study, the analytical method(s), the analyte of interest, preparation notes, and all raw data from analysis.

The method reporting limit (MRL) is based on the level of the low standard used in the instrument calibration and the volumes/weights used in the analysis of samples. The MRL cannot be less than the MDL and is typically 3 to 10 times the MDL. The **Limit of Quantitation (LOQ)** is the concentration of an analyte of interest where the relative confidence in the measured value is $\pm 30\%$ at the 95% confidence level. **LOQs** are estimated as 9 to 12 times the standard deviation from the MDL determination. Whenever possible, BRL sets the MRL to be equivalent to the **LOQ** by adjusting the level of the low standard to be equal to the **LOQ**.

The validity of the **LOQ/MRL** is confirmed **quarterly for each instrument used** with the analysis of **four** laboratory fortified blank samples spiked at 1 – 2 times the level of the **LOQ/MRL**. Recovery of the **LOQ/MRL** LFB is judged against the established method acceptance criteria or client data quality objectives, whichever are more stringent, for **precision and** accuracy.

The instrument detection limit (IDL) is determined at initial set-up of the instrument and after any significant change (such as change in equipment or reagents used, carrier gases, gas pressures, etc.). Additionally, an IDL study may be used as part of an analyst's demonstration of capability as long as their ability to prepare samples is not being evaluated. A minimum of seven analytical spikes prepared at the level of the low calibration standard are analyzed and the IDL is then calculated as the standard deviation of the replicate analysis multiplied by the Student t value ($t_{.99}$) for the number of replicates analyzed (3.143 for seven replicates; 2.998 for eight replicates). The calculated IDL must be less than the MDL for all methods analyzed on the instrument. Additionally, a minimum of four analytical spikes prepared at approximately 10 times the MRL are analyzed. The recovery and standard deviation of these QCS samples must meet sample specific requirements of the method being performed.

11.4 Initial and Continuing Demonstration of Capability

11.4.1 Initial Demonstration of Capability (IDOC)

Every analyst must perform an IDOC study prior to analyzing samples. An MDL study is typically part of an analyst's IDOC, but is not required since it will also be affected by the preparation of the samples and isn't fully indicative of the analyst's ability to properly analyze sample preparations. If an MDL is not part of the IDOC, then an IDL study is performed where a minimum of seven analytical spikes prepared at the level of the low calibration standard by the analyst at the instrument must be analyzed. These samples are analyzed as per an MDL

study and the resulting detection limit must be less than the MDL for the analytical method. In addition, a minimum of four QCS samples are prepared as per the specific analytical method requirements (typically at a concentration that is 10 times the level of the MRL) and analyzed. The average recovery and the RSD yielded by the analysis of the QCS samples must meet the specific requirements of the analytical method being performed. A new IDOC must be performed anytime there is a change in instrument type, personnel, or test method (including changes to either the preparation or analysis of samples). [Specific requirements for a passing IDOC are outlined in BRL SOP BR-1206 \(MDL Studies, Validation, and Demonstration of Capability\)](#).

11.4.2 Continuing Demonstration of Capability (CDOC)

In addition to performing an IDOC prior to beginning analysis, each analyst must demonstrate that he is continuously capable of performing the analysis. This capability is judged annually by reviewing control charts for the methods performed by the analyst, looking at four consecutive batches performed by the analyst to ensure that all batch specific QA was met, or by having the analyst perform another IDOC study while analyzing the annual MDL study to demonstrate that the analyst is still capable of obtaining accurate and precise results. [The full analyte list need not be reviewed for multi-analyte analyses to show continuing capability. At a minimum, 6 analytes will be reviewed, including typically problematic analytes such as selenium, silver, and zinc. Specific requirements for a passing CDOC are outlined in BRL SOP BR-1206 \(MDL Studies, Validation, and Demonstration of Capability\)](#). If the analyst has not demonstrated continuing capability for a method, then the Laboratory Manager will determine if additional training is required and the analyst must successfully perform an IDOC prior to analyzing any further client samples.

11.4.3 Documentation

All raw data, including preparation logs, analytical bench sheets, and instrument printouts, used to perform the IDOC or CDOC study are scanned and attached to the relevant sequence in the LIMS. Additionally, hard copies of the preparation logs and analytical bench sheets are filed by the QA Department and maintained for no less than seven years from when the analyst stops working at BRL. All IDOC and CDOC studies must be reviewed by the QA Department and the QA Manager must annually certify that each analyst is capable of performing their respective duties by completing a Demonstration of Capability Certification Statement form for each method an analyst performs. These forms are kept in the employee training records. A copy of this form is presented on the following page.

11.5 General QC Requirement Statement

The QC requirements previously listed are general requirements only. Specific methods or client-specific Statements of Work may have more stringent requirements that take precedence.

Demonstration of Capability Certification Statement

Date:

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Laboratory Name: **Brooks Rand Labs**
Laboratory Address: **3958 6th Avenue NW**
Seattle, WA 98107

Analyst(s) Name(s):

Prep Tech Name (if applicable):

Matrix:

Method number, SOP#, Rev#, and Analyte or Class of Analytes or Measured Parameters:

Criterion Used (MDL Study, Consecutive Analysis, etc):

The undersigned CERTIFY that:

- 1) The analyst (and prep technician if applicable) identified above, using the cited test method(s), which is in use at this facility for the analyses of samples under the National Environmental Laboratory Accreditation Program, has met the requirements for the Demonstration of Capability.
- 2) The test method(s) was performed by the analyst(s)/prep tech(s) identified above.
- 3) A copy of the test method(s) and the laboratory-specific SOPs are available for all personnel on-site.
- 4) The data associated with the demonstration of capability are true, accurate, complete, and self-explanatory (1).
- 5) All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized assessors.

_____	_____	_____
Technical Director	Signature	Date
_____	_____	_____
Quality Assurance Manager's Name	Signature	Date

This certification form must be completed annually or each time a demonstration of capability study is completed.

- (1) True: Consistent with supporting data.
Accurate: Based on good laboratory practices consistent with sound scientific principles/practices.
Complete: Includes the results of all supporting performance testing.
Self-Explanatory: Data properly labeled and stored so that the results are clear and require no additional explanation.

12.0 Data Reduction, Validation, Reporting and Storage

Prior to release of analytical results, all unknown sample and associated quality control data are subjected to the full review process briefly described below. Refer to BRL SOPs BR-1300, BR-1301, and BR-1302 for a detailed description of the data review procedure.

12.1 Analytical Integration

Analytical instrumentation signal output is integrated by BRL-developed integration software (i.e., Guru™) or by manufacturer specific software (i.e., Perkin Elmer Elan and Chromera software). Analytical runs are stored electronically. Integration software is verified by the QA samples. Any integration software related problem that affects samples would also affect QA samples; therefore, as long as QA criteria are met, the software is assumed to be operating properly. The electronics department at BRL maintains all documentation of integration software upgrades.

12.2 Data Reduction

The analyst is responsible for uploading all data into the LIMS and performing primary validation of the data. Initial data reduction is performed by the instrument software to obtain initial results in units of measured pg, measured ng, or µg/L. This information, along with volumes/masses used in the preparation/analysis of the samples is either uploaded or hand entered into the LIMS where final results are calculated according to the method used to analyze the samples. The following documentation must be present with every data package: preparation notes, SPFs, lab bench sheets, Analysis Sequence printout, and analyst's notes. All instrument printouts are stored electronically as PDF files and must have the analytical batch recorded on them and the sample ID for each instrument response.

12.3 Data Entry

The preparation technician [or analyst](#) is responsible for entering all sample masses/volumes and preparation volumes into the bench sheet in the LIMS, as well as any batch specific QC information. The analyst is responsible for checking this information, entering all analytical specific information into the instrument software, and uploading all of the instrument results into the LIMS. The analyst first ensures that all data is present and that all previous sections on the SPF have been completed and signed-off. All final results are automatically calculated in the LIMS using formulas specific to the analytical method used.

12.4 Primary Data Review

After the data has been acquired and any necessary calculations performed, the primary data review is performed by the analyst. Items to be reviewed include correct upload of the data, sample identity, instrument calibration, QC samples, detection limits, numerical computations, accuracy of transcriptions, sample preparation logs, instrument/analytical logs, and compliance with the individual method. Software used for data entry is verified to be working properly by the data entry verification protocols described in BRL SOPs BR-1300 and BR-1301. Any software problems or

failures are documented as correspondence between the IT Manager and the software manufacturer. The IT Manager keeps all such documentation/correspondence on file.

12.5 Final Data Review and Validation

Following the analyst's review, [the raw data and calculations undergo final review by the QA Group](#). The [QA Group](#) also reviews comments about analytical conditions as well as any interpretations made by the analyst. Additionally, the [QA Group](#) examines the QC sample data and ensures that the analytical results meet or exceed the acceptance criteria for frequency, accuracy, and precision.

Data validation is part of the review process whereby data are inspected and either accepted, rejected, or qualified based on a set of criteria. Evaluation parameters that can be used for validation include, but are not limited to:

- Calibration data
- Specific checks unique to each measurement
- Statistical tests

After final data review and validation is complete, the [QA Group](#) applies any necessary data qualifiers, sets data to be reported to “reportable,” and signs-off on the sample processing form. Only the QA Manager or delegate and, in extreme cases, the Lab Manager or [VP of Analytical Services](#) have authority to change the reportability of data after final data review. All changes in the status of data (e.g. batched, prepared, analyzed, reviewed – primary, reviewed – final, reportable versus non-reportable, etc.) is updated automatically in the LIMS with a time stamp and identity of the person that made the change.

12.6 Data Reporting

Prior to data reporting, the Project Manager responsible for the report reviews that data a final time for any discrepancies. The final client report is generated only when the Project Manager is satisfied that the data is valid and all project specific requirements have been met. [Any Level IV report or reports where issues require additional narration goes through secondary review by another Project Manager or Project Coordinator who then signs-off on the report as well](#). Only then is the report sent to the client.

Typically at BRL, results are reported down to the MDL. Results \leq the MDL are reported at the MDL and qualified “U” as non-detectable. Results at or below the MRL but above the MDL are reported as the calculated result and qualified “B” as an estimate. Results above the MRL are reported as the calculated result without qualification. [For Department of Defense \(DoD\) work, results are either reported only down to the LOQ or by the rules defined in Gray Box 47 of the DoD QSM 4.2](#). All sample results are reported to three significant figures except for percent total solids results and results for QC samples, which are both reported to four significant figures. Sediment and soil results are typically reported on a dry-weight basis by dividing the wet weight result by the percent total solids result. Biota results are typically reported on a wet-weight basis. However, upon request, biota results may be reported on a dry-weight basis as well.

Any sample that yields a non-detectable result and shows <30% recovery of the matrix spike cannot be reported. The sample is qualified “R” to indicate that all generated results for the sample are unusable and no result for the sample is reported. Refer to section 11.3 for differences in how the limits of detection are defined between work performed under the NELAC standard and work performed under the DoD QSM and how this affects how results are reported by BRL.

It is BRL policy to always method blank correct results (with the exception of total solids and total suspended solids). In extreme cases where the client requires results that have not been method blank corrected, the criterion for acceptable method blanks is that the absolute value of the highest method blank concentration for any detectable (> MDL) method blank must be $\leq 10\%$ of any [detectable \(> MDL\)](#) result. Any [detectable](#) result not ≥ 10 times the absolute value of the highest detectable method blank concentration is qualified “X” and narrated as being an estimate due to elevated method blanks with either high or low bias depending on whether the method blank concentration is a positive or negative value.

Another extreme case where it may not be appropriate to blank correct data is when there are highly variable blanks that do not meet the method blank criteria. In such cases, it is better to report results without blank correction as previously described. When reporting results without method blank correction, the reporting limits should not be adjusted. Instead, any results affected due to random or elevated method blanks are appropriately qualified using the “X” qualifier. Refer to Section 11.1.2.1 for further discussion on method blanks.

[Data that is not method blank corrected is reviewed and qualified using the same acceptance criteria as blank corrected data with one caveat. Samples are not reprepared or reanalyzed if failing non-blank corrected QC would have passed if it had been blank corrected as per standard practice. In such cases, the data is qualified accordingly and reported unless specified otherwise in the client contract.](#)

Generally, data are reported in a format generated by the BRL LIMS with a case narrative or a cover letter attached. All of the data, including standard spike recoveries, control samples, duplicate analyses, and results from blank analyses, are reported along with the sample results. Data quality issues are addressed in the [cover letter or case narrative](#), which discuss each batch analyzed in the sequence. Final reports are submitted to all required parties (project dependent). A copy of each report stored electronically as a PDF file for BRL’s internal records (see 12.7 data storage). All laboratory report forms and reporting formats shall be in compliance with the reporting requirements of the applicable project for which they are generated. A specific statement clearly identifying any results that do not meet the specific project requirements (i.e. non-NELAP accredited or non-DoD accredited work performed by BRL) is included, if applicable, in the final report.

Every reasonable effort is made to report data with acceptable associated quality assurance sample (QC) results. However, barring this, data is qualified appropriately to indicate when batch QC does not meet specific acceptance criteria. A list of all data qualifiers and their definitions is included with every data report. While Brooks Rand Labs has its own in-house data qualifiers that are defined on the “Report Information” page of the report, the use of project or accreditation specific qualifiers always take precedence over BRL qualifiers. In such instances, the project specific

qualifier definitions would [over-ride](#) the BRL qualifier definitions on the “Reporting Information” page of the final report and [discrepancies would be narrated](#).

Electronic files may be transferred to a client via electronic data deliverable (EDD) or by email with the following statement:

CONFIDENTIAL

This electronic message transmission (including any attachments) is intended only for use by the addressee(s) named herein; it contains legally privileged and confidential information. If you are not the intended recipient, you are hereby notified that any dissemination, distribution, printing, or copying is strictly prohibited. If you have received this e-mail in error, please notify the sender and permanently delete any copies thereof.

Disclosing information about client results or contracts to any party outside of Brooks Rand Labs without prior permission from the client and Brooks Rand Labs and without following all reporting policies stated in the Brooks Rand Labs Comprehensive Quality Assurance Plan and associated standard operating procedures is forbidden by all personnel. The term “reporting” refers to any electronic, written, or spoken discussion of client data or other confidential and proprietary information. To protect the client’s proprietary rights, data must never be reported over the phone. Additionally, data can only be reported directly to the client with whom Brooks Rand Labs has a legal contract to perform work, [unless BRL has written permission from the client to release the data or report to a third party](#).

12.7 Data Storage

For all data generated by Brooks Rand Labs prior to October 15, 2006, hard copies of all data and documentation will be kept on file for a minimum of five years [unless contract specific requirements call for longer storage](#). Data and documentation to be stored include: SPFs, preparation notes, lab bench sheets, lab notebooks used in reduction, instrument printouts, and any results spreadsheets (i.e., Excel[®] spreadsheets used to calculate values). The QA Manager is responsible for maintaining files of all batch specific hard data. The [last 6 months worth](#) of batch specific hard data is stored in cabinets located in the main office area. The previous year’s batch specific hard data is stored in the overhead space of the [conference room](#). Any earlier batch specific hard data is stored in a secure facility off BRL premises. The Project Manager is responsible for maintaining all client specific files. [Most client files are saved electronically and not in hardcopy](#). All MDL study documentation and other QA documentation are scanned and attached to the relevant sequence in the LIMS. Hard copies of the original data are filed by the QA Department by date. All data generated following October 15, 2006 are scanned and stored electronically for a minimum of ten years. After five years, electronic data may be removed from the server, but is backed up to two separate external hard drives that are stored at separate, secure locations. Any paper work that has not been scanned for any reason will be stored for a minimum of five years.

Note: The following procedure is done for clients with data prior to October 15, 2006 that require data to be maintained for more than 5 years to ensure that data is not inadvertently lost. Hardcopy data prior to October 15, 2006 is pulled from storage and then scanned to the server and stored as electronic data for as long as required by the project.

Electronic summaries of data will be kept for a minimum of 10 years. All computer files are stored both on computer hard drive and on backup disks. Computer files of client reports are organized by sample tracking number, batch spreadsheets are organized by batch number, and all project information is organized by project numbers. All client reports are scanned and stored electronically. These reports contain copies of the original SRL, as well as any information provided by the client including chain-of-custody forms, analysis request forms, airbills (full reports only), etc. Since October 15, 2006, all sequence specific data has also been scanned and stored electronically. The original hardcopy batch data is stored for at least 6 months in the file cabinets in the main office before being shredded. All hard copy data previous to October 15, 2006 will be stored for a minimum of five years from the date of reporting before being shredded. All employees at BRL are authorized to access electronic information. No levels of accessibility for employees exist. The IT Manager monitors the upkeep of computer files.

All hard copies of any documents that could be traced directly to a client are destroyed by shredding prior to disposal.

13.0 Document Control Policies

13.1 SOPs, Manuals, Handbooks, and Plans

All documents important to the internal operations of BRL go through formal procedures as to their writing, approval, implementation, retirement, and sharing.

13.1.1 Writing and Approval of SOPs, Manuals, Handbooks, and Plans

Once it has been determined that a new policy or procedure is required at BRL, the most appropriate employee(s) (i.e., whoever has the most knowledge or experience in the given area) is/are delegated to write a document detailing the policy or procedure. Once the document has been written, it must pass up through a chain of approval specific to the type of document being written.

All SOPs begin with the appropriate person writing the procedure. The Group Leader (if applicable), the QA Manager, and, finally, the [Lab Manager](#) then must approve the SOP (in that order). The CQAP must be approved in order by the QA Manager and the VP of Analytical Services. BRL Handbooks and Plans follow their own specific chain-of-approval processes, with final approval coming from the VP of Analytical Services or President.

If an error is discovered during any portion of the approval process, the person who found the error makes a note of it and sends the document back to the original writer. It is the writer's responsibility to address the error and then reinitiate the approval process from the very beginning.

Upon approval, each person in the chain of approval must sign and date the document. Only upon final approval is the document considered to be in force and all procedures within the document from that date forth are enforced until the document is retired (see section 13.1.3).

13.1.2 Annual Review of SOPs, Manuals, Handbooks, and Plans

All BRL documents are reviewed annually. If no changes in the procedure are required, the reviewer signs and dates the document as being reviewed. If changes are required, the appropriate employee is designated to make the required revisions. The new revision of the document must then go through the same chain of approval it went through for its initial writing. Upon final approval, the new revision is considered in force, and the old revision is retired. Refer to SOP BR-1400 for specific procedures to follow when revising an SOP.

13.1.3 Retirement of SOPs, Manuals, Handbooks, and Plans

When a BRL document is retired, the original is clearly labeled "outdated" and the date of its retirement is also clearly indicated. All copies of the retired document are either destroyed or also clearly labeled as being outdated. The original is then archived as a historical record (either electronically as a PDF file or as a hardcopy) for no less than five years.

13.1.4 Proprietary Information

Many of the analytical methods used at BRL have been developed in-house and are considered proprietary information. Clients or other organizations requesting particular SOPs are required to first sign an “Agreement for Confidential Disclosure and Restricted Use of Proprietary Information.” Whenever possible, “client ready” SOPs, where all proprietary information has been removed, are given to clients instead of full SOPs.

13.1.5 Uncontrolled Documents

Uncontrolled documents are defined as any document (CQAP, SOP, “cheat sheet”, etc.) or portion thereof that has not been signed and dated as being approved for use in the laboratory and is not under the direct control of the QA Manager. No such document is allowed to be posted or used in the laboratory and must be immediately removed upon detection. When referencing the CQAP or an SOP, the current approved version should be opened directly from the server from the following folder: [Y:\SOP & other DOCs](#). All documents in this folder are PDF versions with signed and dated cover pages. If “cheat sheets” or isolated pages from SOPs would be of value in the lab, then these must be approved by the QA Manager who then signs and dates the pages and combines them into a controlled logbook for the laboratory.

13.1.6 Master List of Controlled Documents

The Quality Assurance Manager is responsible for maintaining a master list for the location of all controlled documents. The list must contain the following information:

- Title of controlled document
- Revision number
- Location stored or name person in possession of
- Date printed or sent electronically

13.2 Client Records

All client reports, records of results, and correspondences are maintained by BRL for a period of no less than five years. All project information is electronically stored on the server for a minimum of 10 years. All “Active Client” specific files are maintained by the Project Manager. All client data generated following October 15, 2006 is scanned and stored electronically for a minimum of ten years.

In the event that BRL should go out of business, it is BRL’s stated policy that every attempt will be made to notify all clients (past and present) and ask them how they would wish to have their records maintained or transferred. In the advent of a change in ownership, it is BRL’s policy that all records become the property of the new owner unless specifically requested otherwise by the client. All reasonable demands of the client shall be met and no client information shall be removed from BRL premises without the client’s written consent.

13.3 Employee Records

All employee records, including resumes, training, IDOC and MDL studies, are maintained by BRL for a period of no less than seven years following the departure of the employee.

14.0 Information Systems

14.1 Hardware

A local area network (LAN) connects staff computers and printers for local access, as well as providing external email, faxes, and Internet access. The server computer is a Dell PowerEdge 1900 running Microsoft® Small Business Server 2003 R2. The server is configured as a primary domain controller and print server for networked printers. It is equipped with three 146 gigabyte hard disk drives and employs RAID 5. The redundant array will prevent data loss in the event of a single hard drive failure.

A dedicated server runs the LIMS application and is accessible via the LAN. The hardware is a Hewlett-Packard ProLiant DL180 G5 Server. It has six 250 GB hard disk drives. The data resides on a three disk RAID 5 array. The OS resides on a two disk RAID 1 array. The sixth HDD is a spare hot swappable disk. The OS is Microsoft® Windows Server 2008. The LIMS program runs on SQL Server 2005 application.

A terminal server is configured to provide remote access for offsite employees. The server is a Dell PowerEdge 700 running Microsoft® Small Business Server 2003 R2 and Terminal Services.

14.2 System Backup

Backup software, Retrospect version 7.0, provides scheduling, automation and monitoring of backup for both server and workstation files. The software is run on a networked spare workstation. All data files located on the server are backed up daily. These include the LIMS file (Microsoft® SQL Server), instrument data, and client-related files. Other selected files on the workstation are also backed up weekly.

Three external hard drives are used to perform the backups. The hard drive connected to the backup workstation remains so for three weeks, after which it is removed to an offsite location and the external hard drive with the oldest backed up data is then connected to the backup PC.

14.3 Security

A Netscreen-5GT router/firewall protects the LAN from the public internet. Workstation access is available to all authorized employees via domain logon. Shared data is available throughout the local network. Specific directories or files may be protected from access using Group Policy security settings if the data owner considers it necessary. Data loss is safeguarded through redundancy. Redundancy is accomplished via backups as mentioned and secure storage of data in hard copy.

All computer accounts are password protected so that unauthorized access is not allowed. Individuals are required to logoff of computers when they leave the workstation.

15.0 Corrective Action

15.1 Corrective Action

The laboratory has a corrective action system to identify any situations that may adversely affect data quality. These situations include, but are not limited to:

- Results outside of quality control criteria as outlined in individual SOPs
- Statistically out-of-control-events
- Deviations from normally expected results
- Suspect data
- Deviations from the method
- Special sample handling requirements

Corrective action may also be initiated as a result of other QA activities, such as performance or system audits.

Once a requirement for corrective action has been identified, the Lab Manager and/or the QA Manager must be notified immediately. A verbal notification may be initially made; however, written documentation of the problem is required typically using an incident report form (Refer to [Brooks Rand Labs SOP BR-1204](#)). The QA Manager is responsible for evaluating the situation and determining the appropriate corrective action. The QA Manager has stop work and resume work authority whenever a nonconformance issue may threaten the quality of data produced by Brooks Rand Labs. Corrective action steps include, but are not limited to:

- Problem identification
- Investigation to determine the cause of the condition
- Action to eliminate the problem
- Increased monitoring to evaluate the effectiveness of the corrective action
- Verification that the problem has been eliminated

Documentation of problems requiring corrective action is important to overall laboratory management. Any lab personnel may initiate a corrective action, but it is the QA Manager who is responsible for ensuring that the action is documented. The QA Manager is also responsible for verifying that initial action has taken place and appears effective and, after an appropriate time, for checking to see if the problem has been fully resolved. Examples of corrective action include, but are not limited to:

- Amending forms
- Reanalyzing samples if holding times permit
- Checking instrumentation to make sure that it is operating properly
- Recalibrating with fresh standards
- Replacing suspect reagents
- Examining calculations
- Additional training in sample preparation and analysis

- Evaluating and amending procedures
- Accepting the data and acknowledging the level of uncertainty or inaccuracy by flagging the data and providing an explanation for the qualification

15.2 Client Communication and Complaints

Brooks Rand Labs is committed to providing the best laboratory services available in the industry. To this end it is vital that good and proper communication is always maintained with our clients. Clients' opinions of the services provided by Brooks Rand Labs are very important to us. All client comments, whether positive or negative, are taken seriously. If a client has a complaint, it is recorded and kept on file by the Client Services Manager. Complaints may encompass any aspect of the services provided by BRL, including analytical services, technical services, or quality assurance.

Once a complaint has been recorded, the BRL manager who is most responsible for the service to which the complaint is directed shall handle the matter with the client. If necessary, the BRL manager will initiate a corrective action to deal with any legitimate deficiencies brought to our attention by clients. The resolution of all complaints shall be recorded along with the initial complaint.

Any events that cast doubt on the validity of any test results already reported must be conveyed to the affected client within one business day of when the events become evident to BRL management. In addition to any phone messages, the client must also be promptly notified in writing. This is typically done in the form of an email. If more formal documentation is required, then a signed letter may be provided, as well as copies of any associated corrective actions.

Both negative and positive feedback from clients are reviewed at the end of the year as part of the Managerial Review in an effort to constantly improve the quality system and products and services provided by Brooks Rand Labs.

15.3 External Audits

Corrective action may also be initiated by external audits by regulatory agencies or clients. Brooks Rand Labs considers audits as an opportunity to improve upon our services. Any deficiencies discovered during external audits are documented and corrective actions are initiated to address them.

16.0 Performance and System Audits

16.1 System Audits

16.1.1 Internal Systems Audits

BRL conducts specific function audits on an annual basis, with a different segment of the laboratory being thoroughly audited each quarter of the year. This audit process is used to ensure that:

- Approved procedures are in place and used
- Sample custody is properly maintained and documented
- Analytical methods are performed properly and documented
- Specific equipment is available, calibrated and in proper working order
- Analysts are properly trained and the training is documented
- Record keeping procedures are being followed and appropriate documentation is maintained

Additionally, laboratory walk-through audits are performed monthly throughout the laboratory. The laboratory is divided into four groups (Sample Control Group, Mercury Group, Trace Metals Group, and Sample Preparation Group). Each group is audited separately. Laboratory walk-through audits are not as thorough as the quarterly audits, but serve to ensure that quality assurance procedures are being performed routinely before issues arise. The findings from monthly walk-through audits and any necessary corrective actions are presented in monthly QA reports.

An annual Managerial Review of the quality system is prepared, typically during the month of January. This report consists of a review of the monthly and quarterly audits over the past year, including the documentation, findings, reporting, corrective action, and follow-up. If any findings are still considered open from the past year, then the report should include a list of outstanding findings, a detailed explanation as to how those findings are being addressed, and a form on which to indicate when the findings have been resolved. This review also looks ahead to anticipated issues for the coming year(s). The ultimate purpose of this review is to ensure the continued effectiveness and improvement of the quality systems in place at Brooks Rand Labs.

Various intercalibration exercises with other laboratories also serve as a performance audit of the laboratory analyses.

16.1.2 External Systems Audits

BRL has occasional audits from various clients and accrediting agencies. The principal organizations that conduct audits of BRL's facilities and operations are the Washington State Department of Ecology, the Florida State Department of Environmental Protection as part of the NELAP accreditation, and ACLASS as part of Department of Defense accreditation. BRL views external audits as an excellent tool for evaluating our quality and for finding areas for improvement. BRL always welcomes any client (current or potential) or government agency to conduct on-site audits.

16.2 Performance Audits

Internal Performance Audits must be conducted at least biannually and may consist of blind samples, split samples with another laboratory (interlaboratory comparison study), QC samples (unknown to the analyst), performance evaluation samples, and/or blind spiked samples. BRL frequently participates in assisting agencies to certify reference materials for use as blind interlaboratory samples. Any of the Analytical Technicians may analyze these performance audit samples. The Project Manager and Lab Manager are responsible for overseeing BRL's participation in each study, and all associated documentation, reporting, and record keeping.

External Performance Evaluations are as follows:

<u>Agency</u>	<u>Study Title</u>	<u>Frequency</u>
ERA	Blind PE samples*	Semi-Annually**
RTC	Blind PE samples*	Semi-Annually**

- * As a better indication of overall laboratory performance, PE samples are treated like all other received samples in terms of receipt, preparation, quality control, and analysis.
- ** Participation in additional PE studies may be required as part of corrective action.

16.3 Annual Management Review of the Quality Systems

Brooks Rand Labs management conducts an annual review of the quality systems to ensure that they are still effective. This review typically takes place during the month of January. All reports by managerial personnel, the outcome from all recent internal and external audits, the results from PE studies and interlaboratory comparisons, changes in the volume and type of work performed, feedback from clients, and corrective actions are taken into account during the managerial review.

APPENDIX A – Common Abbreviations

AA	–	Atomic Absorption
ASD	–	Analytical Services Department
BLK	–	Method Blank
BRL	–	Brooks Rand Labs
BS	–	Blank Spike
CCV	–	Continuing Calibration Verification
CDOC	–	Continuing Demonstration of Capability
COC	–	Chain of Custody
CQAP	–	Comprehensive Quality Assurance Plan
CRM	–	Certified Reference Material
CVAFS	–	Cold Vapor Atomic Fluorescence Spectrophotometry
DoD QSM	–	Department of Defense Quality Systems Manual
DUP	–	Method Duplicate
EDD	–	Electronic Data Deliverables
EPA	–	Environmental Protection Agency
ERA	–	Environmental resource Associates
FEP	–	Fluorinated Ethylene Propylene (Teflon™)
FLPE	–	Fluorinated High-Density Polyethylene
HDPE	–	High-Density Polyethylene
HEPA	–	High Efficiency Particulate Air
HGAAS	–	Hydride Generation Atomic Absorption Spectrometry
IDOC	–	Initial Demonstration of Capability
ICP-MS	–	Inductively Coupled Plasma – Mass Spectrometry
ICV	–	Initial Calibration Verification
IMD	–	Instrument manufacturing Department
IT	–	Information Technology
LIMS	–	Laboratory Information Management System
LOD	–	Limit of Detection
LOQ	–	Limit of Quantification
MB	–	Method Blank

MD	–	Method Duplicate
MDL	–	Method Detection Limit
MRL	–	Method Reporting Limit
MS/MSD	–	Matrix Spike / Matrix Spike Duplicate
NELAC	–	National Environmental Laboratory Accreditation Conference
NELAP	–	National Environmental Laboratory Accreditation Program
PQL	–	Practical Quantitation Limit
PM	–	Project Manager
QA	–	Quality Assurance
QC	–	Quality Control
RPD	–	Relative Percent Difference
RSD	–	Relative Standard Deviation
SPF	–	Sample Processing Form
SOP	–	Standard Operating Procedure
SOW	–	Statement of Work
SRM	–	Standard Reference Material
VP	–	Vice President

APPENDIX B - Standard Operating Procedures

Brooks Rand Labs - Standard Operating Procedures

<u>SOP #</u>	<u>Title</u>
	<u>Analysis (BR-0001 through BR-0099)</u>
BR-0002	BRL Procedure for EPA Method 1631, Appendix to (1/01): Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)
BR-0003	Determination of Total and “Acid-Labile” Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)
BR-0005	Total Volatile Mercury in Water by Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
BR-0006	Procedure for EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
BR-0007	BRL Procedure for Determination of Vapor Phase Total Mercury from Stationary Sources Using Dry Sorbent Trap Sampling and Analysis by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) – Modification of EPA Method 324
BR-0011	Determination of Methyl Mercury by Aqueous Phase Ethylation, Trap Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630 (Waters) and EPA Method 1630, Modified (Solids)
BR-0013	Five-Step Selective Sequential Extraction Procedure (SEP) to Quantify Mercury Fractions in Sediments, Soils and Mine Tailings
BR-0015	BRL Procedure for Reactive Mercury in Tissue, Sludge, Sediment and Soil by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS) Modified from EPA 1631
BR-0020	Determination of Selenium (Se) and Arsenic (As) in Environmental Samples by Hydride Generation-Atomic Absorption with Cryogenic Trap Preconcentration
BR-0021	BRL Procedure for the Analysis of Water, Sediment, and Tissue by EPA Method 1632, Revision A (1/01): Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry

Brooks Rand Labs - Standard Operating Procedures

<u>SOP #</u>	<u>Title</u>
	<u>Analysis (BR-0001 through BR-0099 continued)</u>
BR-0060	Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using a Perkin-Elmer ELAN DRC II
BR-0061	Trace Element Speciation by High Performance Liquid Chromatography – Inductively Coupled Plasma – Dynamic Reaction Cell – Mass Spectrometry using a Perkin-Elmer ELAN DRC II
BR-0062	Determination of Ag, Al, As, Cd, Cu, Cr, Ni, Sb, Se, V and Zn in Flue Gas Desulphurization Waste Waters by Inductively Coupled Plasma – Dynamic Reaction Cell – Mass Spectrometry using a Perkin Elmer ELAN DRC II
BR-0063	Determination of Trace Elements in Seawaters and Low Level Waters by Online Column Chelation Preconcentration – Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II
BR-0065	Aqueous Sample Digestion by Closed-Vessel Oven Heating for Total and Total Recoverable Metals
BR-0066	Reductive Precipitation of Total Recoverable and Dissolved Metals from Brackish and Seawater Samples
BR-0067	Reverse Aqua Regia Oven Bomb Digestion for Total Recoverable Metals in Sediments and Soils
BR-0068	“Total” Metals Digestion in Sediments, Soils, Coal, and Fly Ash
BR-0069	Extraction Using Co-APDC for Nickel, Copper, Silver, Cadmium, and Lead in Water
BR-0070	Total Metals Digestion for Biota Matrices
BR-0080	Determination of Iron Speciation in Water Samples by Colorimetric Detection
BR-0085	Determination of Hexavalent Chromium (Cr ⁶⁺) in Sediment and Aqueous Samples
	<u>Sample Preparation (BR-0100's)</u>
BR-0104	Metals “Free” Filtration
BR-0106	Sample Homogenization
BR-0107	Filtration for Collection of Particulate from Water Samples

Brooks Rand Labs - Standard Operating Procedures

<u>SOP #</u>	<u>Title</u>
	<u>Sample Receipt and Storage (BR-0300's)</u>
BR-0300	Receipt of Samples
BR-0301	Sample Custody Maintenance and Tracking
BR-0302	Sample and Client Identification
BR-0303	Sample Storage and Disposal
BR-0304	Sample Processing
BR-0306	Purchase, Receipt, and Storage of Consumable Materials Used for the Technical Operations of the Laboratory
	<u>Decontamination (BR-0400's)</u>
BR-0400	Decontamination of Sample Preparation Equipment
BR-0401	Decontamination of Silicon and Teflon [®] Tubing and Filter Units for Sample Collection
BR-0402	Metals Decontamination of Glassware
BR-0404	Preventing Trace Metals Contamination of Samples
	<u>Reagents and Standards (BR-0500's)</u>
BR-0500	Documentation of Reagents and Standards
	<u>Security (BR-1000's)</u>
BR-1000	Security of Laboratory and Samples
	<u>Training (BR-1100's)</u>
BR-1100	Training of Laboratory Personnel
BR-1101	Prevention and Detection of Improper, Unethical, and Illegal Actions – Brooks Rand Labs's Data Integrity Plan

Brooks Rand Labs - Standard Operating Procedures

<u>SOP #</u>	<u>Title</u>
<u>Quality Control (BR-1200's)</u>	
BR-1200	Maintaining Instrument and Equipment Records and Logbooks
BR-1201	Internal Laboratory Audits
BR-1202	Evaluating Precision and Accuracy and Estimating Uncertainty in Results
BR-1203	Identifying Systematic Errors
BR-1204	Incident Report and Resolution
BR-1205	Preventative Maintenance
BR-1206	MDL Studies, Validation, and Demonstration of Capability
<u>Data Validation and Reporting (BR-1300's)</u>	
BR-1300	Primary Data Review
BR-1301	Final Data Review
BR-1302	Data Flow and Handling
BR-1303	Reporting
<u>Documents (BR-1400's)</u>	
BR-1400	Writing, Reviewing and Revising Standard Operating Procedures (SOPs)
BR-1401	Records of Client Sample Results
BR-1402	Records of QC Results
BR-1403	Document Control for Standard Operating Procedures (SOPs) and Comprehensive Quality Assurance Plan (CQAP)
<u>General Determinations (BR-1500's)</u>	
BR-1500	Total Suspended Solids in Water
BR-1501	Dry Weight Determination
BR-1502	Determination of Hardness in Water by Calculation
BR-1503	Brooks Rand Labs Procedure for SM 2540G: Total, Fixed and Volatile Solids in Solid and Semisolid Samples – Total Volatile Solids (TVS) Ignited at 550 °C
BR-1504	Measurement of the pH of Solid and Aqueous Samples by Suspension, Centrifugal Separation, and Quantification Using an Electrode-Based pH Meter



CERTIFICATE OF ACCREDITATION

ANSI-ASQ National Accreditation Board/AClass
500 Montgomery Street, Suite 625, Alexandria, VA 22314, 877-344-3044

This is to certify that

Brooks Rand Labs, LLC
3958 6th Ave. NW
Seattle, WA 98107

has been assessed by AClass
and meets the requirements of

ISO/IEC 17025:2005 and DoD-ELAP

while demonstrating technical competence in the field(s) of

TESTING

Refer to the accompanying Scope(s) of Accreditation for information regarding the types of tests to which this accreditation applies.

ADE-1447

Certificate Number

AClass Approval



Certificate Valid: 03/30/2012-03/30/2014
Version No. 002 Issued: 04/09/2012



This laboratory is accredited in accordance with the recognized International Standard ISO/IEC 17025:2005. This accreditation demonstrates technical competence for a defined scope and the operation of a laboratory quality management system (refer to joint ISO-ILAC-IAF Communiqué dated January 2009).



ANSI-ASQ National Accreditation Board

SCOPE OF ACCREDITATION TO ISO/IEC 17025:2005 & DoD-ELAP

Brooks Rand Labs, LLC
 3958 6th Ave NW, Seattle, WA 98107
 Frank McFarland Phone: 206-632-6206

TESTING

Valid to: March 30, 2014

Certificate Number: ADE- 1447

I. Environmental

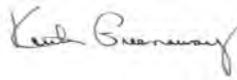
MATRIX	SPECIFIC TEST or GROUP OF ANALYTES**	SPECIFICATION OR STANDARD METHOD (all EPA unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Water Solids Biological Tissue	Elemental Analysis	1638 modified 200.8 modified 6020 modified	ICP-MS
Seawater	Elemental Analysis	1640 modified BR-0060	ICP-MS
Water	Se speciation	BR-0061	HPLC-ICP-MS
Water Biological Tissue	As speciation	1632A	HGAAS
Solids	As speciation	1632A modified	HGAAS
Water	Hg	1631E	CVAFS
Solids Biological Tissue	Hg	1631E (appendix)	CVAFS
Water	Methyl Mercury	1630	CVAFS
Solids Biological Tissue	Methyl Mercury	1630 modified	CVAFS
Water	Hardness – total (as CaCO ₃)	SM 2340 B (20 th Ed.) By calculation of : 1638 modified 200.8 modified 6020 modified	ICP-MS (calc.)



MATRIX	SPECIFIC TEST or GROUP OF ANALYTES**	SPECIFICATION OR STANDARD METHOD (all EPA unless specified)	* KEY EQUIPMENT OR TECHNOLOGY USED
Water	Total Suspended Solids	SM 2540 D (20 th Ed.)	Gravimetric
Solids	Dry weight	SM 2540 E (20 th Ed.)	Gravimetric

Notes:

1. * = As Applicable
2. ** = Refer to Accredited Analyte Listing for specific analytes in which the laboratory is accredited.
3. This scope is part of and must be included with the Certificate of Accreditation No. ADE- 1447



Vice President



Accredited Analytes/Methods (by matrix)

Brooks Rand Labs, LLC

Seattle, WA

Analyte	Matrix										
	Aqueous			Solids			Biological Tissue			Seawater	
Non-Filterable Residue (TSS)	2540D										
Residue-total (total solids)				2540E							
Methyl Mercury	EPA 1630			EPA 1630 (Modified)			EPA 1630 (Modified)				
Arsenic Speciation	EPA 1632 A			EPA 1632 A (Modified)			EPA 1632A				
Selenium Speciation	BR-0061										



State of Florida

Department of Health, Bureau of Public Health Laboratories
This is to certify that



E87982

BROOKS RAND LLC
3958 SIXTH AVE. NW
SEATTLE, WA 98107

has complied with Florida Administrative Code 64E-1,
for the examination of environmental samples in the following categories

NON-POTABLE WATER - METALS, SOLID AND CHEMICAL MATERIALS - METALS, BIOLOGICAL TISSUE - METALS

Continued certification is contingent upon successful on-going compliance with the NELAC Standards and FAC Rule 64E-1 regulations. Specific methods and analytes certified are cited on the Laboratory Scope of Accreditation for this laboratory and are on file at the Bureau of Public Health Laboratories, P. O. Box 210, Jacksonville, Florida 32231. Clients and customers are urged to verify with this agency the laboratory's certification status in Florida for particular methods and analytes.

Date Issued: July 15, 2013 Expiration Date: June 30, 2014



A handwritten signature in black ink that reads "Victor Johnson".

Victor Johnson, Director
Division of Emergency Preparedness and Community Support

DH Form 1697, 7/04

NON-TRANSFERABLE E87982-20-07/15/2013
Supersedes all previously issued certificates



Laboratory Scope of Accreditation

Attachment to Certificate #: E87982-20, expiration date June 30, 2014. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87982

EPA Lab Code: WA00252

(206) 632-6206

E87982

Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Aluminum	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Aluminum	EPA 200.8	Metals	NELAP	9/24/2012
Aluminum	EPA 6020	Metals	NELAP	9/24/2012
Antimony	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Antimony	EPA 1638	Metals	NELAP	7/16/2008
Antimony	EPA 200.8	Metals	NELAP	9/24/2012
Antimony	EPA 6020	Metals	NELAP	9/24/2012
Arsenic	BR-0020 Revision 008/HGAAS	Metals	NELAP	11/16/2009
Arsenic	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Arsenic	EPA 1632	Metals	NELAP	11/16/2009
Arsenic	EPA 1640	Metals	NELAP	9/24/2012
Arsenic	EPA 200.8	Metals	NELAP	9/24/2012
Arsenic	EPA 6020	Metals	NELAP	9/24/2012
Arsenic-III (arsenite)	EPA 1632	Metals	NELAP	9/24/2012
Barium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Barium	EPA 200.8	Metals	NELAP	9/24/2012
Barium	EPA 6020	Metals	NELAP	9/24/2012
Beryllium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Beryllium	EPA 200.8	Metals	NELAP	9/24/2012
Beryllium	EPA 6020	Metals	NELAP	9/24/2012
Bismuth	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Boron	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Cadmium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Cadmium	EPA 1638	Metals	NELAP	7/16/2008
Cadmium	EPA 1640	Metals	NELAP	11/16/2009
Cadmium	EPA 200.8	Metals	NELAP	9/24/2012
Cadmium	EPA 6020	Metals	NELAP	9/24/2012
Calcium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Calcium	EPA 6020	Metals	NELAP	9/24/2012
Chromium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Chromium	EPA 200.8	Metals	NELAP	9/24/2012

Clients and Customers are urged to verify the laboratory's current certification status with the Environmental Laboratory Certification Program.

Issue Date: 7/15/2013

Expiration Date: 6/30/2014

**Laboratory Scope of Accreditation**

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EPA Lab Code: WA00252

(206) 632-6206

E87982

Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Chromium	EPA 6020	Metals	NELAP	9/24/2012
Cobalt	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Cobalt	EPA 200.8	Metals	NELAP	9/24/2012
Cobalt	EPA 6020	Metals	NELAP	9/24/2012
Copper	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Copper	EPA 1638	Metals	NELAP	7/31/2006
Copper	EPA 1640	Metals	NELAP	11/16/2009
Copper	EPA 200.8	Metals	NELAP	9/24/2012
Copper	EPA 6020	Metals	NELAP	9/24/2012
Dimethylarsinate	EPA 1632	Metals	NELAP	9/24/2012
Hardness	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Iron	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Iron	EPA 6020	Metals	NELAP	9/24/2012
Lead	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Lead	EPA 1638	Metals	NELAP	7/31/2006
Lead	EPA 1640	Metals	NELAP	11/16/2009
Lead	EPA 200.8	Metals	NELAP	9/24/2012
Lead	EPA 6020	Metals	NELAP	9/24/2012
Lithium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Magnesium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Magnesium	EPA 6020	Metals	NELAP	9/24/2012
Manganese	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Manganese	EPA 200.8	Metals	NELAP	9/24/2012
Manganese	EPA 6020	Metals	NELAP	9/24/2012
Mercury	EPA 1631	Metals	NELAP	7/31/2006
Methyl mercury	BR-0011 Revision 013/CVAFS	Metals	NELAP	11/16/2009
Methyl mercury	EPA 1630	Metals	NELAP	7/31/2006
Molybdenum	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Molybdenum	EPA 200.8	Metals	NELAP	9/24/2012
Molybdenum	EPA 6020	Metals	NELAP	9/24/2012
Monomethylarsonate	EPA 1632	Metals	NELAP	9/24/2012

Clients and Customers are urged to verify the laboratory's current certification status with the Environmental Laboratory Certification Program.

Issue Date: 7/15/2013

Expiration Date: 6/30/2014

**Laboratory Scope of Accreditation**

Attachment to Certificate #: E87982-20, expiration date June 30, 2014. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87982

EPA Lab Code: WA00252

(206) 632-6206

E87982

Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Nickel	BR-0060 Revision 003/ICP-MS	Metals	NELAP	11/16/2009
Nickel	EPA 1638	Metals	NELAP	11/16/2009
Nickel	EPA 1640	Metals	NELAP	11/16/2009
Nickel	EPA 200.8	Metals	NELAP	9/24/2012
Nickel	EPA 6020	Metals	NELAP	9/24/2012
Potassium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Potassium	EPA 6020	Metals	NELAP	9/24/2012
Selenium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Selenium	EPA 1638	Metals	NELAP	7/31/2006
Selenium	EPA 200.8	Metals	NELAP	9/24/2012
Selenium	EPA 6020	Metals	NELAP	9/24/2012
Selenium (IV)	BR-0061 Revision 000/HPLC-ICP-MS	Metals	NELAP	11/16/2009
Selenium (VI)	BR-0061 Revision 000/HPLC-ICP-MS	Metals	NELAP	11/16/2009
Silver	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Silver	EPA 1638	Metals	NELAP	7/31/2006
Silver	EPA 1640	Metals	NELAP	9/24/2012
Silver	EPA 200.8	Metals	NELAP	9/24/2012
Silver	EPA 6020	Metals	NELAP	9/24/2012
Sodium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Sodium	EPA 6020	Metals	NELAP	9/24/2012
Strontium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Thallium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Thallium	EPA 1638	Metals	NELAP	7/31/2006
Thallium	EPA 200.8	Metals	NELAP	9/24/2012
Thallium	EPA 6020	Metals	NELAP	9/24/2012
Tin	BR-0060 Revision 003/ICP-MS	Metals	NELAP	11/16/2009
Titanium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Tungsten	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Uranium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/24/2012
Uranium	EPA 200.8	Metals	NELAP	9/24/2012

Clients and Customers are urged to verify the laboratory's current certification status with the Environmental Laboratory Certification Program.

Issue Date: 7/15/2013

Expiration Date: 6/30/2014



Laboratory Scope of Accreditation

Attachment to Certificate #: E87982-20, expiration date June 30, 2014. This listing of accredited analytes should be used only when associated with a valid certificate.

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EPA Lab Code: WA00252

(206) 632-6206

E87982

Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Uranium	EPA 6020	Metals	NELAP	9/24/2012
Vanadium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Vanadium	EPA 200.8	Metals	NELAP	9/24/2012
Vanadium	EPA 6020	Metals	NELAP	9/24/2012
Zinc	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Zinc	EPA 1638	Metals	NELAP	7/31/2006
Zinc	EPA 1640	Metals	NELAP	9/24/2012
Zinc	EPA 200.8	Metals	NELAP	9/24/2012
Zinc	EPA 6020	Metals	NELAP	9/24/2012

Clients and Customers are urged to verify the laboratory's current certification status with the Environmental Laboratory Certification Program.

Issue Date: 7/15/2013

Expiration Date: 6/30/2014



Laboratory Scope of Accreditation

Attachment to Certificate #: E87982-20, expiration date June 30, 2014. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87982

EPA Lab Code: WA00252

(206) 632-6206

E87982

Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
Antimony	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Arsenic	BR-0021 Revision 004/HGAAS	Metals	NELAP	6/27/2011
Arsenic	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Beryllium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Cadmium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Chromium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Cobalt	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Copper	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Lead	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Mercury	BR-0002 Revision 10/CVAFS	Metals	NELAP	7/16/2008
Mercury	EPA 1631	Metals	NELAP	7/31/2006
Methyl mercury	BR-0011 Revision 013/CVAFS	Metals	NELAP	11/16/2009
Molybdenum	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Nickel	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Selenium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Silver	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Strontium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Thallium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Zinc	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008

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State Laboratory ID: E87982

EPA Lab Code: WA00252

(206) 632-6206

E87982
Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Biological Tissue

Analyte	Method/Tech	Category	Certification Type	Effective Date
Aluminum	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Antimony	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Arsenic	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Arsenic	EPA 1632	Metals	NELAP	6/27/2011
Arsenic-III (arsenite)	EPA 1632	Metals	NELAP	9/24/2012
Barium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Beryllium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Boron	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Cadmium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Calcium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Chromium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Cobalt	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Copper	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Dimethylarsinate	EPA 1632	Metals	NELAP	9/24/2012
Iron	BR-0060 Revision 003/ICP-MS	Metals	NELAP	6/27/2011
Lead	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Magnesium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	9/26/2011
Manganese	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Mercury	BR-0002 Revision 10/CVAFS	Metals	NELAP	7/16/2008
Mercury	EPA 1631	Metals	NELAP	7/31/2006
Methyl mercury	BR-0011 Revision 013/CVAFS	Metals	NELAP	11/16/2009
Molybdenum	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Monomethylarsonate	EPA 1632	Metals	NELAP	9/24/2012
Nickel	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Selenium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Silver	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008

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State Laboratory ID: E87982

EPA Lab Code: WA00252

(206) 632-6206

E87982

Brooks Rand LLC
3958 Sixth Ave. NW
Seattle, WA 98107

Matrix: Biological Tissue

Analyte	Method/Tech	Category	Certification Type	Effective Date
Thallium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Titanium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Vanadium	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008
Zinc	BR-0060 Revision 003/ICP-MS	Metals	NELAP	7/16/2008

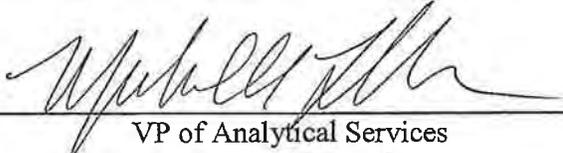
SOP #BR-0066

**Reductive Precipitation of Total Recoverable and Dissolved Metals from
Brackish and Seawater Samples**

Brooks Rand Labs

Revision 002a
Written 3/25/05
Revised 01/22/10

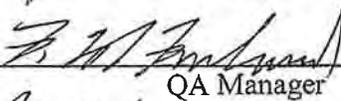
Reviewed



VP of Analytical Services

1/25/10

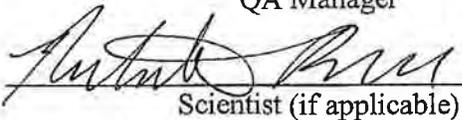
Date



QA Manager

1/25/10

Date



Scientist (if applicable)

1/25/10

Date

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Reductive Precipitation of Total Recoverable and Dissolved Metals from Brackish and Seawater Samples

1 SCOPE AND APPLICATION

1.1 Brackish and seawater samples present matrix interferences for trace metal analysis, especially samples high in salt levels. The method in this Standard Operating Procedure (SOP) describes a preparation for brackish and seawater samples to be analyzed by inductively coupled plasma - mass spectrometry (ICP-MS).

1.2 The preparation method described in this SOP not only functions to remove the analyte(s) of interest from the interfering matrix, but in the process the sample is also concentrated 4-fold. This improves detection limits, allowing for successful quantification of ambient seawater concentrations more often.

2 SUMMARY OF METHOD

2.1 Samples are preserved to 0.2% (v/v) with pre-tested concentrated HNO₃. Samples analyzed for dissolved metals require a filtration through a 0.45- μ m filter according to Brooks Rand SOP #BR-0104 and are preserved following filtration.

2.2 This method involves a reductive precipitation of all metals by sodium borohydride (NaBH₄) followed by a filtration of the precipitate through a pre-cleaned 0.2- μ m filter. The majority of the salt matrix is removed and remains in the filtrate.

2.3 The metals on the filter are digested and oxidized with nitric acid (HNO₃) and hydrogen peroxide (H₂O₂). The samples are then analyzed by ICP-MS.

2.4 The procedure concentrates the samples by a factor of 4 and is a useful method for achieving a low level of detection for brackish and seawaters.

3 DEFINITIONS

3.1 Refer to Draft EPA Method 1638, Section 18.0, for definitions for method blank, spikes, and dissolved metals.

4 CONTAMINATION AND INTERFERENCES

4.1 All reagent water and bottles of concentrated nitric acid are tested to ensure there is no contamination above the minimum thresholds. Method blanks are also prepared to monitor possible contamination. Ultra-clean handling techniques should be used in preparing the samples.

4.2 Prior to use, filters are heated in an oven overnight in [REDACTED] acid solution [REDACTED]. They are removed from the oven and allowed to sit

in the acid solution [REDACTED], then rinsed well with DIW to remove contaminants.

4.3 Method blanks and low samples should be filtered before higher samples and matrix spikes to avoid carry-over. The filtering apparatus requires a strict cleaning procedure between samples. [REDACTED]

4.4 Iron, palladium, lanthanum, and terbium (Fe, Pd, La, and Tb) are used in high concentrations for this preparation. It is important to be aware of the risk of carry-over for the analysis of these elements in other samples.

4.5 High Pd concentrations interfere with both silver isotopes (^{107}Ag and ^{109}Ag) and ^{111}Cd because of the PdH^+ ion and an interference with the MoO correction equation. Monitor these isotopes carefully, and if the quality control samples indicate interference, an alternative preparation (such as Co-APDC Coprecipitation, Brooks Rand SOP #BR-0069) should be considered.

4.6 Organic chelates occurring naturally in the environment may interfere with the precipitation reaction. This matrix affect may be overcome by preparing the samples with [REDACTED] HNO_3 closed-vessel oven digestion (Brooks Rand COP #BR-0065) prior to precipitation by this SOP. This requires more ammonium hydroxide (NH_4OH) in the neutralization step (See Section 7).

4.7 See Draft EPA Method 1638, Section 4.0 ("Contamination and Interferences") for a more detailed list of possible interferences and contaminations.

5 SAFETY

5.1 Hydrofluoric acid (HF) is particularly dangerous and should be used with extreme caution. HF may not cause immediate pain but is still very harmful. If there is any contact, quickly rinse under water followed by an application an unopened tube of calcium gluconate gel. Then go directly to the hospital. There should always be at least one tube in the lab during any procedure involving the use HF. The MSDS should be consulted prior to the use of HF and prior training is required by an experienced staff member. [Note: HF is not used unless Cr is an analyte of interest. If Cr is not an analyte of interest, then filters should be used dry (not acid cleaned), and no HF is used in the sample preparation process.]

5.2 Nitric acid, sodium borohydride, and ammonium hydroxide are very caustic and adequate protective gear should be worn when working with acids or bases, including eye protection, gloves with the appropriate resistance, and a lab coat. An adequate fume hood should be used when working with all acids and bases.

5.3 The toxicity and/or carcinogenicity of some reagents are not well established. Always refer to the MSDS for all reagents and standards. Use caution with the Pd/Fe/La/Tb mixed standard and any spiking standards needed.

6 APPARATUS AND MATERIALS

6.1 Routine preventative maintenance for the equipment used in this procedure is described in detail in the standard operating procedure BR-1205 (Preventative Maintenance).

6.2 Clean-room gloves, powder-free, vinyl - tested low for trace metals prior to use.

6.3 Polypropylene tweezers - rinsed between samples with 2% HCl and water and stored in the trace-metals vat.

6.4 Clean-air hood - class-100 particulate-free clean air station with HEPA filter.

6.5 250 mL Teflon bottles with lids

6.6 pH paper - minimum range of 6-10.

6.7 A balance - that masses up to 250 grams.

6.8 Vacuum pump with water trap - a water trap to protect the vacuum pump from water vapor should be used.

6.9 Coarse-frit glass filter support with funnel - 47-mm diameter and 300-mL capacity; a Neoprene stopper is used to connect the support to the filter flask.

6.10 Polycarbonate 0.22- μ m filters - 47-mm diameter.

6.11 Glass funnel - 47-mm diameter and 300-mL capacity; a spring clamp to hold funnel to the filter support is also needed.

6.12 Filter flasks - at least 1-L capacity.

6.13 Teflon[®] vials - 15-mL size with screw caps.

6.14 Hot plate - to heat up to 150° C (300° F).

6.15 Concentrated nitric acid (HNO₃), [REDACTED] - tested to be low for metals prior to use.

6.15.1 HNO₃ solution, [REDACTED]

- 6.16 Hydrofluoric acid, [REDACTED] - tested to be low for metals prior to use.
- 6.17 Reagent water - deionized water should be used; all water should be tested monthly for metals to ensure that levels are low enough for use.
- 6.18 Sodium borohydride, 99% pure - can be tested for contamination by analyzing a blank prepared with only NH_4OH and then subtracting any NH_4OH contribution from a method blank result.
- 6.19 Ammonium hydroxide, trace metal grade - tested prior to use.
- 6.20 Hydrogen peroxide (H_2O_2), [REDACTED] - tested prior to use.
- 6.21 Certified reference material (CRM) - [REDACTED]
- 6.22 Pd/Fe/La/Tb solution - [REDACTED]
- 6.23 NaBH_4 solution, [REDACTED]

7 PROCEDURE

7.1 Pour 200 g of sample into a Teflon bottle using a balance. Prepare matrix duplicate (DUP), matrix spike (MS), and matrix spike duplicate (MSD) samples in the manner. Prepare CRMs in the same manner, though a smaller volume may be desired to accommodate high-concentration CRMs. CRMs to be analyzed at a smaller volume should be dilute to 200 mL with 0.2% (v/v) HNO₃.

7.2 Prepare 4 (minimum 3) method blanks by adding 200 mL of 0.2% (v/v) HNO₃ to each jar.

7.3 Two seawater Blank Spikes (BS) can be prepared by setting up three samples. The first sample is seawater collected from the Edmonds Dive Park. The second sample is an MRL spike on top of the Edmond's seawater. The third sample is a spike equal to that of the desired matrix spike levels. The seawater blank should be logged in as a sample in the LIMS and the Blank Spikes should be entered as matrix spikes.

7.4 Matrix spike samples should be fortified with all of the analytes of interest. A spiking level of 2-5x the native concentration is desirable; therefore, consult historical concentrations if they are available. Do not spike samples at a level lower than the minimum reporting limit (MRL). If there is limited sample, a MSD may not be possible. In this case, prepare a DUP and MS on an additional sample.

7.5 Add [REDACTED] the Pd/Fe/La/Tb solution to each jar. [REDACTED]

7.6 Adjust the pH of each sample [REDACTED] with NH₄OH. Small aliquots of sample can be pipetted onto pH paper to monitor the pH. [REDACTED]

7.7 Add [REDACTED] NaBH₄ to each sample. The solution will turn black.

7.8 Let the samples sit [REDACTED]

7.9 Filter the samples as follows:

7.9.1 Rinse the acid-washed filter support and funnel well with reagent water.

7.9.2 With the polypropylene tweezers, place an acid-washed polycarbonate 0.22- μ m filter on the filter support and clamp the funnel on to the support.

7.9.3 Swirl the sample, pour the contents into the funnel, and apply a vacuum. Rinse the bottle with ~10 mL of DIW and the cap with ~5 mL of DIW, and pour the rinsates into the funnel. Rinse down the sides of the funnel with DIW. [REDACTED]

[REDACTED]

7.9.4 Stop the vacuum and use the tweezers to carefully fold the filter [REDACTED]. Place the folded filter in a 15-mL Teflon[®] vial.

7.9.5 The filtering apparatus requires a strict cleaning procedure between samples. [REDACTED]

7.9.6 Filtrate may be disposed of down the drain.

7.10 Digest the samples on the filters as follows:

7.10.1 Add [REDACTED] HNO₃ to each Teflon[®] vial. Use a clean pipette tip to press the filter to the bottom of the vial and to move the filter around in the acid to ensure that the acid is reaching all parts of the filter.

7.10.2 Tightly cap each vial and place on a hotplate [REDACTED]. This allows the acid to completely break down the organic complexes that precipitated the sample. Allow samples to cool.

7.10.3 Add [REDACTED] H₂O₂ to each vial. Cap the vials tightly and place each vial again on a hotplate [REDACTED]. Allow samples to cool.

7.10.4 Add [REDACTED] DIW to each vial and cap tightly. Heat the vials again on a hotplate [REDACTED].

7.11 Store samples. [REDACTED]

8 QUALITY ASSURANCE

8.1 Four method blanks (minimum of 3) should be prepared for every batch of 20 or less samples to assess the reagents, handling procedures, and apparatus used.

8.2 Efficiency factors should be determined for each analyte. Efficiency factors are based on historic recoveries of CRMs and appropriately spiked seawater collected from Puget Sound. The efficiency factors are derived from control charts and should be based on a minimum of 20 data points.

8.3 A matrix spike/matrix spike duplicate (MS/MSD) set should be prepared and analyzed at a minimum frequency of 10%. The spiking level should be 2-5 times the concentration of the native sample or 5 times the MRL, whichever is greater. The recovery of the spikes must fall within 70-130% with an RPD \leq 30%.

8.4 A method duplicate (DUP) is prepared and analyzed upon request of the client. If a DUP is requested and there is limited sample, a MSD may not be possible on the same sample. In this case, prepare another DUP/MS or MS/MSD set on an additional sample. The acceptance criterion for DUP analysis is an RPD \leq 30%.

8.5 For every batch of 20 or less samples that are digested, at least one relevant matrix CRM and two seawater blank spikes should be prepared and analyzed. The appropriate CRM for seawater samples is CASS-4. For those elements that CASS-4 is not certified (refer to the certificate for CASS-4 scanned to the LIMS standards and reagents entry), a native and a spike of the CRM should be prepared. The CRM should be spiked at approximately 10 times the element specific MRL.

8.6 See Brooks Rand SOP #BR-0060 for instrumental quality assurance measures and for additional information on QA criteria.

9 REFERENCES

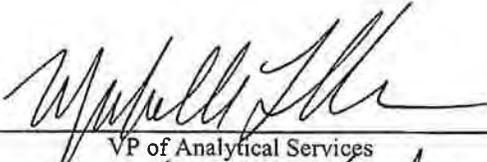
- 9.1 Draft EPA Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry, January 1996.
- 9.2 Draft EPA Method 1640: Determination of Trace Elements in Ambient Waters by On-line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry, April 1997.
- 9.3 Nakashima, S., R.E. Sturgeon, S.N. Willie, and S.S. Berman. 1988. "Determination of Trace Elements in Sea Water by Graphite Furnace Atomic Absorption Spectrometry After Preconcentration by Tetrahydroborate Reductive Precipitation," *Analytica Chimica Acta*, 207: 291-299.

SOP #BR-0060

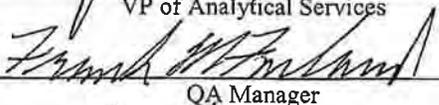
Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II

Brooks Rand Labs

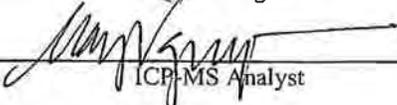
Written 3/24/2005
Revised 05/24/10
Revision 003c



VP of Analytical Services



QA Manager



ICP-MS Analyst

5/24/10

Date

5/24/10

Date

5/24/10

Date

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Determination of Trace Elements by Inductively Coupled Plasma – Mass Spectrometry using a Perkin-Elmer ELAN DRC II

1.0 DESCRIPTION

- 1.1 This procedure describes a mode of analysis for the determination of dissolved and total recoverable trace elements in waters using inductively coupled plasma – mass spectrometry (ICP-MS). This procedure is intended for samples with total dissolved solids (TDS) of less than 1000 mg/L. Sample dilution may be required in order to achieve an optimum TDS level. The calibration range for the instrument is dependant on the analyte of interest.
- 1.2 This procedure is written specifically for use with a Perkin-Elmer ELAN DRC II ICP-MS. The instrument software is ELAN Version 3.4 for use on Windows XP®.
- 1.3 This procedure can be utilized to determine a large list of analytes. However, at this time the method has been fully validated only for Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Pt, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, and Zn. In addition, the following analytes have validated methods developed in DRC Mode: Ag, Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, Se, V, and Zn. Following this method will aid in the method development and validation for the analysis of other analytes.
- 1.4 Matrices other than waters may be analyzed using this procedure. Sample preparations techniques can be utilized for the analysis of seawaters, municipal and industrial influents and effluents, human biomonitoring samples (such as urine, blood, and plasma/serum), and dilute digestates of sediments, soils, rocks, biota/tissues, or petroleum products.
- 1.5 This procedure is a modification of Draft EPA Method 1638. The EPA method validation study (reference 11.5) reported that the “EPA intends to revise Method 1638 to recommend use of response factor or weighted linear regression calibrations, allowing unweighted linear regress as an acceptable calibration technique.” As the lowest standards are more of an influence in weighted linear regressions than “fit-through-zero” calibrations, Brooks Rand intends to primarily use weighted linear regression calibrations. For samples that are measured at or near the highest standards, a “fit-through-zero” approach may be appropriate.
- 1.6 This procedure must be followed to assure accuracy and reproducibility of the samples results generated by all of the operating chemists. An analyst must first be fully trained in the use of ICP-MS, including the interpretation of spectral and matrix interferences and procedures for their correction, as well as ultra-clean sample handling.

2.0 SUMMARY OF METHOD

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- 2.1 An aliquot of homogenous sample is prepared for analysis. The determination of dissolved elements requires the sample be filtered through a 0.45- μm pre-cleaned filter unit as in BR-0104, and then preserved with acid. The determination of total and total recoverable elements in water samples requires the samples be digested with a combination of heat and acid, or the metals must be extracted from the sample matrix. Solid samples require matrix specific digestion steps before introduction into the instrument. All sample preparation procedures are detailed in depth in separate Brooks Rand Labs SOPs.
- 2.2 A prepared, aqueous sample is pumped through a nebulizer, where the liquid forms aerosol droplets as it enters a spray chamber. The aerosol separates into a fine aerosol mist and larger aerosol droplets. The larger droplets exit out the bottom of the spray chamber and are pumped off as waste. The finer droplets are transported out of the spray chamber and enter the ICP torch through an injector tube.
- 2.3 Inside the ICP torch, the aerosol droplets are transported into a high-temperature plasma, where they become atomized and ionized as they are introduced through a radio frequency (RF) load coil. The ions are transported into the plasma through a differentially-pumped interface. The ion stream is then focused by a single ion lens, which focuses the ions through a cylinder with a carefully controlled electrical field. The focused ion stream is directed into the dynamic reaction cell (DRC) where, when operating in DRC mode with a pressurized cell, the ion beam will undergo chemical modifications to reduce elemental interferences. When not operating in DRC mode the ion stream will remain focused as it passes through the cell with no chemical modification taking place.
- 2.4 The ion stream is then transported to the quadrupole mass filter, where only ions having a specific mass-to-charge ratio (m/z) are passed through at any moment in time. The ions exiting the mass filter are detected by a solid-state detector and processed by the data handling system.

3.0 DEFINITIONS

- 3.1 A partial list of definitions is presented below. Most definitions can be found for specific terms in the sections where they are first mentioned. Many of the definitions mentioned in this method are based on those found in the glossaries of EPA Methods 1638 and 1640. Please refer directly to these methods for a more detailed list.
- 3.2 **Ambient Water:** Waters from the natural environment, such as river or lake water, as opposed to effluents.
- 3.3 **Analyte:** A metal tested for by this method.

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- 3.4 Dissolved Analyte: The concentration of analyte in an aqueous samples that will pass through a 0.45 µm filter membrane prior to the sample being acidified.
- 3.5 Internal Standard (IS): Pure analyte(s) added to each sample (client and QC) at the instrument in known amounts and used to measure the relative response of other method analytes that are components of the samples. The IS must be an analyte that is not a sample component.
- 3.6 Linear Dynamic Range: The concentration range over which the instrument response to an analyte is linear.
- 3.7 m/z: mass-to-charge ratio
- 3.8 May: This action is optional.
- 3.9 May Not: This action is prohibited.
- 3.10 Must: This action is required.
- 3.11 Should: This action is suggested, but not required.

4.0 EQUIPMENT

- 4.1 Routine preventative maintenance for the equipment used in this procedure is described in detail in the standard operating procedure BR-1205 (Preventative Maintenance).
- 4.2 Facility: An ultra-clean laboratory environment is critical for the successful production of quality data at ultra-low levels. All sample preparation must take place in a clean hood (Class-100). Metallic pieces should be kept to a minimum in the lab and coated with an acrylic polymer gel. Adhesive floor mats should be used at entrances to the lab and changed regularly to prevent the tracking of dust and dirt from the outside environment. Clean-room gloves must be worn and changed whenever contact is made with anything non-ultra-clean. The lab floor should be wiped regularly to remove any particles without stirring up dust.
- 4.3 Instrumentation: ICP-MS (Perkin-Elmer ELAN DRC II) with a free-running 40 MHz RF generator; controllers for nebulizer, plasma, auxiliary, DRC gas A, and DRC gas B flow control; and a getter is equipped for work with ammonia gas. The quadrupole mass spectrometer has a mass range of 5 to 270 atomic mass units (amu). The turbo molecular vacuum system achieves 10^{-6} torr or better.
- 4.4 ESI SC-4 auto-sampler.
- 4.5 ESI FAST high-flow valve.
- 4.6 An RF coil designed for axial torch arrangement.

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- 4.7 Platinum skimmer and sampler cones.
- 4.8 A Ryton Scott-type spray chamber for analysis with HF and an ESI PC³ peltier cooled quartz cyclonic spray chamber for all other analysis.
- 4.9 Alumina injector with 2 mm inner diameter (ID) for HF analysis and a quartz or sapphire injector with 2 mm ID for other matrices.
- 4.10 ESI PFA ST nebulizer.
- 4.11 Polyvinyl chloride (PVC) tubing (¼” OD, ⅛” ID) for nebulizer gas and for waste.
- 4.12 Peristaltic pump tubing: Waste; Pharmed, green-green, 1.855-mm ID, and sample; PVC black-black, 0.76-mm ID, internal standard; PVC orange-green 0.38mm ID.
- 4.13 Carbon fiber support autosampler probe (0.8mm i.d-ESI N0777285 REV.A) with lines to connect to SC-FAST switching valve.
- 4.14 Sample loop of desired volume for analysis, typically 1.25mL for a full suite of metals.
- 4.15 Connection from SC-FAST switching valve to nebulizer with ST fitting.
- 4.16 Connector for sample and internal standard line.
- 4.17 Waste unit with tubing holes.
- 4.18 Gases: high-purity grade liquid argon (> 99.996%), ultra-x grade, 99.9999% minimum purity oxygen, and electronic grade, 99.99% minimum purity ammonia. The gases are stored in a ventilated gas storage cabinet.
- 4.19 Variable-speed peristaltic pump for solution delivery to the nebulizer.
- 4.20 Analytical Balance: a standard laboratory balance suitable for sample preparation and capable of measuring to 0.1-mg.
- 4.21 Clean-room gloves (tested low in trace-metals).
- 4.22 Sample bottles constructed of fluoropolymer (FEP or PTFE), polyethylene (HDPE or LDPE), polycarbonate (PC), polypropylene (PP), or glass. HDPE bottles are preferred. All bottles must be pre-cleaned by SOP BR-0400.
- 4.23 Auto-sampler cups (15-mL and 50-mL) pre-cleaned by soaking in 2% nitric acid for at least 24 hours, rinsed three times with DIW, and dried in a clean hood.
- 4.24 Volumetric flasks, class-A, cleaned by SOP BR-0400.

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- 4.25 Assorted calibrated pipettes for volumes from 0.005-10 mL. Pipettes are calibrated according to SOP BR-0400. Should include the assorted pipette tips for 2 - 10 mL, 1 - 5 mL, 0.1 - 1 mL and 0.005 - 0.200 mL pipettes.
- 4.26 Reagent bottles, 10-mL to 2000-mL, must be from any of the plastics listed in 2.20 and cleaned by SOP BR-0400.
- 4.27 Wash bottles, squeeze type, 500-mL, cleaned by SOP BR-0400.
- 4.28 Filter units, 150-mL and 500-mL, pre-cleaned with 4% nitric acid in DIW.
- 4.29 Vacuum pumps for sample filtration.
- 4.30 Silicon vacuum tubing with 8-mm ID and 14-mm OD.
- 4.31 pH meter.
- 4.32 Zip-type bags of various sizes.
- 4.33 Kimwipes.
- 4.34 A sonicator to clean cones and RF coils.

5.0 CONTAMINATION and INTERFERENCES

5.1 Contamination

- 5.1.1 Contamination of the samples during sample collection is a great risk, and extreme care should be taken to avoid this. Potential sources of contamination during sampling include using metallic or metal-containing labware, containers, and sampling equipment.
- 5.1.2 Sample collection equipment such as tubing, pumps, filters, and homogenization equipment should be non-metallic (whenever possible) and tested for metals through the analysis of equipment blanks.
- 5.1.3 Contamination of samples by airborne particulate matter is a concern. Sample containers should remain closed as much as possible. Container lids should only be removed briefly and in a clean environment during sample preservation and processing, so that exposure to an uncontrolled environment is minimized.
- 5.1.4 Laboratory

- 5.1.4.1 All labware (including pipette tips, ICP-MS autosampler vials, sample and digestion bottles, extraction apparatus, and reagent bottles) should be tested for the presence of trace-metals. If necessary, the labware should be acid-cleaned, rinsed with DIW, and dried in a clean hood.
- 5.1.4.2 All auto-sampler vials are cleaned by storing them in 2% (v/v) HNO₃ for at least 24 hours and then rinsed three times with DIW. The vials are then dried in a clean hood before use. Glass volumetric flasks should be soaked in ~5% HNO₃ overnight prior to use.
- 5.1.4.3 All reagents and gases used for analysis and sample preparation should be tested for the presence of trace metals prior to use in the lab. Due to the ultra-low detection limits of this method, it is imperative that all the reagents and gasses be as low as possible. It is often required to test several different sources of reagents until an acceptable source has been found. Metals contamination can vary greatly from lot to lot. Once an acceptable reagent lot has been identified, several cases of the lot number should be sequestered from the supplier. A logbook should be maintained to better track the acids and is stored in the ICP-MS lab.
- 5.1.4.4 Metals concentrations in both reagent DIW and HNO₃ are monitored each day at the instrument. These samples are uploaded into every LIMS sequence as IBLs. Although there are no established limits for the blanks, the data is useful for troubleshooting.
- 5.1.4.5 Great care should be taken to keep the facility free from all sources of metals contamination. Clean hood HEPA filters must be replaced with new filters on a regular basis to reduce the risk of airborne contaminants. Metal corrosion of any part of the facility should be addressed and replaced. Every piece of apparatus that is directly or indirectly used in the collection, preservation, or processing of samples should be trace metals free. Additionally, the lab should be free of clutter to minimize contamination from other sources.

5.2 Elemental interferences

- 5.2.1 Interference sources that may inhibit the accurate collection of ICP-MS data for trace elements are addressed below.
- 5.2.2 Isobaric elemental interferences are isotopes of different elements that form singly or doubly charged ions of the same mass-to-charge ratio (m/z) and cannot be resolved by the mass spectrometer.
- 5.2.3 Data obtained with isobaric overlap must be corrected for by:

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- 5.2.3.1 Measuring the signal from another isotope of the interfering element and estimating the contribution from the interfering isotope on the isotope of interest. This should not be determined using relative isotopic abundance alone, but instead by spiking actual samples with varying amounts of the interfering element. The relative ratio of counts per second that appear on the interfered mass and a non-interfered isotope for the interfering element can be compared to determine an appropriate correction factor (CF). The correction equation can be entered into the corrections column on the equations page of the analysis method. An example is listed below.

$$CF = I/A$$

Where CF is the correction factor, I is the measured increase on the interfered target isotope in terms of counts per second, and A is the measured increase of an isotope of the interfering element for which no isobaric overlap exists, in terms of counts per second. Analytical data can then be corrected by:

$$T = M - CF * X$$

Where T is the true counts per second of the target analyte, M is the measured counts per second of the target analyte, CF is the correction factor, described above, and X is the measured counts per second of the interfering element at the mass used to determine the correction factor.

- 5.2.3.2 The correction equation for the example above would look as follows:

$$\text{Cd 114} = \text{mass 114} - (\text{Correction Factor}) * (\text{Sn 118})$$

- 5.2.4 Abundance sensitivity occurs when part of an elemental peak overlaps an adjacent peak. This often occurs when measuring a small mass-to-charge ratio (m/z) peak next to a large m/z peak. The abundance sensitivity is affected by ion energy and quadropole operating pressure. Proper optimization of the resolution during tuning will minimize the potential for abundance sensitivity interferences.
- 5.2.5 Isobaric Polyatomic Interferences are interferences caused by ions, composed of multiple atoms, which have the same m/z as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or the interface system from the support gases or sample components. The objective of DRC analysis is to remove these interferences, and as a result, correction factors should not be necessary. If they are determined to be present, then they can be corrected by the following:
- 5.2.5.1 Spiking a sample, matrix matched to the samples of interest, with varying amounts of a polyatomic parent (i.e., Ca for the production of CaO, which can be detected at mass 56) and calculating a correction factor based on the

change in counts per second at the parent mass and the change in counts per second at the analyte mass. Once a correction factor has been determined, it can be added to the corrections tab in the method file in the Elan 3.4 software.

5.2.5.2 Polyatomic interferences are highly dependent on the sample matrix. Corrections should be considered at the time of analysis.

5.3 Physical Interferences occur when there are differences in the response of the instrument from the calibration standards and the samples. Physical interferences 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.

5.3.1 Physical interferences can be associated with the transfer of solution to the nebulizer at the point of nebulization, transport of aerosol to the plasma, or during excitation and ionization processes in the plasma. High levels of TDS in a sample can result in physical interferences. Proper internal standardization (choosing standards that have analytical behavior similar to the associating elements) can compensate for many physical interferences.

5.4 Memory Interferences - Carryover of elements in a previous sample in the sample tubing, cones, torch, spray chamber, connections, and autosampler probe are minimized by rinsing the instrument with a reagent blank after samples high in metals concentrations are analyzed.

5.4.1 If carryover is suspected, the sample should be reanalyzed after a long rinse period or after the analysis of an acceptable blank (less than the MRL. Note: Tighter criteria may apply to different regulatory requirements).

6.0 SAFETY

6.1 Refer to Draft EPA Method 1638, section 5.0, for safety issues associated with the use of the method.

6.2 Hydrofluoric acid (HF) is particularly dangerous and should be used with extreme caution. HF may not cause immediate pain but is still very harmful. If there is any contact, quickly rinse under water followed by an application an unopened tube of calcium gluconate gel. Then go directly to the hospital. There should always be at least one tube in the lab during any procedure involving the use HF. The MSDS should be consulted prior to the use of HF and prior training is required by an experienced staff member.

6.3 Nitric acid and hydrochloric acid are very caustic and adequate protective gear should be worn when working with these acids, including eye protection, gloves with the

appropriate resistance, and a lab coat. An adequate fume hood should be used for all acids.

- 6.4 Many of the chemicals have toxicities that are not well established and should be handled with care. For all known chemicals used, the MSDS should be consulted in advance.
- 6.5 Reference 11.3 in Section 11 lists the local Washington state OSHA regulations. King County local sewer limits should be posted near the ICP-MS waste disposal sinks and no materials higher than the limits should be disposed of.
- 6.6 The ICP-MS emits UV light when the plasma is on. Goggles should be worn if working near the plasma.
- 6.7 The instrument generates high levels of radio frequency (RF) energy and is very hot when the plasma is on. In the case of an instrument failure, be aware of these potential dangers.
- 6.8 DRC gases should be stored safely in a closed cabinet. Adequate caution should always be used with pressurized gasses. Prior training or experience is necessary to change any gas cylinders. Oxygen gas can be explosive with certain materials and ammonia has a very low odor threshold and is corrosive to tissue.

7.0 REAGENTS AND STANDARDS

- 7.1 Reagents may contain elemental impurities that could negatively affect high data quality. High-purity reagents should always be used. Each reagent lot should be tested and test low for the elements of interest before being used in the laboratory.
- 7.2 Deionized Water (DIW) (ASTM Type I) demonstrated to be free from the metals of interest and potentially interfering substances.
- 7.3 Nitric Acid (HNO_3), concentrated, tested low (limits are found in the Bottle Washing SOP BR-0400).
 - 7.3.1 1% (v/v) HNO_3 - Stock standard preparation diluent and sample diluent.
 - 7.3.2 2% (v/v) HNO_3 - Tube soaking solution.
 - 7.3.3 5% (v/v) HNO_3 - Pipette cleaning solution and rinse station solution.
- 7.4 Stock Standard Solutions - obtained from a reputable and professional commercial source.

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- 7.4.1 Single element standards are obtained for each determined metal as well as for any metals used as internal standards and interference checks.
- 7.4.2 A second source is obtained for each determined metal.
- 7.5 Multi-element stock standard solution-elements must be compatible and stable in solutions together.
 - 7.5.1 "IV-19" Second source stock solution obtained from Inorganic Ventures. 100 mg/L As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Se, Ti, Tl, V, and Zn.
 - 7.5.2 "IV-7" Second source stock solution obtained from Inorganic Ventures. 1000 mg/L K; 100 mg/L Al, Ag, B, Ba, and Na; 50mg/L Si.
 - 7.5.3 "QCS-26" Second source stock solution obtained from High-Purity Standards. 100 mg/L Al, Cd, Pb, Se, Sb, Ca, Mg, As, Cr, Mn, Ag, Ba, Co, Mo, Na, Zn, Be, Cu, Ni, Tl, B, Fe, K, and Ti.
 - 7.5.4 Dilute single element stock standards appropriately in order to prepare multi-element standards in 1% HNO₃. These standards will be stable for six months from date of preparation. These standards may change in composition as the needs for different calibrations change.
 - 7.5.5 "TM-A" Standard (mg/L): 2000 Ca; 1000 Na; 500 Fe; 100 B; 25 Cr; 10 Ti, As, Ni, Cu, Sr; 5.0 Co; 1.0 Cd; and 0.5 Tl.
 - 7.5.6 "TM-B" Standard (mg/L): 10 Se; 5.0 V; 2.5 Sn and Pb; 1.0 Be; and 0.50 Th, and U.
 - 7.5.7 "TM-C" Standard (mg/L): 2000 Mg; 1000 K; 500 Al; 50 Zn; 25 Mn, Ba; and 5.0 Mo.
 - 7.5.8 "ML-1" Standard (mg/L): 0.01 Tl and U; 0.02 Mo, Th, and Cd; 0.05 Be, Mn, Sr, and Pb; 0.1 Co; 0.15 V, Cr and Sn; 0.2 Ba, Ti, As, Ni, Cu, and Zn; 0.5 Se; 1.0 B, Al; 3.0 Mg; 4.0 K; 5.0 Fe; 15 Na; and 30 Ca.
 - 7.5.9 Ag Standard Solutions at 2.0 and 0.02 mg/L
 - 7.5.10 Sb Standard Solutions at 1.0 and 0.02 mg/L
 - 7.5.11 Additional elements can be added to these standard mixes in 1% HNO₃. Attention should be given to the compatibility of the elements added.
- 7.6 Internal Standard Solution - Dilute stock standard solutions of Ge, In, ⁶Li, Pt, Rh, Tm, and Sc to give approximately 500,000 counts per second when run at a 4:1 sample to internal standard mix. [REDACTED]

- 7.9.1 The ICV is made by diluting 25 μL of QCS-26 and 25 μL of a 10-fold dilution of QCS-26, to 50-mL of 1% HNO_3 . Additional ICVs are prepared as needed.
- 7.9.2 Alternatively or additionally, a mixed solution standard of all elements at exactly 10-50 times the low calibration standard and may be obtained from CPI.
- 7.10 "Daily" optimization and tuning solution - [REDACTED]
- 7.11 Dual detector calibration solution - [REDACTED]
- 7.12 Certified reference material (CRM) - CRMs of various matrices (drinking water, seawater, sediment, soil, tissue, river water, etc).
- 7.13 Interference check solution - BRL analyzes an aliquot of the river water CRM NIST 1643e with every batch. NIST 1643e is similar in composition to standard interference check solutions for ICP-MS analyses and it offers a real world check of the validity of the interference correction.

8.0 SAMPLE COLLECTION, FILTRATION, PRESERVATION, AND STORAGE

- 8.1 Samples should be received as described in SOP BR-0300.
- 8.2 Samples for dissolved metals determination must be filtered (if not field-filtered) through a 0.45- μm or a 0.2- μm pre-cleaned disposable filter unit within 48 hours of collection. Otherwise, all data for the dissolved metals will be qualified "H" for inappropriate sample handling prior to receipt. Filtering procedures are described in BRL SOP BR-0104.
- 8.3 Samples must be preserved to a pH less than or equal to 2. The following provides a list of common preservation schemes:
- 8.3.1 Preserve to 0.2% (v/v) with HNO_3 for reductive precipitation (RP) extractions.
- 8.3.2 Preserve to 0.099% (v/v) with HNO_3 for Co-APDC extractions.
- 8.3.3 Preserve to 1% (v/v) with HNO_3 for dissolved metals determination and for some total recoverable metals digestions.

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- 8.3.4 Preserve to 1.8% (v/v) HNO₃ and 0.2% hydrofluoric acid (HF) for some total recoverable metals digestions.
- 8.4 Store the preserved samples for a minimum of 48 hours before analysis to completely desorb the metals from the container walls. The sample pH should be verified to be less than pH 2 prior to sample preparation.
- 8.5 Preserved samples can be stored in a secure area of the laboratory at room temperature until analysis.
- 8.6 Human biomonitoring samples should be shipped frozen and stored frozen until the time of analysis; however, short-term storage of urine and plasma/serum samples at 2-4 °C is acceptable.

9.0 PROCEDURE (PRE-CALIBRATION, CALIBRATION AND STANDARIZATION)

9.1 Sample Preparation

- 9.1.1 For the determination of dissolved analytes, samples should be preserved with HNO₃ to 1% (v/v) after filtration. Rinse pipette tip two times with a 1% HNO₃ pipette rinsing solution and add 10-mL of a filtered preserved sample to a pre-cleaned 15-mL autosampler vial. If the sample is suspected to be high in metals or total dissolved solids (TDS), then dilute the sample with 1% HNO₃. In the case of a high concentration of metals dilute the sample until the concentration of the metals at the dilution fall within the calibration range of the instrument. In the case of a high TDS, dilute the samples until the TDS count is less than 1000 mg/L.
- 9.1.2 As a general guideline, normal seawater and sediment digest samples are diluted 50x, tissue samples are diluted 10x, and influent wastewater samples are diluted 5x.
- 9.1.3 Biomonitoring samples:
- 9.1.3.1 Urine samples are diluted 10x with 1% (v/v) HNO₃.
- 9.1.3.2 Whole blood samples are diluted 50x with 1% (v/v) HNO₃.
- 9.1.4 For the determination of total recoverable analytes, there are several digestion and preservation techniques that can be used. Evaluation of the sample matrix, detection limits, analytes of interest, and the client's needs is required before deciding on an appropriate preparation technique. Current methods include SOP BR-0065 (1% HNO₃ digestion), BR-0066 (RP), BR-0067 (Co-APDC extraction),

BR-0068 (reverse aqua regia digestion), BR-0069 (HF/HNO₃/HCl digestion), and BR-0070 (tissue digestion).

- 9.1.5 When the metals concentration of a sample is unknown, the samples should be diluted or analyzed using a total quantification method prior to being run undiluted or with a comprehensive quantitative method. This protects the instrument and the sample introduction system from potential contamination and damage.

9.2 Instrument Startup

- 9.2.1 Turn on the computer, printer, and monitor. Load Windows XP®. Load the ELAN software by choosing the ELAN icon from the desktop or by choosing the ELAN software from the programs menu in the start menu.

9.2.2

- 9.2.3 Follow the ICP-MS daily maintenance logbook as you complete the following checks.

9.2.3.1 Change the peristaltic pump tubing as needed. The tubing requires changing if the internal standard shows RSD values above 1.5% for the initial calibration blank. **Note:** The PharMed green-green peristaltic pump tubing for the waste can be used for a month or more.

9.2.3.2 Check that all tubing and connections are in good condition.

9.2.3.3 Check the sample waste container level. Neutralize and dispose of sample waste if needed.

9.2.3.4 Check the sampler and skimmer cones and inspect the o-rings for damage or wear. Replace or clean if needed. Clean the cones by swabbing with DI water. If this is insufficient

9.2.3.5 Check the quartz torch, RF load coil, and quartz injector for damage and wear. Replace or clean if needed.

9.2.3.6 Check for the proper alignment of the injector, torch, and RF coil. Perform Z adjustment if not properly aligned and anytime that the spray chamber is changed, the cones are changed, the injector or torch is changed, or the RF coil is cleaned. The following procedure should be followed when performing the Z adjustment.

9.2.3.6.1 [REDACTED]

9.2.3.6.2 [REDACTED]

9.2.3.6.3 [REDACTED]

9.2.3.7 Check that the Argon pressure to the instrument is [REDACTED]. The plasma must be on to check this, and it's behind the instrument and difficult to get to. Alternatively, check that the regulator for Ar on the wall above the instrument reads at [REDACTED] and that all readings are normal on the Instrument Panel in ELAN.

9.2.3.8 If running in DRC mode, check the DRC gases in the safety cabinet. Both should be at around [REDACTED].

9.2.3.9 Check the recirculator coolant level. Make sure the red light is not on and add coolant if needed. Check the filter, and clean if needed.

9.2.3.10 Check that the instrument vent is on and working properly.

9.2.3.11 Check the pump oil levels and condition of the pump oil. Change the pump oil when it develops the color and transparency of tea or when it appears dirty or turbid. Refer to page 4-34 of the ELAN DRC II hardware guide to change the pump oil. The oil in the high vacuum roughing pump (left) should be changed about every three months. The right roughing pump oil should be changed about every two months or more frequently if high TDS samples or analysis with Ammonia as a DRC gas have been run

9.2.3.12 Enter the instrument window of the ELAN software and choose the front panel tab. The system status indicator should indicate "Ready" if all of the system hardware is running properly and the plasma can be ignited. If the system status indicator displays "Not ready", choose the diagnostic display tab to help determine the reason for this instrument status.

9.2.3.13 Click the plasma "Start" box on the front panel tab to start the plasma ignition process (plasma can also be ignited manually by pushing the green "start" button on the front of the instrument). The plasma ignition process takes about one minute.

9.2.3.13.1 If the plasma fails to ignite or arcing is observed push the yellow stop button on the front of the instrument immediately and wait one minute before opening up the torch box for investigation. Check for damage to the coil, torch, and auxiliary and plasma gas connections to the torch caused from arcing. Determine the reason for the ignition failure.

- 9.2.3.13.1.1 Check for moisture in the injector tube and torch assembly.
 - 9.2.3.13.1.2 Check the o-rings on the injector for damage or wear that could lead to loss of vacuum.
 - 9.2.3.13.1.3 Tubing should be checked for damage or poor connections that may be allowing air into the system.
 - 9.2.3.13.1.4 Check for proper installation and alignment of the injector, torch, and RF coil.
 - 9.2.3.13.1.5 Check the drain connection and tubing leaving the spray chamber to ensure a proper connection.
 - 9.2.3.13.1.6 Push the plasma start button again. If the plasma still will not ignite then refer to page 5-2 in the ELAN DRC II hardware guide or to page 2-6 of the ELAN version 3.0 software guide.
- 9.2.3.14 After the plasma has ignited, the peristaltic pump should automatically begin to rotate counter-clockwise. Alternatively, the pump can be turned on automatically by going to the Devices window, putting “6” in the rpm window, and clicking on the counter-clockwise button.
- 9.2.3.15 Place the carrier fluid probe into a vial of 1% HNO₃ and observe consistent fluid flow. If the flow is inconsistent, determine the cause and continue. Optimize the peristaltic pump levers to a tension that minimizes pump pulsing but keeps a continuous and rapid flow.
- 9.2.3.16 Let the plasma stabilize for at least ██████████ before beginning optimization.
- 9.2.3.17 If the instrument has been off for an extended period of time or if it has been moved or had major components replaced, refer to page 2-4 of the ELAN version 3.0 software guide for special startup instructions.

9.3 X-Y Adjustment

- 9.3.1 The X-Y adjustment of the sample introduction system needs to be performed whenever the cones are cleaned or replaced or after performing maintenance procedures in the torch chamber.
- 9.3.2 Place the carrier fluid probe into the “Daily” solution (section 6.10).
- 9.3.3 Open the “1-xy” method and the current daily performance dataset, ie, “Daily Performance IV”.

- 9.3.4 In the “samples” window, choose the “manual” tab and then click on “Analyze sample”.
- 9.3.5 In the “real-time” window, click on [REDACTED] in the “analytes available” window, and then click on “Add analyte”. Repeat the same steps for [REDACTED] to observe the background signal. Adjust the setting of the window to optimize the viewing of the signals.
- 9.3.6 Lift the top cover of the instrument to access the X and Y adjustment knobs. While observing the intensity signal in the real-time graphics window, adjust the Y knob (closer to the operator) to obtain the maximum intensity on the vertical plane. While observing the intensity signal in the real-time graphics window, adjust the X knob to obtain the maximum intensity on the horizontal plane.
- 9.3.7 Repeat the X and Y adjustments several times until the maximum signal intensity is achieved.

9.4 Tuning

- 9.4.1 Tuning should be performed whenever there are changes to the instrument’s electronics, whenever there is a need to modify the resolution for elements, or monthly (at a minimum).
- 9.4.2 The tuning file is needed to manage the instrument’s quadrupole mass filtering performance. The tuning controls are used to perform either of two operations:
 - 9.4.2.1 A mass calibration is used to adjust the instrument’s electronics to ensure accuracy of the mass spectrometer.
 - 9.4.2.2 A resolution measurement and adjustment is used to ensure that the instrument’s resolution at each mass of interest is within the defined range.
- 9.4.3 Place the carrier fluid probe in the “Daily” solution (section 6.10).
- 9.4.4 In the Smart Tune window, click on the “Edit List” button and add “Mass Calibration and Resolution” to the “Selected” section. Close the “Edit List” tab.
- 9.4.5 Click on the “Setup” tab and ensure the correct optimization, tuning and dataset files are selected, and that the autosampler position is set to 0.
- 9.4.6 In the optimization list click on the Mass Calibration and Resolution and ensure that the “1-tuning” method is selected.
- 9.4.7 Click “Optimize”

- 9.4.8 When complete, check to see that the measured masses are ± 0.1 amu of the actual mass value. Check the resolution (measured peak width) to see that it is between 0.650 – 0.750 for all measured masses.
- 9.4.8.1 The interactive graphics window is used to view the results of the tuning adjustment.
 - 9.4.8.2 If one or more of the measured masses falls outside the acceptable range then retune the instrument. Continue retuning until all the masses are within the acceptable criteria.
 - 9.4.8.3 If one or more of the resolution values falls outside of the acceptable range, adjust the resolution DAC value in the following manner:
 - 9.4.8.3.1 To increase the resolution (narrow the peak width), increase the DAC setting. Increasing the DAC setting by 30 will increase the resolution by 0.1 amu.
 - 9.4.8.3.2 To decrease the resolution (broaden the peak width), decrease the DAC setting. Decreasing the DAC setting by 30 will decrease the resolution by approximately 0.1 amu.
- 9.4.9 The tuning is optimized when all of the measured masses and resolution values are within the acceptable range. Save the tuning file (default.tun).
- 9.4.10 Print the tuning report to PDF. Go to the “interactive” window, click the “Analyte” box, and add all the analytes. Printout the spectral data for each analyte. Add the PDF to the Mass Calibration and Resolution file on the server.

9.5 Nebulizer Gas Flow Optimization

- 9.5.1 The nebulizer gas flow optimization should be performed daily or as needed.
- 9.5.2 Place the carrier fluid probe in the “Daily” solution (section 6.10).
- 9.5.3 Open the Smart tune window
- 9.5.4 Click on the “Edit List” button and bring Nebulizer Gas Flow to the “selected” side.
- 9.5.5 In the optimization tree box, choose nebulizer gas flow (NEB).
- 9.5.6 Select the appropriate method, typically “1-Neb Gas Optimization.”

- 9.5.7 In the criteria section, select the Intensity and Formula boxes. Select In 114.904 as the analyte for intensity and “CeO 155.9” as the first analyte “/” for the operator and “Ce 139.905” as the second analyte for formula.
- 9.5.8 In the “Range” window, select [REDACTED].
- 9.5.9 In the Optimization tree, right click on “Nebulizer Gas Flow (NEB)” and select “Quick Optimize.”
- 9.5.10 When complete go to the interactive window to view the optimization curve. Check that the optimization curve increases, attains a maximum point, then decreases.
- 9.5.11 Save the optimization file as “default.dac”. Printout the optimization curve and add to the ICP-MS optimization logbook.
- 9.5.12 The DRC Mode NEB is automatically set to the same value as the standard mode NEB, however, it is good practice to re-analyze the nebulizer gas flow for the target analytes, in the exact matrix in which the analysis will be performed.

9.6 Optimizing the Autolens Voltage

- 9.6.1 The autolens optimization should be performed daily.
- 9.6.2 Place the carrier solution probe in the “Daily” solution (6.10).
- 9.6.3 Open the “Smart Tune” window.
- 9.6.4 Click on the “Edit List” button.
- 9.6.5 Move “Autolens” to the selected side.
- 9.6.6 Click on “Autolens” in the optimization tree and then on the “Setup” tab.
- 9.6.7 Load the correct method file, typically “1-autolens-FAST.mth.”
- 9.6.8 In the range box, select [REDACTED].
- 9.6.9 Right click on “Autolens” in the optimization tree and select “Quick Optimize”
- 9.6.10 Printout the autolens plots in the interactive window by clicking on the box with four little arrows. Add the plot to the ICP-MS logbook. Initial the plot and record the type of spray chamber.

9.6.11 The lens can also be optimized for a single element by adding “Lens Voltage” to the Optimization tree and performing the above procedure.

9.7 Instrument Performance Check: “Daily”

9.7.1 The instrument performance check is done before the start of each analytical run to ensure proper functioning and sensitivity of the instrument. It is often educational to run a daily before and after optimization in order to observe how performing optimizations change the instrument response.

9.7.2 Place the carrier fluid probe in the “Daily” solution (6.10).

9.7.3 Open the “Smart Tune” window and add “Daily Performance” to the Optimization tree.

9.7.4 Click once on “Daily Performance” in the optimization tree and select the “Setup” tab.

9.7.5 Load the appropriate method file, typically “1-daily-FAST.mth,” and ensure that the correct criteria are selected.

9.7.6 Right click on “Daily Performance Check” in the optimization tree and select “Quick Optimize.”

9.7.7 Review the results in the report view to check for background counts, sensitivity, double-charged element levels, and oxide levels. Minimum performance specifications are listed on page 4-39 of the ELAN version 3.0 software guide. The specifications should fall within the following guidelines:

Background level at mass 220: < 5 cps

Mg sensitivity: > 8,000 cps/1 ppb

In sensitivity: > 40,000 cps/1 ppb

U sensitivity > 30,000 cps/1ppb

CeO/Ce: ≤ 2.5%

Ba⁺⁺/Ba: ≤ 2.5%

9.7.8 If the performance check is satisfactory, the instrument is ready to begin sample analysis. Place the autosampler probe in the rinse position to begin flushing the system.

9.7.9 If the performance check is not satisfactory, begin the following steps:

9.7.9.1 Manually adjust the nebulizer gas flow by going into the “Optimize” window and selecting the “Manual adjust” tab.



9.7.9.2 Check the pump tubing, cones, torch, and injector for alignment and cleanliness.

9.7.9.3 Check the nebulizer for blockages and cleanliness.

9.7.9.4 Perform the optimizations steps again (X-Y, tuning, nebulizer gas flow, and autolens), perform a daily after each step to observe the changes.

9.7.9.5 If the daily is still not satisfactory, a full optimization may be necessary.

9.8 Section 9.8 intentionally left blank.

9.9 Full Optimization

9.9.1 A full optimization should be performed when the status of the instrument is unknown, after a major servicing or repair, or when the daily optimizations fail to meet criteria.

9.9.2 Before beginning a full optimization, the daily optimization procedures should be completed. This includes the sample introduction system check, the X-Y adjustment, tuning, nebulizer gas flow optimization, and autolens.

9.9.3 Detector Voltages.

9.9.3.1 Place the carrier fluid and internal standard probes in DIW.

9.9.3.2 Open the Smart Tune window and add detector voltages to the optimization tree.

9.9.3.3 Click once on Detector Voltages in the optimization tree and then on the “setup” tab. Check that the correct methods are loaded in the method window. Typically the Pulse Method File will be “Pulse Stage Optimization” and the Analog Method File will be “Analog Stage Optimization.”

9.9.3.4 In the “Criteria” section check that the analyte for the



9.9.3.5 In the Range section click “Get Defaults.”

9.9.3.6 Right click on detector voltages in the Optimization Tree and select “Quick Optimize.”

9.9.3.7 In the optimization window a plot of the pulse intensity vs. pulse stage voltage is displayed. The diamond symbol indicates the optimum point that the software picked. Evaluate the plot to ensure that the correct value has been chosen. Print the plot and add to the ICP-MS optimization logbook.

9.9.3.8 Save the optimizations file.

9.9.4 Performing Dead Time Correction

9.9.4.1 The dead time correction is a mathematical equation that is used to correct for erroneous readings at high-count rates. The dead time function corrects for the anomaly that two pulses will hit the detector at the same time. The dead time correction should not change as the detector ages and should only need to be adjusted when the detector is replaced.

9.9.4.2 Move the carrier fluid and internal standard probes to DIW.

9.9.4.3 Open the workspace "Setting Dead Time Correction.wrk".

9.9.4.4 In the optimization window, click the dual detector calibration tab, and click "Get analyte list".

9.9.4.5 Ensure that "analog 80" appears in the analyte field and click "Get defaults"

9.9.4.6 Click "Calibrate". When the scanning is complete, note the correlation coefficient (under the heading coefficient).

9.9.4.7 From the options menu, click configuration. In the dialog box that appears, note the value of the dead time correction and increase the value of dead time (ns) by 5. Click OK and Exit.

9.9.4.8 Open the dataset window and highlight the last two samples: the "dual calibration blank" and the "dual calibration". Keep these two samples highlighted while you calibrate at different dead time corrections.

9.9.4.9 Leaving the two samples highlighted in the dataset window, go back to the dual detector tab in the optimization window.

9.9.4.10 Click "Clear calibration", "Get analyte list", and "Calibrate from dataset".

9.9.4.11 Note the correlation coefficient again.

9.9.4.11.1 If the correlation coefficient has increased, access the options menu again and click configuration. Increase the dead time value by another . Go back to the dual detector tab in the optimization window and click "Clear

calibration”, “Get analyte list”, and “Calibrate from dataset”. Continue the above steps until the highest (i.e., closest to 1.000000) correlation coefficient is found.

9.9.4.11.2 If the correlation coefficient has decreased, access the options menu again and click configuration. Decrease the dead time value by another [REDACTED]. Go back to the dual detector tab in the optimization window and click “Clear calibration”, “Get analyte list”, and “Calibrate from dataset”. Continue the above steps until the highest correlation coefficient is found.

9.9.4.12 The typical dead time correction value is [REDACTED]. As a guideline, the dead time correction should stay within the range of [REDACTED]. Even if the calibration yields the best correlation coefficient with a dead time setting of [REDACTED], do not set the dead time above [REDACTED].

9.9.4.13 Save the dead time correction value. Record the dead time value in the ICP-MS optimization logbook.

9.9.4.14 On a daily basis and any time the ELAN software has been shut down. The set dead time correction value should be verified as the last recorded value in the optimization logbook. This can easily be done while running the “daily performance check” as the current selected dead time correction value will be listed near the top of the daily performance report.

9.9.5 Dual Detector Cross Calibration

9.9.5.1 The dual detector calibration should be performed only after the above steps of the full optimization have been completed. The dual calibration is used to extend the dynamic range of the detector by normalizing the analog stage voltage of the detector and the pulse stage voltage.

9.9.5.2 The dual detector calibration method file and solution should contain each element that is desired for quantification using the extended dynamic range, including internal standards.

9.9.5.3 Move the carrier fluid and internal standard probes to the dual calibration solution (Section 6.11).

9.9.5.4 Open the “Smart Tune” window and add “Dual Detector Calibration” to the optimization tree.

9.9.5.5 Click once on “Dual Detector Calibration” in the optimization tree and then click on the “Setup” tab.

9.9.5.6 Check that the appropriate method is loaded in the “method” box, typically this is “1-dual.mth.”

9.9.5.7 Check that in the “Range” section, the “Start” value is 2, the “end” value is 13 and the “Step” value is 0.250.

9.9.5.8 Right click on “Dual Detector Calibration” in the optimization tree and select “Quick Optimize.”

9.9.5.9 In the “Dual calibration” tab, check the correlation coefficients of all the analytes and the number of counts measured. The correlation coefficient r-value should be at least 0.999 (or closer to 1.000) for each analyte. There should be a minimum of 5 points for each metal. If little or no counts are measured for an analyte, check the dual calibration solution for the presence and the concentration of the analyte(s) in question. Counts for the elements should be in the [REDACTED] counts range (note: this is counts, and not cps; therefore, to evaluate this, you need to change your settings). The dual detector calibration is only important if counts exceed [REDACTED].

9.9.5.10 In the interactive window, click on “analytes” and add the analytes five at a time. Review and print the plots for all analytes. Add the plots to the ICP-MS optimization logbook.

9.9.5.11 Save the optimization file.

9.9.6 Optimizing the Autolens Voltage

9.9.6.1 An autolens optimization must be performed following a dual detector calibration.

9.9.6.2 Follow Section 8.6.

9.9.7 Instrument Performance Check: “Daily”

9.9.7.1 A daily performance check will need to be performed following a full optimization. The nebulizer gas flow may need to be adjusted a little manually to optimize the oxides and doubly charged ions.

9.9.7.2 Follow Section 8.7 or 8.8 for automated optimization.

9.10 Cell Rod Offset

9.10.1 If the background is increasing or the detector has been changed, this procedure can be performed.

9.10.2 This procedure is not part of the full optimization and should not be performed as part of a routine optimization. Usually, a new detector is installed in the instrument by a Perkin-Elmer service technician and that person will perform this optimization as part of the installation and maintenance check.

- 9.10.3 Open the “Smart Tune” window and add “Cell Rod Offset Std. (CRO)” to the optimization tree.
- 9.10.4 Click once on “Cell Rod Offset (CRO)” in the optimization tree and click on the “Setup” tab.
- 9.10.5 Ensure the correct method file is loaded, typically this is “Cell Rod Offset Std.mth.”
- 9.10.6 In the Criteria box, check that “intensity” is selected and that the analyte is “In 114.904.” The comparator should be “Maximum.”
- 9.10.7 Click “Get defaults”.
- 9.10.8 In the optimization criteria group, choose “Ramp”.
- 9.10.9 Place the carrier fluid and internal standard probes in the “Daily” solution (6.10).
- 9.10.10 Right click on “Cell Rod Offset (CRO)” in the optimization tree and select “Optimize”.
- 9.10.11 In the real-time graphics window, find the setting that yields a minimum for the two background signals (8.5 and 220) while obtaining the maximum signal for In. In the intensity vs. time profile, note the point for the optimum In signal.
- 9.10.12 In the interactive graphics window, click on the intensity point 114.904 in the intensity vs. time profile for In.
- 9.10.13 After clicking on this point, the optimization file will automatically be updated.
- 9.10.14 In the “Optimization” window, select “File” and “Save”.

9.11 Cell Path Voltage

- 9.11.1 The cell path voltage adjusts the voltage applied to the reaction cell lenses. This is not part of a full optimization procedure and should not be performed as part of routine optimization. In general, this optimization is performed at installation and should not have to be adjusted.
- 9.11.2 Open the workspace “Optimizing cell path voltage.wrk.”
- 9.11.3 In the optimization window, select the “Auto optimize” tab.
- 9.11.4 In the parameter description list box, click “Cell path voltage.”
- 9.11.5 Click “Get analyte list” and select In 114.904.

9.11.6 Click “Get defaults”.

9.11.7 In the optimization criteria group, choose “Ramp.”

9.11.8 Place the auto-sampler probe in the “Daily” solution (section 6.10).

9.11.9 In the optimization window, click “Optimize.”

9.11.10 In the real-time graphics window, find the 3 analyte ions that yield a minimum for the two background signals (8.5 and 220). The signal for these two masses should be below 2 cps while obtaining the maximum signal for In. In the intensity vs. time profile, note the point for the optimum In signal.

9.11.11 In the real-time graphics window, note the In intensity at the optimum point on the intensity vs. time profile.

9.11.12 Click on the optimum In intensity point in the interactive graphics window. The software will automatically update the optimized cell path voltage value.

9.11.13 In the “Optimization” window, select “File” and “Save.”

9.12 Internal Standardization and Calibration

9.12.1 Following Pre-calibration optimizations, the following calibration table should be used with internal standardization as defined in **BOLD**. The unit of measure for all calibration points in the table is $\mu\text{g/L}$.

9.12.2 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full mass range scans, 3-5 internal standards should be used. Internal standards must be present in all samples, standards, and blanks at identical levels. Internal standards are added using a second channel of the peristaltic pump at a level of [REDACTED] counts.

9.12.3 The instrument is typically calibrated using 8 points. Calibration points may be omitted from the calibration, but only at the high or the low end. If low-end calibration points are omitted, the MRL may require adjustment up such that the MRL is \geq the lowest calibration point used. A minimum of 3 non-zero calibration points for each analyte determined is required.

9.12.4 Multiple isotopes for some analytes may be measured, with only the most appropriate isotope (as determined by the analyst) being reported.

Typical ICP-MS Calibration Curve Concentrations

Analyte	CAL1	CAL2	CAL3	CAL4	CAL5	CAL6	CAL7	CAL8
⁶Li								
Be	0.05	0.1	0.5	1	2	4	10	20
B	1	2	10	50	100	500	1000	2000
Na	15	30	150	500	1000	5000	10000	20000
Mg	3	6	30	200	2000	10000	20000	40000
Al	1	2	10	50	500	2500	5000	10000
K	4	8	40	100	1000	5000	10000	20000
Ca	30	60	300	1000	2000	10000	20000	40000
Sc								
Ti	0.2	0.4	2	5	10	50	100	200
V	0.15	0.3	1.5	5	10	20	50	100
Cr	0.15	0.3	1.5	12.5	25	125	250	500
Mn	0.05	0.1	0.5	2.5	25	125	250	500
Fe	5	10	50	250	500	2500	5000	10000
Co	0.1	0.2	1	2.5	5	25	50	100
Ni	0.2	0.4	2	5	10	50	100	200
Cu	0.2	0.4	2	5	10	50	100	200
Zn	0.2	0.4	2	5	50	250	500	1000
Ge								
As	0.2	0.4	2	5	10	50	100	200
Se	0.2	0.4	2	10	20	40	100	200
Sr	0.05	0.1	0.5	5	10	50	100	200
Mo	0.02	0.04	0.2	0.5	5	25	50	100
Ag	0.02	0.04	0.2	1	2	10	20	40
Cd	0.01	0.02	0.1	0.5	1	5	10	20
In								
Sn	0.15	0.3	1.5	2.5	5	10	25	50
Sb	0.02	0.04	0.2	1	2	4	10	20
Ba	0.05	0.1	0.5	2.5	25	125	250	500
Tm								
W	0.02	0.04	0.2	1	2	10	20	40
Tl	0.01	0.02	0.1	0.25	0.5	2.5	5	10
Pb	0.05	0.1	0.5	2.5	5	10	25	50

9.13 Sample Analysis

9.13.1 Creating a method

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9.13.1.1 A method is created to instruct the instrument what analytes (masses) to measure during a run. It is also used to set the data acquisition, processing, and calibration information that will be used to control the determination.

9.13.1.2 A method can either be created new from a blank template or as a modification of an earlier saved method.

9.13.1.3 Under the file menu, click method and new. OR, use the HugeOne-J.mth file as a template.

9.13.1.4 Save the method as a name with the Element sequence number followed by the SOP used for the analysis, followed by the instrument name, followed by the analyst's initial. The method name for the analysis of sequence 0900150, analyzed with SOP BR-0060, using the ICP-MS Darcy, with an analyst with the initials ACM would be "0900150-0060-Darcy-ACM."

9.13.1.5 Click on the Timing tab.

9.13.1.5.1 In the analyte column, enter in the analytes of interest followed by specific mass (i.e.Se78). Right clicking on the analyte column will allow the user to choose from the periodic table of elements which masses to use. Enter in the internal standards to be used. Using the "Edit" menu, define the groups of elements and identify the internal standard for each group. For monitoring elements only, enter the elements near the bottom of the page and do not associate them with a group or internal standard.

9.13.1.5.2 For elements that are to be quantitatively determined and for internal standards, set the dwell time to [REDACTED]. For monitoring elements, set the dwell time to [REDACTED].

9.13.1.5.3 Select a sample loop for the analysis based on the approximate sample volume required for each run. [REDACTED] There should be a buffer of at least 33% when calculating the required sample volume.

9.13.1.5.3.1 [REDACTED]

9.13.1.6 Click on the Equations tab.

9.13.1.6.1 Correction equations are entered in this page. The software will provide a list of common interferences for each mass.

9.13.1.7 Click on the Calibration tab.

9.13.1.7.1 Enter in the concentrations of the calibration standards for each element. Leave the rows with the internal standards blank.

9.13.1.7.2 Right click on the units column and choose $\mu\text{g/L}$ from the drop down list. Make all the units $\mu\text{g/L}$.

9.13.1.7.3 Ensure that the calibration curve type reads “Weighted Linear”, unless otherwise requested.

9.13.1.8 Click on the Sampling tab.

9.13.1.8.1 In the “A/S” column, enter in the autosampler location of the calibration standards.

9.13.1.8.2 Set the sample flush times for all the calibration standards to 1 second, as this number is simply a place holder when using the FAST sample introduction system.

9.13.1.8.3 Set the sample flush, wash and delay and analysis speed [REDACTED].

9.13.1.8.4 Set the read delay to [REDACTED].

9.13.1.8.5 Set the wash time to [REDACTED].

9.13.1.8.6 The times above can be altered in selected circumstances. For example, if only As and Se are being analyzed by DRC, a sample uptake time [REDACTED] is acceptable if the FAST method is adjusted to match.

9.13.1.8.7 If there is no autosampler selected, click on “Select”, and choose “As-93plus” from the drop-down menu. In the “Tray” box, click on “Select” and choose “c:\program files\esi\esi sc\esi.try”.

9.13.2 Sample Window

9.13.2.1 The sample window is used to identify the samples in a sequence, control the order in which samples are measured, and initiate the measurements.

9.13.2.2 The sample window contains two tabs: “Manual” and “Batch”. The manual window is used to individually identify samples for manual control of a determination. The manual window is useful for reanalyzing calibration standards that did not meet criteria during initial analysis. The batch window is used to identify a group of samples for an automated determination, to control the order in which the samples are measured, and to initiate the measurements. Most sample analysis is performed using the batch window.

9.13.2.3 Click the “Batch” tab at the top of the sample window.

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9.13.2.4 Enter the appropriate autosampler location for each sample in the A/S column.

9.13.2.5 In the “Batch ID” column, enter in the batch number of the sample batch to be run. This column should be left blank for rinses, calibrations, CCVs, instrument blanks, etc.

9.13.2.6 In the “Sample ID” column, enter the unique sample name for each sample.

9.13.2.7 The “Measurement Action” column defines when to run standard and blank solutions, in addition to specifying the running of the sample solution. In the measurement action cell, right click the mouse to show a drop down menu with a list of actions to choose from. For the calibration, select “Run blank, stds. and sample”. Choosing this action will analyze the calibration blank and the standards that are specified on the calibration tab of the method. For all other samples, choose “Run sample”.

9.13.2.8 The method column specifies which method should be used for measuring the sample. In the method cell, right click the mouse to display the “Select method file dialog”. From the file list, select the desired method and click OK.

9.13.2.8.1 The description cells provide a field for entering in specific information or notes about the sample. Currently this is used by the Element software to determine the appropriate blank correction factor, for samples diluted 10 times, enter “10x.”

9.13.2.9 In the “Aliquot Volume” and “Diluted to Volume” columns, enter the initial and final volume (in milliliters, mL) of sample if the sample is diluted in the autosampler cups. Leave these columns empty if the sample is not diluted.

9.13.3 Dataset window

9.13.3.1 The dataset window records every analysis and the order they have been analyzed. Information in the fields cannot be modified. The dataset should be saved with an identification number that corresponds directly to the Element sequence number i.e. “0900150.”

9.13.4 Calibration view

9.13.4.1 The calibration view window is used for post-acquisition viewing and interpretation of calibration curves generated from the measurement of the calibration standards. Statistical information and graphical plots can be evaluated in the calibration window.

9.13.4.2 To evaluate the effects of eliminating individual calibrations points from the curve, click on the point and it will be removed from the calibration calculation. Click on the point again to introduce it back into the calibration.

9.13.4.3 Evaluate the calibration curve. If all of the calibration points meet the analysis requirements, the calibration should be saved under a file name with a similar identification to the corresponding method file (i.e., 0900150 for analysis consisting of the 150th sequence analyzed in 2009).

9.13.5 Starting an Automated Analysis

9.13.5.1 Highlight the samples to be analyzed in the “Sample” window. Then, click on “Analyze Batch”.

9.13.5.2 Immediately following the calibration, an Initial Calibration Blank (ICB) should be analyzed. This demonstrates that there is no carryover of the analytes of interest and that the analytical system is free from contamination.

9.13.5.3 Immediately following the ICB, a calibration verification should be analyzed. This is called the Initial Calibration Verification (ICV).

9.13.5.4 A minimum of three reagent blanks should be analyzed following the ICV. These blanks are called Instrument Blanks (IBL).

9.13.5.5 Two certified reference materials (CRM) should be analyzed following the IBWs. Common CRMs used for the analysis of waters are NIST 1640 (fresh water), NIST 1643e (river water), and CRM TMDW (drinking water). If analyzing seawater samples, CRM TMSW can be used. If analyzing for hardness, then CRM WasteWatR Hardness should be analyzed.

9.13.5.6 A continuing calibration verification (CCV) standard should be analyzed every ten samples and at the end of the run. The CCV standard should be the mid-point calibration standard.

9.13.5.7 A blank should be analyzed after each CCV, this blank is called a continuing calibration blank (CCB). This demonstrates that there is not carryover and that the analytical system is free from contamination.

9.13.5.8 For every 10 client samples, prepare and analyze a matrix spike (MS) and a matrix spike duplicate (MSD). Matrix spikes should be spiked at a level two to five times the background concentration or at the practical quantitative limit (PQL), whichever is greater.

9.13.5.9 For every 10 client samples, prepare and analyze a matrix duplicate (MD) sample.

9.13.5.10 Method of Standard Additions (MSA) curves must also be performed any time that matrix interference is suspected, such as when matrix spikes or post-digestion spikes fail to meet acceptance criteria. In general, a three point MSA curve for solid digests should be prepared.

9.13.5.11 At the end of the run, flush the system with a rinse, DIW, and air. These steps will rinse out the instrument and sample introduction system, remove any acids that could wear down the sample introduction system, and dry the sample introduction system.

9.13.5.12 When the sample information file is complete, highlight all remaining samples to be analyzed. Go to the “Scheduler” window and select the “Analyze Samples” and “Autostop” tabs. In the Details column select the relevant Sample and Dataset file. Click “Start”. The instrument will shut down the plasma, stop the peristaltic pump action, and return the autosampler probe to the rinse vial position after the last sample is analyzed. The auto stop can be selected at any time during analysis.

9.13.5.13 The plasma can be extinguished at any time by clicking plasma “Stop” on the front panel of the instrument page or, if need be, manually by pressing the yellow “off” button on the front of the instrument.

9.13.6 Exporting and Reprocessing Instrument Data

9.13.6.1 Reprocess the data in the “Dataset” window by highlighting the runs and clicking “Reprocess” after analysis has finished.

9.13.6.2 Click on the report tab on the far right hand side of the method window to edit the instrument outputs.

9.13.6.3 To print a copy of the instrument data select “Send to printer”, and that the appropriate printer is selected. To print a calibration report select “1-CalReport” as the Report Output and reprocess any run. To print a copy of the raw data select “Quant-1” as the Report Output.

9.13.6.4 To export data to LIMS select the “Send to file” box and select “Processforinput1wcalcoeff” as the report output file. Name the produced report by the following: Data\(\year_data)\Instrument Files – seq\Sequence Number, i.e., \\Curie\lab\Data\09_data\Instrument Files - seq\0900150.

9.13.6.5 Return to the dataset window and select all relevant runs, click “Reprocess.”

10.0 PROCEDURE FOR ANALYSIS USING DYNAMIC REACTION CELL (DRC)

10.1 For elements that suffer from isobaric or polyatomic interferences (see section 4.2), it is advantageous to utilize the DRC mode operation of the instrument. For non-interfered ions, the DRC mode can be optimized to enhance the standard mode performance.

10.2 When the reaction cell is pressurized with a reactive gas, the polyatomic or isobaric interferants can be converted to a different mass where they no longer interfere with the correct measurement of a desired element or the reaction gas will convert the desired element of interest to a mass which is not interfered upon. Chemical processes that occur in the DRC include charge transfer, proton transfer, and condensation and association reactions. The following procedure describes the process involved with running samples while utilizing the dynamic reaction cell to modify the ion stream chemistry.

10.3 The ELAN DRC II ICP-MS can be operated in three ways.

10.3.1 Using the dynamic reaction cell. The reaction cell is pressurized with a reaction gas (i.e., ammonia or oxygen).

10.3.2 With the dynamic reaction cell vented. In this manner, the instrument will emulate a conventional ICP-MS.

10.3.3 Both modes in sequence. Sample information can sequentially be collected in DRC mode and then in standard mode.

10.4 Interferences in DRC Mode

10.4.1 Isobaric interferences from doubly charged ions at the same m/z as described in section 4.2. can still cause interferences in DRC mode. It is important to ensure that the double-charged ratio associated with Ba^{++}/Ba is less than 2.5% when performing the daily performance check. A daily performance check in DRC mode can be done to verify low levels of Ba^{++} .

10.4.2 Isobaric interferences from polyatomic species are, when optimized properly, reduced to background levels in DRC mode. Reaction chemistry can result in an increase in background levels when not optimized. Specific chemistry within the cell should be understood thoroughly to perform quality analyses.

10.4.3 DRC Gas

10.4.3.1 The DRC gases are separated into two channels. Ammonia is in channel A and is referred to as Cell Gas A. Other gases, typically Oxygen, are in channel B and are called Cell Gas B. Ammonia passes through a "Getter" to dry the ammonia and

remove trace levels of Oxygen. Cell Gas B bypasses the getter and goes directly to the DRC. Be extra careful to not reverse the gases, as this will contaminate the getter.

10.4.3.2 The type of DRC gas will remove interferences differently. This technology still has not been extensively researched and it is still unknown how certain analytes will behave with certain gases. A guideline of possible DRC gases and their relative effectiveness on certain analytes can be found on the last page of the ELAN DRC Accessory Training Manual.

10.4.4 Optimization using DRC

10.4.4.1 Optimization of the sample introduction system, plasma, and ion optics is the same for DRC mode as in standard mode. Follow sections 8.3 through 8.8. Proper optimization in standard mode will greatly enhance the DRC performance. Further optimization can be performed for a single element if needed (i.e., lens voltage at a single mass instead of using the autolens feature).

10.4.4.2 Following the daily (and full, if needed) optimization in standard mode, the reaction cell should be conditioned prior to optimization in DRC mode.

10.4.4.3 In the optimize window, select manual adjust and enter a value for either cell gas A (ammonia) or cell gas B (oxygen). A typical value will be around [REDACTED]. If using both gases for analysis, enter a value for cell gas A only. Allow the reaction cell to condition in this manner for at least [REDACTED]. If the cell has not been pressurized for a long period, or if there are problems, conditioning for [REDACTED] may be necessary.

10.4.4.4 Performing a DRC mode daily performance check will ensure the proper functioning and sensitivity of the instrument and will verify the sensitivity of isotopes that are interfered with by plasma-based interferences.

10.4.4.4.1 Open the template method file for the desired analysis, possibly "As Se DRC."

10.4.4.4.2 Enter the method window and confirm the presence of the analytes of interest to be determined and save.

10.4.4.4.3 For the analytes added to the method, verify the cell gas flow rate and the RPq are set to what is typical. If these values are unknown (i.e., pre-method development), then do not perform the daily performance.

10.4.4.4.4 Aspirate a solution containing 1 ppb of the analytes of interest.

10.4.4.4.5 Open the sample window and click analyze sample.

10.4.4.4.6 Compare the intensity of the DRC mode analytes with previous DRC mode instrument performance data to verify that the interference reduction is acceptable.

10.4.4.4.7 If the performance check is satisfactory, the instrument is ready to begin sample analysis.

10.4.4.5 Method development is an integral part of running samples utilizing the DRC feature. Method development includes optimizing a reaction cell gas flow and an RPq parameter. Response to the reaction cell will vary greatly with sample matrix, so it is important that for every new sample matrix ran in DRC mode an appropriate reaction gas, cell gas flow rate, and RPq parameter is found. Once a method has successfully been developed for a particular sample matrix, the cell gas flow and RPq value should not change.

10.4.4.6 Optimizing DRC Parameters

10.4.4.6.1 Optimizing the cell gas flow in DRC mode requires a matrix- matched blank and a matrix matched standard spike [REDACTED] of the analyte of interest.

10.4.4.6.2 Open the method "1-DRC Method Development.mth". Modify the method so it lists only the analytes of interest. A convenient first approximation for the stability parameter RPq and the cell gas flow rates are [REDACTED]

10.4.4.6.3 In the "Optimize" window, select the "Auto Optimize" tab and Click "Get Analyte List." In the Parameter Description area, select the Cell Gas or RP value to be optimized. In the "Parameter Range" area select a range of values to be evaluated and the step value used. In the "Optimization Criteria" area select "Ramp."

10.4.4.6.4 Move the sample probe into the desired matrix blank and allow sufficient time for the sample to be aspirated.

10.4.4.6.5 Click "Optimize" to begin the optimization

10.4.4.6.6 When finished, move the sample probe to the matrix matched spiked solution.

10.4.4.6.7 In the sample window, click on the manual tab and enter a spike related ID that will be easily identifiable later.

10.4.4.6.8 Click "Optimize" to begin the optimization.

10.4.4.6.9 When the second optimization is finished, go to the “Interactive” window, choose “Cell Param Optimize” from the drop-down list and click composite.

10.4.4.6.10 In the cell gas optimize options dialog, click the select buttons to locate and open the blank and spiked sample from the appropriate dataset folder.

10.4.4.6.11 Type in the concentration of the spiked matrix matched sample.

10.4.4.6.12 Click “Calculate”.

10.4.4.6.13 Go to the interactive graphics window and choose the analyte of interest from the drop-down list.

10.4.4.6.14 Three plots appear in the interactive window. The matrix blank, matrix spike, and estimated detection limit.

10.4.4.6.15 Select the flow rate that gives the best-estimated detection limit while still maintaining an acceptable number of counts. The counts will depend on the ionization potential of the element. Put the flow rate in method. Alternate between Gas Flow Optimizations and RPq Optimizations until settings have been found which give the required interference resistance and sensitivity.

10.4.4.7 Little or no adjustment is necessary for the RPa value because most sequential chemistry takes place at a lower mass than the analyte. [REDACTED]
[REDACTED] The RPa can be used to analyze samples which would normally saturate the detector. This should be done with very careful consideration. Further information can be found in the instrument manual.

10.4.4.8 The Cell Path Voltage (CPV), Cell Rod Offset (CRO), and Quadrupole Rod Offset (QRO) are voltage settings that are optimized at installation and generally do not have to be adjusted. Refer to sections 4-81 through 4-83 of reference 11.1 for procedures on optimizing these settings.

10.4.4.9 Once appropriate values for the reaction cell gas flow and RPq are obtained they should be entered into the method in the timing page and in the cell parameters in the optimize window.

10.4.4.10 In the early stages of method development, it is useful to set up the method to analyze several replicates of a mass using [REDACTED].

10.5 Current DRC methods – New DRC methods are being developed for different analyte/matrix combinations on a regular basis. The table below is not intended to be all-inclusive, but only a representation of what methods have been fully developed and validated as of the last revision date of this SOP.

Analyte/Internal Standard	Gas	Matrix	RPq	Cell Gas Flow
⁹¹ (AsO)/ [REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁷⁸ Se/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁸⁰ Se/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
¹⁰⁹ Ag/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
²⁶ Al/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁵² Cr/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁵³ Cr/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁶³ Cu/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁶² Ni/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁶² Ni/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁵¹ V/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁶⁶ Zn/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]
⁶⁶ Zn/[REDACTED]	[REDACTED]	All Matrices	[REDACTED]	[REDACTED]

10.5.1 As every matrix may have slight variance, analysis should include more isotopes of the same element if possible and RPq and cell gas flows should be measured [REDACTED] for each analyte to ensure best DRC conditions.

10.5.2 The table above lists the general cell conditions optimized for multi-analyte analyses. Cell conditions, especially cell gas flow rates, may be optimized for specific analyte/matrix combinations, as needed. In such cases, the optimized methods will often have slightly different RPq and cell gas flow values. [REDACTED]

11.0 QUALITY CONTROL

11.1 All BRL quality control criteria are summarized in Section 16.0. Project specific quality control requirements may differ and always take precedence over BRL requirements. Refer to Addendum A for additional project specific criteria currently used at BRL.

11.2 Preventative maintenance - The ICP-MS daily optimization logbook lists routine maintenance and checks that should be performed on a daily basis. Refer to section 4 of the ELAN DRC II hardware guide for details on daily, weekly, and monthly preventative maintenance. All maintenance should be documented in the ICP-MS daily optimization logbook.

11.3 Instrument optimization is an integral part of quality control. Sometimes optimizing the instrument takes the whole day.

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11.4 Pipettes must be calibrated weekly, or whenever the status of a pipette is unknown, checked daily. Refer to BRL SOP BR-1205 for further instruction on the calibration of pipettes.

11.5 The correlation coefficients of the weighted-linear calibration curves for each element must be ≥ 0.995 to proceed with sample analysis. If the correlation coefficient for any element is < 0.995 , the results for that element may not be reported from that run. If high standards begin to decrease in sensitivity and do not fall into the linear regression, this might indicate that a cross calibration of the dual detector is needed and a full optimization would be required.

11.6 The percent recovery of the ICV standard must be 85-115% for each element being determined. If the percent recovery is not within the control limits of 85-115%, for any element, the results for that element may not be reported from that run, unless approved by both the Quality Assurance Officer and the Laboratory Manager.

11.7 Instrument rinses should be performed after any samples suspected to be high in metals and before any method blanks to ensure baseline sensitivity has been achieved.

11.8 Each analytical or digestion batch must have at least 3 preparation (or method) blanks associated with it if method blank correction is to be performed (1 method blank may be acceptable if sample results are not being blank corrected). The blanks are treated the same as the samples, and must go through all of the preparative steps. All of the samples should be corrected for the mean concentrations of these blanks. Three times the standard deviation of these blanks is the estimated method detection limit (EMDL) for that batch. The EMDL is evaluated against the MDL determined as per 40 CFR 136. Ideally, the EMDL should be at or below the MDL.

11.9 For every 10 client samples, a matrix duplicate (MD) sample should be analyzed. Generally, the relative percent difference (RPD) for the replicate should be $\leq 20\%$ for waters and $\leq 30\%$ for solids and seawaters prepared by RP or Co-APDC if the sample concentrations are greater than 5 times the MRL. A duplicate matrix spike (MSD) may be substituted for the MD, with the same control limits unless client-specific data quality objectives require an MD sample.

11.10 For every 10 client samples, a matrix spike (MS) and a matrix spike duplicate (MSD) should be performed. The percent recovery of the spikes should be 75-125% with an RPD $\leq 20\%$ for waters and 70-130% with an RPD $\leq 30\%$ for solids and seawaters prepared by RP or Co-APDC. If the spike recovery is outside of the control limits, a MSA curve that has been prepared and analyzed may be used to correct for the matrix effect. Samples may be corrected by the slope of the MSA curve if the correlation coefficient of the MSA curve is ≥ 0.995 . If the sample concentration levels are sufficiently high, the sample may be diluted to reduce the matrix effect. Spike sets should be performed at the same dilution factor as the native sample. Spike at 1-5 times the level of a historical sample of a client, or if unknown, spike 1-5 times a typical value for the matrix; however, spiking levels should also be no

lower than 5x the MRL. For multi-element analyses, allowances can be made for spiking with mixed standards.

11.11 The percent recoveries of the CRMs should be 75-125%. If the results are not within control limits for each analyte, the sample results may not be reportable. However, it should be noted that for sediment and soil CRMs, nearly all CRMs are certified for “total” metals; whereas, BRL typically prepared these types of samples with a reverse aqua regia (RAR) bomb digestion, which produces results for “total recoverable” metals. For some metals that are less labile (i.e., Cr, Ba, etc.), CRM recoveries may be low and outside of the control limits; however, this would not cause concern for the validity of the data and would not require any corrective action. The Addendum to the Certificates of Analysis for NIST SRMs 2709, 2710, and 2711 do a good job of explaining this issue clearly, and offer a good guide for comparing recovery results for total and total recoverable metals.

11.12 The percent recoveries of the CCV standards should be within 75-125%. If the CCV results are not within the control limits for any analyte, the sample results may not be reportable for that element.

11.12.1 Unless otherwise instructed by the client, sample results may be CCV corrected using the mean recovery of the bracketing CCVs. Only after careful evaluation of the data should this be done. The instrument should show a trending drift of CCV recoveries and not just a few anomalous outliers. The project manager or group leader should be consulted before CCV correcting data.

11.13 CCBs should be monitored for the effects of carry-over and for possible system contamination. If carry-over of the analyte at levels greater than 10 times the MDL is observed, the sample results may not be reportable.

11.14 Results for samples prepared with reductive precipitation (RP) and APDC extractions may be corrected by an efficiency factor that is calculated quarterly based on the previous year’s recovery data for CRMs, blank spikes, and MS/MSDs.

11.15 The absolute response of any one internal standard should not vary from the original response in the calibration blank by more than 60-125%. Some analytical samples, such as those containing concentrations of the internal standard and tissue digestates, can have a serious effect on the internal standard intensities, but this does not necessarily mean that the analytical system is out of control. In some situations, it is appropriate to reprocess the samples using a different internal standard monitored in the analysis. Careful evaluation of the data and notification to the project manager should be given before doing this.

12.0 METHOD PERFORMANCE

12.1 All method detection limits (MDLs) were achieved by performing a full MDL study as described in 40 CFR 136, Appendix B. The MDLs for all analytes are listed in the BRL Analytical Services Table and are available upon request, as are the data from the actual

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MDL studies. The quality control acceptance criteria listed in Tables 16.1 and 16.2 are developed from the EPA methods and are validated as achievable at BRL in control charts maintained for the method.

13.0 POLLUTION PREVENTION

13.1 Whenever feasible, lab personnel should use pollution prevention techniques to limit waste generation. The cost involved in purifying used acids makes such recycling unpractical at BRL. Instead, every effort is made to reduce any volumes necessary to still produce the best possible results. This analysis requires very small volumes to analyze sample preparations and standards. Standards should be prepared in volumes consistent with the laboratory use to minimize the volume of disposed standards to be disposed.

14.0 WASTE MANAGEMENT

14.1 All waste is disposed of in accordance with state and federal regulations either by sewer disposal (only if concentrations are less than the King County sewer limits) or through a licensed hazardous waste disposal facility such as Philips Services.

15.0 REFERENCES

- 15.1 Software Guide-ELAN Version 3.0, Perkin-Elmer part number WE1002821, 2003 Edition Perkin-Elmer/MDS SCIEX instruments, 71 Four Valley Drive, Concord, ON L4K 4V8.
- 15.2 Hardware Guide-ELAN DRC II, Perkin-Elmer part number WE1002727A, 2001, Perkin-Elmer Instruments LLC, 710 Bridgeport Avenue, Shelton, Connecticut, 06840.
- 15.3 "Safety and Health Core Rules" OSHA regulation for Washington State, Chapter 296-800 WAC.
- 15.4 "ELAN DRC Accessory Training Manual". Perkin-Elmer, N0225044, Revision A, 2005.
- 15.5 EPA SW-846 Method 6020. "Inductively Coupled Plasma –Mass Spectrometry." Revision 2. December 1996.
- 15.6 EPA Method 1638. "Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma – Mass Spectrometry." January 1996.
- 15.7 EPA Method 1640. "Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma – Mass Spectrometry." January 1996.

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- 15.8 EPA Method 200.8, Revision 5.5. "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry." October 1999.
- 15.9 EPA Method 6020A, Revision 1. "Inductively Coupled Plasma – Mass Spectrometry." SW-846 Methods. February 2007.
- 15.10 NIST Certificate of Analysis for SRM 2709 – San Joaquin Soil, National Institute of Standards and Technology, Gaithersburg, Maryland, 2003.
- 15.11 CDC Laboratory Procedure Manual, Urine Multi-Element ICP-DRC-MS, Method No. ITU001B, February 16, 2006.
- 15.12 CDC Laboratory Procedure Manual, Blood Lead and Cadmium ICP-DRC-MS, Method No. ITB001A, September 9, 2004

16.0 TABLES

Table 16.1 BRL QA Criteria for Water Samples Prepared by BR-0065 and Analyzed by BR-0060

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Calibration Standards	Linearity of the calibration curve	Analyzed once per analytical day; Minimum of 5 calibration points	Correlation coefficient ≥ 0.995 , 1 st standard \leq PQL, low standard recovery = 75-125%, all other standard recoveries = 80-120%	Reanalyze suspect calibration standard. High calibration standard(s) may be omitted as long as all samples results are still below the highest calibration standard use. If criteria still not met, then re-prepare standards and recalibrate the instrument.
Internal Standards	Variation in sample properties between samples and standards	Each standard, blank, and sample is spiked with internal standard	60-125% recovery compared to calibration blank	If the responses of the internal standards in the following CCB are within the limit, rerun the sample at an additional 2x dilution. If not, then samples must be re-analyzed on a new calibration.
Interference Check Solution (ICS)/Certified Reference Material (CRM)	Check the validity of the interference correction and method accuracy	At the beginning of each analytical run	All non-certified analytes $<$ RL; other analytes within $\pm 25\%$ or \pm RL if $<$ 5x RL	If CRM true value is $\geq 5x$ the MRL and if the recovery is outside of the control limits, then halt analysis, identify and correct problem, recalibrate if necessary, and reanalyze affected samples.
Independent Calibration Verification (ICV)	Independent check of system performance	1 following instrument calibration	Recovery = 85-115%	Correct problem prior to continuing analysis, recalibrate if necessary
Check Calibration Verification (CCV)	Accuracy	1 per 10 sample preparations and at the end of the analytical run	Recovery = 75-125%	Halt analysis, correct problem, recalibrate, and reanalyze affected samples. CCV-correction may be allowed. Note: If internal standards are not run, then CCV standards must be analyzed at various concentrations.
Method Blanks (MB)	Contamination from reagents, lab ware, etc.	Minimum of 3 per batch	Mean \leq PQL; SD \leq MDL or MBs $<$ 1/10 th sample result	Reanalyze to confirm results. MBs may be omitted if they meet the Grubb's Outlier test and if a minimum of 3 MB remain. If MBs are still high following rejection of any Grubb's outlier, then a batch specific MDL is estimated (EMDL) by multiplying the standard deviation of the remaining MBs by 3x. The batch specific MRL is estimated (EMRL) by multiplying the EMDL by 3x. All results are evaluated against the EMDL and EMRL, and data is qualified if necessary.
Method Duplicates (MD)	Method precision within a given matrix	Minimum of 1 per 10 client samples (prepared at instrument)	RPD $\leq 20\%$ or \pm PQL if results $\leq 5x$ PQL	If RPD criteria not met, then sample may be reanalyzed, but this is not required. Sample matrix may be inhomogeneous, in which case the results would be qualified.
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	Method accuracy and precision within a given matrix	Minimum of 1 per 10 client samples (prepared at instrument)	Recovery = 75-125% and RPD $\leq 20\%$	If MS/MSD criteria not met, samples must be qualified. Samples may be reanalyzed at a greater dilution, but this is not required. Matrix effects may be present, in which case the results would be qualified. If RPD criteria not met, then sample may be reanalyzed, but this is not required. Sample matrix may be inhomogeneous, in which case results would be qualified.

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Table 16.2 BRL QA Criteria for Seawater Samples Prepared by BR-0066/BR-0069 and Analyzed by BR-0060

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Calibration Standards	Linearity of the calibration curve	Analyzed once per analytical day; Minimum of 5 calibration points	Correlation coefficient ≥ 0.995 , 1 st standard \leq PQL, low standard recovery=75-125%, all other standard recoveries=80-120%	Reanalyze suspect calibration standard. If criteria still not met, then reprepare standards and recalibrate the instrument
Internal Standards	Variation in sample properties between samples and standards	Each standard, blank, and sample is spiked with internal standard	60-125% recovery compared to calibration blank	If the responses of the internal standards in the following CCB are within the limit, rerun the sample at an additional 2x dilution. If not, then samples must be re-analyzed on a new calibration.
Interference Check Solution (NIST 1643e) (NIST 1640)	Check the validity of the interference correction	At the beginning of each analytical run	All non-certified analytes $<$ RL; other analytes within $\pm 25\%$ or \pm RL if $< 5x$ RL	Halt analysis, identify and correct problem, recalibrate if necessary, and reanalyze affected samples
Independent Calibration Verification (ICV)	Independent check of system performance	1 following instrument calibration	Recovery = 85-115%	Correct problem prior to continuing analysis, recalibrate if necessary
Check Calibration Verification (CCV)	Accuracy	At beginning and end and 1 per 10 sample preparations	Recovery = 75-125%	Halt analysis, correct problem, recalibrate, and reanalyze affected samples (Note: If internal standards are not run, then CCV standards must be analyzed at various concentrations.)
Method Blanks (MB)	Contamination from reagents, lab ware, etc.	Minimum of 3 per batch	Mean \leq PQL; SD \leq MDL or MBs $< 1/10^{\text{th}}$ sample result	Reanalyze to confirm results. MBs may be omitted if they meet the Grubb's Outlier test and if a minimum of 3 MB remain. If MBs are still high following rejection of any Grubb's outlier, then a batch specific MDL is estimated (EMDL) by multiplying the standard deviation of the remaining MBs by 3x. The batch specific MRL is estimated (EMRL) by multiplying the EMDL by 3x. All results are evaluated against the EMDL and EMRL, and data is qualified if necessary.
Method Duplicates (MD)	Method precision within a given matrix	Minimum of 1 per 10 client samples	RPD $\leq 30\%$ or \pm PQL if results $\leq 5x$ PQL	If RPD criteria not met, then sample may be reprepared and reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion duplicate (PDD) can be analyzed to evaluate instrument precision.
Matrix Spikes/ Matrix Spike Duplicates (MS/MSD)	Method accuracy and precision within a given matrix	Minimum of 1 per 10 client samples	Recovery = 70-130% and RPD $\leq 30\%$ (may be adjusted to accommodate efficiency factors for RP and APDC preps)	If RPD $> 25\%$, results must be qualified. If RPD criteria not met, then sample may be reprepared and reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion spike (PDS) can be analyzed to evaluate instrument accuracy and also to determine if matrix interference is occurring at the prep stage or at the analytical stage. An MSA curve may be prepared and analyzed along with the samples to quantify and correct for interference.
Post-Digestion Spike (PDS)	Check for matrix interference	When required (samples spiked too low/high, dilution test fails, etc.)	Recovery = 75-125%	Samples must be analyzed using MSA or results flagged accordingly.
Laboratory Fortified Blanks (LFB)	Method accuracy	When no suitable CRM available	Recovery = 75-125%	If LFB recovery is outside of the control limit, then batch must be reprepared and reanalyzed.
Certified Reference Material (CRM)	Method accuracy	Must be matrix matched to samples; Minimum of 1 per batch	Recovery = 75-125% unless limits set by CRM manufacturer are greater or element/CRM specific limits have been established	If CRM true value is $\geq 5x$ the PQL and if the recovery is outside of the control limit, then batch must be reprepared and reanalyzed.

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Table 16.3 BRL QA Criteria for Sediment and Biota Samples Analyzed by BR-0060

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Calibration Standards	Linearity of the calibration curve	Analyzed once per analytical day	Correlation coefficient ≥ 0.995 , 1 st standard \leq PQL, low standard recovery=75-125%, all other standard recoveries=80-120%	Reanalyze suspect calibration standard. If criteria still not met, then reprepare standards and recalibrate the instrument
Internal Standards	Variation in sample properties between samples and standards	Each standard, blank, and sample is spiked with internal standard	60-125% recovery compared to calibration blank	If the responses of the internal standards in the following CCB are within the limit, rerun the sample at an additional 2x dilution. If not, then samples must be re-analyzed on a new calibration.
Interference Check Solution (ICS)	Check the validity of the interference correction	At the beginning of each analytical run	All non-certified analytes $<RL$; other analytes within $\pm 25\%$ or $\pm RL$ if $<5x RL$	Halt analysis, identify and correct problem, recalibrate if necessary, and reanalyze affected samples
Independent Calibration Verification (ICV)	Independent check of system performance	1 following instrument calibration	Recovery = 85-115%	Correct problem prior to continuing analysis, recalibrate if necessary
Check Calibration Verification (CCV)	Accuracy	At beginning and end and 1 per 10 sample preparations	Recovery = 75-125%	Halt analysis, correct problem, recalibrate, and reanalyze affected samples
Method Blanks (MB)	Contamination from reagents, lab ware, etc.	Minimum of 3 per batch	Mean $\leq PQL$; SD $\leq MDL$ or MBs $<1/10^{th}$ sample result	As per with sediments (Table 16.3).
Method Duplicates (MD)	Method precision within a given matrix	Minimum of 1 per 10 client samples	RPD $\leq 30\%$ or $\pm 2x PQL$ if results $\leq 5x PQL$	If RPD criteria not met, then sample may be reprepared and reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion duplicate (PDD) can be analyzed to evaluate instrument precision.
Matrix Spikes/ Matrix Spike Duplicates (MS/MSD)	Method accuracy and precision within a given matrix	Minimum of 1 per 10 client samples	Recovery = 70-130% and RPD $\leq 30\%$	If RPD $> 30\%$, results must be qualified. If RPD criteria not met, then sample may be reprepared and reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion spike (PDS) can be analyzed to evaluate instrument accuracy and also to determine if matrix interference is occurring at the prep stage or at the analytical stage. An MSA curve may be prepared and analyzed along with the samples to quantify and correct for interference.
Post-Preparation Spike (PPS)	Check for matrix interference	When required (samples spiked too low/high, dilution test fails, etc.)	Recovery = 75-125%	Samples must be analyzed using MSA or results flagged accordingly.
Laboratory Fortified Blank (LFB) or Blank Spike (BS)	Method accuracy	Minimum of 1 per batch	Recovery = 75-125%	If LFB recovery is outside of the control limit, then batch must be reprepared and reanalyzed.
Certified Reference Material (CRM)	Method accuracy	Must be matrix matched to samples; minimum of 1 per batch	Recovery = 75-125% unless limits set by CRM manufacturer are greater or element/CRM specific limits have been established	If CRM true value is $\geq 5x$ the PQL and if the recovery is outside of the control limit, then batch must be reprepared and reanalyzed. See comments in section 10.11.

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Addendum A: Client Specific QA Criteria

Table A1. Department of Defense Quality Systems Manual, Version 4.2, Requirements

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Instrument Tuning	Optimization of the instrument	Prior to ICAL each day	Mass Cal ≤ 0.1 amu from true; resolution < 0.9 amu full width at 10% peak height. Stability, RSD $\leq 5\%$ for 4 replicates.	Retune instrument. Flagging of data is not acceptable. No analysis may be performed without a valid MS tune.
Calibration Standards	Linearity of the calibration curve	Analyze once per analytical day	Correlation coefficient ≥ 0.995 , 1 st standard \leq MRL with $\pm 20\%$ rec.	Reanalyze suspect calibration standard. If criteria still not met, then reprepare standards and recalibrate the instrument
Internal Standards	Variation in sample properties between samples and standards	Each standard, blank, and sample is spiked with internal standard	30-120% recovery compared to calibration blank	If the responses of the internal standards in the following CCB are within the limit, rerun the sample at an additional 2x dilution. If not, then samples must be re-analyzed on a new calibration.
Interference Check Solution ICS-A ICS-AB	Check the validity of the interference correction	At the beginning of each analytical run	All non-spiked analytes $< LOQ^*$; other analytes within $\pm 20\%$ or $\pm RL$ if $< 5x RL$	Halt analysis, identify and correct problem, recalibrate if necessary, and reanalyze affected samples
Independent Calibration Verification (ICV)	Independent check of system performance	1 following instrument calibration	Recovery = 90-110%	Correct problem prior to continuing analysis, recalibrate if necessary
Check Calibration Verification (CCV)	Accuracy	At beginning and end and 1 per 10 sample preparations	Recovery = 90-110%	Halt analysis, correct problem, recalibrate, and reanalyze affected samples (Note: If internal standards are not run, then CCV standards must be analyzed at various concentrations.)
Calibration Check Blank (CCB)	Contamination at the instrument	Following each CCV	$< LOQ^*$	Determine and eliminate cause of contamination. Affected samples must be reanalyzed
Method Blanks (MB)	Contamination from reagents, lab ware, etc.	Minimum of 3 per batch	$\leq \frac{1}{2} RL$ or $\leq 10\%$ of any sample. Or $\leq 10\%$ of regulatory limit	Determine and eliminate cause of contamination. Affected samples must be reprepared and reanalyzed.
Method Duplicates (MD)	Method precision within a given matrix	Minimum of 1 per 10 client samples	RPD $\leq 20\%$ or results within the PQL if $< 5x PQL$	If RPD criteria not met, then sample may be reprepared and reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion duplicate (PDD) can be analyzed to evaluate instrument precision.
Matrix Spikes/ Matrix Spike Duplicates (MS/MSD)	Method accuracy and precision within a given matrix	Minimum of 1 per 10 client samples	Recovery = 80-120%; RPD $\leq 20\%$	If RPD $> 20\%$, results must be qualified. If RPD criteria not met, then sample may be reprepared and reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion spike (PDS) can be analyzed to evaluate instrument accuracy and also to determine if matrix interference is occurring at the prep stage or at the analytical stage.
Dilution Test	Check for matrix interference	Minimum of 1 per batch, sample $> 50x LOQ/MRL$	Five-fold dilution must be within $\pm 10\%$ of original result	Perform post-digestion spike addition.
Post-Digestion Spike (PDS)	Check for matrix interference	When dilution test fails or all sample results $< 100x MDL$	Recovery = 75 - 125%	Samples must be analyzed using MSA or apply J qualifier to all samples with same matrix for the specific analyte(s) associated with the post-digestion spike addition.
Laboratory Fortified Blanks (LFB)	Method accuracy	When no suitable CRM available	Recovery = 80 - 120%	If LFB recovery is outside of the control limit, then batch must be reprepared and reanalyzed.
Method of Standard Additions (MSA)	N/A	If post-digestion spike fails	Document use of MSA	N/A
Lab Control Sample (LCS) / Blank Spike (BS)	Method accuracy	One per batch containing all analytes to be reported	QC acceptance criteria specified by DoD, if available. Default of 80-120%	Correct problem and reprepare and reanalyze all samples for failed analytes if available sample mass. If cannot reprepare, then affected results are qualified and explained in the case narrative.
Standard Reference Material (SRM)	Method accuracy	Must be matrix matched to samples; minimum of 1 per batch	Recovery = 75 - 125%, unless limits set by SRM manufacturer are greater	If CRM true value is $\geq 5x$ the PQL and if the recovery is outside of the control limit, then batch must be reprepared and reanalyzed. See comments in section 10.11.

* DoD work at BRL is only reported down to the LOQ.

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Appendix A: Analytical Differences between EPA Methods 1638, 200.8, 6020, and Brooks Rand Labs SOP BR-0060.

EPA Method 1638	EPA Method 200.8	EPA Method 6020	SOP BR-0060
<p>Method is performance based. Modifications are allowed if the laboratory can demonstrate that data quality is not affected. Method is in Draft (unpromulgated) status, and QC criteria are based on a limited set of data.</p>	<p>Method is promulgated and is not performance based.</p>	<p>Method is performance based. Modifications are allowed if the laboratory can demonstrate that data quality is not affected.</p>	<p>SOP is performance based. Modifications are allowed to improve data quality or to make allowances for non-routine samples, but all modifications must be clearly documented.</p>
<p>1.1-1.3 Method is written solely for ambient water samples and for a very limited number of metals (9).</p>	<p>1.1 Method applicable for 21 metals in waters, sludges, and soils. 1.3 Solids preparation involves a HNO₃/HCl digestion on a hotplate.</p>	<p>1.3 Method applicable for 15 metals. A variety of preparation methods are used to most appropriately analyze different metals in waters, sludges, and soils. Preparation methods are documented in their own EPA methods including 3005, 3010, or 3015 for aqueous samples and 3050 or 3051 for solids.</p>	<p>8.1.2 A variety of preparation methods are used to most appropriately analyze different analytes and matrices. Preparation methods are documented in their own SOPs are not a part of this SOP.</p>
<p>7.7 Tuning solution should contain Be, Mg, Co, In, and Pb. Tuning should be performed daily until it's shown that instrument meets the performance criteria without tuning. Tuning solution should be analyzed at least 5 times with RSD of ≤ 10%.</p>	<p>7.7 Tuning solution should contain Be, Mg, Co, In, and Pb. Tuning of instrument is required daily, and tuning report is included with data.</p>	<p>5.8 Tuning solution should contain Li, Co, In, and Tl. Tuning of instrument is required daily, and tuning report is included with data (Resolution < 0.9 amu full width ant 10% peak height.) Tuning solution must be analyzed four times with RSD < 5%.</p>	<p>8.4 Tuning is performed as per the instrument manufacturer recommendations. Tuning solution contains Mg, In, Ce, Pb, and ambient ¹²C and ⁷⁶Ar. Tuning is done at least monthly or as needed. Newer instrument do not require tuning as often.</p>
<p>9.7 Ongoing Precision and Recovery prepared with each batch.</p>	<p>7.9 Laboratory Fortified Blank (blank spike) prepared with each batch.</p>	<p>8.7 A Laboratory Control Sample (LCS) should be prepared and analyzed for each sample batch up to 20 samples or less. 8.8.3 Limits within (+/-) 10%.</p>	<p>8.1.1.5.4 Two Standard reference materials (SRMs) are prepared with each calibration. Additionally, an LFB and CRMs are prepared for solid and seawater matrices.</p>
<p>9.2.4 QCS (2nd source standard) required quarterly.</p>	<p>9.2.3 QCS (2nd source standard) required quarterly.</p>	<p>7.8 ICV (2nd source standard) is required daily. Limits within (+/-) 10%.</p>	<p>10.6 ICV must be analyzed daily.</p>

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EPA Method 1638	EPA Method 200.8	EPA Method 6020	SOP BR-0060
<p>9.6.1 1 or more Laboratory Method Blank (MB) per batch of 20 samples. Blank correction allowed if minimum of 3 blanks are analyzed. Mean MB + 2 SD must be less than the regulatory compliance level.</p>	<p>9.3.1 1 Laboratory Reagent Blank (LRB) per batch of 20 samples. No blank correction performed. LRB must be < 10% of the sample concentration or < 2.2x the MDL.</p>	<p>5.5 One Calibration blank and one preparation blank must be performed. A rinse blank of 2% HNO₃ must be analyzed between every calibration standard and sample. 8.8.4 The calibration blank must be < 3 times the current instrument IDL.</p>	<p>10.8 At least 3 Method Blanks (MB) per batch of samples (up to 60 samples). Blank correction performed. Mean MB must be < PQL with a SD < MDL.</p>
<p>9.3 MS/MSD go through entire preparation as a native sample.</p>	<p>9.4 MS/MSD go through entire preparation as a native sample.</p>	<p>8.6 Post Digestion Spike addition should be 75-125% of the known value or within laboratory derived acceptance criteria. 8.10 Analyze one duplicate sample per batch of 20 samples. RPD < 20%.</p>	<p>8.11.5.7 To estimate appropriate spiking levels of water samples, MS/MSD for water samples are spiked post-digestion. Water samples are digested in their original bottle. For solid samples, MS/MSD go through entire preparation process with native samples.</p>
<p>9.3 If there is no monitoring occurring, spike at 1-5 times the sample concentration or the ML, whichever is higher.</p>	<p>9.4 Spiking levels are set at 40-500 µg/L in water and 50 – 100 mg/kg in solids.</p>	<p>8.6 The Post Digestion Spike addition should be based on the indigenous concentration of the sample.</p>	<p>10.10 Spike at 1-5 times the level of a historical sample of a client, or if unknown, spike 1-5 times a typical value for the matrix. For multi-element analyses, allowances can be made for spiking with mixed standards.</p>
<p>9.6 Field and equipment blanks required.</p>	<p>8.5 Field and equipment blanks required.</p>	<p>Field and equipment blanks are not addressed.</p>	<p>Field and equipment blanks are recommended, but this is not included in the ICP-MS analysis SOP.</p>
<p>10.3 Internal standards include at least 3 of the following analytes: Li⁶, Sc, Y, Rh, In, Tb, Ho, Lu, Bi. Control limits: 60-125%.</p>	<p>10.3 Internal standards include at least 3 of the following analytes: Li⁶, Sc, Y, Rh, In, Tb, Ho, Lu, Bi. Control limits: 60-125%.</p>	<p>3.3 Internal standards include at least 3 of the following analytes: Li⁶, Sc, Y, Rh, In, Tb, Ho, Bi. Control limits: 30-120%. If internal standard fails criteria, reanalyze at a fivefold dilution.</p>	<p>6.6 Internal standards typically used are Li⁶, Sc, Ge, Rh, Tm, Lu, and In. These may be modified for interferences. DRC mode typically uses Ga and Rh as internal standards. Control limits: 60-125%.</p>
<p>10.4 Calibrations are based on the mean of calibration factors with an RPD < 15%.</p>	<p>10.4 At one or more concentration levels, the calibration is determined from an average response of 3 replicate integrations.</p>	<p>7.6 At one or more concentration levels within the linear dynamic range. The calibration is determined from an average response of 3 replicate integrations.</p>	<p>10.4 Calibrations are based on a weighted linear fit with R > 0.995. Control limits: 75-125% for lowest calibration standard; 80-120% for all other calibration points.</p>

EPA Method 1638	EPA Method 200.8	EPA Method 6020	SOP BR-0060
10.5 Calibration verification sample criteria is element specific.	9.3.4 CCVs within 15% of the calibration. 10-15% deviation required recalibration.	8.8.2 – 8.8.3 CCVs are run at beginning, after every 10 analyses, and at end. ICV must be 90-110%.	10.6 & 10.12-13 CCV criterion is within 25% of the calibration for all elements. ICV recovery is within 15% of the expected value. Samples may be CCV-corrected, if appropriate.
12.0 Total dissolved metals analysis requires the addition of HCl.	11.3 Samples with high turbidity requires additional HCl.	5.1 Concentrations of Sb and Ag between 50-500ug/L require 1% HCl for stability.	7.3 All aqueous samples not prepared by reductive precipitation extraction are treated with a nitric acid digestion. No HCl is used.
13.8 Do not perform blank subtraction on sample results.	Blank correction not addressed.	Blank correction not addressed.	Results are routinely instrument and method blank corrected as per standard industry practices.
Interference check solutions not addressed. Sections 4.4.1 & 4.4.2 discuss use of specific isotopes free from isobaric elemental interferences and adjusting the spectrometer resolution to minimize potential wing overlap.	Interference check solutions not addressed. Sections 4.1.1 & 4.1.2 discuss use of specific isotopes free from isobaric elemental interferences and adjusting the spectrometer resolution to minimize potential wing overlap.	5.6 An Interference Check Solution should be analyzed following the calibration, every ten analytical samples and after the last sample.	Tables 12.1 & 12.2 NIST 1640 and NIST 1643e used as interference check solutions. Analyzed with each batch.
9.2.4 MDL should be determined annually, when a new operator begins work or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate.	9.2.1 MDLs should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate.	8.2 IDLs must be determined at least every 3 months and kept with the instrument log book.	MDL annually for waters and biennially for solids or whenever significant modifications made to the instrument or analytical procedure. IDOCs, including all of the elements of an IDL or MDL study, performed for each new analyst prior to analyzing client samples.
Specific dilution tests not discussed.	Specific dilution tests not discussed.	8.5 Dilution test (run at 5x, result 90-110%) required on 5% of samples.	Not routinely done as part of analysis. Is performed upon request.
Post-digestion spikes and MSA curve not discussed.	Post-digestion spikes and MSA curve not discussed.	8.6 Post-digestion spike with recovery of 75-125% required or MSA curve required.	10.12 As per SW-846 Method 6020.
18.15 Defines what a laboratory duplicate is, but the method does not define any requirements for its analysis.	3.7 Defines what a laboratory duplicate is, but the method does not define any requirements for its analysis.	8.10 One matrix dupe (MD) per 20.	10.9 One MD per every 10 samples, RPD ≤ 25% for waters and RPD ≤ 30%.
Table 1.2 Approved elements are Ag, Cd, Cu, Ni, Pb, Sb, Se, Ti, and Zn.	Table 1.1 Approved elements are Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Th, Ti, U, V, and Zn.	Table 1 Approved elements are Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Ti, and Zn.	1.6 Validated for Ag, Al, As, B, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, U, V, & Zn so far.

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SOP #BR-0006

**Procedure for EPA Method 1631, Revision E: Mercury in Water by
Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence
Spectrometry**

Brooks Rand Labs

Revision 004e
Written 05/30/00
Revised 05/24/10

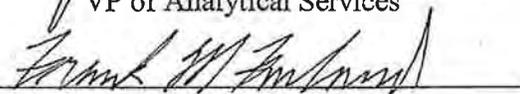
Reviewed _____



VP of Analytical Services

5/24/10

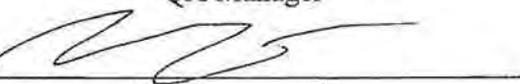
Date



QA Manager

5/24/10

Date



Scientist (if applicable)

5-24-10

Date

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Procedure for EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

1.0. SCOPE AND APPLICATION

1.1. Method BR-0006 is the performance-based procedure followed at Brooks Rand Labs (BRL) as a modification of EPA Method 1631E. BRL has been performing mercury analysis by cold vapor atomic fluorescence since 1989, and during this time has identified several modifications to EPA Method 1631E that improve the quality of the data and the efficiency of the analytical process. These improvements and specific information about the equipment and forms used are detailed within this SOP, following the organizational format of Method 1631E. Unless specifically stated otherwise in this document, all apparatus, materials, reagents, standards, and procedures as stated in EPA Method 1631E are used at BRL.

1.2. Though EPA Method 1631E was written specifically for water samples, this method may be modified, as described in this SOP, for the analysis of many types of aqueous samples, including (but not limited to) chemicals, wastes, and biomonitoring samples (urine and plasma).

2.0. SUMMARY OF METHOD

2.1. Prior to instrumental analysis, the aqueous samples must be prepared according to the procedure discussed in EPA Method 1631E.

2.2. Refer to EPA Method 1631E, section 2.0, for the summary of the method employed at Brooks Rand Labs.

2.3. Refer to the Appendix at the end of this document for a summary of differences between EPA Method 1631, Revision E, and BRL SOP #BR-0006.

3.0. DEFINITIONS

3.1. A partial list of definitions is presented below. Most definitions can be found for specific terms in the sections where they are first mentioned. Many of the definitions mentioned in this method are based on those found in the glossary for EPA Method 1631E. Please refer directly to this method for a more detailed list.

3.2. May: This action is allowed, but not required.

3.3. May Not: This action is prohibited.

3.4. Must: This action is required.

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3.5. Shall: This action is required.

3.6. Should: This action is suggested, but is not required.

4.0. CONTAMINATION AND INTERFERENCES

4.1. Refer to EPA Method 1631E, section 4.0, for a detailed account of possible contamination routes and interferences that may be encountered during the analysis, and descriptions of how these may be avoided or minimized at BRL.

5.0. SAFETY

5.1. Refer to EPA Method 1631E, section 5.0, for safety issues associated with the use of this method.

5.2. Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of this, only highly trained personnel familiar with the dangers and precautions to take when working with mercury compounds should ever handle standards and/or high level samples.

5.3. Material safety data sheets (MSDSs) are maintained for all chemicals used in this method. The MSDS sheets are stored in the sample receiving laboratory in appropriately marked binders.

5.4. Refer to the latest revision of the Chemical Hygiene Plan (CHP) for additional safety precautions and required protective equipment.

6.0. APPARATUS AND MATERIALS

6.1. Refer to EPA Method 1631E, section 6.0, for a list of materials used in this method.

6.2. Routine preventative maintenance for the equipment used in this procedure is described in detail in the standard operating procedure BR-1205 (Preventative Maintenance).

6.3. Detailed instructions for the decontamination of bottles and other equipment are described in BRL SOPs #BR-0400 (Decontamination of Sampling Containers) and #BR-0404 (Preventing Mercury Contamination of Samples).

6.4. Specific equipment used at BRL is listed below. Any modifications to EPA Method 1631E are described and explained.

6.4.1. Brooks Rand Labs Model III Atomic Fluorescence Spectrophotometer (BRL part #07002): To achieve the low detection levels and small, interference-free sample aliquots claimed by this method, a very sensitive CVAFS detector is required. Such systems are built at BRL (Model III) based on the principals discussed in the literature. Refer to the “Brooks Rand LLC Model III Operations Manual” for instrument operating instructions. [REDACTED]

6.4.2. Brooks Rand Labs Amalgamation Control Module (BRL part #02100): Controls the heating of the gold-coated sand traps [REDACTED] and then the cooling of the traps following desorption of Hg from the trap.

6.4.3. Brooks Rand Labs flow meter/needle valve (BRL part #08510): Capable of controlling and measuring gas flow to the purge vessel at 200-500 mL·min⁻¹.

6.4.4. Teflon[®] adapters (BRL part #08401 through #08404) and tubing (BRL part #08405 through #08407): Connections between components and traps are made using 3.2-mm OD pre-cleaned Teflon[®] FEP tubing and Teflon[®] friction-fit or threaded tubing connectors.

6.4.5. Soda lime pre-trap (BRL part #03410): For preventing acid-fumes and moisture from degrading the gold-coated sand or gold wire traps. A 10 cm x 0.9 cm (diameter) Teflon[®] tube containing 2-3 grams of commercially available reagent grade, non-indicating, [REDACTED] soda lime chunks, packed in between plugs of silanized glass wool. This trap is purged of Hg by placing it on the output of a clean cold vapor generator, partially filled with deionized water (DIW) and [REDACTED] stannous chloride (SnCl₂), and purging [REDACTED] with nitrogen (N₂) at [REDACTED]. Bubbler blanks are analyzed first so that any indication of unclean pre-traps would be evident immediately.

6.4.6. Cold vapor generator (BRL part #03200): A 220-mL flask with a standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the flask bottom.

6.4.7. Teflon[®] split bottle: Used for measurement and pre-reduction of original oxidized samples prior to analysis. A 125-mL blank tested Teflon[®] bottle with a unique identifier is permanently associated with a corresponding cold vapor generator.

6.4.8. Gold wire traps or gold-coated sand traps (BRL part #03010 or #03020): Used for trapping gaseous elemental mercury. Gold-coated sand traps made with gold-coated [REDACTED] quartz sand are used to analyze water samples. Both gold-coated sand traps and gold wire traps are used to analyze air samples. [REDACTED]

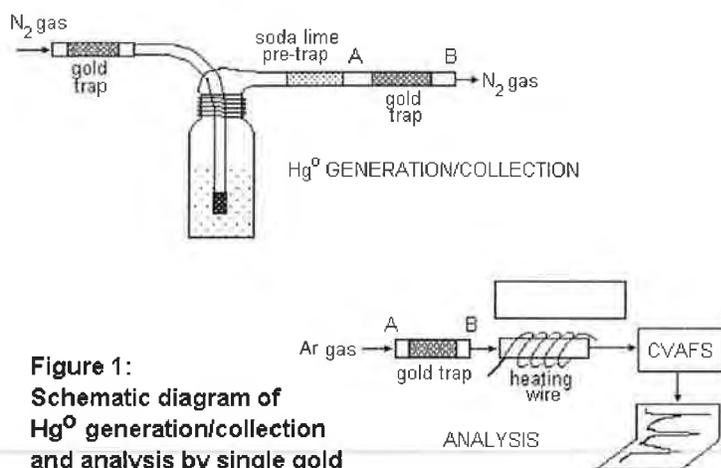


Figure 1:
Schematic diagram of
Hg⁰ generation/collectio
and analysis by single gold
amalgamation/CVAFS

6.4.9. Recorder: BRL uses direct data acquisition with the BRL Guru integration software instead of a chart recorder or integrator as described in EPA Method 1631E, section 6.6. The BRL Model III comes complete with the Hg Guru™ integrating software. Refer to the “Brooks Rand LLC Model III Operations Manual” for Hg Guru™ software/integrator operating instructions. Hg Guru™ software requires an IBM compatible computer (minimum requirements are a Pentium II® processor running at 400 MHz, a CD-ROM Drive, 128 MB RAM, and 50 MB free space on the hard-drive) and runs MS Windows® 98 or higher. Use of this integration software is faster, eliminates the expense of chart recorders and/or integrators, allows for storage of data in diskette form, and eliminates possible transcription errors.

6.4.10. Pipettes: All plastic pneumatic fixed volume and variable pipettes in the range of 10 µL to 5.0 mL.

6.4.11. Sampling Bottles: BRL uses clean and blank tested glass and fluoropolymer lined (FLPE) bottles for sample collection and preparation. For further information on the cleaning (or decontamination) and testing of bottles refer to SOP #BR-0400.

6.4.12. Nichrome wire coil (BRL part #08300) with plug (#08301): Used for heating the gold trap to thermally desorb the mercury.

7.0. REAGENTS AND STANDARDS

7.1. Water: Reagent water is monitored for Hg on a daily basis when calibration blanks are analyzed. A minimum of four 100 mL aliquot of fresh reagent water, each with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and SnCl_2 , are analyzed at the beginning of the run sequence. The average results must be < 20 pg Hg with a standard deviation < 7.5 pg Hg. A high level of mercury detected in the reagent water analysis may also be attributed to the bubbler itself, the SnCl_2 , or the soda lime pre-traps. Regardless of the source, all analysis is stopped until the source of contamination is determined and the problem is corrected. The results are stored with each batch.

7.2. Air: It is vital that the laboratory air be low in both particulate and gaseous mercury in order to reduce the risk of contamination. The BRL sample preparation lab clean room is equipped with a laminar flow hood that provides incoming air to the lab. Outside air, which is very low in Hg, is filtered through a particulate filter and then through HEPA filters before entering the mercury lab. Positive pressure is maintained to ensure that there is no incoming air through routes other than the laminar flow hoods. Sticky mats are located at the entrance as an additional precautionary measure. The mercury lab, the sample preparation lab, and the shipping and receiving area are monitored monthly for atmospheric mercury levels to ensure that these levels are sufficiently low for ultra-trace level mercury analysis. Air from each lab is pumped through a soda lime pre-trap and onto either a gold wire or gold-coated sand trap at a flow rate of 1 L/min until at least 20 L of air have been collected per trap. A warning level has been established at 15 ng Hg/m³ with a shutdown control level at 25 ng Hg/m³. Results from the monthly air tests are stored electronically on the BRL computer server.

7.3. Hydrochloric acid: Trace-metal purified reagent HCl is purchased and analyzed for Hg before use. In general, it is possible to obtain acid containing less than 5 pg/mL Hg. When a lot number meeting this specification is found, several cases are purchased. Generally, lower values can be obtained in this manner than by re-distilling acid in the laboratory. Only "trace-metal" grade acid should be used. Acids labeled as "ULTRA-PURIFIED" have historically had higher concentrations of mercury and should be avoided. All open cases of acids for trace metal work are stored in the locked storage area located in the north mezzanine level of the building.

7.4. Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), stannous chloride (SnCl_2), and bromine monochloride (BrCl): Each of these reagents is prepared according to instructions listed in section 7.0 of Method 1631E. Reagent blanks must be analyzed each time that BrCl is made anew. The SnCl_2 and $\text{NH}_2\text{OH}\cdot\text{HCl}$ are tested daily whenever calibration blanks are analyzed.

Note: BrCl is tested whenever a new bottle is prepared prior to use with samples. During initial testing, reagent blanks are prepared in fluorinated polyethylene (FLPE) bottles at five different concentrations of BrCl (1.0%, 2.0%, 5.0%, and 10%). The BrCl is prereduced in the split bottle and then added to the bubbler with stannous chloride. A linear regression is performed to determine the level of contamination due to the bottles ($b = y$ intercept) and the true

concentration of Hg in the reagents. The acceptance criterion for the linear regression is an r^2 value ≤ 0.9 (If 2 or more of the points are less than the low standard, 25 pg Hg, then r^2 criteria may not be relevant and the lot of BrCl must be approved by QA). The amount of Hg per reagent unit (reagents used in a 1.0% BrCl method blank) must be ≤ 20 pg. If BrCl is prepared using the same lot of KBr and $KBrO_3$ as a lot of BrCl already tested for linearity, then only two reagent blanks need be made at 10% BrCl to ensure the continued purity of the reagents. All lots of HCl are pretested and must already be shown to be pure prior to any use in reagents. As such, linearity testing of new BrCl is not required if only the HCl lot has changed.

7.5. Stock mercury standard: A commercially available 1000 $\mu\text{g/mL}$ mercury standard that is traceable to NIST is used. This stock standard should be replaced by the manufacturer's expiration date.

7.6. Intermediate mercury standard solution: 0.100 mL of the stock solution is diluted to 100.0 mL with DIW containing 2.0 mL of BrCl. This solution contains 1000 ng/mL Hg, and must be kept refrigerated in a tightly closed Teflon[®] bottle. This solution should be replaced annually.

7.7. Mercury working standards: 2.50 mL of the intermediate mercury standard solution is diluted to 250 mL with high purity water containing 2.50 mL BrCl solution, to make a 10.0 ng/mL working solution (as discussed in EPA Method 1631E, section 7.9). A 1.00 ng/mL working standard should be made by diluting 0.250 mL of the intermediate mercury standard to 250 mL with DIW containing 2.50 mL BrCl solution. These working standards of 10.0 ng/mL and 1.00 ng/mL are added in appropriate aliquots to reagent water and analyzed to create the calibration curve and CCV samples.

7.8. Independent Calibration Verification (ICV) Standard: 0.250 mL of the standard reference material (SRM) NIST 1641d (mercury in water) is added 247.25 mL DIW and 2.5 mL BrCl for a final volume of 250 mL. After adjusting for the density of the SRM, the final value for this standard is 16.01 ng/L. NIST 1641d is purchased directly from the National Institute of Standards and Technology.

7.9. Nitrogen: Grade 4.8 (99.999% purity) minimum nitrogen that has been further purified by the removal of Hg using a gold coated sand trap.

7.10. Helium or Argon: Grade 4.8 (99.999% purity) minimum inert gas which has been further purified by the removal of Hg using a gold-coated sand trap.

8.0. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1. Refer to EPA Method 1631E, section 8.0, and EPA Method 1669 (*Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels*) for a detailed description of sample collection, preservation, and storage methods.

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9.0. QUALITY CONTROL

9.1. Refer to EPA Method 1631E, section 9.0, for a detailed description of the quality control procedures employed at BRL for this method. Consult Section 18 of this SOP for the current MDL (method detection limit) and ML (minimum limit) determined at BRL for the analysis of mercury using Method 1631E (Table 1). The ML is sometimes referred to as the method reporting limit (MRL). Acceptance criteria and corrective action procedures are listed in Table 2.

9.2. All quality control data should be maintained and available for easy reference and/or inspection.

9.3. Samples containing high analyte concentrations should be analyzed at a reduced volume. For all quantified results, peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed and above the peak area obtained from the lowest standard analyzed in the calibration curve.

9.4. Analysts who have not performed EPA Method 1631E previously at BRL must complete an initial demonstration of capability (IDOC) study, which includes the analysis of samples for MDL determination. Refer to Table 3 in Section 18 of this SOP for the general analytical sequence for the IDOC.

9.5. When analyzing client samples, BRL will follow the general analytical sequence found in Table 4 of Section 18 of this SOP. Note that in order to avoid potential carryover from high-level samples, samples projected to have only low levels of mercury (field blanks, method blanks, and samples otherwise expected to be low based on historical data or small amounts of particulate matter) should be analyzed at the beginning of the run sequence. Although EPA Method 1631E suggests (in section 9.1.7) that method blanks may be analyzed intermittently throughout the analysis, BRL analysts should analyze all method blanks at the beginning to avoid potential carryover and to verify that all method blanks meet criteria before proceeding with sample analysis. In addition, whereas Method 1631E only requires analysis of two CCV samples (at the start and at the end of the run sequence), it is BRL policy to run additional CCV samples (one after every 10 client samples) to ensure ongoing control of the system.

9.6. EPA Method 1631E states that spiking levels of the MS/MSD shall be equal to the regulatory compliance limit or 1-5 times the background concentration of the sample, whichever is greater. This is achieved in aqueous samples at BRL by analyzing the sample to be spiked prior to the addition of the spiking solution.

9.7. A minimum of 3 method blanks per batch of 20 client samples must be run. Method blanks must be prepared with the same lot of BrCl used to prepare the samples. [REDACTED]

[REDACTED] Brooks Rand routinely prepares and analyzes 4 method blanks to allow for the possible outlier.

10.0. CALIBRATION AND STANDARDIZATION

10.1. Refer to EPA Method 1631E, section 10.0, for a detailed description of instrument calibration.

10.2. Instrument Calibration: BRL has adopted the following procedure.

10.1.1. The mercury analyzers built and used at BRL are capable of achieving extremely low detection limits. As such, BRL calibrates its instruments down to 25 pg. The standards typically used to calibrate the instruments for total mercury at BRL are 25 pg, 100 pg, 500 pg, 2500 pg, and 10,000 pg. The standards are added to the split bottle, pre-reduced with $\text{NH}_2\text{OH}\cdot\text{HCl}$, and then poured into the bubbler. The calibration is based on the measured picograms of mercury in the bubbler and not on concentration.

10.2.2. Sections 9.0 and 10.0 of EPA Method 1631E do not state a frequency requirement for calibration. BRL performs a new calibration each day and whenever CCV recovery fails to meet the acceptance criteria as outlined in Method 1631E, Table 2. Additionally, analysis of the ICV standard must also meet the criterion in Table 2 for the calibration to be validated.

10.2.3. Section 9.4.1.3 of EPA Method 1631E suggests that the mean peak area for all bubbler blanks (including those analyzed during the analytical sequence to ensure that no carryover occurs from high-level samples) should be subtracted from all raw data before results are calculated. This does not allow for the continuous determination of whether QA results are in control, thereby forcing the analyst to analyze all samples prior to determining if all QA criteria are met. BRL subtracts the average peak area measurement of the first four bubbler blanks (or one blank for each split bottle and bubbler used in the analysis of samples) analyzed at the beginning of the analytical run from all raw data for result calculations. The acceptance criterion for the initial bubbler blanks (referred to as calibration blanks) is each ≤ 40 pg, average ≤ 20 pg, and standard deviation ≤ 7.5 pg. The criterion for subsequent bubbler blank checks is that each blank must be ≤ 40 pg and ± 20 pg from the calibration blank mean.

10.2.4. BRL uses the following equation to calculate the calibration factor (CF_x) for Hg in each of the standards:

$$\text{CF}_x = (C_x) / (A_x - A_{\text{CB}})$$

Where:

C_x = mass of Hg in standard analyzed (pg)

A_x = peak area for Hg in standard

A_{CB} = mean peak area for Hg in calibration blanks

This calculation differs from the calculation given in 1631E in that the numerator and denominator are reversed.

11.0. PROCEDURE

11.1. Sample Preparation: Refer to EPA Method 1631E, section 11.0, for more detailed guidelines regarding sample preparation and analysis. Practices employed specifically by BRL are outlined below and in the appendix to this SOP.

11.1.1. Four method blanks are prepared with each batch of samples. All method blanks are preserved to [REDACTED] BrCl. This is allowable because BRL tests each new batch of BrCl made to prove that it maintains linearity with increased concentration.

11.1.2. The samples are then preserved to a percentage of BrCl that is dependant upon amount of particulate in sample. A clear sample would get [REDACTED] BrCl; a fairly clear sample with some particulate would get [REDACTED] BrCl; a sample with lots of particulate would get [REDACTED]. If a sample has a yellow tinge to it, an amber sticker is placed on top of the bottle to indicate that the coloration is due to the matrix and not necessarily due to any BrCl added to the sample during preparation. After the addition of BrCl, the samples are left to oxidize for at least 24 hours.

NOTE: [REDACTED]

11.1.3. After a minimum of 24 hours, a 24 hour check is performed. The 24 hour check consists of looking at each sample individually to check that the sample is still yellow, which indicates the BrCl was added in excess. Any sample that is suspected of not having excess BrCl, or a sample with an amber sticker on top is tested with starch iodide indicator paper. If the paper turns purple, then the sample is presumed to be adequately preserved. If the paper stays white, more BrCl is added to the sample. If additional BrCl was added to any of the samples in a batch, a subsequent 24 hour check is required. If a batch is to be analyzed within less than 24 hours from prep, it should be heated for 4 hours at 65 °C and the "24 hour" check should be performed prior to analysis.

11.1.4. Urine samples should be oxidized with [REDACTED] BrCl by default. They must be checked for excess BrCl using starch iodide paper as the BrCl color will be indistinguishable from the color of the urine itself.

11.2. Instrumental Analysis: BRL has adopted the following modifications from EPA Method 1631E.

11.2.1. Samples and standards are purged [REDACTED]

[REDACTED]

11.2.2. Four 100-mL aliquots of water are poured into each of the bubblers prior to calibration. [REDACTED] of SnCl_2 is added to each bubbler and the aliquots are used to condition the soda-lime pre-traps [REDACTED], as noted in 6.4.4 of this SOP. Following this pre-trap conditioning step, the purged water is discarded and 100 mL aliquots of DIW along with [REDACTED] $\text{NH}_2\text{OH}\cdot\text{HCl}$ are poured from the four split bottles into their associated bubblers. [REDACTED] SnCl_2 is added to this water, which is then purged [REDACTED] onto a gold amalgamation trap and analyzed for Hg. A high level of mercury in the calibration blanks may be attributed to the split bottle, the bubbler, the reagents, or the soda lime pre-traps. Regardless of the source, all analysis using the contaminated bubbler/split bottle/trap combination is stopped until the source of contamination is determined and the problem is corrected. Use of all uncontaminated bubblers, split bottles, and traps may continue during this process.

11.2.3. All calibration standards and QC samples are added to 100 mL aliquots of DIW in a thoroughly rinsed split bottle prior to transfer to a bubbler for analysis.

11.2.4. Aliquots of the original oxidized sample of approximately 100 mL are weighed into split bottles. [REDACTED] $\text{NH}_2\text{OH}\cdot\text{HCl}$ is added directly to the split bottle and allowed to react [REDACTED] prior to transfer to the bubbler for purging onto a gold amalgamation trap for analysis. Split bottles and bubblers are rinsed a minimum of three times with DIW in between sample aliquots.

11.2.5. Urine samples should be pipetted into split bottles, as the density of urine is not equivalent to the density of water. A maximum of 25 mL will be used (giving an MRL/MDL 4x higher than for water samples). Urine samples can be analyzed in the same batch as water samples but must have QC performed on at least 1 urine sample.

11.2.6. As discussed in Method 1631E and in section 9.4 of this SOP, follow the attached analytical sequence (Table 4). Generally, analysts should follow the suggestion in Method 1631E that samples suspected to contain the lowest concentration of mercury (i.e., known blank samples) should be analyzed first followed by samples containing potentially higher levels (i.e., known influent samples).

11.2.7. As discussed in section 9.4 of this SOP, the analyst may choose to analyze CCV samples more frequently than required by Method 1631E. A CCV must be analyzed after every 10 client samples (not counting quality control samples) to verify ongoing control of the system.

11.2.8. The PMT and offset are recorded on the bench sheet at the beginning of each day after auto zeroing the instrument previous to measuring the noise. [REDACTED]



11.2.9. BRL has found that checking for mercury carryover in a bubbler by analyzing a bubbler blank is not necessary unless an unusually high level sample has been purged. Carryover tests, performed using spikes of 10,000 pg, 20,000 pg, 40,000 pg, and 100,000 pg, resulted in carryover of less than 50 pg Hg from the bubbler and trap. To avoid carryover from the bubbler or split bottle, the analyst should rinse each bubbler and split bottle three times with DIW between all samples. To avoid carryover from the trap, the analyst should heat the mid- and downstream sections of any traps associated with a higher-level sample (such as any sample above the calibration range) for an additional 3 minutes following sample desorption. If a purged sample contains > 20,000 pg Hg, the analyst must follow the above corrective actions and analyze a bubbler blank and split bottle blank check using fresh DIW and the associated bubbler, split bottle and trap. The analysis of the split bottle blank should be performed on a different bubbler to facilitate proper contamination identification. Using previously purged DIW is not necessary for the bubbler blank. If any bubbler or split bottle blank fails (> 40 pg Hg and/or > \pm 20 pg from average calibration blank on associated bubbler and trap), the analyst must identify and correct the source of contamination, and demonstrate that the bubbler and trap pass the blank criterion before sample analysis can continue using that bubbler, split bottle, and trap.

11.2.10. Any samples run in a bubbler, split bottle and/or on a trap associated with a carryover sample (e.g., a sample with > 20,000 pg Hg) must be reanalyzed, if sufficient sample volume exists.

11.2.11. After analysis is complete, split bottles and bubblers are rinsed with DIW three times and filled with DIW.



11.3. Gold traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling trap will become damaged, giving low and/or irreproducible results. Suspect traps should be checked with at least two consecutive standard runs before continued use. Traps should be replaced quarterly or as soon as possible after quality control results indicate their

degradation. Additionally, traps should be replaced whenever integration peaks become abnormally shaped (no longer symmetrical with steep slopes).

11.4. Section 11.3.2 of Method 1631E states that before each trap is analyzed, argon should be passed through the trap for approximately two minutes to drive off condensed water vapor prior to heating and desorbing for three minutes. Historically, BRL has not experienced significant analytical problems associated with water vapor on traps. However, if the analyst observes peaks that desorb prior to the mercury peak, this technique may be employed.

12.0. DATA ANALYSIS AND CALCULATIONS

12.1. The following equations are used at BRL to calculate sample results.

12.2. To calculate the amount of mercury measured during an analytical run (P), employ the following formula:

$$P = \text{Hg (pg)} = CF_m (A_S - A_{CB})$$

Where:

CF_m = mean calibration factor

A_S = gross peak area measured in sample analysis

A_{CB} = mean peak area for Hg in calibration bubbler blanks

12.3. To determine the concentration of total mercury in a sample, the calculation is performed as follows:

$$\text{Hg (in ng/L or ppt)} = \{[(P/V_A) * V_D] - MB\} / V_O$$

Where:

P = Hg (pg) from equation in section 12.2

V_A = volume (mL) of the sample preparation that was analyzed

V_D = final dilution volume (mL) of the sample preparation

V_O = volume (mL) of the original sample used in the preparation

MB = multiple of the average result (in total pg Hg) for the 0.5% BrCl method blanks.

Note: The multiplier of the average [REDACTED] BrCl method blank result is based on the concentration of BrCl in the prepared sample. [REDACTED]

This is only allowed if the linear regression yielded by the initial reagent blank testing as described in Section 7.4 of this SOP yields the following: $r^2 \geq 0.9$ and $b \leq 0.2$ ng/L. Otherwise, method blanks must be prepared at each of the BrCl concentrations used to prepare the samples. (These

criteria do not apply if the reagent blank units are less than 1 pg since all of the method blank testing results for the different BrCl concentrations would be below the MDL.)

12.4. It is BRL's policy to method blank correct sample results unless specifically requested not to do so by the client.

12.5. Method 1631E states that results below the ML should be reported as less than the level of the ML or as required by the regulatory authority, and that field blank results below the ML but above the MDL should be reported to 2 significant digits. Because BRL is not always aware of the original source of a sample or the specific needs or requirements of our clients, all results above the BRL determined MDL are reported to 3 significant digits.

13.0. METHOD PERFORMANCE

13.1. Refer to EPA Method 1631E, section 13.0, for information regarding the verification of this method.

13.2. The detection limits reported in Table 1 were achieved by performing a full MDL study as described in 40 CFR 136, Appendix B. The quality control acceptance limits reported in Table 2 are developed from the EPA methods and are validated as achievable at BRL in the control charts maintained for the method.

14.0. POLLUTION PREVENTION

14.1 Refer to EPA Method 1631E, section 14.0, for EPA recommendations regarding pollution prevention techniques.

14.2 Whenever feasible, lab personnel should use pollution prevention techniques to limit waste generation. The cost involved in purifying acids makes such recycling unpractical at BRL. Instead, every effort is made to reduce volumes necessary to still produce the best possible results. This analysis requires small amounts of acid to be used in the preparation of the samples [REDACTED]. When making standards, they should be prepared in volumes consistent with their use in the laboratory to minimize the volume of expired standards to be disposed.

15.0. WASTE MANAGEMENT

15.1. Refer to EPA Method 1631E, section 15.0, for information and references related to managing waste produced by application of this method.

15.2. All waste is disposed of in accordance with state and federal regulations either by sewer disposal (only if concentrations are below the King County sewer limits) or through a licensed and bonded hazardous waste disposal facility such as Philips Services.

16.0. REFERENCES

- 16.1. EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, August 2002 (including references cited in section 16.0).
- 16.2. Model III (CVAFS Mercury Analyzer) Operating Manual, September 2004. Brooks Rand LLC, 3958 6th Ave NW, Seattle, WA.
- 16.3. EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, July 1996.

17.0. GLOSSARY

17.1. Refer to EPA Method 1631E, section 17.0, for additional definitions of terms used throughout the text of 1631E.

18.0. FIGURES (1631E), TABLES, AND BENCHSHEETS

18.1. BRL has adopted the following modifications to the figures illustrated in EPA Method 1631E, section 18.0.

18.1.1. Figure 1: Schematic Diagram of Bubbler Setup and Figure 2: Schematic Diagram of the Bubbler, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System. Instead of the setup shown in these figures, BRL uses the setup illustrated in Figure 1 of this document, BR-0006, Section 6.3.6.

18.1.2. Figure 3: Schematic Diagram of the Flow-Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System. This system is not employed by BRL.

Table 1. Current Method Detection Limits and Minimum Levels Determined at Brooks Rand Labs for the Analysis of Total Mercury in Water Using EPA Method 1631

Matrix	Preparation Method	Method Detection Limit (MDL)¹	Minimum Level (ML)²
Water	Digestion	0.15 ng/L	0.40 ng/L

NOTES:

1. MDL as determined by the procedure 40 CFR Part 136, Appendix B. MDL and ML reported here are for method blank corrected results.
2. At BRL the ML is often referred to as the method reporting limit (MRL).

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Table 2. Quality Control Criteria and Corrective Action Procedures for the Analysis of Total Mercury by CVAFS

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Calibration Blanks / Bubbler Blank	Contamination from split bottles / bubblers	1 per split bottle / bubbler used	each ≤ 40 pg avg ≤ 20 pg std ≤ 7.5 pg	Clean and test split bottles / bubblers until criteria met prior to any further analysis
Calibration Standards	Acceptability of the calibration curve	Daily (first batch of the day) or when ICV/CCV fail	RSD of response factors $\leq 15\%$; Recovery of Low Standard = 80 – 120%	Reanalyze suspect calib stand w/diff trap/bubbler. If criteria still not met, then remake standards and recalibrate the instrument.
Continuing Calibration Verification (CCV)	Accuracy	1 immediately after calibration followed by 1 every 10 samples and 1 at the end of each batch)	Recovery = 77 – 123%	Correct problem and reanalyze CCV. If criteria met, reanalyze samples backwards until 2 consecutive results w/RPD $\leq 20\%$. Otherwise, recalibrate system.
Carryover Check Bubbler Blank	Contamination due to carryover in the bubbler/trap	Perform on same bubbler/trap combination following any measured result $\geq 20,000$ pg	≤ 40 pg (within ± 20 pg of avg bubbler blank before used for additional analyses)	Remake and condition the soda-lime trap. Clean and continue to test bubbler/trap combo until criteria met prior to further use. Samples analyzed using same bubbler and/or trap following a result $\geq 20,000$ pg must be reanalyzed.
Method Blank ( BrCl in reagent water)	Contamination from reagents, lab ware, etc.	3 per batch	Each MB ≤ 0.5 ng/L and StDev $\leq 2/3$ the MDL or highest MB < 0.1 times the lowest reported result.	Correct problem until criteria met. All samples affected by high method blanks (sample $< 10x$ the highest MB) must be qualified accordingly.
Independent Calibration Verification (ICV)	Independent check of system performance	1 per batch	Recovery = 85 – 115%	Correct problem prior to continuing analysis. Otherwise, recalibrate system.
Matrix Spike / Matrix Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Recovery = 71 – 125%; RPD $\leq 24\%$	If recoveries similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If RPD criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicate	Precision within a given matrix	As per client request	RPD $\leq 24\%$ or if results $< 5x$ the MRL then \pm the MRL of one another	If RPD criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.

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Table 3. Quality Control Acceptance Criteria and General Analytical Run Sequence for the Initial Demonstration of Capability for the Analysis of Total Mercury.

Run	Run Name	Section Name	Analyze	Requirements
1	CB	Calibration	Split bottle blank	< 40 pg; ave. < 20 pg; stdev < 7.5 pg
2	CB		Split bottle blank	
3	CB		Split bottle blank	
4	CB		Split bottle blank	
5	25 pg std	Calibration	25 pg Hg	RSD of CF < 15%; recovery of low standard = 80-120%
6	100 pg std		100 pg Hg	
7	500 pg std		500 pg Hg	
8	2500 pg std		2500 pg Hg	
9	10000 pg std		10000 pg Hg	
10	IPR std (500 pg)	Initial Precision and Recovery	500 pg Hg	Ave. recovery 79-121%, RSD < 21%
11	IPR std (500 pg)		500 pg Hg	
12	IPR std (500 pg)		500 pg Hg	
13	IPR std (500 pg)		500 pg Hg	
14	Method Blank	Method Blanks for MDL	Method blanks prepared at same BrCl level as MDL samples	Each ≤ 0.5 ng/L StDev ≤ 0.07 ng/L
15	Method Blank			
16	Method Blank			
17	Method Blank			
18	MDL sample	Method Detection Limit	DIW + 0.1-0.5 ng/L	MDL ≤ 0.1 ng/L
19	MDL sample		DIW + 0.1-0.5 ng/L	
20	MDL sample		DIW + 0.1-0.5 ng/L	
21	MDL sample		DIW + 0.1-0.5 ng/L	
22	MDL sample		DIW + 0.1-0.5 ng/L	
23	MDL sample		DIW + 0.1-0.5 ng/L	
24	MDL sample		DIW + 0.1-0.5 ng/L	
25	CCV (500pg std)	Continuing Calibration Verification	500 pg Hg	Recovery 77-123%

Notes

1. All standards and samples are corrected for mean calibration blank.
2. All samples are corrected for mean method blank.

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Table 4. Quality Control Acceptance Criteria and General Analytical Run Sequence for the Analysis of Total Mercury.

Run	Run Name	Section Name	Analyze	Requirements
1	CB	Calibration Blanks	Split bottle blank	Each < 40 pg; Ave. < 20 pg; StDev < 7.5 pg
2	CB		Split bottle blank	
3	CB		Split bottle blank	
4	CB		Split bottle blank	
5	25 pg std	Calibration	25 pg Hg	StDev < 15% of Ave. RF Recovery of 25 pg std = 80-120%
6	100 pg std		100 pg Hg	
7	500 pg std		500 pg Hg	
8	2500 pg std		2500 pg Hg	
9	10000 pg std		10000 pg Hg	
10	ICV (1000pg std)	Independent Calibration Verification	1000 pg (different standard)	Recovery 85-115%
11	CCV (500pg std)	Continuing Calibration Verification	500 pg Hg	Recovery 77-123%
12	Method Blank 01	Method Blank	BrCl MB	All MB ≤ 0.5 ng/L
13	CCB	Continuing Calibration Blank	Same split bottle and bubbler associated w/the 10000 pg std.	< 40 pg and within ± 20 pg of the average CB
14	Method Blank 02	Method Blank	BrCl MB	Each ≤ 0.5 ng/L StDev ≤ 0.07 ng/L
15	Method Blank 03		BrCl MB	
16	Method Blank 04		BrCl MB	
Next	Field, Equipment, or Bottle Blanks	Field, Equipment, or Bottle Blanks	Field, Equipment, or Bottle Blanks	< ML or < 1/5 th of associated sample conc.
Next	1 st Half of Samples (including MS1 and MSD1)	Sample Analyses Matrix Spike Matrix Spike Duplicate	Sample X X + spike X + dup. Spike Other Samples	Recovery 71-125%; RPD < 24% Recovery 71-125%; RPD < 24%
Next	CCV (500pg std)	Continuing Calibration Verification	5.0 ng/L	Recovery 77-123%
Next	2 nd Half of Samples (including MS2 and MSD2)	Sample Analyses Matrix Spike Matrix Spike Duplicate	Sample Y Y + spike Y + dup. Spike Other Samples	Recovery 71-125%; RPD < 24% Recovery 71-125%; RPD < 24%
Last	CCV (500pg std)	Continuing Calibration Verification	500 pg Hg	Recovery 77-123%

Notes

- All standards and samples are corrected for mean calibration blank.
- All samples prepared with one level of BrCl are corrected by multiplication of the BrCl MB result by the factor required to produce a result equivalent to that of the BrCl level used to oxidize the sample.
- Field and equipment blanks are only analyzed if provided by clients. Bottle blanks are analyzed for the bottles provided by Brooks Rand Labs.
- A carry-over blank is run following any high-level sample (≥20,000 pg measured). The carry-over blank is analyzed using the same split bottle, bubbler, and trap associated with the high-level sample.
- Field blanks and other potentially low-level samples should be analyzed at the beginning of the analytical run; samples suspected to contain comparatively high levels of mercury should be run at the end of the sequence.
- Reagent blanks must be analyzed when new BrCl is made and must average less than 20 pg of Hg per blank unit.
- Equipment blanks are analyzed only on a project-specific basis.

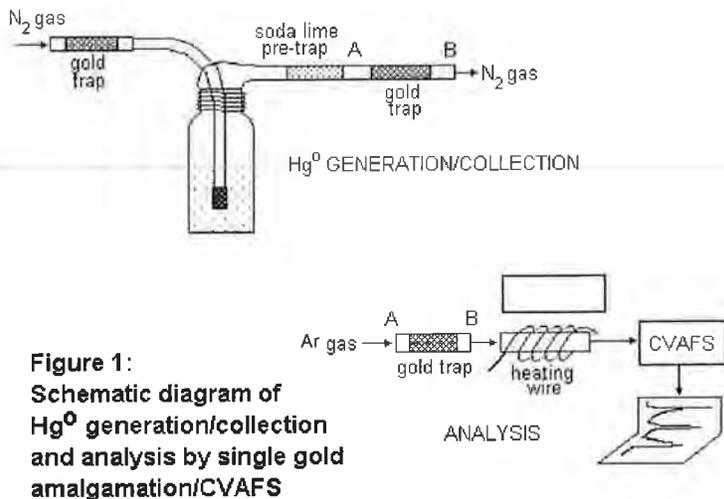
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Appendix to Brooks Rand Labs Procedure for EPA Method 1631, Revision E (02/05)

Differences between EPA Method 1631, Revision E, and Brooks Rand Labs SOP #BR-0006

The following differences exist between EPA Method 1631, Revision E (with relevant sections marked in boldface), and the practices employed by Brooks Rand Labs (SOP #BR-0006):

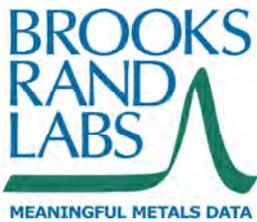
- **Figures 1 and 2** (referenced within **sections 2.6 and 2.7**) give schematic diagrams of the bubbler, purge and trap, CVAFS analytical system. In contrast, Brooks Rand Labs (BRL) purges samples with nitrogen in bubblers onto sample traps. After samples are purged, the sample traps are disconnected from the bubbler system and desorbed using argon, as shown below:



- **Section 6.4.3** specifies the use of acid fume pretraps consisting of 8-14 mesh soda lime chunks and which are purged for 1 hour with nitrogen. BRL uses pretraps consisting of [REDACTED] soda lime chunks and which are purged [REDACTED] with nitrogen.
- **Section 6.5** discusses the use of a dual-trap Hg(0) pre-concentration system. In contrast, BRL uses a single trap pre-concentration system. This allows for shorter analysis times without masking of potential problems on the sample collection trap.
- BRL uses direct data acquisition with the BRL “Hg Guru” integration software instead of a chart recorder or integrator as described in **section 6.6**.
- Method 1631E identifies two working standards at 10.0 ng Hg/mL and 0.10 ng Hg/mL (**sections 7.9 and 7.10**) used for instrument calibration. Instead of the 0.10 ng Hg/mL working standard, BRL uses a 1.0 ng Hg/mL standard, along with the 10 ng Hg/mL standard, for calibration.

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- **Section 9.3.1** states that the concentration of the spike for matrix spike (MS) and matrix spike duplicate (MSD) samples shall be at 1-5 times the background level of the native sample. After the determination of the concentration of the native sample, appropriate spike volumes will be added to an aliquot of the native sample in the Teflon split bottle prior to pre-reduction.
- **Section 9.4.1.3** specifies that the mean result for all bubbler blanks analyzed during an analytical batch should be subtracted from all raw data before results are calculated. Instead, BRL subtracts the average peak area measurement of the first four split bottle blanks analyzed prior to the calibration from all raw data. Split bottles are used for the measurement and/or transfer of all standards, client samples, and quality control samples to the bubblers.
- **Section 9.4.7** specifies that 5% of any lot of bottles should be tested. BRL has found that there is little variation within any given lot of FLPE bottles, glass bottles, or glass vials. Therefore, BRL randomly tests only 10% of the bottles or vials from the first opened case from each lot before accepting or rejecting the lot, up to a maximum of 10 cases per lot number. A minimum of 10% of the cases of any given lot number are tested. BRL uses the tighter acceptance criterion of $\text{THg} \leq 0.2 \text{ ng/L}$, as opposed to $\leq 0.5 \text{ ng/L}$, for passing a lot number of bottles. In addition, four method blanks are prepared with every batch (> 10% of any given batch) using the same bottles that the samples are collected and prepared in, which serves as a further indicator of any potential contamination due to the bottles.
- **Section 10.1** does not state a frequency requirement for calibration. BRL performs a new calibration at the beginning of each analytical day and whenever CCV recovery fails to meet the acceptance criteria as outlined in 1631E, Table 2.
- **Section 10.2.2.1** lists calibration points of 50 pg, 500 pg, 2500 pg, 5000 pg, and 10000 pg Hg created from aliquots of working standards discussed above. BRL uses a calibration curve with points of 25 pg, 100 pg, 500 pg, 2500 pg, and 10000 pg. These points are produced by adding 0.025 mL and 0.100 mL of a 1.0 ng Hg/mL standard (50 pg and 100 pg respectively) and by adding 0.050 mL, 0.250 mL, and 1.0 mL of a 10.0 ng Hg/mL standard (500 pg, 2500 pg, and 10000 pg respectively). BRL does not add aliquots of the working standard directly to the bubblers; instead aliquots of standards are added to approximately 100 mL of DI water in a split bottle prior to transfer to the bubbler.
- **Section 11.2.1.2** states that samples are purged with nitrogen for 20 minutes at gas flow rate of 300-400 mL/min. BRL purges all [REDACTED]. High-level standard recoveries and subsequent bubbler blanks indicate that [REDACTED] is an adequate purge time to volatilize and collect mercury.
- BRL has not found the step described in section 11.3.2 (passing argon through the sample trap prior to desorption) to be necessary to eliminate condensed water vapor prior to trap desorption.



Brooks Rand Labs Memorandum

Re: Blank Correction of Trace Metals Data

Dated: February 11, 2011

While blank-correction of data is generally discouraged by the EPA, this is not always true for the analyses of low-level metals. When the EPA promulgated EPA Methods 1631E (for total mercury) and 1630 (for methylmercury), those methods explicitly allowed for blank-correction of the data if at least three method blanks were prepared and analyzed with the samples. EPA Method 1630 actually calls for blank-corrected data (Section 12.4.1) and does not even offer the option of not blank-correcting. Based on conversations between our staff and staff at the EPA's Office of Water (Bill Telliard and Richard Redding, specifically), we believe that once other 1600-series low-level metals methods are fully promulgated (e.g., Draft EPA Methods 1638, 1640, etc.), the same blank-correction policy will be incorporated into those methods. At Brooks Rand Labs (BRL), we prepare and analyze four method blanks with every batch of samples and if the standard deviation of those blanks meets our strict acceptance criteria, then the mean of the method blank results is subtracted from the sample results automatically by our LIMS.

Blank correction of the data is the only way to report truly accurate analytical results for low-level trace metals. For example, method blanks for total mercury (Hg) by EPA Method 1631E can be anywhere from 0.03 – 0.35 ng/L, depending on the batch of reagents used for the preparation of the bromine monochloride (BrCl). Ambient water concentrations for total Hg can often be < 1 ng/L. Without blank correction, the reported data can be biased high by a significant amount!

Nearly all of the data produced by our laboratory is method blank corrected. All of our control charts and QC control limits are based only on blank-corrected data. For the very rare clients that require data to not be blank corrected for some reason (<1% of our total workload), we require higher SDG minimums and we impose additional fees.

BRL has been involved in many high-profile government projects where we are providing data over the past several years (including for many ORAP sites), and in every case where the issue of blank-correcting the data has come up, the decision has been made to continue to have BRL blank-correct our data.

The industry standard amongst labs performing low-level trace metals analyses is to method blank-correct the data. If the goal of the project is to achieve the most accurate data at low concentrations, method blank-correction is crucial. Otherwise, low-level data can be biased. At BRL, we are dedicated to providing our clients with the most accurate data possible, and to that end, we blank-correct all data. This is clearly explained to our clients up-front in our quotations, because we realize this is different from how standard-level metals data is treated, and we want our clients to understand how important it is when we are reporting samples results at very low levels.

If you have any further questions regarding BRL's blank-correction policy, please feel free to contact Michelle Briscoe, Vice President of Analytical Services, at 206-632-6206 (ext. 117) or via e-mail at michelle@brooksrands.com.

SOP-XXXX
Metals in Tissue

[Reserved]

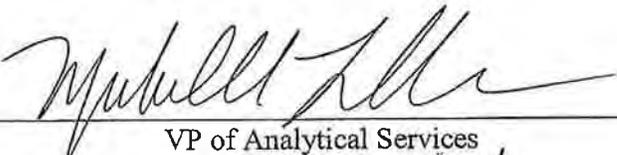
SOP #BR-0002

BRL Procedure for EPA Method 1631, Appendix to (1/01): Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

Brooks Rand Labs

Revision 010c
Revised 02/11/10

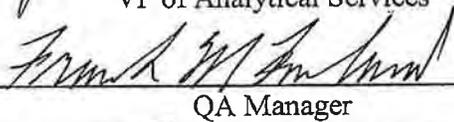
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VP of Analytical Services

2/15/10

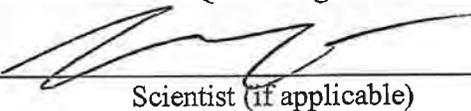
Date



QA Manager

2/12/10

Date



Scientist (if applicable)

2-12-10

Date

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BRL Procedure for EPA Method 1631, Appendix to (1/01): Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

1.0 SCOPE AND APPLICATION

1.1 Method BR-0002 is modification of Appendix to EPA Method 1631 and is based on peer-reviewed, published articles for the determination of total mercury in a wide range of biological and geological matrices. All samples must be subject to an appropriate digestion step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid samples must be acid digested to break down the sample matrix and oxidized to convert all mercury species to mercuric ions.

2.2 Method BR-0002 is a cold vapor atomic fluorescence technique, based upon the fluorescence of 253.7 nm radiation by excited elemental mercury (Hg^0) atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg^0 using stannous chloride (SnCl_2), and then purged onto gold amalgamation traps using nitrogen gas as a means of preconcentration. Mercury vapor is thermally desorbed into the fluorescence cell. Fluorescence intensity is measured as a function of total mercury collected, which is converted to concentration by the size of the aliquot purged.

2.3 The actual detection limits for this method will be dependent upon the specific techniques used to prepare the samples. Current detection limits as determined by Brooks Rand Labs (BRL) are found in Table 1 of this document.

3.0 DEFINITIONS

3.1 A partial list of definitions is presented below. Most definitions can be found for specific terms in the sections where they are first mentioned. Many of the definitions mentioned in this method are based on those found in the glossary for EPA Method 1631e. Please refer directly to this method for a more detailed list.

3.2 May: This action is allowed, but not required.

3.3 May Not: This action is prohibited.

3.4 Must: This action is required.

3.5 Shall: This action is required.

3.5 Should: This action is suggested, but is not required.

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4.0 INTERFERENCES

4.1 Due to the strong oxidation step there are no observed interferences with this method.

4.2 The potential exists for destruction of the gold traps (and consequently, low recoveries) if free halogens are purged onto them. When these instructions are followed accurately, this outcome is unlikely.

4.3 Water vapor may collect in the gold traps, and be released into the fluorescence cell where it condenses, giving a false peak due to scattering of the excitation radiation. This can be minimized with the use of a soda lime pre-trap.

4.4 As always with atomic fluorescence, the fluorescent intensity is strongly dependent upon the inertness of the carrier gas. Using only ultrapure gases minimizes the possibility of quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas is used and that the analytical train is leak-free.

5.0 SAFETY

5.1 Refer to EPA Method 1631E, section 5.0, for safety issues associated with the use of this method.

5.2 Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of this, only highly trained personnel familiar with the dangers and precautions to take when working with mercury compounds should ever handle standards and/or high level samples.

5.3 Material safety data sheets (MSDSs) are maintained for all chemicals used in this method. The MSDS sheets are stored in the mercury laboratory in appropriately marked binders.

5.4 Refer to the latest revision of the Chemical Hygiene Plan (CHP) for additional safety precautions and required protective equipment.

6.0 APPARATUS AND MATERIALS

6.1 Routine preventative maintenance for the equipment used in this procedure is described in detail in the standard operating procedure BR-1205 (Preventative Maintenance).

6.2 Atomic fluorescence spectrophotometer (BRL part #AF-03): To achieve the low detection levels a very sensitive CVAFS detector is required. Such systems are built at BRL (BRL Model III) based on the principles discussed in the literature. Refer to the "Brooks Rand, LLC Model III Operation Manual" for instrument operating instructions.

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6.3 Flow meter/needle valve (BRL part #AF-60): Capable of controlling and measuring gas flow to the purge vessel at 200-500 mL·min⁻¹.

6.4 Fluoropolymer adapters (BRL part #s AF-80 through AF-84) and tubing: Connections between components and traps are made using 3.2 mm O.D. precleaned fluoropolymer tubing, and fluoropolymer friction-fit or threaded tubing connectors.

6.5 Acid-fume and moisture pre-trap: A 10 cm x 0.9 cm diameter fluoropolymer tube containing 2-3 grams of reagent grade, non-indicating 6-12 mesh soda lime, packed between plugs of silanized glass wool. This trap is purged of Hg by placing it on the output port of a clean cold vapor generator, filled with ultrapure deionized water, and purging for at least 20 minutes with N₂ at 400 mL·min⁻¹.

6.6 Cold vapor generator (BRL part #AF-31): A 200 mL flask with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit which extends to within 0.2 cm of the flask bottom.

6.7 Gold wire traps or gold-coated sand traps (BRL part #AF-19 or AF-20): Used for trapping gaseous Hg⁰.

6.8 Recorder: The BRL Model III comes complete with Guru[®] integrating software. Refer to the "Brooks Rand, LLC Model III Operation Manual" for Guru[®] software/integrator operating instructions. Guru[®] software requires an IBM compatible computer (Pentium[®] II, 400MHz, 128MB RAM minimum) and running MS Windows[®] 98SE/ME/NT4/NT2000/XP.

6.9 Pipettors: Pneumatic fixed volume and variable pipettors in the range of 10 µL to 5.0 mL.

6.10 Refluxing digestion flask: 20 mL (small mass) or 40 mL glass VOA vials with fluoropolymer lined lids. Acid-cleaned 1-inch diameter glass marbles are used over the vial mouth as pressure relief valves. Alternatively 100mL volumetric flasks can be used in place of VOA vials. Securely capped 18.2 mL or 25.6 mL fluoropolymer vials can also be used. When the vials are placed in a sand bath (approximately 150 °C) the contents will reflux.

6.11 Cold digestion vials: 40 mL glass VOA vials with fluoropolymer lined lids or 60 mL Environmental Express Digestion Tubes.

6.12 Nichrome wire coil (BRL part #AF-40) with plug (BRL part #AF-41): Used for heating the gold trap to thermally desorb the mercury.

7.0 REAGENTS

Document standard or reagent preparation in the standards and reagents log in the LIMS. Record the standard or reagent type, identification number, preparation date, lot number, expiration date, and analyst name in the appropriate fields. Record the standard or reagent type, identification number, preparation date, analyst's initials and expiration date on the container.

7.1 Water: 18 megohm ultrapure deionized water (DIW) originating from a pre-purified source. The water system is located in the northwest corner of the bottom floor of the building. Water should be monitored for Hg by analysis of bubbler blanks, especially after ion exchange beds are changed.

7.2 Nitric acid (HNO₃): Trace-metal reagent grade pre-analyzed, low mercury (<5.0 ng·L⁻¹ Hg) concentrated nitric acid.

7.3 Sulfuric acid (H₂SO₄): Trace-metal reagent grade pre-analyzed, low mercury (<5.0 ng·L⁻¹ Hg) concentrated sulfuric acid.

7.4 Hydrochloric acid (HCl): Trace-metal reagent grade pre-analyzed, low mercury (<5.0 ng·L⁻¹ Hg) concentrated hydrochloric acid.

7.5 Stannous chloride: [REDACTED]

7.6 Bromine monochloride (BrCl): [REDACTED]

Caution: This process generates copious quantities of free chlorine, which are released from the bottle. Add the KBrO₃ slowly and in a well operating fume hood! The fumes from this reagent are very irritating and corrosive.

[REDACTED]. The solution is stored in 2.5 L glass bottles and in 125 mL and 250 mL fluoropolymer bottles, tightly capped, in the absence of light at room temperature. This reagent must be tested prior to use. Refer to BRL SOP BR-0006 for full a description of this testing procedure.

7.7 Hydroxylamine hydrochloride (NH₂OH·HCl): [REDACTED]

[REDACTED] This reagent must be tested along with the BrCl

reagent prior to use in the analysis of samples. Method blanks are analyzed with each analytical batch to ensure that contaminated reagents, including $\text{NH}_2\text{OH}\cdot\text{HCl}$, are not used in the analysis of samples.

7.8 Stock mercury standard: [REDACTED]

[REDACTED] This stock standard should be replaced by the manufacturer's expiration date. Store this standard in an appropriate location separate from the working standards such as the "high level standards and samples" cabinet located on the south wall of the shop.

7.9 Intermediate mercury standard solution [REDACTED]

7.10 Mercury working standards: [REDACTED]

7.11 Independent Calibration Verification (ICV) Standard: [REDACTED]

7.12 Nitrogen: Grade 4.8 (99.999% purity) nitrogen [REDACTED]

7.13 Argon or Helium: Grade 4.8 (99.999% purity) inert gas [REDACTED]

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Samples should be collected into glass, polyethylene, or fluoropolymer jars. Polyethylene bags are also acceptable for all but very low level and/or very wet solid samples. Dry samples such as coal and ores may be collected and stored in heavy gauge paper pouches.

8.2 Samples containing biota (i.e. wet or dry sludge), and all wet sediment samples are shipped to the laboratory at 0-4 °C and stored at < 4 °C for up to 1 year. Dry samples such

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as ores, paper, and wood may be shipped unrefrigerated and stored indefinitely in a cool, dry location low in mercury.

8.3 Biota samples are to be frozen at $< -15\text{ }^{\circ}\text{C}$ (standard freezer on coldest setting) until use. Samples may be stored for a maximum holding time of 1 year.

8.4 Freezing and thawing of sediment samples may adversely affect their homogeneity. Ideally, sediment samples will not be frozen, however, projects often require multiple analyses on the same sample including speciation analysis which requires the samples to stay frozen until analysis. To reduce the impact of freezing on the sample, aliquots for all analyses are taken at the same time to reduce the freeze/thaw cycles. If the client requests it, the sediment samples can be aliquoted and weighed at the laboratory prior to freezing to further negate the impact of freezing on homogeneity. If wet sediment samples have been frozen prior to preparation, they must be sequentially homogenized into smaller aliquots as follows. First the whole sample must be emptied into a clean weigh boat and thoroughly homogenized. Then half of the sample is transferred back into the original container. The sample remaining in the weigh boat is thoroughly homogenized before half is transferred back into the original container again. The procedure is continued until the appropriate sample preparation weight is left and is then placed the sample preparation vial. Refer to SOP BR-0106 for further discussion of sample homogenization. Additionally, any other associated sample preparations to be performed with the sample (such as percent solids analysis) should homogenized and aliquoted at the same time to ensure that the aliquots are similar in sample characteristic. All remaining sample is stored in the original sample container at $< -15\text{ }^{\circ}\text{C}$ for up to 1 year.

To better assure homogeneity, large particles such as rocks and sticks can be removed by screening the samples through a 2.0 mm sieve. Though to prevent contamination as much as possible, the typical practice at BRL is to pick out large particles prior to aliquoting for sample prep.

8.5 All dissection, homogenization, and other handling of the samples are to occur by clean room gloved personnel in an environment free of mercury contamination.

9.0 PROCEDURE

9.1 Sample Preparation

9.1.1 General considerations: Dissect and/or homogenize the sample with clean stainless steel tools. Sediment and soil samples may be homogenized with an acid-cleaned fluoropolymer spatula. Clean the stainless steel tools with ultrapure deionized water and a mild detergent (such as Alconox[®]) between sample aliquots. Refer to SOP BR-0106 for instructions in the homogenization of various sample matrices.

9.1.2 Hot re-fluxing $\text{HNO}_3/\text{H}_2\text{SO}_4$ digestion: This procedure is used for **biota**, wood, paper, tissue, sludge, or other soils high in organic content. An aliquot of

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homogenized sample of [REDACTED] is weighed directly into a [REDACTED] glass vial with a fluoropolymer-lined lid. To prep homogenization blanks, pipette [REDACTED] of the homogenization blank water into a vial then prep as normal.

Glass vials are tested by lot number prior to use to ensure that they are not a potential source of mercury contamination. Glass vials are triple rinsed with DIW prior to use in the preparation of samples. Cleaned and tested fluoropolymer vials may also be used. If necessary, up to 2-3 mL of DIW may be used to rinse the sample down to the bottom. [REDACTED] of HNO₃ and [REDACTED] of H₂SO₄ are pipetted into the sample, and the preparation is swirled.

Caution: This mixture gets hot and emits caustic fumes!

Acid washed fluoropolymer cones or glass marbles are placed on each glass vial to allow refluxing of the preparation. Samples are next placed on a hotplate, and brought up to a refluxing boil in temperature increments to avoid excessive foaming, especially common with tissue samples. At BRL a hotplate is used, the samples are digested at a temperature of [REDACTED] °C for [REDACTED] and then refluxed at a hotplate temperature of [REDACTED] °C for [REDACTED]. The samples are allowed to cool prior to removal from the hotplate. [REDACTED] of BrCl is added to each sample, and then the samples are diluted to the [REDACTED] mark with deionized water. Experience and numerous intercalibration studies show that undigested rock material or animal fat does not affect the accuracy of this digestion for Hg, because these fractions are both very low in initial Hg content, and are effectively leached by the boiling acid.

Alternative method: If fluoropolymer vials are used, the caps should be tightened so that the threads make good contact. If a sand bath is used, then samples are digested at [REDACTED] °C for [REDACTED] and then refluxed at a sand bath temperature of [REDACTED] °C for [REDACTED], or until all organic matter is dissolved, the solution looks substantially colorless or light yellow, and the brown gas above the liquid has almost disappeared.

As a substitute, [REDACTED] volumetric flasks may be used. After addition of the HNO₃/H₂SO₄ mixture, a clean glass marble is placed over the mouth, and the samples are allowed to predigest at room temperature for [REDACTED]. Samples are then heated in the same manner as previously described. After digestion the flasks should be allowed to cool, and [REDACTED] of BrCl is added and the volume brought up to the [REDACTED] mark with ultrapure deionized water. A section of parafilm is secured over the flask opening, and the samples are thoroughly homogenized by gentle agitation prior to analysis.

9.1.3 Alternative cold aqua regia digestion: This procedure is for geological media such as coal, ores, **sediments, and soils**. Since the matrix is leached rather

than dissolved, the sample must be pulverized prior to digestion if the total mercury content is desired.

Weigh to the nearest mg approximately [REDACTED] into a [REDACTED] vial or [REDACTED] Environmental Express Digestion Tube. In a fume hood, add [REDACTED] of concentrated HCl, swirl, and add [REDACTED] of concentrated HNO₃. The vial may be loosely capped (tightening the lid may cause the vial to explode). The preparation should then be allowed to digest at room temperature [REDACTED].

For all samples other than those high in elemental carbon (i.e. coal), add [REDACTED] BrCl and dilute the digestate to [REDACTED] with deionized water, shake vigorously, and allow to fully settle prior to analysis. For coal samples, and other samples high in elemental carbon, dilute the digestate to [REDACTED] with up to 0.07 N (35%) BrCl solution to prevent any mercury from re-adsorbing to the carbon particles.

Note: More organic samples may require higher levels of BrCl. BRL typically adds [REDACTED] of BrCl to most aqua regia preparations, but more organic samples may require higher levels of BrCl (levels between [REDACTED] BrCl). Additionally, reagent water without BrCl may be used if the samples are appropriate to such preparation and very low method blanks are required.

9.1.4 Preparation of Capillary Collected Blood Samples at Micro Volumes: The following method is for blood that is collected in capillary tubes only. If the blood is collected in a vial with adequate volume, the standard biota prep should be used unless otherwise specified.

9.1.4.1 Pipette [REDACTED] of DIW into a [REDACTED] glass vial. If the blood is not already in a capillary tube, use a pre-cleaned capillary tube to draw up an aliquot of the blood sample. Weigh the tube with the blood aliquot to the nearest 0.1 mg. Place one end of the capillary tube just below the surface of the DIW and using a modified pipette tip, force the blood into the water. Due to the high viscosity of the blood, it may be necessary to rinse out the capillary tube several times. Each time ensure that all of the liquid has been forced out of the capillary tube by observing bubbles in the solution. It is important to remove the capillary tube from the liquid while bubbles are still forming to prevent any sample being drawn back into the tube. The tube is then reweighed and the sample mass is calculated by difference. A final sample mass of ~20 mg is typical.

9.1.4.2 Then [REDACTED] of a 7:3 HNO₃:H₂SO₄ mixture is added to each vial, the vial is covered with a clean marble or fluoropolymer cone, and the samples are heated at [REDACTED] °C for [REDACTED]. Then the temperature is raised to

█ °C and the samples are heated for an additional █. The samples are then removed from the heat and allowed to cool to room temperature. █ of BrCl is added and each sample preparation is made up to █ with deionized water.

Additional Notes: The SRM used for blood analysis (SRM-966) comes in two levels of trace metals. Only Level 2 is certified for mercury. Only Level 2 should be used as an SRM for this analysis. The level of mercury in this SRM is high enough that 20 mg of the SRM is sufficient. The SRM should be weighed out in the same manner as the samples.

9.2 Analysis: A diagram of the purging/concentration step and the desorbition/detection step is shown in Figure 1. █ of deionized water and █ of NH₂OH·HCl are placed into a split bottle. The contents are then added to the bubbler and █ of SnCl₂ solution is added. A gold trap is connected to the soda lime pre-trap and purged for █ with Hg-free N₂ at █. This value is the bubbler blank or calibration blank used for calibration. To analyze samples, add █ of NH₂OH·HCl reagent to each split bottle to destroy the excess BrCl. Cap and gently swirl the sample and allow approximately █ to ensure that no trace halogens remain. PURGING OF FREE HALOGENS ONTO THE GOLD TRAPS WILL RESULT IN DAMAGE, AND LOW IRREPRODUCIBLE RESULTS THEREAFTER. Gold traps are placed onto the soda lime pre-trap outlet and then an aliquot of the digestate, usually in the range of █ (due to trap degradation by acid fumes), is added to █ of deionized water in a split bottle. The contents of the split bottle are poured into a bubbler and █ of SnCl₂ is pipetted into the bubbler. The caps are replaced and secured to the vessel with a bubbler clamp, and the sample is purged for █. The instant that SnCl₂ and the sample aliquot are combined, reduction of mercuric ions to volatile Hg⁰ begins. The analyst should minimize the time between sample reduction and the start of sample collection. In order to best minimize potential loss of the volatile Hg⁰, the analyst must have the gold trap in place prior to adding SnCl₂ to the purge vessel and connects the N₂ purge gas after the bubbler top is clamped in place.

To analyze the mercury adsorbed on a gold trap, the trap is placed into the Nichrome wire coil of the Amalgamation Control Module (ACM), and the gas connections made to the trap from the incoming Hg-free argon and from the trap to the analyzer. The run is then started with the Guru[®] software, which will simultaneously begin the trap heating/desorption cycle and will begin collecting the instrument signal. The trap heating and run times in the software should be set to █. The electrical current of the ACM should be set so that the coil █ for gold coated sand traps, or █ for a gold wire trap. For gold coated sand traps it is very important that the traps are not heated above █ °C otherwise thermal expansion of the quartz sand leading to irreparable trap damage will result. As another gauge for appropriate heating temperature, the retention time when using gold-coated sand traps should be

approximately [REDACTED], and the retention time when using gold wire traps should be about [REDACTED]

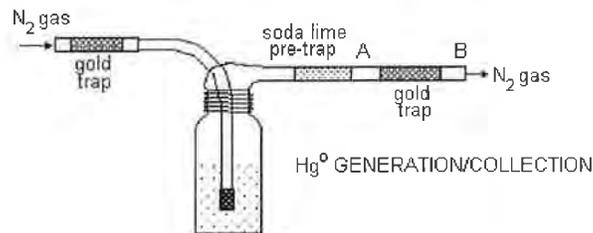
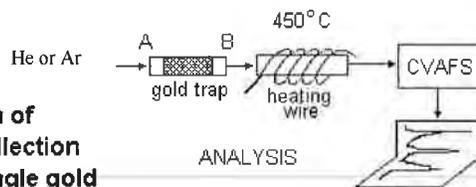


Figure 1:
Schematic diagram of
Hg⁰ generation/collecton
and analysis by single gold
amalgamation/CVAFS



Following the recording of the fluorescence intensity, the ACM will automatically stop heating and begin the cooling cycle. Once the gold-coated sand trap has cooled sufficiently (30-60 seconds) the gold trap is removed from the gas stream, and the fluoropolymer end plugs replaced until its next use. The next sample trap is placed in line, and the procedure repeated.

Peaks generated using this technique should display a very sharp and symmetrical peak. Broad or asymmetrical peaks are indicative of an analytical problem, possibly including: low gas flow, water vapor on the trap, or the trap being damaged by chemical fumes or overheating. The last possibility is definitely the case if a secondary small broad peak is observed following a sharp peak. If the gold trap has been damaged, the trap and the fluoropolymer tubing downstream from it should be discarded, due to the possibility of gold migration to downstream surfaces.

9.3 It is required that a calibration curve of at least 5 points be prepared prior to the analysis of samples to verify linearity and quantify sample concentrations. A new calibration curve must be prepared at the beginning of each analytical day and whenever continuing calibration verification (CCV) recovery fails to meet acceptance criteria and cannot be traced to a bad trap or bubbler. Standards to be analyzed for calibration should include 25 pg, 100 pg, 500pg, 2500 pg, and 10,000 pg standards.

9.4 To run standards, aliquots of working standard solution and [REDACTED] NH₂OH·HCl of [REDACTED] are added to a split bottle containing approximately [REDACTED] of ultrapure deionized water. The total contents of the split bottle are added directly to the bubbler and [REDACTED] of SnCl₂ is added and the analysis is run as per a sample. Refer to SOP BR-0006 for a full description of the use of split bottles.

9.5 Gold traps should be tracked using unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling trap will become damaged, giving low and irreproducible results. Suspect traps should be checked with a CCV level standard run before continued use.

9.6 The major cause of analytical problems with this method results from using the soda lime pre-traps too long. These traps should be purged for at least [REDACTED] prior to use (see section 4.4) and used for [REDACTED]. Longer use risks irreproducibility, as the traps may begin retarding the flow of Hg^0 . Also, as they become very wet, there is a risk of NaOH-saturated water vapor coming out onto the gold trap.

Note: If sample aliquots with too much acid [REDACTED] are being analyzed, [REDACTED]. The acid fumes in combination with water vapor, when trapped in soda lime pre-traps, can potentially trap Hg^0 and resulting in low recoveries.

9.7 Method blanks, matrix spike duplicates, certified reference materials, and check standards should be routinely analyzed, as discussed in section 8.

9.8 Calculations are made as follows:

9.8.1 Bubbler/Calibration Blanks – A minimum of four bubbler blanks, one per bubbler used in the analysis, must be prepared and analyzed prior to instrument calibration and/or calibration verification. Each individual bubbler blank must be less than 40 pg of Hg, the mean of the calibration blanks must be less than 20 pg of Hg and the standard deviation of all calibration blanks must be less than 7.5 pg of Hg in order for the calibration blanks to be valid. Calculate the mean peak area generated by the bubbler blanks (A_{BB}). Only the first four bubbler blanks analyzed prior to the calibration standards are used for blank correcting the calibration and the analyzed samples. Any bubbler blanks analyzed following the calibration standard are used only to check for carryover and other potential contamination.

9.8.2 Calculations for the calibration are as follows:

9.8.2.1 Mean Calibration factor (CF_m): Divide each standard amount (pg of Hg) by each net standard result (peak area of standard minus mean peak area of bubbler blanks or A_{BB}) in the calibration, to yield the "pg Hg/peak area." Pool all of the "pg Hg/peak area" values for a given calibration, to obtain a mean "pg Hg/peak area" value called the mean calibration factor (CF_m).

9.8.2.2 Relative Standard Deviation (RSD) and Recovery of the Low Standard: The RSD of the “pg Hg/peak area” values must be <15% in order for the calibration to be considered valid. The recovery of the low standard must be $\pm 25\%$ of the expected value.

9.8.3 To calculate the amount of total mercury measured in the analyzed aliquot of the sample preparation (P_S), employ the following formula:

$$P_S = \text{measured Hg (in pg)} = CF_m(A_S - A_{BB})$$

Where A_S is the measured peak area for the analyzed sample. If a customer does not desire blank correction, then A_{BB} is not subtracted.

9.8.4 To determine the concentration of total mercury in a sample, the calculation is performed as follows:

$$\text{Hg (in ng/g or ppb)} = [(P_S/V_A)V_D - P_{MB}]/M$$

Where V_D is the final dilution volume of the digestate in mL, V_A is the volume of digestate analyzed in mL, M is the digested sample mass in mg, and P_{MB} is the mean total Hg (pg) from the preparation of the method blanks. If a customer does not desire blank correction, then P_{MB} is not subtracted.

9.8.5 To determine the amount of total mercury from the preparation of the method blanks (P_{MB}), use the following formula for each method blank:

$$P_{MB} = [(A_{MB} - A_{BB}) CF_M \cdot V_D] / V_A$$

Where A_{MB} is the peak area of the method blank, V_D is the final dilution volume of the method blank and V_A is the volume of the method blank analyzed. Sediment and soil results are typically dry weight corrected by dividing the wet weight result by the percent total solids result. Although biota results are typically reported on a wet weight basis, they may be dry weight corrected upon request.

9.8.6 The Method Detection Limit (MDL) is determined as per 40 CFR 136, Appendix B. A minimum of seven replicate samples or laboratory fortified blanks (LFB), that are approximately the same concentration as the expected MDL, are analyzed and the standard deviation of the resulting concentrations is calculated. The MDL is then determined by multiplying the calculated standard deviation by the Student's t value ($\alpha=0.01$) for the number of replicate samples analyzed (2.998 for eight samples). The MDL may have to be adjusted to account for the sample weights, dilution factors, and/or analyzed volumes used in the analyses of various samples if these weights and volumes differ from those used in the MDL study.

10.0 QUALITY CONTROL

All Brooks Rand Labs (BRL) SOPs are Proprietary Information and protected by WA state law. Proprietary Information shall be kept in the strictest confidence & shall not be used or appropriated to benefit any party without prior written consent from BRL.

Current method detection limits are listed in Table 1. For easy reference for QC criteria refer to Table 2, which outline typical run sequences and required QA samples and Table 3, which describes all required QA frequency requirements and QA acceptance criteria along with corrective actions for failed QA.

10.1 All quality control data should be maintained and available for easy reference or inspection.

10.2 Calibration data must be composed of a minimum of 4 calibration blanks (one per bubbler used) and 5 non-zero point standards. Such a calibration must be analyzed daily prior to beginning analysis and run whenever continuing calibration verification (CCV) samples fail to meet acceptance criteria and the failure cannot be attributed to poorly performing bubbler and/or trap.

10.3 Samples containing high analyte concentrations may be run following dilution. The amount of total mercury measured in the sample aliquot analyzed (P_s) must ultimately fall below the peak area obtained from the highest standard analyzed and above the adjusted MRL.

10.4 Calibration checks must be analyzed every ten samples, and at the end of the analytical batch. Calibration checks shall consist of analysis of a certified, traceable standard, referred to as a CCV, at a level in the low to mid-range of the calibration (i.e. 500 pg) and a bubbler blank, also referred to as a continuing calibration blank (CCB). The CCB only needs to be run after the calibration. In addition, a standard from a source other than the one used to make the calibration standards must be run prior to the analysis of samples. This standard is referred to as the independent calibration verification (ICV) standard. The ICV is analyzed at the mid-range of the calibration (i.e. 1000 pg). The CCV standards must be within $\pm 23\%$ (77-123%) of the certified value and the ICV standard must be within $\pm 15\%$ (85-115%) for analysis to continue.

Carryover check bubbler blanks must be immediately analyzed following any sample result that exceeds one half of the "carryover threshold". The carryover threshold is determined by repeatedly analyzing standards with higher concentrations until a bubbler blank analyzed immediately after the standard, using the same bubbler/trap combination, yields a result that is > 40 pg and/or deviates from the average calibration blank by more than 20 pg. Currently, the carryover threshold has been determined to be 100,000 pg. Therefore, a carryover check bubbler blank is required following any sample result $> 50,000$ pg. Neither the bubbler nor the trap may be used to analyze client samples until it has met all bubbler blank criteria. Any samples analyzed using either the bubbler or the trap before the bubbler/trap combination has met the blank criteria must be reanalyzed using a different bubbler/trap combination.

10.5 A minimum of 3 method blanks per batch of 20 client samples must be run. The criterion for the method blanks is average method blank less than two times the MDL and standard deviation less than 0.67 times the MDL or less than $1/10^{\text{th}}$ of the associated

client samples. Brooks Rand routinely prepares and analyzes 4 method blanks to allow for the possible outlier.

10.6 Matrix spike (MS) and matrix spike duplicate (MSD) recoveries are analyzed at a minimal frequency of one per every 10 client samples. At least one matrix spike sample and matrix spike duplicate sample set must be analyzed per batch and at least two must be analyzed if more than 10 client samples are in a batch. Criterion for MS/MSD analysis is recoveries of 70-130% with a relative percent difference $\leq 30\%$ for sediment and biota and 65-135% with a relative percent difference of $\leq 35\%$ for blood or other samples using the micro method. The target spiking concentration is 2 – 5 times the level of the native sample. If there is no historic data on which to base the spike concentration, then the following default spiking levels should be used:

Sediment Samples: 1000 ng/g
Biota Samples: 1000 ng/g

10.7 Certified reference materials (CRM) for mercury in tissues and sediments are analyzed at a minimal frequency of once per every batch of client samples. At least one appropriate CRM must be run for each different type of matrix being analyzed in a batch. So if a batch contained two distinct biota matrices, then two appropriate CRMs, if available, should be prepared and analyzed. The criterion for CRMs is determined using control charts. If control charts are not available then CRM results should be within 25% of the certified value for the analysis to be considered valid. CRM sample results not meeting this criterion shall be reprepared and analyzed or qualified at the discretion of the lab manager. A list of CRMs currently in stock at BRL is included as Table 4.

10.8 Method duplicate (MD) samples should be prepared and analyzed in conjunction with the MS/MSD samples and whenever samples are deemed to have matrices that are so heterogeneous that it might affect the analysis of the sample. The acceptance criterion for duplicate analysis is RPD $\leq 30\%$ or \pm two times the MRL if the sample results are \leq five times the MRL.

10.9 Refer to Section 14 for copies of the sample preparation log and analytical bench sheets that must be used when preparing and analyzing all batches containing client samples.

11.0 METHOD PERFORMANCE

11.1 Refer to the Appendix to EPA Method, section 13.0, for information regarding the verification of this method.

11.2 The detection limits reported in Table 1 were achieved by performing a full MDL study as described in 40 CFR 136, Appendix B. The quality control acceptance limits reported in Table 3 are developed from the EPA methods and are validated as achievable at BRL in the control charts maintained for the method.

12.0 POLLUTION PREVENTION

12.1 Refer to EPA Method 1631E, section 14.0, for EPA recommendations regarding pollution prevention techniques.

12.2 Whenever feasible, lab personnel should use pollution prevention techniques to limit waste generation. The cost involved in purifying acids makes such recycling unpractical at BRL. Instead, every effort is made to reduce volumes necessary to still produce the best possible results. When making standards, they should be prepared in volumes consistent with their use in the laboratory to minimize the volume of expired standards to be disposed.

13.0 WASTE MANAGEMENT

13.1 Refer to EPA Method 1631E, section 15.0, for information and references related to managing waste produced by application of this method.

13.2 All waste is disposed of in accordance with state and federal regulations either by sewer disposal (only if concentrations are below the King County sewer limits) or through a licensed and bonded hazardous waste disposal facility such as Philips Services.

14.0 REFERENCES

14.1 Bloom, N.S. and Crecelius, E.A. (1983). "Determination of Mercury in Seawater at Subnanogram per Liter Levels." *Mar. Chem.* 14:49.

14.2 Bloom, N.S. and Fitzgerald, W.F. (1988). "Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapour Atomic Fluorescence Detection." *Anal. Chim. Acta.* 208:151.

14.3 EPA Appendix to Method 1631. (2001). "Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation."

14.4 EPA Method 1631.E. (8/02). "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry."

- 14.5 Fitzgerald, W.F., and Gill, G.A. (1979). "Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis." *Anal. Chem.* 15:1714.
- 14.6 Liang, L., and Bloom, N.S. (1992). "Determination of Total Hg by Single-Stage Gold Amalgamation with Cold Vapor Atomic Spectrometric Detection." *JAAS*. June 8:001

15.0 TABLES AND BENCHSHEETS

Table 1. Current Method Detection Limits and Minimum Levels Determined at BRL for the Analysis of Total Mercury in Solids Using EPA Method 1631, Appendix

Matrix	Preparation Method	Method Detection Limit (MDL)^{1,2}	Minimum Level (ML)
Sediment/Sludge	Aqua regia cold digestion (██████ BrCl)	0.05 ng/g	0.15 ng/g
Coal (samples high in elemental carbon)	Aqua regia cold digestion (██████ BrCl)	0.20 ng/g	0.50 ng/g
Biota/Sediment	HNO ₃ /H ₂ SO ₄ hot digestion (██████ BrCl)	0.04 ng/g	0.10 ng/g
Biota – Blood in Capillary tubes	HNO ₃ /H ₂ SO ₄ hot digestion (██████ BrCl)	1.5 ng/g	4.5 ng/g
Hair (w/washing step)	HNO ₃ /H ₂ SO ₄ hot digestion (██████ BrCl)	0.80 ng/g	2.50 ng/g

NOTES:

1. MDL as determined by the procedure 40 CFR Part 136, Appendix B.
2. All MDLs are calculated using a default mass of 1000 mg (wet weight)

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Table 2. Run Sequence for Total Hg in Solids (suggested)

Run	Run Name	Section Name	Analyze	Requirements
01	Calib. Blank	Calibration Blanks	IBL	each CB <40 pg Ave. <20 pg StDev <7.5 pg
02	Calib. Blank		IBL	
03	Calib. Blank		IBL	
04	Calib. Blank		IBL	
05	25 pg std	Calibration*	25 pg Hg	RSD<15% Rec. Low Std. = 80-120%
06	100 pg std		100 pg Hg	
07	500 pg std		500 pg Hg	
08	2500 pg std		2500 pg Hg	
09	10000 pg std		10000 pg std	
10	CCV (500 pg std)	Continuing Calibration Verification	500 pg	Recovery 77-123%
11	ICV (1601 pg std)	Independent Calibration Verification	1601 pg std, NIST 1641d	Recovery 85-115%
12	Method Blank	Method Blank	BLK	See Below
13	Cont. Calib. Blank	Carryover Check for High Std	CCB	< 40 pg, ± 20 pg from ave.
14	Method Blank	Method Blanks	BLK	Average < 2 x MDL and St. Dev. < 2/3 rd of MDL or High MB < 1/10 th sample
15	Method Blank		BLK	
16	Method Blank		BLK	
17	CRM-1	Certified Reference Materials	CRM	Recovery = 75-125% Blood CRM Rec. = 65-135%
18	BS	Laboratory Fortified Blank	Blank Matrix Spiked at 4.0 ng	Recovery = 70-130% (use only if no CRM available)
19	Sample 01	Sample Analysis	Sample 01 Native	RPD≤30% or ±2xMRL if results ≤5xMRL
20	Sample 01DUP1	Duplicate Analysis	Sample 01 Duplicate	
21	Sample 01MS1	Matrix Spike Analysis Spike	01 + Spike	Recovery = 70-130% RPD≤30%**
22	Sample 01MSD1	Duplicate Analysis	01 + Spike	
23	Sample 02	Sample Analysis	Sample 02	
24	Sample 03		Sample 03	
25	Sample 04		Sample 04	
26	Sample 05		Sample 05	
27	Sample 06		Sample 06	
28	Sample 07		Sample 07	
29	Sample 08		Sample 08	
30	Sample 09		Sample 09	
31	Sample 10		Sample 10	
32	CCV (500 pg std)		Continuing Calibration Verification	
33	Sample 11	Sample Analysis	Sample 11 Native	RPD≤30% or ±2xMRL if results ≤5xMRL
34	Sample 11DUP2	Duplicate Analysis	Sample 11 Duplicate	
35	Sample 11MS2	Matrix Spike Analysis Spike	11 + Spike	Recovery = 70-130% RPD≤30%**
36	Sample 11MSD2	Duplicate Analysis	11 + Spike	
37	Sample 12	Sample Analysis	Sample 12	
38	Sample 13		Sample 13	
39	Sample 14		Sample 14	
40	Sample 15		Sample 15	
41	Sample 16		Sample 16	
42	Sample 17		Sample 17	
43	Sample 18		Sample 18	
44	Sample 19		Sample 19	
45	Sample 20		Sample 20	
46	CCV (500 pg std)		Continuing Calibration Verification	

* Calibration Curve may be adjusted depending on expected concentration range of samples and on the linear range due to instrumentation.

** Matrix spike / spike duplicate acceptance criteria for blood and small mass samples is recovery = 65-135% with an RPD ≤ 35%.

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Table 3. Quality Control Criteria for the Analysis of Mercury in Solids by CVAFS

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Bubbler Blank (IBL)	Contamination from bubblers	1 per bubbler used prior to analysis	each ≤ 40 pg avg ≤ 20 pg std ≤ 7.5 pg	Clean and test bubblers until criteria met prior to any analysis
Calibration Standards (CAL)	Acceptability of the Calibration Curve	Each day prior to analyzing samples and whenever CCV/CRM analysis fails	RSD of response factors $\leq 15\%$; Recovery of Low Standard = 80 – 120%	Reanalyze suspect calibration standard. If criteria still not met, then remake standards and recalibrate the instrument
Independent Calibration Verification (ICV)	Test of the entire analytical system	1 per batch following the calibration (following calibration blanks if verifying past calibration)	Recovery = 85 – 115%	Correct problem prior to continuing analysis, recalibrate system if required
Continuing Calibration Verification (CCV)	Accuracy	2 per batch (one at the beginning and one at the end of each batch)	Recovery = 77 – 123%	Correct problem and reanalyze CCV. If criteria met, reanalyze samples backwards until 2 consecutive results w/RPD $\leq 20\%$
Carryover Check Bubbler Blank (CCB)	Contamination due to carryover in the bubbler/trap	On same bubbler/trap following any result exceeding $\frac{1}{2}$ the carryover threshold of 100,000 pg	≤ 40 pg and within ± 20 pg of avg bubbler blank	Clean and continue to test bubbler/trap combo until criteria met prior to further use. Samples analyzed following a result $\geq \frac{1}{2}$ the carryover threshold must be reanalyzed
Method Blank (BLK)	Contamination from reagents, lab ware, etc.	3 per batch	Avg $< 2 \times$ MDL StDev $< 2/3^{\text{rd}}$ of MDL or High MB $< 1/10^{\text{th}}$ of associated samples	Correct problem until criteria met. All samples associated with a contaminated method blank must be reanalyzed.
Certified Reference Material (CRM)	Accuracy	1 per batch	Recovery = 75 – 125%; Capillary Blood CRM Rec. = 65 – 135%	Correct problem prior to continuing analysis
Matrix Spike/Spike Duplicate (MS/MSD)	Accuracy and Precision within a given matrix	1 per 10 client samples	Recovery = 70 – 130%; RPD $\leq 30\%$ Blood and Small Mass Criteria Recovery = 65 – 135%; RPD $\leq 35\%$	If recoveries similar but fail recovery criteria, interference may be present in the sample and the result must be qualified. If RPD criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicate (DUP)	Precision within a given matrix	In conjunction with MS/MSD samples and when deemed necessary	RPD $\leq 30\%$ Blood and Small Mass Criteria RPD $\leq 35\%$	If RPD criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.

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Table 4. Certified Reference Materials Applicable to this SOP and in Stock at BRL

Agency	Name (ID)	Matrix	Certified Level of Hg
National Institute of Standards and Technology			
NIST	966 (Level 2)	Bovine Blood	31.4 $\mu\text{g}\cdot\text{L}^{-1}$ (29.8 $\mu\text{g}\cdot\text{kg}^{-1}$)
	2976	Mussel Tissue	0.061 $\text{mg}\cdot\text{kg}^{-1}$
Institute for Reference Materials and Measurements			
IRMM	BCR-580	Marine Sediment	132 $\text{mg}\cdot\text{kg}^{-1}$
National Resource Council of Canada			
NRCC	DORM-3	Fish Homogenate	0.382 $\text{mg}\cdot\text{kg}^{-1}$
	DOLT-4	Fish Liver	2.58 $\text{mg}\cdot\text{kg}^{-1}$
	TORT-2	Lobster Hepatopancreas	0.270 $\text{mg}\cdot\text{kg}^{-1}$
	PACS-2	Marine Sediment	3.04 $\text{mg}\cdot\text{kg}^{-1}$
	MESS-3	Marine Sediment	0.091 $\text{mg}\cdot\text{kg}^{-1}$
GBW	GBW 07604	Poplar Leaves	0.026 $\text{mg}\cdot\text{kg}^{-1}$
International Atomic Energy Agency			
IAEA	IAEA-085	Human Hair	23.2 $\text{mg}\cdot\text{kg}^{-1}$
	IAEA-086	Human Hair	0.573 $\text{mg}\cdot\text{kg}^{-1}$
	IAEA-140	Sea Plant Homogenate	0.038 $\text{mg}\cdot\text{kg}^{-1}$

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Appendix A to BR-0002: Modifications to EPA Method 1631, Appendix

EPA Method 1631		BRL SOP BR-0002	
SECTION	DESCRIPTION	SECTION	DESCRIPTION
A1.2	These conditions allow determination of Hg at concentrations ranging from 1.0 to 5000 ng/g in solid and semi-solid matrices.	7.2	These conditions allow measurements of Hg concentrations in the range of 0.03 – 16,000 ng/g. Dilutions can be made at the time of analysis to extend the range if necessary.
A1.3	The MDL for Hg has been determined to be in the range of 0.24 to 0.48 ng/g when no interferences present. The MRL has been established as 1.0 ng/g. These levels assume a sample size of 0.5 g.	7.1 & 10, Table 1	Sample size is [REDACTED], MDL=0.03-1.5, MRL=0.1 – 4.5 ng/g depending on matrix and prep type.
A4.4	The use of hydroxylamine hydrochloride to remove free halogens is not needed for solid sample digestates.	7.2	[REDACTED] of hydroxylamine hydrochloride is added to the samples at analysis.
A8.3.3	Wet sediment samples must be aliquotted and weighed at the laboratory and prior to freezing. Wet sediment samples may be held for 1 year if frozen at <-15 C.	6.2, 6.4	Wet sediment samples are refrigerated at <4 C until analysis. If speciation is needed on the same sample, the sample is stored frozen until analysis then thawed and homogenized prior to analysis.
A9.4.2	Method blank—For each batch of 20 samples (Section 9.1.7 of Method 1631B), digest and analyze a method blank using the most appropriate reference matrix (Appendix Section A7.1). The laboratory may process a greater number of method blanks, if desired, and average the results. The method blank must include all sample processing steps; e.g., homogenization (Appendix Section A8.3.2.1).	8.5	4 Method Blanks are prepped with each batch of samples; a minimum of three should be used to calculate the average. Homogenization blanks are prepared separately if the sample needs more homogenization than stirring with a spatula.
A9.5.1	Analyze an aliquot of the appropriate reference matrix (see Appendix Section A7.1), spiked at the concentration in the IPR.	8	Blank spikes at the MRL are prepared and analyzed, but there is no matrix added to them.
A11.2.2	Cap the vessel with a clean glass marble or inverted fluoropolymer cone.	7.1.3	For sediments, the vial caps are loosely placed on top of the vials during digestion.
A12.1	Pipette a 0.01- to 5.0-mL volume of diluted digestate (Appendix Section A11.1.4, A11.2.3, or A11.2.4) directly into a bubbler containing approximately 100 mL of pre-purged SnCl ₂ -containing water.	7.2	The maximum aliquot is [REDACTED]. The digestate is added to [REDACTED] of DIW in a split bottle with [REDACTED] hydroxylamine hydrochloride. The entire contents of the split bottle are added to the bubbler then [REDACTED] stannous chloride is added.
A12.2	Purge the solution onto a gold trap for 20 minutes. These conditions allow measurement of Hg concentrations in the range of 1 – 5,000 ng/g (parts per billion).	7.2	The samples are purged in the bubblers for [REDACTED]. These conditions allow measurements of Hg concentrations in the range of 0.03 – 16,000 ng/g.
A12.3	Change the SnCl ₂ -containing water in the bubbler after a total of 10 mL of digestate has been added. Water must be placed in the bubbler and purged for a minimum of 10 minutes prior to addition of another digestate aliquot.	7.2	The bubblers are emptied, rinsed and filled with fresh DIW between every sample. The DIW used is sufficiently low in ambient Hg and does not need to be purged prior to use.

[See Appendix B: Differences between EPA Method 1631e and BR-0006 for any analysis modifications, as they may also be applicable to BRL-0002.]

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Appendix B: Brooks Rand Labs Procedure for EPA Method 1631, Revision E (02/05)

Differences between EPA Method 1631, Revision E, and Brooks Rand Labs SOP #BR-0006

The following differences exist between EPA Method 1631, Revision E (with relevant sections marked in boldface), and the practices employed by Brooks Rand Labs (SOP #BR-0006):

- **Figures 1 and 2** (referenced within **sections 2.6 and 2.7**) give schematic diagrams of the bubbler, purge and trap, CVAFS analytical system. In contrast, Brooks Rand Labs (BRL) purges samples with nitrogen in bubblers onto sample traps. After samples are purged, the sample traps are disconnected from the bubbler system and desorbed using argon, as shown below:

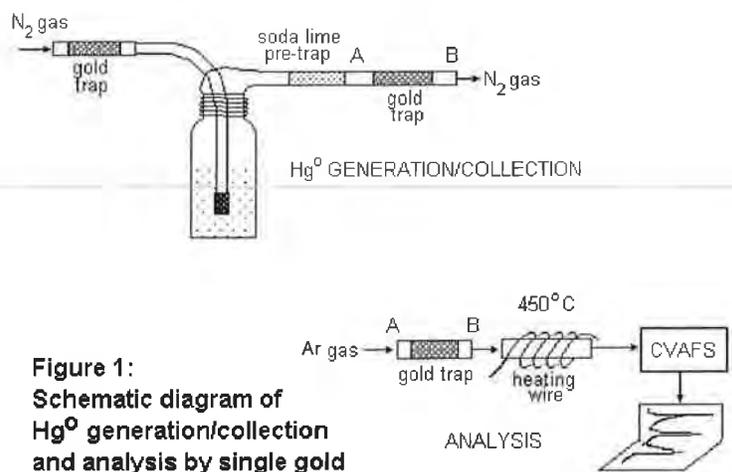


Figure 1:
Schematic diagram of
Hg⁰ generation/collection
and analysis by single gold
amalgamation/CVAFS

- **Section 6.4.3** specifies the use of acid fume pretraps consisting of 8-14 mesh soda lime chunks and which are purged for 1 hour with nitrogen. BRL uses pretraps consisting of [REDACTED] soda lime chunks and which are purged for [REDACTED] with nitrogen.
- **Section 6.5** discusses the use of a dual-trap Hg(0) pre-concentration system. In contrast, BRL uses a single trap pre-concentration system. This allows for shorter analysis times without masking of potential problems on the sample collection trap.
- BRL uses direct data acquisition with the BRL “Hg Guru” integration software instead of a chart recorder or integrator as described in **section 6.6**.
- Method 1631E identifies two working standards at 10.0 ng Hg/mL and 0.10 ng Hg/mL (**sections 7.9 and 7.10**) used for instrument calibration. Instead of the 0.10 ng Hg/mL working standard, BRL uses a 1.0 ng Hg/mL standard, along with the 10 ng Hg/mL standard, for calibration.

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- **Section 9.3.1** states that the concentration of the spike for matrix spike (MS) and matrix spike duplicate (MSD) samples shall be at 1-5 times the background level of the native sample. After the determination of the concentration of the native sample, appropriate spike volumes will be added to an aliquot of the native sample in the Teflon split bottle prior to pre-reduction.
- **Section 9.4.1.3** specifies that the mean result for all bubbler blanks analyzed during an analytical batch should be subtracted from all raw data before results are calculated. Instead, BRL subtracts the average peak area measurement of the first four split bottle blanks analyzed prior to the calibration from all raw data. Split bottles are used for the measurement and/or transfer of all standards, client samples, and quality control samples to the bubblers.
- **Section 9.4.7** specifies that 5% of any lot of bottles should be tested. BRL has found that there is little variation within any given lot of FLPE bottles, glass bottles, or glass vials. Therefore, BRL randomly tests only 10% of the bottles or vials from the first opened case from each lot before accepting or rejecting the lot, up to a maximum of 10 cases per lot number. A minimum of 10% of the cases of any given lot number are tested. BRL uses the tighter acceptance criterion of $\text{THg} \leq 0.2 \text{ ng/L}$, as opposed to $\leq 0.5 \text{ ng/L}$, for passing a lot number of bottles. In addition, four method blanks are prepared with every batch (> 10% of any given batch) using the same bottles that the samples are collected and prepared in, which serves as a further indicator of any potential contamination due to the bottles.
- **Section 10.1** does not state a frequency requirement for calibration. BRL performs a new calibration at the beginning of each analytical day and whenever CCV recovery fails to meet the acceptance criteria as outlined in 1631E, Table 2.
- **Section 10.2.2.1** lists calibration points of 50 pg, 500 pg, 2500 pg, 5000 pg, and 10000 pg Hg created from aliquots of working standards discussed above. BRL uses a calibration curve with points of 25 pg, 100 pg, 500 pg, 2500 pg, and 10000 pg. These points are produced by adding 0.025 mL and 0.100 mL of a 1.0 ng Hg/mL standard (50 pg and 100 pg respectively) and by adding 0.050 mL, 0.250 mL, and 1.0 mL of a 10.0 ng Hg/mL standard (500 pg, 2500 pg, and 10000 pg respectively). BRL does not add aliquots of the working standard directly to the bubblers; instead aliquots of standards are added to approximately 100 mL of DI water in a split bottle prior to transfer to the bubbler.
- **Section 11.2.1.2** states that samples are purged with nitrogen for 20 minutes at gas flow rate of 300-400 mL/min. BRL purges all samples for [REDACTED]. High-level standard recoveries and subsequent bubbler blanks indicate that [REDACTED] is an adequate purge time to volatilize and collect mercury.
- BRL has not found the step described in section 11.3.2 (passing argon through the sample trap prior to desorption) to be necessary to eliminate condensed water vapor prior to trap desorption.

Field Forms



3958 6th Avenue NW
 Seattle, WA 98107
 Phone: 206-632-6206
 Fax: 206-632-6017

samples@brooksrands.com
 www.brooksrands.com

Chain of Custody Record

White: LAB COPY
 Yellow: CUSTOMER COPY

Client:	Address:	COC receipt confirmation? Y / N
Contact:		If so, by: email / fax (circle one)
Client project ID:		Email:
PO #:	Phone #:	Fax #:

Requested TAT in business days: <input type="checkbox"/> 20 (standard) <input type="checkbox"/> 15 <input type="checkbox"/> 10 <input type="checkbox"/> 5 <input type="checkbox"/> Other ____ <i>Surcharges apply for expedited turn around times.</i>	Collection		Miscellaneous				Field Preservation			Analyses required							Comments
	Date	Time	Sampler (initials)	Matrix type	# of containers	Field filtered? (Y/N)	Unpreserved / ice only	HCl / HNO ₃ (circle one)	Other (specify)	Total Hg, EPA 1631	Methyl Hg, EPA 1630	ICP-MS Metals (specify)	As / Se species (specify)	% Solids	Filtration	Other (specify)	
Sample ID																	
1																	
2																	
3																	
4																	
5																	
6																	
7																	
8																	
9																	
10																	

Relinquished by:	Date:	Time:	Relinquished by:	Date:	Time:
Received by:	Date:	Time:	Received at BRL by:	Date:	Time:
Shipping carrier:	# of coolers:		BRL work order ID:		BRL project ID:

General Site Information								
Date:			Time:			Field Crew:		
Weather:			Sample ID:			Sample Location:		
Northing:			Easting:			GPS Point Saved	YES	NO
Total Depth (m):			Brine Depth (m):			Secchi Depth (m):		
Vertical Profile File Name:				Photo Numbers and descriptions:				
Surface Water Samples (check when done)								
0.2 m from	DO		Mercury		Metals		Sulfate	
0.5 m from	DO		Mercury		Metals		Sulfate	
Profile Samples (check when done)								
Depth (m)	TDS	Density	Depth (m)	TDS	Density	Depth (m)	TDS	Density
0.2								
Brine Shrimp Samples (check when done)								
Tow 1		Tow 2		Tow 3		Composited:		
Tow 4 (taxon)								