

Evaluation of Sample Preparation and Spiking for the Great Salt Lake Selenium Samples

PREPARED FOR: Great Salt Lake Science Panel, Utah Division of Water Quality
PREPARED BY: Project Team
DATE: March 20, 2007

Background

Frontier Geosciences Inc. (FGS) has been performing selenium analyses of water samples for the Great Salt Lake Selenium project per protocol included in the project QAPP. Both raw acidified and filtered acidified samples have been analyzed by the Hydride Generation-Atomic Fluorescence Spectrometry (HGAFS) method developed by FGS. This is the same methodology that was used in the round robin event that was used to select the analytical method by the Science Panel for the Great Salt Lake water quality studies.

At the November 30-31, 2006 Science Panel meeting, project team members expressed concern that no deep brine water samples had been spiked to date. CH2M HILL investigated and requested FGS to spike a deep brine water sample in early December. Results received in January indicated low recoveries in matrix spike/matrix spike duplicate analyses (MS/MSDs) that resulted in analyses of further MS/MSDs and the analysis described below. Summary information of the deep brine MS/MSD recoveries is presented in Table 1 below. A separate Microsoft Excel workbook titled, "Analytical_Matrix_Spike_Recoveries" is included that provides the "raw" data that was used to create the summary tables and graphs within this memorandum.

Sample QC

FGS follows their internal standard operating procedures that are included as part of the QAPP for the sample preparation and analysis. FGS selected samples randomly for matrix spike/matrix spike duplicate analyses in the absence of directions on the chain-of-custody. FGS followed the QAPP Method Quality Objectives when matrix spike recoveries did not meet criteria by reviewing other data quality indicators such as Laboratory Control Sample recoveries and investigating the cause and/or performing additional QC analyses as necessary. Additional details are provided in the following sections.

TABLE 1
Deep Brine Layer MS/MSD Recoveries

Native ID	Recovery
2565 7.5 M_120606 RAMS	72
2565 7.5 M_120606 RASD	52
2565 6.5M FA - Dissolved	20
2565 6.5M FA - Dissolved	11
2565 6.5 M RA- Total	18
2565 6.5 M RA- Total	31
2565 8.0 M_110106 FA	14
2565 8.0 M_110106 FA	22
2565 8.0 M_110106 RA	12
2565 8.0 M_110106 RA	10
3510 8.0M_120706 FA	22
3510 8.0M_120706 FA	22
3510 8.0M_120706 RA	5.
3510 8.0M_120706 RA	16

Sample Preparation and Analysis

Frontier Geosciences developed the following sample preparation processes for the determination of selenium by HGAFS:

- 1) Samples are collected and stored in capped high density polyethylene bottles.
- 2) Upon sample receipt, the laboratory verifies the field preservation to a pH of 2.
- 3) The samples remain capped in the original sample bottle until an aliquot is removed. The bottle is shaken and then the aliquot is transferred to a 50-ml centrifuge tube. Each sample aliquot is capped and oven digested by heating overnight at 85° Celsius. (Note that the heating process often loosens the cap until the cooling process is complete.) FGS performs the oven digestion to aid in the digestion of organic matter and mineral precipitates.
- 4) The samples are then digested by adding a predetermined amount of 40% hydrochloric acid and potassium persulfate solution (persulfate digestion).

This step is performed to reduce all inorganic and organic selenium to selenium (IV). The sample aliquot used for the persulfate digestion is not shaken, to prevent undigested solid material from entering the instrument during analysis.

- 5) Because the oven-digested sample must be cool prior to beginning the persulfate step, this step can be performed several days earlier. However, once the persulfate digestion is performed, the sample is analyzed the same day to ensure selenium remains in a reduced state.
- 6) The persulfate-digested samples are reacted with sodium borohydride and analyzed by an atomic fluorescence detector to obtain the selenium concentration.

Instrument Calibration and Verification

The instrument's initial calibration standards (ICALs) and the continuing calibration standards (CCVs) are prepared using selenium (IV). The ICAL ranges from 50 ng to 3000 ng with an instrument blank the first point in the ICAL. The ICAL is calculated using a linear regression with a correlation coefficient greater than 0.995. These ICAL and CCV standards are not oven digested or persulfate digested, because these standards are made from selenium (IV). However, the ICALs, CCVs and continuing calibration blanks have potassium persulfate added to them prior to analysis to matrix-match the samples and standards.

Two second source standards are analyzed. These are prepared from selenomethionine sources and are persulfate digested. These standards are prepared at the mid-level of the calibration range and have consistently yielded recoveries between 90 and 100+ %.

Laboratory Control Sample QC Analyses

Laboratory control sample/laboratory control sample duplicates (LCS/LCSDs) are prepared from a National Institute of Standards and Technology (NIST) 1640 source of selenium (IV). The LCS/LCSDs undergo oven digestion and persulfate digestion and yield recoveries within the QAPP recovery limits of 80-120%. The LCS/LCSD is spiked at approximately 20 ug/L.

Matrix Spike and Matrix Spike Duplicate and Analytical Spike and Analytical Spike Duplicate Analyses

MS/MSDs are randomly selected and spiked near the midpoint of the initial calibration (approximately 1.8 ug/L) with selenium IV prior to oven digestion and persulfate digestion. The average recovery of all MS/MSDs is 77%. The overall range of recoveries is roughly 6% to 110%. The average recovery for MS/MSDs in the deep brine is only 22%. Additional data were received on March 9, 2007 that indicated very poor MS/MSD recoveries in the deep brine. The range of spike

recoveries ranged from roughly 6% to 72%. Additionally, MS/MSD samples analyzed from Brad Marden's program demonstrated an average recovery of only 66%. The exact sample locations are still being correlated with Brad, but these samples are not believed to contain deep brine layer material. Attachment 1 includes a more detailed summary of the MS/MSD spike recoveries along with a chart indicating the recoveries from the earliest to latest analysis dates as you move from left to right in the chart.

Analytical spike/analytical spike duplicates (AS/ASDs) are spiked with selenomethionine without oven digestion and before persulfate digestion. Selenomethionine is used for the AS/ASD and the second source standards to ensure the persulfate digestion is properly reducing the organic form of selenium to inorganic selenium. The average recovery of the AS/ASDs is 92%. The minimum recovery was 61% and the maximum recovery was 121%. The deep brine and samples from Brad Marden's program have average recoveries of 96% and 92%, respectively. Attachment 2 at the end of the memorandum includes a summary of the AS/ASDs and associated spike recoveries along with a chart indicating the recoveries from the earliest to latest analysis dates as you move from left to right in the chart.

Additional Evaluation of the Sampling and Analytical Procedures for the Deep Brine Samples

The following tasks were identified during a conference call with the project team on March 14 as a first step to further investigate low recoveries identified in MS/MSDs. The team has initiated the completion of these tasks but anticipates further discussion at the Science Panel meeting on March 21, 2007.

1. If sufficient sample volume remains at FGS, three MS/MSD paired samples will be reprepared and analyzed using the most recently collected deep brine samples without using the oven digestion procedure but spiking with selenomethionine in addition to selenite. The oven digestion procedure has been identified as a step that may impact the recovery of selenite in the MS/MSD (as well as potentially the measurements of total selenium in native samples). The oven digestion procedure's effect on the recovery of selenomethionine has not been determined.
2. During the next sampling event, 3 deep brine samples will be collected using a Kemmerer sampler along with filtered and unfiltered samples as collected in prior events. The use of the Kemmerer sampler is intended to aid in evaluating if the current prior sample collection procedures are introducing a bias to the sample data.
3. Additional samples will be collected to determine if selenium is being lost due to volatilization during the sample filtration process. The trapped filtered solids collected during sampling will be analyzed for total selenium at the University of

Utah. The total selenium concentration of the solid material collected during the filtration process will be added to the result from the filtrate and then compared to the "raw" sample result. During data evaluation, if the sum of the solids and the filtrate is within 80% of the raw result then the loss of selenium through volatilization will not be considered significant.

4. Tom May of the USGS Columbia Environmental Research Center will analyze split samples from several locations in the next sampling event.

Path Forward

Discussions with FGS and the project team indicate that one or more of the following factors may be a cause of the low recoveries in the deep brine layer:

- Selenite spiked into the deep brine layer MS/MSDs is lost through precipitation
- Selenite is lost through volatilization
- Sampling Method/Laboratory anomaly

While the exact reason for the loss of the selenite in the deep brine layer MS/MSDs may not be determined by the additional sampling and analysis, the data should aid in evaluating the current data. Further discussion with the Science Panel is needed to determine how existing deep brine sample data may be used.

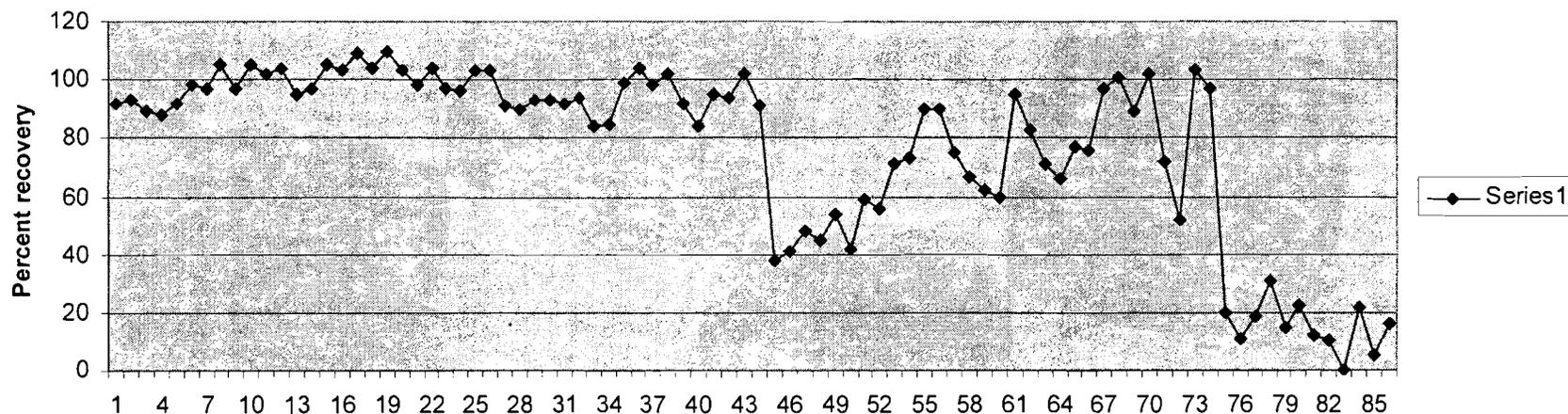
Attachment 1 – MS/MSD Recoveries

NativeID	Matrix	QAQC Type	Sample Date	Sample Time	Recovery
BR1-250506 1430 FAMS	Water	MS	5/25/2006	14:30	92
BR1-250506 1430 FASD	Water	SD	5/25/2006	14:30	93
LEE CREEK 120506 1017 FAMS	Water	MS	5/12/2006	10:15	89
LEE CREEK 120506 1017 FASD	Water	SD	5/12/2006	10:15	88
3510 0.2M 230506 1230 RAMS	Water	MS	5/23/2006	12:30	92
3510 0.2M 230506 1230 RASD	Water	SD	5/23/2006	12:30	98
GOGGIN DRAIN- RA TOTALMS	Water	MS	5/17/2006	10:45	97
GOGGIN DRAIN- RA TOTALSD	Water	SD	5/17/2006	10:45	105
GOGGIN DRAIN_060606-RA TOTALMS	Water	MS	6/6/2006	13:30	97
GOGGIN DRAIN_060606-RA TOTALSD	Water	SD	6/6/2006	13:30	105
WR 170506 1325 RAMS	Water	MS	5/17/2006	13:25	102
WR 170506 1325 RASD	Water	SD	5/17/2006	13:25	104
2267 4.0m_061906- RA TOTALMS	Water	MS	6/19/2006	15:50	95
2267 4.0m_061906- RA TOTALSD	Water	SD	6/19/2006	15:50	97
2767 3.0M 230506 1130 RAMS	Water	MS	5/23/2006	11:30	105
2767 3.0M 230506 1130 RASD	Water	SD	5/23/2006	11:30	103
3510 0.2m_062006- RA TOTALMS	Water	MS	6/20/2006	11:30	109
3510 0.2m_062006- RA TOTALSD	Water	SD	6/20/2006	11:30	104
GD99 170506 0940 FAMS	Water	MS	5/17/2006	9:40	110
GD99 170506 0940 FASD	Water	SD	5/17/2006	9:40	103
OGBA-3-WMS	Water	MS	6/23/2006	10:50	98
OGBA-3-WSD	Water	SD	6/23/2006	10:50	104
2767 3.0M FAMS	Water	MS	7/27/2006	15:00	97
2767 3.0M FASD	Water	SD	7/27/2006	15:00	96
LC RAMS	Water	MS	7/12/2006	13:30	103
LC RASD	Water	SD	7/12/2006	13:30	103
WR 080806 0950 TMS	WATER	MS	8/8/2006	9:50	91
WR 080806 0950 TSD	WATER	SD	8/8/2006	9:50	90
WR_090706 FAMS	WATER	MS	9/7/2006	9:10	93
WR_090706 FASD	WATER	SD	9/7/2006	9:10	93
WR_090706 RAMS	WATER	MS	9/7/2006	9:10	92
WR_090706 RASD	WATER	SD	9/7/2006	9:10	94
10010020_092606-RAMS	WATER	MS	9/26/2006	12:30	84
10010020_092606-RASD	WATER	SD	9/26/2006	12:30	85
2767 2.7M-RAMS	WATER	MS	6/3/2006	12:50	99
2767 2.7M-RASD	WATER	SD	6/3/2006	12:50	104
3510 0.2M-RAMS	WATER	MS	6/3/2006	9:15	98
3510 0.2M-RASD	WATER	SD	6/3/2006	9:15	102
2565 0.2m_092806 RAMS	WATER	MS	9/26/2006	12:30	92
2565 0.2m_092806 RASD	WATER	SD	9/26/2006	12:30	84
2267 3.5m_092706 RAMS	WATER	MS	9/26/2006	13:05	95
2267 3.5m_092706 RASD	WATER	SD	9/26/2006	13:05	94
BR1 10/10/06 1515 RAMS	WATER	MS	10/10/2006	11:43	102

NativeID	Matrix	QAQC Type	Sample Date	Sample Time	Recovery
BR1 10/10/06 1515 RASD	WATER	SD	10/10/2006	11:43	91
Program 7/Site 1/ GSL WaterMS	WATER	MS	7/26/2006	0:00	38
Program 7/Site 1/ GSL WaterSD	WATER	SD	7/26/2006	0:00	41
Program 9/Site 7/GSL WaterMS	WATER	MS	7/26/2006	0:00	48
Program 9/Site 7/GSL WaterSD	WATER	SD	7/26/2006	0:00	45
Program 8/Site 3/GSL WaterMS	WATER	MS	7/26/2006	0:00	54
Program 8/Site 3/GSL WaterSD	WATER	SD	7/26/2006	0:00	42
Program 8/Site 9/GSL WaterMS	WATER	MS	8/22/2006	0:00	59
Program 8/Site 9/GSL WaterSD	WATER	SD	8/22/2006	0:00	56
Program5/Site2/GSL WaterMS	WATER	MS	5/24/2006	0:00	71
Program5/Site2/GSL WaterSD	WATER	SD	5/24/2006	0:00	73
Program6/Site7/GSL WaterMS	WATER	MS	5/24/2006	0:00	90
Program6/Site7/GSL WaterSD	WATER	SD	5/24/2006	0:00	90
2767 0.2m_110306 RAMS	WATER	MS	11/1/2006	12:30	75
2767 0.2m_110306 RASD	WATER	SD	11/1/2006	12:30	67
3510 0.2m_110306 RAMS	WATER	MS	11/1/2006	10:00	62
3510 0.2m_110306 RASD	WATER	SD	11/1/2006	10:00	60
GD_110906 FAMS	WATER	MS	11/1/2006	13:00	95
GD_110906 FASD	WATER	SD	11/1/2006	13:00	83
2767 0.2m RA-TotalMS	WATER	MS	11/20/2006	14:00	71
2767 0.2m RA-TotalSD	WATER	SD	11/20/2006	14:00	66
Program12/Site 4/GSL WaterMS	WATER	MS	11/20/2006	0:00	77
Program12/Site 4/GSL WaterSD	WATER	SD	11/20/2006	0:00	76
LC_122106 RAMS	WATER	MS	12/7/2006	12:15	97
LC_122106 RASD	WATER	SD	12/7/2006	12:15	101
Program13/Site 7/GSL WaterMS	WATER	MS	12/2/2006	11:44	89
Program13/Site 7/GSL WaterSD	WATER	SD	12/2/2006	11:44	102
2565 7.5 M_120606 RAMS	WATER	MS	12/6/2006	11:25	72
2565 7.5 M_120606 RASD	WATER	SD	12/6/2006	11:25	52
GD_013107 1440 RAMS	WATER	MS	1/31/2007	14:40	103
GD_013107 1440 RASD	WATER	SD	1/31/2007	14:40	97
2565 6.5M FA - Dissolved	WATER	MS			20
2565 6.5M FA - Dissolved	WATER	SD			10.7
2565 6.5 M RA- Total	WATER	MS			18.4
2565 6.5 M RA- Total	WATER	SD			30.8
2565 8.0 M_110106 FA	WATER	MS			14.5
2565 8.0 M_110106 FA	WATER	SD			22.4
2565 8.0 M_110106 RA	WATER	MS			12.5
2565 8.0 M_110106 RA	WATER	SD			10.4
3510 8.0M_120706 FA	WATER	MS			21.8
3510 8.0M_120706 FA	WATER	SD			22
3510 8.0M_120706 RA	WATER	MS			5.06
3510 8.0M_120706 RA	WATER	SD			16.3

Cells shaded in magenta were hand entered from PDF

Matrix Spike/Duplicate Recoveries



Average Recovery	87 %		
Min recovery	6 %		
max recovery	110 %		
avg recovery deep brine	22 %	min = 5.6%	Max = 72%
avg recovery shallow brine	90 %	min = 60%	Max = 109%
avg recovery brad sites	66 %	min = 38%	Max = 102%

Please note that the following samples were removed from the table/chart because Frontier specified that these samples were not spiked:

FGS	2565 7.5 M_120606 RAMS	WATER	MS	12/7/2006	11:25	8.6
FGS	2565 7.5 M_120606 RASD	WATER	SD	12/7/2006	11:25	6.2

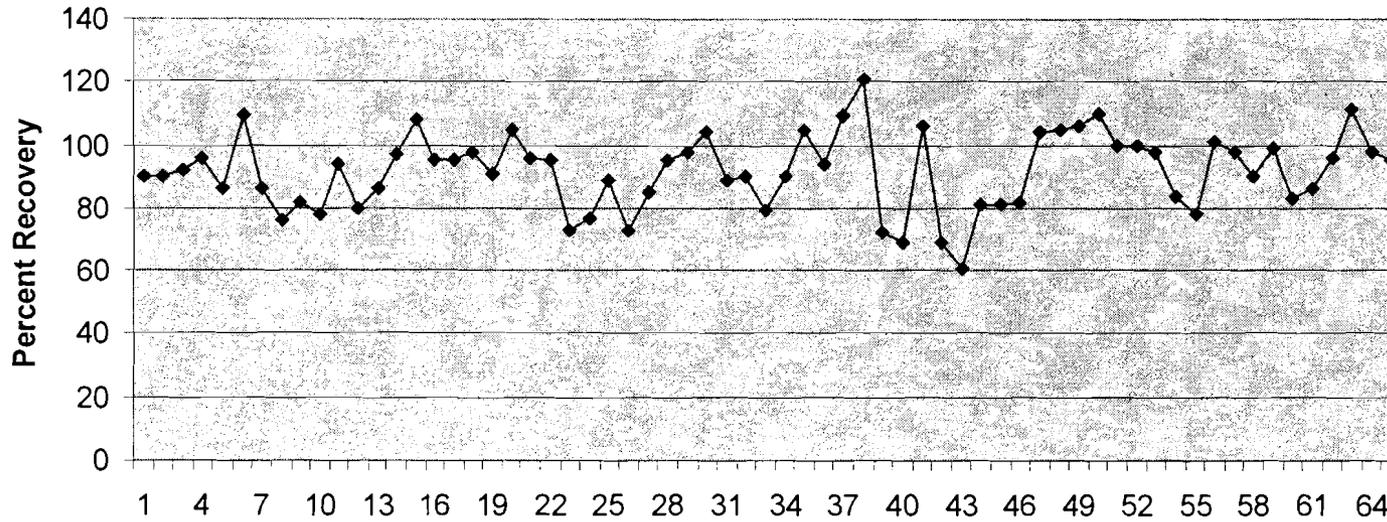
Attachment 2- AS/ASD Recoveries

NativeID	Matrix	QAQC Type	Sample Date	Sample Time	Recovery
BR1-250506 1430 RAAS	Water	AS	5/25/2006	14:30	90
BR1-250506 1430 RAAD	Water	AD	5/25/2006	14:30	90
WATER -GSLM COLONYAD	Water	AD	8/8/2006	11:23	92
WATER -GSLM COLONYAS	Water	AS	8/8/2006	11:23	96
BR1 030506 1425 RAAD	WATER	AD	5/3/2006	14:25	86
ANTI-1-WAS	WATER	AS	6/16/2006	9:15	109
BR1_062106- FA DISSAS	WATER	AS	6/21/2006	13:45	86
2767 3.0M 230506 1130 FAAD	WATER	AD	5/23/2006	11:30	76
BR1 030506 1425 RAAS	WATER	AS	5/3/2006	14:25	82
2767 3.0M 230506 1130 FAAS	WATER	AS	5/23/2006	11:30	78
2267 4.0m_061906- FA DISSAS	WATER	AS	6/19/2006	15:50	94
BR1_062106- FA DISSAD	WATER	AD	6/21/2006	13:45	80
BR1_062106- RA TOTALAD	Water	AD	6/21/2006	13:45	86
2267 0.2m_061906- RA TOTALAS	Water	AS	6/19/2006	15:35	97
ANTI-1-WAD	WATER	AD	6/16/2006	9:15	108
2267 0.2m_061906- RA TOTALAD	WATER	AD	6/19/2006	15:35	95
BR1_062106- RA TOTALAS	Water	AS	6/21/2006	13:45	95
2267 4.0m_061906- FA DISSAD	Water	AD	6/19/2006	15:50	98
WR RAAD	Water	AD	7/12/2006	9:30	91
FB RAAD	Water	AD	7/18/2006	11:00	105
WR RAAS	WATER	AS	7/12/2006	9:30	96
FB RAAS	WATER	AS	7/18/2006	11:00	95
WR 080806 0950 TAS	Water	AS	8/8/2006	9:50	73
WR 080806 0945 TAS	Water	AS	8/8/2006	9:50	77
WR 080806 0950 TAD	Water	AD	8/8/2006	9:50	89
WR 080806 0945 TAD	Water	AD	8/8/2006	9:50	73
WR_090706 FAAD	Water	AD	9/7/2006	9:10	85
WR_090706 FAAS	Water	AS	9/7/2006	9:10	95
BR1 10/10/06 1515 RAAD	Water	AD	10/10/2006	11:43	98
BR1 10/10/06 1515 RAAS	Water	AS	10/10/2006	11:43	104
Program 9/Site 7/GSL WaterAD	WATER	AD	7/26/2006	0:00	89
Program 9/Site 7/GSL WaterAS	WATER	AS	7/26/2006	0:00	90
Program 7/Site 1/ GSL WaterAD	WATER	AD	7/26/2006	0:00	79
Program 7/Site 1/ GSL WaterAS	WATER	AS	7/26/2006	0:00	90
Program 8/Site 3/GSL WaterAS	WATER	AS	7/26/2006	0:00	105
Program 8/Site 3/GSL WaterAD	WATER	AD	7/26/2006	0:00	94
Program 8/Site 9/GSL WaterAD	WATER	AD	7/26/2006	0:00	109
Program 8/Site 9/GSL WaterAS	WATER	AS	7/26/2006	0:00	121
Program5/Site2/GSL WaterAS	WATER	AS	5/24/2006	0:00	72
Program5/Site2/GSL WaterAD	WATER	AD	5/24/2006	0:00	69
2767 0.2m_110306 RAAS	WATER	AS	11/1/2006	12:30	106

NativeID	Matrix	QAQC Type	Sample Date	Sample Time	Recovery
3510 0.2m_110306 RAAD	WATER	AD	11/1/2006	10:00	69
3510 0.2m_110306 RAAS	Water	AS	11/1/2006	10:00	61
2767 0.2m_110306 RAAD	Water	AD	11/1/2006	12:30	81
2767 0.2m RA-TotalAD	WATER	AD	11/20/2006	14:00	81
2767 0.2m RA-TotalAS	WATER	AS	11/20/2006	14:00	82
GSL-3AS	WATER	AS	12/4/2006	0:00	104
GSL-3AD	WATER	AD	12/4/2006	0:00	105
2565 7.5 M_120606 RAAD	Water	AD	12/7/2006	11:25	106
2565 7.5 M_120606 RAAS	Water	AS	12/7/2006	11:25	110
2565 7.5 M_120606 RAAD	WATER	AD	12/6/2006	11:25	100
2565 7.5 M_120606 RAAD	WATER	AD	12/6/2006	11:25	100
2565 7.5 M_120606 RAAS	WATER	AS	12/6/2006	11:25	98
2565 6.5M FA - Dissolved	WATER	AS			84
2565 6.5M FA - Dissolved	WATER	AD			78
2565 6.5 M RA- Total	WATER	AS			101
2565 6.5 M RA- Total	WATER	AD			98
2565 8.0 M_110106 FA	WATER	AS			90
2565 8.0 M_110106 FA	WATER	AD			99
2565 8.0 M_110106 RA	WATER	AS			83
2565 8.0 M_110106 RA	WATER	AD			86
3510 8.0M_120706 FA	WATER	AS			96
3510 8.0M_120706 FA	WATER	AD			111
3510 8.0M_120706 RA	WATER	AS			98
3510 8.0M_120706 RA	WATER	AD			95

Cells shaded in magenta were hand entered from PDF

Analytical Spike/Spike Recoveries



Average Recovery	91 %		
Min recovery	61 %		
max recovery	121 %		
avg recovery deep brine	96 %	Min= 78%	Max = 111%
avg recovery shallow brine	84 %	Min = 61%	Max = 106%
avg recovery brad	92	Min = 69%	Max = 121%