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Analysis of Ionic Mercury Species in SRR Samples Measured by SRNL and Eurofins FGS

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May 2020

SRNL-STI-2020-00081, Revision 0

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Revision

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May 2020

Savannah River National Laboratory®

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

Savannah River Remediation (SRR) requested the development of mercury speciation capabilities at the Savannah River National Laboratory (SRNL) to support the Liquid Waste Operations at SRS.[i] As part of that method development, SRR requested that SRNL Analytical Development (AD) compare their results with those obtained from their outside contract laboratory, Eurofins Frontier Global Sciences (FGS). This document reports on this method development work performed at SRNL as well as the comparative analyses conducted between the two laboratories.

Development, optimization, and validation were undertaken at SRNL to produce a method for the species-specific analysis of ionic mercury. This method was developed as a secondary step to an existing method, L16.1-ADS-1579 Purgeable Mercury Cold Vapor Atomic Fluorescence Spectrophotometry. As such, much of the development and validation were performed in service of development of L16.1-ADS-1579.

Six samples, representing two consecutive quarterly Tank 50 batches, were tested for ionic mercury by SRNL-AD and Eurofins FGS. The mean values reported by each lab for ionic mercury differed by less than one standard deviation, therefore the values reported by both labs were considered to be in agreement. SRNL-AD reported values for the six samples that differed by -5.56 mean percent, relative to Eurofins FGS. Together with comparable quality control data reported by each laboratory, these data represent a high level of agreement among both laboratories.

With a viable method for ionic mercury that matches the data quality provided by outside commercial laboratories, SRNL-AD has demonstrated competency in measuring methylmercury, ethylmercury, total mercury, soluble & particulate mercury, purgeable mercury, and ionic mercury species in a variety of radioactive tank samples.

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[i].Gray, R. J. "SRNL Mercury Speciation Capability Development", X-TTR-H-00069, Rev. 1, Savannah River Remediation, Aiken, SC 29808 (September 2018).

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LIST OF ABBREVIATIONS

AD	Analytical Development
CVAFS	Cold vapor atomic fluorescence spectroscopy
DGM	Dissolved gaseous mercury
DSPM	Dense separate phase mercury
ECC	External calibration curve
EF	Eurofins FGS
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometer
LOD	Limit of detection
LOQ	Limit of quantitation
P&T	Purge and trap
QC	Quality Control
SAM	Standard addition method
SCM	Suspended Colloidal Mercury
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TD	Thermal desorption

1.0 Introduction

The high-activity nuclear waste tanks and legacy waste processing systems at the Savannah River Site (SRS) contain over 60 metric tons of mercury in various forms and species. [1] Mercury has been used for over 50 years at SRS as a catalyst for the dissolution of aluminum alloys, aluminum-uranium cermets, and cladding from targets and fuels. [2] The use of mercuric ions continues today in the nuclear material processing facilities for the dissolution of various aluminum-based materials. [3] Fourth quarter CY2014 samples from Tank 50 showed relatively high levels of total and organomercury, at approximately 76 and 25 mg/L, respectively, relative to the formation mechanisms predicted by models and leachate testing. [1] Efforts have been undertaken to develop quantitative capabilities for organic and inorganic mercury speciation at Savannah River National Laboratory (SRNL) for use in high-activity tank samples.

Novel methods have been developed and optimized at SRNL to separate and quantify inorganic and organic mercury species of interest in High-Level Waste using modular analytical systems housed within radiochemical hoods. [4-5] The work presented here focused on the development of in-house methods for the analysis of ionic mercury species (Hg(I) and Hg(II)), in the liquid tank waste streams.[3] This work built heavily upon prior method development on the analysis of purgeable mercury in liquid tank waste solutions.

Methods for the determination of mercury species involve a combination of sample preparation techniques, such as purge and trap (P&T), adsorbent trapping, and alkyl derivatization. Additionally, diverse ionization and detection techniques, such as inductively couple plasma ionization (ICP) and cold-vapor atomic fluorescence, have existed in the literature for decades.[6-9] While effective standard methods exist for the determination of mercury species in aqueous samples,[10-11] typically prescribed sample handling and manipulation (e.g., modification with NH_2OH, oxidation *via* bromine monochloride, secondary adsorption to carbon and nitric acid digestion, for example) make many commonplace methods for inorganic mercury analysis incompatible with the As Low As Reasonably Achievable (ALARA) principles of radionuclear analytical work and may increase the potential for inadvertent personnel contamination. Therefore, streamlined, modular, low-maintenance methods have been utilized at SRNL for the speciation of mercury.

SRNL undertook work on the development, optimization, validation, and application of a fully-contained, modular method for the separation and analysis of ionic mercury in SRR samples.[4, 12-14] For this method, it was proposed that samples could be first purged with inert gas to remove any purgeable mercury species (e.g., elemental mercury, colloidal mercury, dense separate phase mercury, etc.). Then, with treatment by stannous chloride, ionic mercury could be volatilized and trapped on gold prior to analysis by thermal desorption and atomic fluorescence spectroscopy. This developed procedure was applied to comparison between values for purgeable mercury measured by SRNL and Eurofins FGS in quarterly SRR samples.

2.0 Experimental Procedure

Being a continuation of prior work on purgeable mercury, the experimental setup for this analysis (including development, optimization, and implementation) drew heavily from existing published sources, including SRNL-STI-2019-00300, "Development and Comparison of Purgeable Mercury Values in SRR Samples Measured by SRNL and Eurofins FGS," and SRNL-STI-2018-00250, "Comparison of Methyl- and Ethylmercury Values in SRR Samples Measured by SRNL and Eurofins Frontier Global Sciences." For the purposes of completion and to allow this document to stand alone, some aspects of the experimental procedure and method development, particularly where it concerns the removal of purgeable mercury, will repeat portions (where referenced) from the aforementioned documents. Proper reference has been added where this occurs.

2.1 <u>Instrumentation and Calibration</u>[14]

The instrumentation within the contaminated area (CA) hood was configured to allow maximum efficiency and maneuverability, minimal worker exposure, and limited sample handling. The setup of instrumentation can be seen diagrammed in Figure 2-1. The CA hood (A) enveloped the working area, including a (B) 4-vessel Purge and Trap (P&T) system (Brooks Rand Instruments, Seattle, WA), (C) Dual Trap Thermal Desorption Module (TDM-II) thermal desorption system (Brooks Rand Instruments) containing the sample inlet and (D) Model III (Brooks Rand Instruments) Cold-Vapor Atomic Fluorescence Spectroscopy (CVAFS). Data analysis, handling, and signal processing was performed at an (F) external workstation running Microsoft Excel (Microsoft Corporation, Redmond, WA) and Mercury Guru software (Brooks Rand Instruments), connected to the Model III CVAFS digitally *via* a RS-232 communication port. (H) Carrier and purge gas lines (ultra-high purity grade 5 argon and laboratory grade 4.5 nitrogen, respectively, with 1/8" outer diameter Teflon tubing) were fed through the back of the CA. A small (E) control pad was installed within the CA, connected to the external workstation digitally *via* (G) USB that enabled operation of basic functions of the instrument, as well as control over simple data processing and analysis from within the CA.
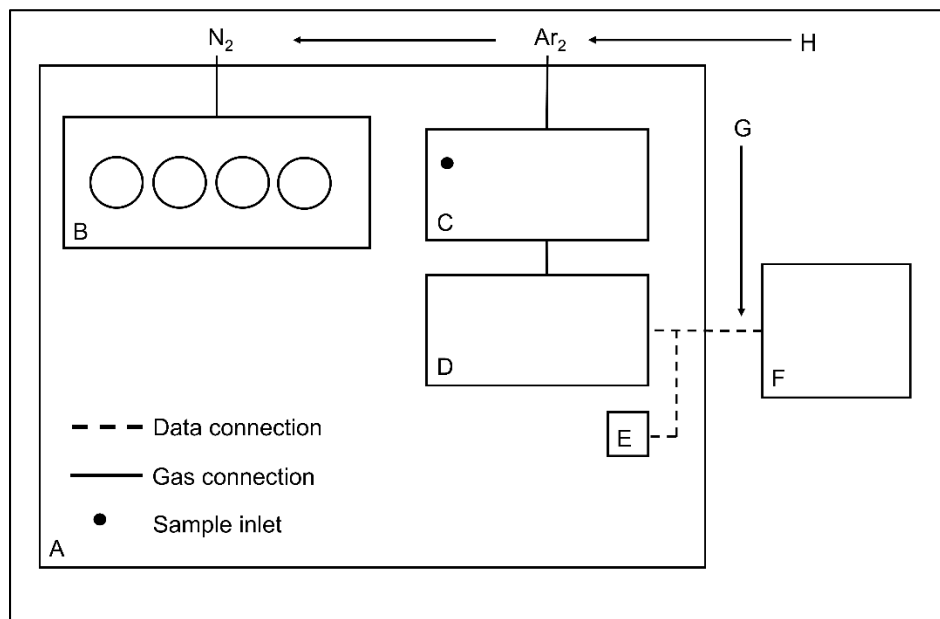
Figure 2-1. Schematic of the configuration of the P&T-TD-CVAFS within the contamination area demonstrating (A) the radiological hood, (B) purge and trap system, (C) thermal desorption device and sample inlet, (D) atomic fluorescence detector, (E) digital instrumental control pad, (F) instrumental control computer, (G) digital and electronic connections, and (H) purge and carrier gas lines.

Initial parameters for instrumental operation were obtained from standardized methods and vendor recommendation:[11] N_2 purge flow rate of 25 mL/min, carrier gas flow rate of 30 mL/min Ar_2, a N_2 purge time of 35 minutes, 10.6 V for the heating coil on the flow-rate of TDM-II, TDM-II heating and cooling times of 3 minutes each. For optimization purposes, purge flow rate, purge time, and matrix modification were investigated. For development and calibration, gas-phase mercury was used as the measured form of mercury, and following stannous chloride reduction, will be gas-phase elemental mercury.

Calibration was obtained by external calibration and standard addition. For generating standards, known amounts of mercury were withdrawn from the headspace of a gas-tight box containing liquid mercury and mercury-saturated headspace (Brooks Rand Instruments).[15] These gas aliquots were injected in-line with the experimental setup. Mass of mercury withdrawn was calculated using the volume of mercury withdrawn at ambient atmospheric pressure, ambient temperature in Kelvin (T_K) of the radiation hood, and an empirically derived equation of state for real gases provided by the vendor (Brooks Rand Instruments):[15-17]

Equation 1: $\log(ng/mL) = (-3104/T_K) + 11.709$

Standard addition calibration, matrix spike samples, and recovery analysis data were generated in-line at the purge vessels by spiking known amounts of mercury vapor through the septum of a quartz-T connector into the N_2 purge gas flow upstream of the purge vessels. For experimental consistency, mercury vapor was

used to represent all purgeable mercury species. Matrix spikes were generated by injecting mercury vapor in-line with the purge gas through deionized water or simulated tank waste.

Data analysis proceeded in accordance with manufacturer recommendation. As this method contained no chromatography, all "peaks" observed in the detector following each analysis were presumed to be purged mercury and summed to determine total mass (ng) of mercury purged and detected. Incomplete or otherwise unusable purge runs were occasionally observed. For this method, three quality assurance rules were developed to eliminate unusable or low-quality data based on the detector peak profile alone:

1. To remove incomplete desorption data, any run in which a "peak" did not return to the baseline by the end of detection period was removed;
2. To identify contaminated gold-traps, any detector signal profile containing more than five identified peaks were considered contaminated and were re-run;
3. The QC acceptance criteria was ±50% of the expected value

2.2 Two-step sparge for Purgeable and Ionic Mercury

As the analytical instrumentation is not selective on mercury species, prior to analysis for ionic mercury, all purgeable mercury was removed from the sample. As such, the method outlined in SRNL-STI-2019-00300 is first performed, followed by the developed method presented here. All samples were first purged to remove all volatile mercury species, including elemental mercury, suspended colloidal mercury particulates, dense-phase mercury, and any volatile organomercury species. In the analysis of ionic mercury alone, no analytes are trapped in this step. Following initial purge, stannous chloride is used to reduce ionic mercury (Hg(I) and Hg(II)) to Hg(0). Finally, a second purge is performed to remove the reduced ionic mercury, where it can then be trapped on gold-coated beads. See Figure 2-2.

Stannous chloride stock solution was prepared using 200 g of stannous chloride combined with 100 mL of hydrochloric acid. This solution was brought to 1 L with deionized water and purged overnight with nitrogen at 500 mL/min to ensure removal of all traces of mercury. To each sample, quality control sample, and black, 0.5 mL of stannous chloride solution was added and the vessel was allowed to purge for 17.5 minutes.
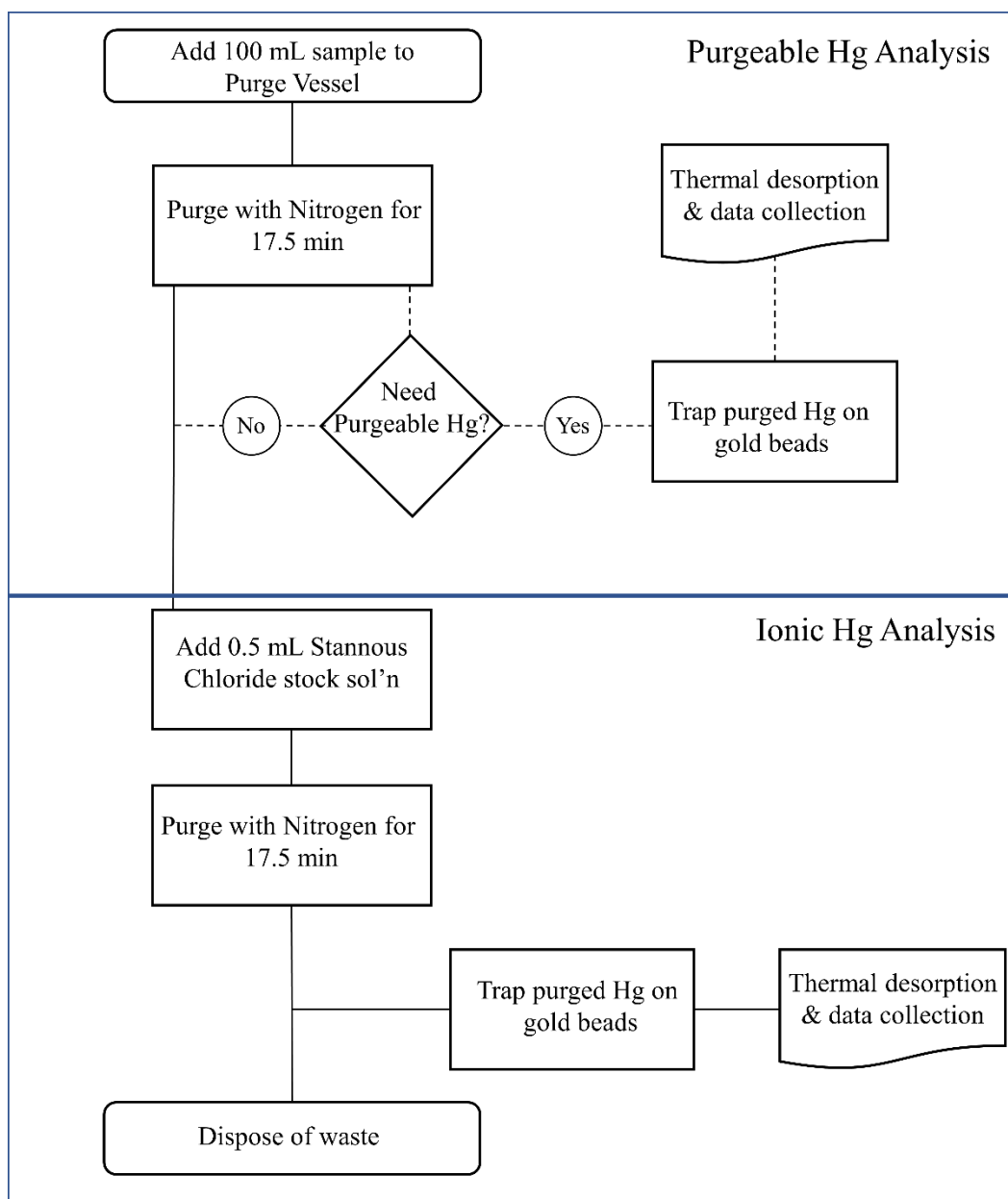
Figure 2-2. Simplified process flow illustrating procedure L16.1-ADS-1579 for the analysis of both purgeable mercury species and ionic mercury species.

2.3 Sample Processing and Data Handling

Quarterly samples were collected in small, stainless steel bottles with limited headspace. The bottles were transferred to SRNL where, for high activity samples, 1:100 aqueous dilutions by volume were performed with deionized water into a Teflon bottle. These dilutions were performed prior to immediate transfer to refrigeration at 4 °C. For low activity waste (including Tank 50 samples), no initial dilution is performed.

For ionic mercury analysis, a further 1:1000 dilution was performed in deionized water and 100 mL was transferred to the purge vessel. [1]

Percent recovery of elemental mercury was determined in water, simulated tank waste, or Tank 50 liquid waste samples from SRR. Percent recovery was calculated according to equation 2, as described by Method 1631 from the Environmental Protection Agency (EPA).[11]

$$\textbf{Equation 2}: \%R = 100 \times \frac{(A-B)}{T}$$

Where, A is the measured concentration of purgeable mercury after spiking, B is the measure concentration of the analyte before spiking, and T is the true concentration of the mercury vapor spike. The uncertainty of recovery is equal to the standard deviation of the mean recoveries for each sample. [11, 18]

2.4 Quality Assurance

The work described in this Report was performed in accordance with the Task Technical & QA Plan SRNL-RP-2016-00788 from SRNL and the Technical Task Request X-TTR-H-00069, Rev. 1 from SRR Requirements for performing reviews of technical reports and the extent of review are established in manual E7, 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

The QA level requirement defined by SRR was Function Classification: Production support. The procedures and work protocols used in the development, implementation, and ongoing execution of this work comply with the required QA level and functional classification established by the customer. All activities were performed and documented with Manual E7 and Manual 1Q.

Unless otherwise stated, reported variance in this work is at the 95% confidence intervals. The ionic mercury data available for statistical evaluation included measurements of Quality Control (QC) standards analyzed by SRNL Analytical Development (AD) and of QC standards analyzed by Eurofins FGS (EF) as well as results from tank samples that were analyzed by both AD and EF.

3.0 Results and Discussion

3.1 Development and Optimization

Development and optimization was performed on the analysis of gaseous mercury, being the final measured species in this analytical process. Therefore, separate optimization was not performed for ionic mercury-

instead only purgeable mercury was optimized. Presented here is the method optimization performed on purgeable mercury.[14]

Three variables were optimized simultaneously for the analysis of elemental mercury using a 3x3 reduced factorial multivariate experiment and changes in their parameters were tested for significance. No cross-combination of parameters was significantly predictive of response. However, taken as univariate experiments, individual correlations were discovered. Optimal experimental parameters included: purge flow rate of 65 mL/min, 17.5 minute purge time for both purges, and 0% salt matrix modification.

Total cumulative recovery was determined for the optimized procedure. Mean percent recovery was 100. ±7% (n=5) when measured by injection of elemental mercury vapor without the purge and trap system, 99.4 ±10.6% when purged through into deionized water, and 91.6 ±14.9% when purged through 1:1000 diluted and blank-corrected Tank 50 liquid waste sample. Overlap was observed in the 95% confidence range of recoveries in spiked Tank 50 samples, spiked DI water, and non-purged gaseous mercury measured directly. A comparison of recovery values, showing 95% confidence levels, can be found in Figure 3-1. Similar recoveries achieved from pre-spiked and purged tank samples and deionized water suggest a lack of matrix effect in the liquid tank waste samples.
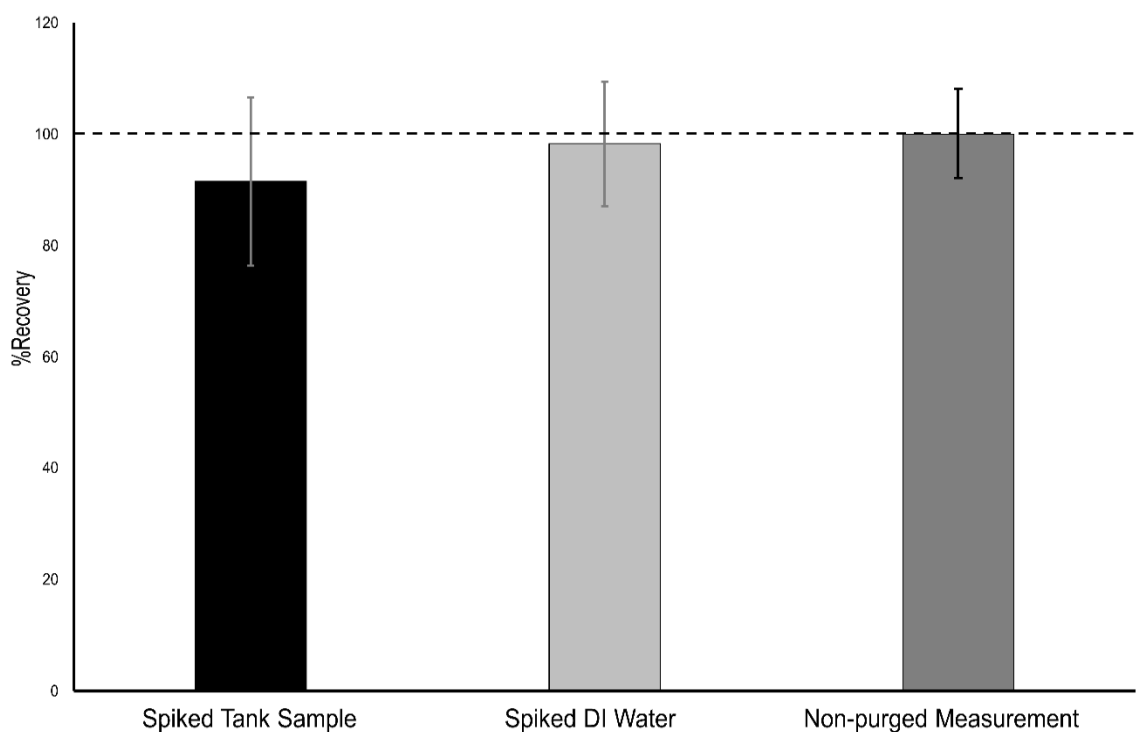
Figure 3-1. A comparison of analytical recovery of mercury vapor spiked and purged through SRR waste sample, deionized water, and measured directly without purge

External calibration maintained linearity over 3 orders of magnitude, with a coefficient of determination of 0.9999. Mean accuracy over this calibration curve was 101 ±5%. Standard addition calibration was obtained over three points, comprised of 10, 25, and 50 μL mercury vapor additions spiked and purged through liquid tank waste diluted at 1:1000 with deionized water, with a coefficient of determination of 0.9999. Mean accuracy over this calibration curve was 99.9 ±1.7%. External calibration and standard addition calibration can be seen in Figure 3-2, where the standard addition has been blank-corrected to display only peak area associated with the spiked mercury vapor. Volume of mercury vapor injected was temperature-corrected, using equation 1, to present the data as a function of mass of mercury injected.
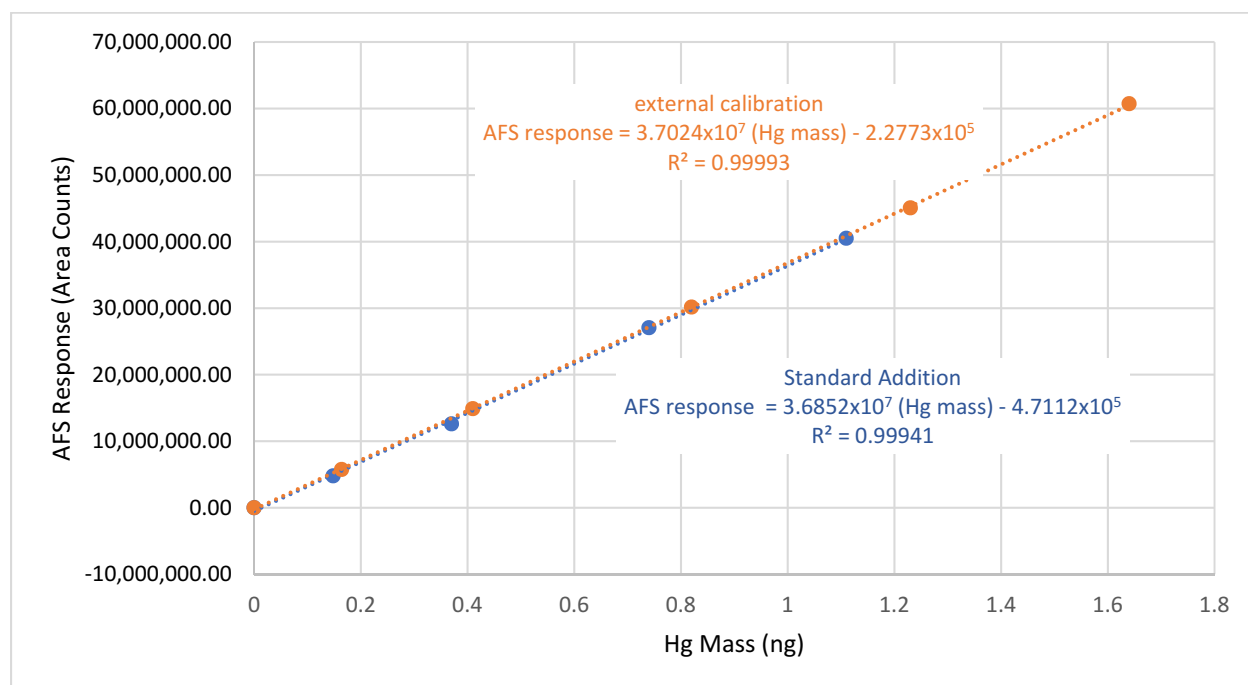
Figure 3-2. Calibration techniques performed directly (external calibration) or *via* purge through SRR samples (standard addition)

3.2 Quality Control and Validation

Quality control replicate analyses were performed to determine internal method quality. Table 3-1 provides the mass (ng) of mercury injected, the mass (ng) of mercury measured, and the percent difference between the two. These results were generated by injecting gaseous elemental mercury vapor in-line with the purge gas flow and sparged through 100 mL of 1:1000 diluted simulated Tank 50 liquid waste. Mercury vapor was used for initial QC testing to determine the functionality of the instrumentation and overall analytical system.

Table 3-1. Performance of Eurofins FGS and SRNL-AD method quality control replicates for mercury matrix spike samples

Sample Name	Sub-Type	% Recovery	
Eurofins FGS QC	Matrix Spike	113	
Eurofins FGS QC	Matrix Spike	65.4	
Eurofins FGS QC	Matrix Spike	64	
Eurofins FGS QC	Matrix Spike Dup	139	
Eurofins FGS QC	Matrix Spike Dup	105	
Eurofins FGS QC	Matrix Spike Dup	103	
Eurofins FGS QC	LCS	101	
Eurofins FGS QC	LCS Dup	117	
Eurofins FGS QC	LCS	105	
Eurofins FGS QC	LCS Dup	105	
Eurofins FGS QC	Matrix Spike	103	
Eurofins FGS QC	Matrix Spike Dup	108	
Eurofins FGS QC	LCS	112	
Eurofins FGS QC	LCS Dup	119	
Eurofins FGS QC	Matrix Spike	96.3	
Eurofins FGS QC	Matrix Spike Dup	115	
	Mean		104
SRNL-AD	QC	112	
SRNL-AD	QC	111	
SRNL-AD	QC	104	
SRNL-AD	QC	132	
SRNL-AD	QC	103	
SRNL-AD	QC	88.9	
SRNL-AD	QC	58	
SRNL-AD	QC	97.6	
SRNL-AD	QC	93.5	
SRNL-AD	QC	60.3	
SRNL-AD	QC	108	
SRNL-AD	QC	80	
	Mean		95.7

Included in these comparisons is a statistical test of the hypothesis of equal variances for the two sets of results. Further statistical analysis can be found in Exhibit A-1. The outcome of Levene's test with its p-value of 0.3831 indicates that this hypothesis cannot be rejected at a significance level of 5% (i.e., at a p-value of 0.05). Thus, the results indicate comparable precision in the measurement of QCs for the two laboratories. A t-test for the hypothesis of equal means for the two sets of relative differences yields a p-value of 0.2581, indicating that this hypothesis cannot be rejected at the 5% significance level. Thus, there is no indication of a relative bias between the two laboratories in the measurements of these QCs.[14]

3.3 Comparison between SRNL-AD and Eurofins FGS in SRR Tank Samples

Following development and validation of this method for the analysis of ionic mercury in contaminated samples, two consecutive quarterly tank samples were prepared simultaneously for shipment to Eurofins FGS and SRNL-AD. Six total samples labeled, representing separate aliquots from batches named 2Q19 Tank 50 and 3Q19 Tank 50, were analyzed by both laboratories. Comparison data can be found in Figure 3-3 and Table 3-2.
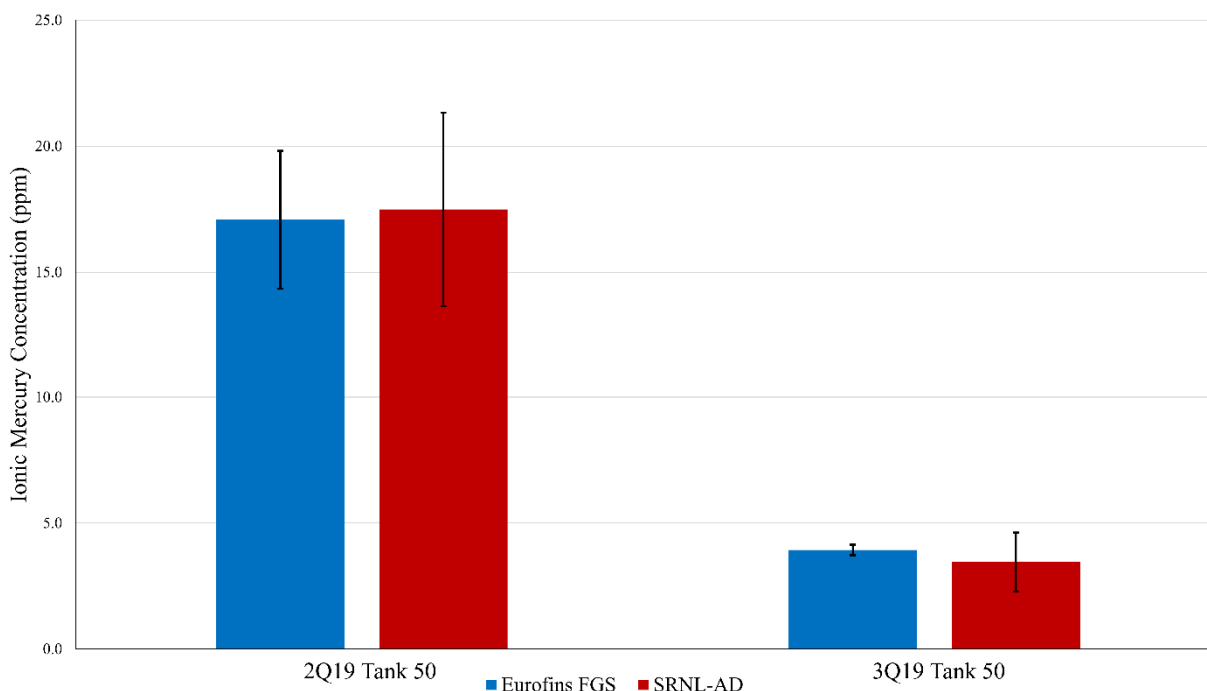
Figure 3-3. Comparison between Eurofins FGS and SRNL-AD of six consecutive SRR Tank Samples, prepared from two quarterly batch aliquots, showing mean and 1-sigma relative deviation

On the analysis of mean ionic mercury concentration, Eurofins FGS produced a value of 17.1 ±16% (1σ) for the samples in the 2Q19 aliquot, and 3.90 ±5.3% for 3Q19. SRNL-AD produced a value of 17.5 ±21% for 2Q19 and 3.50 ±33% for 2Q19. At the 1σ level, no difference is observed in the mean concentration observed in each quarterly batch of samples between the two labs. Mean variance observed in each laboratory differed: Eurofins FGS recorded an average standard deviation of 10.7%, while SRNL-AD reported an average standard deviation of 27%.

This difference in observed variance is reasonable given that Eurofins FGS employs a proprietary analytical method that maximizes automation and maintains the ability to re-analyze samples. SRNL-AD, however, must work within hood-constraints and minimize High Level Waste generation. A trade-off is made,

therefore, between the highly automated and residue-heavy method employed by Eurofins FGS, and the hands-on method used by SRNL-AD that generates little-to-no High Level Waste.

See Table 3-2 for a detailed examination of each sample submitted for analysis for each laboratory and a comparison between them. SRNL-AD results were biased 5.56% low relative to Eurofins FGS, however this bias is within the variance observed in Figure 3-3. Therefore, no statistically relative bias is observed between the two labs. Further, upon implementation of an approved measurement control plan and control charts for this method, the result from SRNL-AD for sample 9859 would likely be rejected as an outlier. Hypothetically rejecting sample 9859 results in a mean %Delta of just 1.98%, demonstrating a high level of agreement between the laboratories.

Table 3-2. Comparison between Eurofins FGS and SRNL-AD of six consecutive SRR Tank Samples, prepared from two quarterly batch aliquots, showing percent difference

		Eurofins FGS (ppm)	**SRNL-AD (ppm)**	**%Delta**
2Q19	9397	17.2	16.4	-4.5
	9398	19.8	21.8	10.3
	9399	14.3	14.3	0.1
3Q19	9858	4.00	4.11	2.83
	9859	3.70	2.10	-43.2
	9860	4.10	4.15	1.17
			Mean	-5.56

4.0 Conclusions and Recommendations

Both SRNL-AD and Eurofins FGS have demonstrated robust, high quality laboratory methods for the analysis of ionic mercury in contaminated samples. No statistically significant bias was observed in the mean concentrations of ionic mercury determined in two consecutive quarterly batches of samples between SRNL-AD and Eurofins FGS. Of note, however, SRNL-AD reported greater standard deviation on all analyzed sample batches: 10.7% vs. 27%. However, a bias of only -5.5% was observed in SRNL-AD, relative to Eurofins FGS, representing a high level of agreement between the two high quality laboratories.

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6.0 Appendix A

Exhibit A-1: Further Statistical Analysis of QC Precision and Means from SRNL-AD and Eurofins FGS

Oneway Anova
Summary of Fit

Rsquare	0.048912
Adj Rsquare	0.012332
Root Mean Square Error	19.74227
Mean of Response	0.682527
Observations (or Sum Wgts)	28

t Test
EF-AD

Assuming equal variances

Difference	8.718	t Ratio	1.156336
Std Err Dif	7.539	DF	26
Upper CL Dif	24.215	Prob > |t|	0.2581
Lower CL Dif	-6.779	Prob > t	0.1290
Confidence	0.95	Prob < t	0.8710

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Lab	1	521.150	521.150	1.3371	0.2581
Error	26	10133.683	389.757		
C. Total	27	10654.833			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
AD	12	-4.2991	5.6991	-16.01	7.416
EF	16	4.4188	4.9356	-5.73	14.564

Std Error uses a pooled estimate of error variance

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
AD	12	-4.2991	21.4735	6.1989	-17.94	9.345
EF	16	4.4188	18.3693	4.5923	-5.37	14.207

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
AD	12	21.47353	16.30331	15.99430
EF	16	18.36926	11.72656	11.58125

Exhibit A-1: Further Statistical Analysis of QC Precision and Means from SRNL-AD and Eurofins FGS (*continued*)

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.2606	1	26	0.6140
Brown-Forsythe	0.6715	1	26	0.4200
Levene	0.7872	1	26	0.3831
Bartlett	0.3012	1	.	0.5831
F Test 2-sided	1.3665	11	15	0.5633

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