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Development and Comparison of Purgeable Mercury Values in SRR Samples Measured by SRNL and Eurofins FGS

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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 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 dissolved gaseous mercury (DGM) in samples from SRR. It was determined that DGM present in SRR samples represented a combination of various soluble and volatile mercury species- and is thus referred to in this document as purgeable mercury.

A method has been developed and analytically validated for the analysis of purgeable mercury in caustic nuclear waste. Using multivariate optimization method, purge flow rate was determined to be highly correlated with increased response (p=0.023). Total recovery of spiked purgeable mercury from deionized water was 99.4 ±10.6% and 91.6 ±14.9% from spiked high-activity tank waste samples. Calibration, by external calibration and standard addition calibration, maintained a mean accuracy of 101 ±5% and 99.9 ±1.7%, respectively. This method represents a decrease in sample handling and processing over currently standard methods and represents a more amenable method for purgeable mercury analysis in liquid nuclear waste.[1] An interlaboratory comparison was performed between SRNL and Eurofins FGS in the co-analysis of three quarterly Tank 50 samples. Two samples demonstrated no statistically significant difference (p=0.271, p=0.0811), with one sample biased 30% low to a statistically significant degree (p=0.0432). Large mean uncertainty was present in the results reported by both laboratories (±15% and 40% from SRNL and Eurofins), with no significant difference observed in uncertainty (p=0.934). Across all co-analyzed samples, no significantly difference was observed in precision (p=0.205) or reported values (p=0.352) between SRNL and Eurofins. These results indicate that SRNL-AD may provide data to the customer of statistically similar quality.

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LIST OF ABBREVIATIONS

SRS	Savannah River Site
SRNL	Savannah River National Laboratory
SCM	Suspended Colloidal Mercury
DSPM	Dense separate phase mercury
DGM	Dissolved gaseous mercury
P&T	Purge and trap
ICP	Inductively coupled plasma
ALARA	As low as reasonable achievable
ICP-MS	Inductively coupled plasma mass spectrometer
TD	Thermal desorption
CVAFS	Cold vapor atomic fluorescence spectroscopy
LOD	Limit of detection
LOQ	Limit of quantification
ECC	External calibration curve
SAM	Standard addition method

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. [2] Mercury, in the presence of nitric acid and heat, 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. [3] The use of mercuric ions continues today in the nuclear material processing facilities for the dissolution of various aluminum-based materials. [4]

Fourth quarter 2014 samples from Tank 50 showed relatively high levels of organomercury, at approximately 100 mg/L, relative to the formation mechanisms predicted by models and leachate testing. [2] 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.

Mercury species of interest to SRR include organomercury (including methylmercury, ethylmercury, and dimethylmercury), particulate and dissolved elemental mercury (Hg^0), and ionic mercury (Hg^+ and Hg^{2+}) in the liquid waste stream. [2] Novel methods have been developed and optimized at SRNL to separate and quantify organomercury species of interest in high-level liquid waste using direct aqueous alkyl derivatization, gas chromatography, and fluorescence spectroscopy. [5-6] This work focused on the development of in-house methods for the analysis of particulate and dissolved elemental mercury (deemed "purgeable mercury) in the liquid tank waste streams.[4]

Given the high concentrations of mercury in the tanks at SRS, it was anticipated that all elemental mercury within the tanks should exist in equilibrium at its solubility point in aqueous solution. [2] General agreement states that the solubility limit of purgeable mercury exists between 0.2 µmol/L and 0.7 µmol/L in aqueous solution (though strongly dependent upon the ionic activity of solution). [7] It is reasonable to presume, however, that sub-sample aliquots taken from large-volume solutions may contain dense-phase or suspended colloidal mercury forms. As this aliquot is diluted with deionized water, a shift is equilibrium may dissolve some previously non-solubilized mercury. For this reason, the term "purgeable mercury" will be used in this work to refer to the sum of all potentially purgeable mercury species.

Methods for the determination of purgeable 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.[8-11] While effective standard methods exist for the determination of mercury species in aqueous samples,[12-13] typically prescribed sample handling and manipulation (e.g. modification with NH_2OH, oxidation *via* bromine monochloride, secondary adsorption to carbon and nitric acid digestion), make many commonplace methods for inorganic mercury analysis incompatible with the As Low As Reasonably Achievable (ALARA) principles of radionuclear analytical work. While ICP mass spectrometry (ICP-MS) may provide highly accurate mercury quantification and, when paired with an appropriate chromatographic separation, could provide high quality species information, the footprint associated with an ICP-MS is cost-prohibitive to radio-hood containment.[5]

SRNL undertook work on the development, optimization, validation, and application of a fully-contained, modular, high-throughput method for the separation and analysis of purgeable mercury in SRR samples. For this work, it was proposed to separate purgeable mercury from organomercury species in high activity waste by leveraging volatility and the affinity between inorganic mercury and gold-coated bead traps. 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

2.1 Instrument Configuration

The instrumentation within the 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.
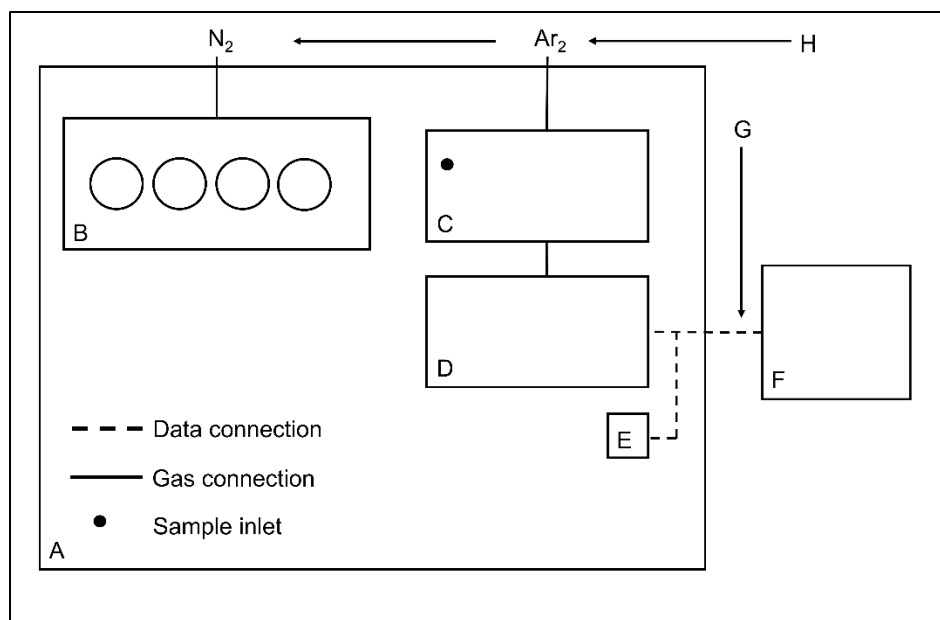
Figure 2-1: Schematic of the configuration of the P&T-TD-CVAFS within the contamination area demonstrating (A) the radiological hood, (B) purge and trap system, (C) thermal desorption device and sample inlet, (D) atomic fluorescence detector, (E) digital instrumental control pad, (F) instrumental control computer, (G) digital and electronic connections, and (H) purge and carrier gas lines**.**

As seen in figure 1, the CA hood (A) enveloped the working area, including a (B) 4-vessel P&T system (Brooks Rand Instruments, Seattle, WA), (C) Dual Trap TDM-II thermal desorption system (Brooks Rand Instruments) containing the sample inlet and (D) Model III (Brooks Rand Instruments) CVAFS. Data analysis, handling, and signal processing was performed at an (F) external workstation PC 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 [O.D.] 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.

Initial parameters for instrumental operation were obtained from standardized methods and vendor recommendation:[13] 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.

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 vial containing liquid mercury. 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):[7, 14-15]

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

Standard addition calibration, matrix spike samples, and recovery analysis samples 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 downstream of the purge vessels. For experimental consistency, mercury vapor was used to represent all soluble, volatile mercury species. During "matrix spiking," the spiked mercury vapor was bubbled through deionized water or simulated tank waste- creating a relatively low residence time between mercury vapor and solution. As such, this setup did not fully replicate the time of interaction between purgeable mercury species in stored tank samples- which may be stored for several weeks (and up to 180 days). However, for the purpose of standardizing method development and optimization, this setup is referred to as a "matrix spike." This experimental design limitation should be considered.

2.2 Multivariate Development

To detect large main effects in the optimization of this method, a 3x3 reduced factorial multivariate experimental design was employed, using 3 variables measured at 3 levels each. [16] For each of three levels designated for each variable, a mid-point was selected that represented the standard method variable setting, and low / high levels that represented reasonable extreme parameters.[17] Table 3-1 demonstrates the experimental design encompassing purge flow, purge time, and matrix addition measured at low/mid/high points taken from standard and commonplace methods,[13, 18-19] of 25/45/65 mL/min, 5/17.5/30 minutes, and 0/10/20% NaCl addition, respectively.

Table 2-1. Three variable – three level multivariate optimization experimental design

	Purge Flow (mL/min)	Purge Time (min.)	Matrix Addition (%)
1	25	5	0
2	25	5	10

3	25	5	20
4	25	17.5	0
5	25	17.5	10
6	25	17.5	20
7	25	30	0
8	25	30	10
9	25	30	20
10	45	5	0
11	45	5	10
12	45	5	20
13	45	17.5	0
14	45	17.5	10
15	45	17.5	20
16	45	30	0
17	45	30	10
18	45	30	20
19	65	5	0
20	65	5	10
21	65	5	20
22	65	17.5	0
23	65	17.5	10
24	65	17.5	20
25	65	30	0
26	65	30	10
27	65	30	20

2.3 <u>Sample Processing and Data Handling</u>

Quarterly samples were collected in small, stainless steel bottles with zero headspace. The bottles were transferred to the SRNL where 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 purgeable mercury analysis, a further 1:1000 dilution was performed in deionized water and 100 mL was transferred to the purge vessel. [2]

Comparison testing was performed *via* statistical analysis at the 95% confidence interval and a standard hypothesis testing value of p=0.05 using two-tailed T-test of independent means. Unless indicated, all uncertainty and standard deviation is given as a percentage relative to the mean value. Methods limits of detection and quantification (LOD, LOQ) were calculated using equations 2, where σ_n is the standard deviation of n samples:

$$\textbf{Equation 2}: LOD = \sigma_n \times t_{95,n-1}$$

$$LOQ = LOD \times 3.33$$

Percent recovery of purgeable mercury was determine in a Tank 50 liquid waste sample from SRR. Percent recovery was calculated according to equation 3, as prescribed by Method 1631 from the Environmental Protection Agency (EPA).

Equation 3: $\%R = 100 \times \frac{(A-B)}{T}$

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. [13, 20]

Bias was assessed in this work and is largely treated as synonymous with recovery. [20] Combined bias in the purging and trapping steps was determined on 15 consecutive samples with 0.422 ±0.042 ng spiked mercury vapor. Mean concentration values obtained using P&T were compared with mean concentration valued obtained by directly injecting the indicated mass of mercury vapor into the AFS detector without P&T. Each reported measured value in this work generated by purge and trap, was calculated as the product of the raw calculated measurement value and a bias correction of +28.9 ±3.3%.

3.0 Results and Discussion

3.1 Development and Optimization.

Three variables were optimized simultaneously 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 could be discovered per variable. Figure 3-1 demonstrates the results at the low and high ends of each optimization experiment. Figure 3-1A demonstrates the nonsignificant difference (p=0.23) in response between matrix solutions prepared at 0% and 20% ionic activity with potassium chloride (n=5). Figure 3-2B shows the highly trending, but nonsignificant difference (p=0.18) in response between samples purged with N_2 for 5 minutes and 30 minutes (n=5). Figure 3-2C shows the significant difference (p=0.023) in samples purged at a flow rate of 25 mL/min and 65 mL/min(n=5). Figure 3-2D demonstrates the significant (p=0.00019) decrease in replicate variance as sample purge rate is increased. Figure 2-D displays the variance associated with the mean (n=9) of AFS peak area data collected at each unique purge flow rate (25/45/65 mL/min), regardless of purge times and matrix addition schemes. The observed data provides a

reasonable match with theoretically optimal performance. [21] This suggests that the kinetics of the described sparging system are relatively fast, and not the rate-limiting step.
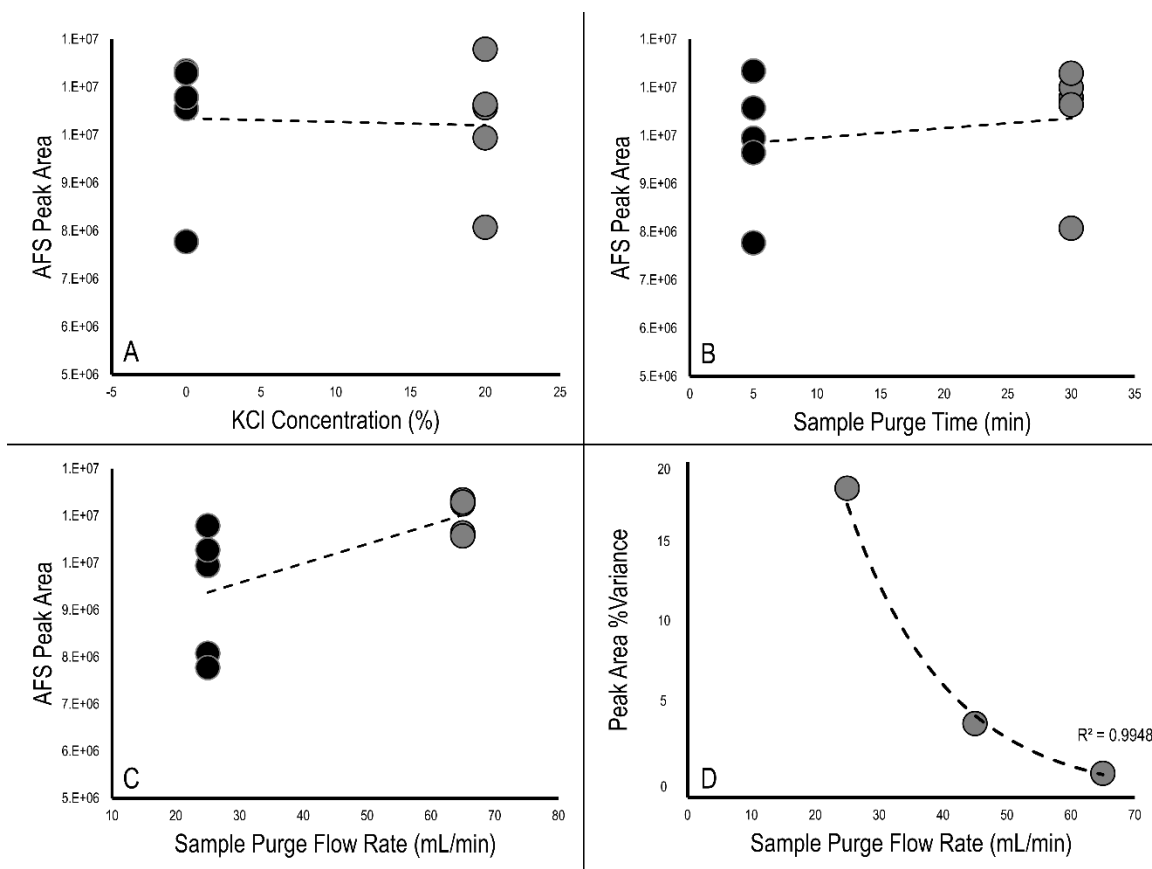
Figure 3-1: Univariate results of multivariate optimization experiments, showing (A) matrix ionic activity response, (B) sample purge time, (C) flow rate of nitrogen purge gas, and (D) relationship between purge flow rate and response variance, showing a polynomial regression and coefficient of determination (R^2). Dashed lines in A – C connect the mean of each group to add visual clarity.

Total cumulative recovery was determined for the optimized procedure. Mean percent recovery was 100. $\pm$7% (n=5) when measured directly without the purge and trap system, 99.4 $\pm$10.6% when purged through into deionized water, and 91.6 $\pm$14.9% when purged through 1:1000 diluted and blank-corrected Tank 50 liquid waste sample. Recovery in Tank 50 samples was not significantly different than non-purged spikes measured directly (p=0.77) or spikes purged through deionized

water (p=0.57). Recovery in deionized water was not significantly different from non-purged spikes, as well (p=0.58). A comparison of recovery values, showing 95% confidence levels, can be found in figure 3-2. Statistically similar recoveries achieved from pre-spiked and purged tank samples and deionized water demonstrate a lack of matrix effect in the liquid tank waste samples.
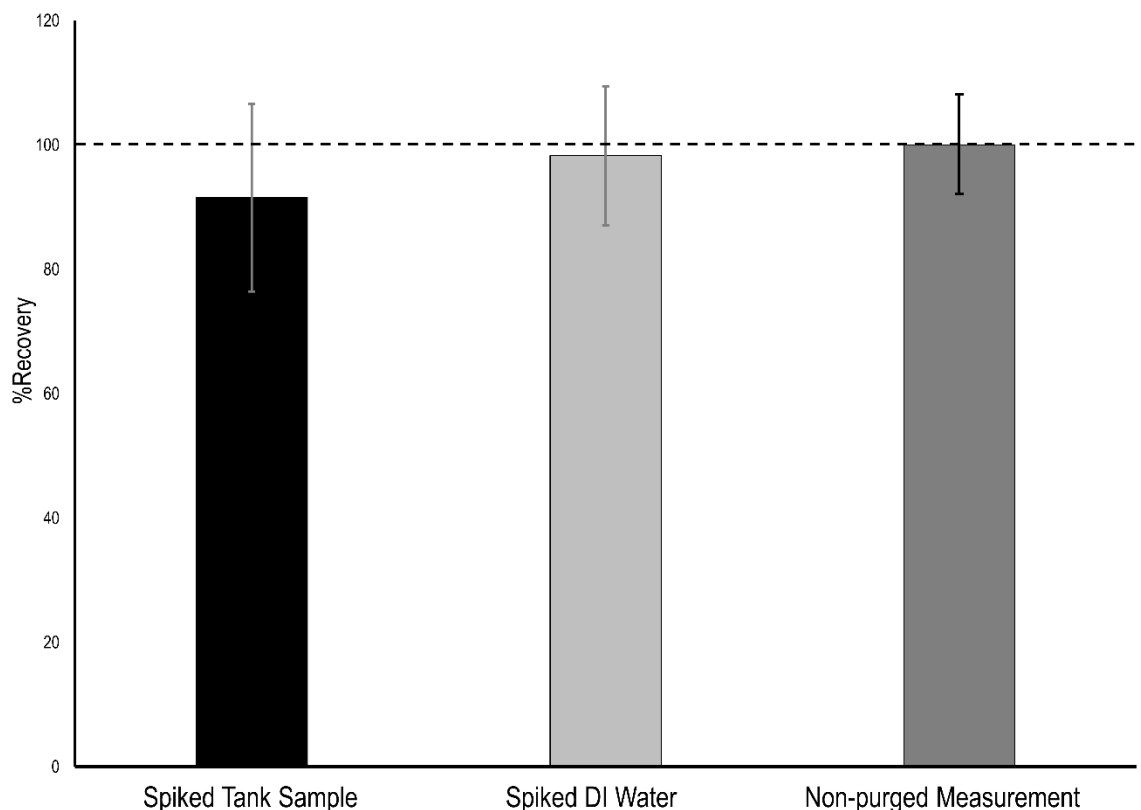
Figure 3-2. A comparison of analytical recovery of mercury vapor spiked and purged through SRR waste sample, deionized water, and measured direction without purge

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%. Mean accuracies of the two calibration methods were not significantly different (p=0.68). External calibration and standard addition calibration can be seen in figure 3-3, where the standard addition has been blank-corrected to display only peak area associated with the spiked mercury vapor.

Figure 3-3. Calibration techniques performed directly (external calibration) or *via* purge through SRR samples (standard addition)
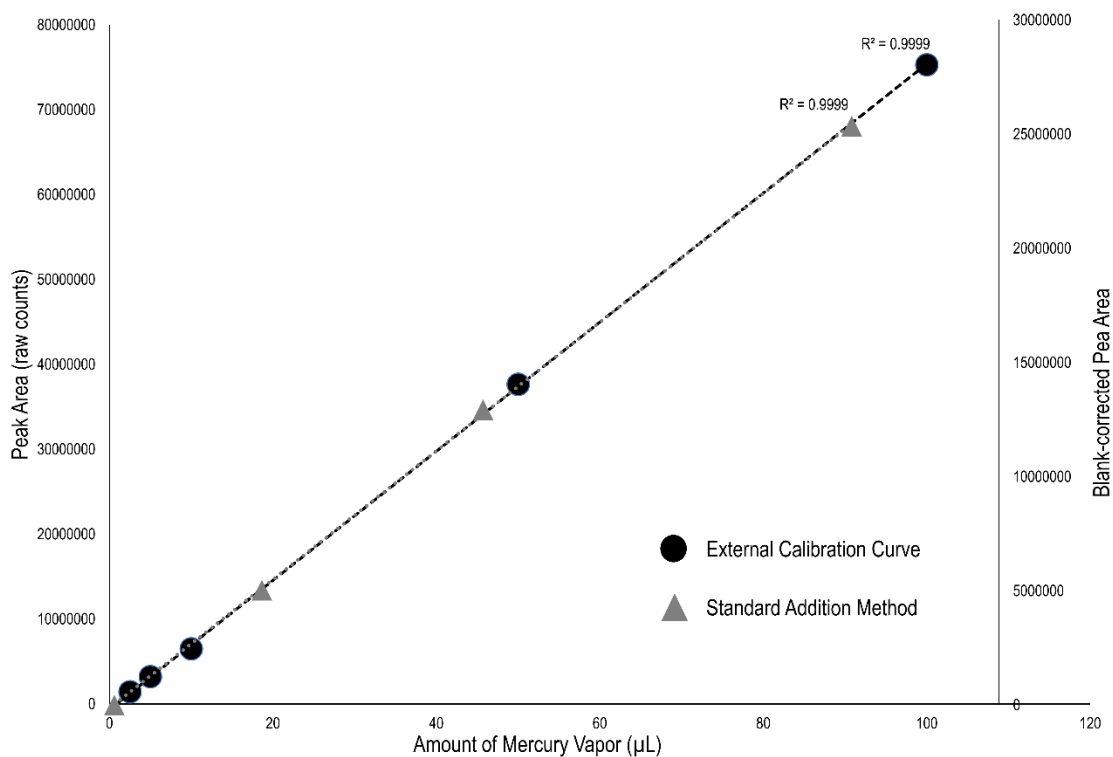
3.2 Comparison between SRNL and Eurofins FGS

A comparison was performed between results obtained for purgeable mercury by SRNL and Eurofins FGS. Results of the comparison can be found in Table 3-1.

Table 3-1. Comparison between SRNL-AD and Eurofins FGS in the analysis of three SRR Tank samples

	AD		Eurofins FGS		
1Q18 Tank 50					
	Concentration (mg/L)	%RSD	Concentration (mg/L)	%RSD	Delta (%)
Concentration	0.431	9	0.677	1	
Calibration Accuracy	100	6.2			
Matrix Spike Recovery	N/A				
7936	0.599	15	0.673	N/A	-11
7937	0.354	3	0.682	N/A	-48
7938	0.339	9	0.676	N/A	-50
Mean	0.431		0.677		-36
3Q18 Tank 50					
	Concentration (mg/L)	%RSD	Concentration (mg/L)	%RSD	Delta (%)
Concentration	0.917	7	1.64	32	
Calibration Accuracy	98.2	1.5			
Matrix Spike Recovery	93.3	N/A			
8305	0.932	7	0.87	N/A	N/A
8306	0.467	104	1.6	N/A	-71
8307	1.35	7	1.67	N/A	-19
Mean	0.917		1.380		-45
4Q18 Tank 50					
	Concentration (mg/L)	%RSD	Concentration (mg/L)	%RSD	Delta (%)
Concentration	0.819	31	0.355	85	
Calibration Accuracy	99.6	1.1			
Matrix Spike Recovery	97.9				
8477	0.654	56	0.293	N/A	123
8478	0.809	7	0.0907	N/A	N/A
8479	0.995	118	0.683	N/A	46
Mean	0.819		0.356		84
Total Mean					+1.1

Both SRNL and Eurofins FGS rejected replicate samples or whole bottle results when the reported measurement returned a statistical outlier. In SRNL, the results for samples 8306 and 8479 returned one replicate each that were deemed outliers, as the reported concentration in these replicates was less than the detection limit. The reported values for these bottles were based upon one replicate. For Eurofins FGS, bottles 8478 and 8305 failed as an outlier and no value was reported, as Eurofins does not perform replicate analysis per bottle.

For the 1Q18 Tank 50 sample, SRNL reported a mean value biased 36% low relative to Eurofins. Due to the low mean uncertainty obtained by SRNL and Eurofins for this sample (± 9 and 1%), the reported concentration values were significantly different (p=0.0432). The 3Q18 Tank 50 sample value reported by SRNL was biased 45% low, however, given the high mean uncertainty obtained by SRNL and Eurofins for this sample (± 7% and 32%), no significant difference between the mean values was observed (p=0.271). For the 4Q18 Tank 50 sample, the SRNL value was biased 84% high relative to Eurofins. The high mean uncertainty obtained by SRNL and Eurofins for this sample (± 31% and 85%) produced no significant difference between the observed values (p=0.0811).

Intra-laboratory quality control analyses were performed in SRNL. Mean calibration accuracy across the 1Q18, 3Q18, and 4Q18 Tank 50 samples was 100%, 98.2%, and 99.6%. Matrix spike recovery from 3Q18 and 4Q18 Tank 50 samples was 93.3% and 97.9%. No quality control data is available from Eurofins. Same-bottle replicate analyses in SRNL produced a mean %RSD of 14%, but when %RSD was calculated across all three submitted bottles per sample, a mean %RSD of 34% was obtained. Same-bottle replicates demonstrated less variance than between bottles.

Though the sample size was relatively low, the large data scatter observed by both analytical labs, given the low mean bias (+1.1%), disparity between per-bottle replicate %RSD and between-bottle %RSD found in SRNL, and the high-fidelity SRNL quality control data, there is evidence that the large uncertainty observed by both laboratories may be associated with sample collection, processing, and storage procedures.

Uncertainty in reported Eurofins data over time is plotted in figure 3-4. No significant difference in uncertainty was observed in either all-time reported measurements from Eurofins and SRNL (p=0.934), or for the three co-analyzed samples (p=0.404). Figure 3-5 illustrates concentration data with 95% confidence intervals and demonstrates the statistical similarity between the values produced by SRNL and Eurofins.
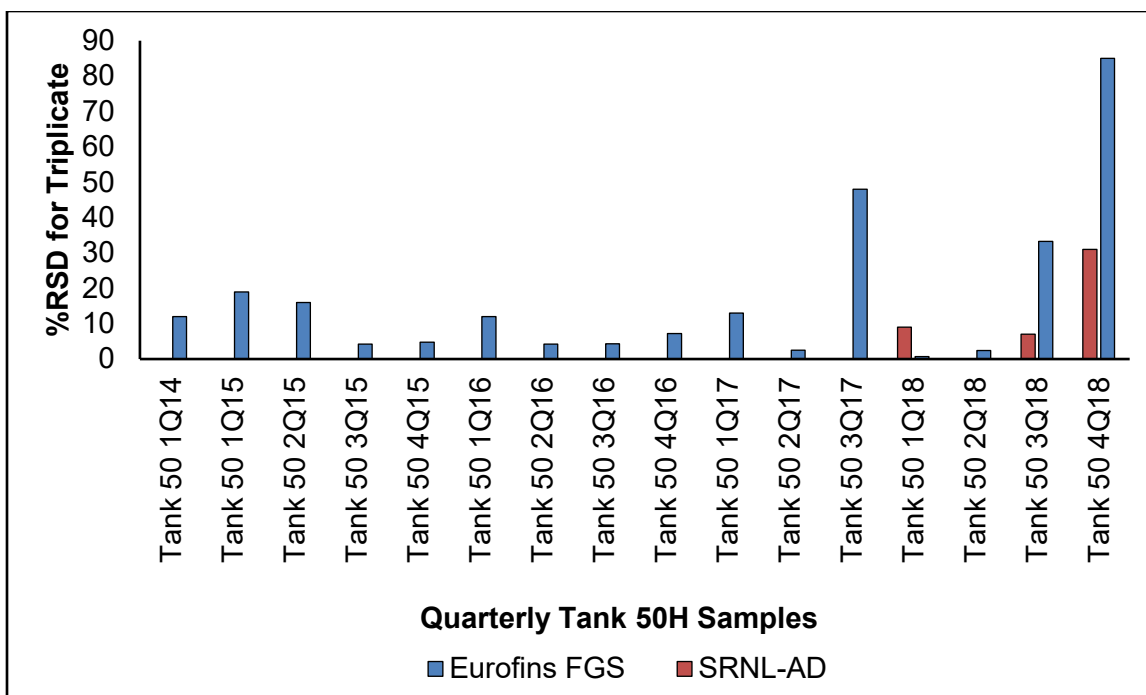
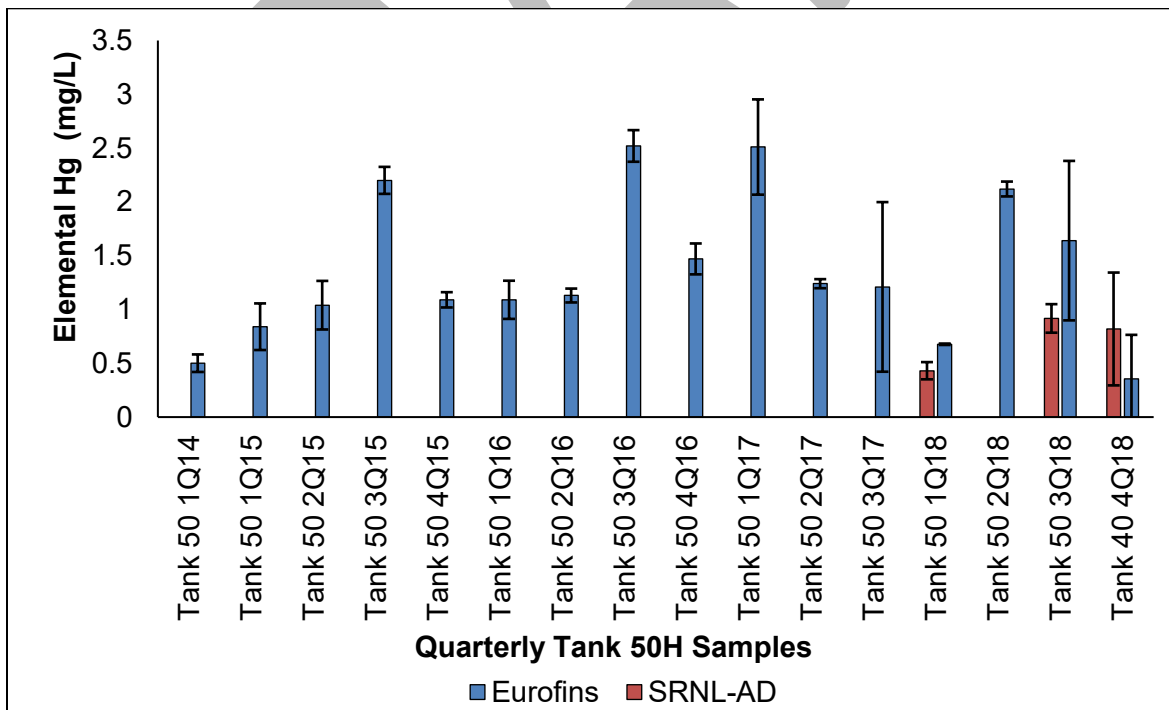**Figure 3-4.** Observed uncertainty in quarterly sample analyses from SRNL and Eurofins

Figure 3-5. Results of elemental mercury analysis in quarterly tank samples from SRNL and Eurofins, showing 95% confidence

4.0 Conclusions

A method has been developed and internally validated at SRNL for the separation and analysis of purgeable mercury species from quarterly SRR tank samples. This method has been further validated by inter-laboratory comparison. Statistically similar variance and low total mean bias across the three co-analyzed samples provides evidence that SRNL is capable of producing data for the customer of statistically similar quality, relative to Eurofins FGS.

5.0 Recommendations

Purgeable mercury, in comparison with other mercury speciation efforts, is composed of various forms of mercury, as discussed in this work. Further illumination of the precise mechanisms of species formation, destruction, and conversion could provide clarity as to the most effective storage, preparation, and collection methods to prevent formation or loss of species. Investing in research to determine the precise mechanisms that form each mercury species in the tank process may help prevent the large inter-bottle variance observed in this work.

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