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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 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 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, an efficient and sensitive method was produced. 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. An interlaboratory comparison was performed between SRNL and Eurofins FGS in the co-analysis of three quarterly SRR Tank 50 samples.

The statistical evaluations presented in this document support the following conclusions: for internal validation data, the two laboratories demonstrate biases of -4.3% for SRNL and 4.4% for Eurofins FGS, though neither are statistically significant at the 5% level. While the percent relative standard deviation for each of the laboratories is rather large (21.5% for SRNL and 18.4% for Eurofins FGS), there is no indication of a statistically significant difference between the two laboratories in the precision of these results. For the three sets of SRR quarterly Tank 50 samples, there is no indication of a statistically significant bias between the two laboratories at the 5% significance level.

These results indicate that SRNL may provide data to the customer of statistically similar quality to Eurofins FGS.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ALARA	As low as reasonable achievable
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 quantification
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, 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. [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 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. [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.

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. [1] 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. [4-5] This work focused on the development of in-house methods for the analysis of dissolved and / or volatile mercury species that can be removed by gas sparging, referred to herein as purgeable mercury, in the liquid tank waste streams.[3]

Capture of gaseous mercury on gold-film demonstrates low specificity for particular mercury species.[6] Researchers have demonstrated that both elemental mercury and dimethylmercury may be trapped with similar efficiency with gold-film beads. Therefore, differentiation of “elemental mercury” from “purgeable mercury” was necessary.[6]

Given the high concentrations of mercury in the tanks at SRS, it was anticipated that elemental mercury within the tanks should exist in equilibrium at its solubility point in aqueous solution. [1] The solubility limit of elemental mercury, a primary species contributing to purgeable mercury, ranges from 0.2 µmol/L (0.02 mg/L as Hg) to 0.7 µmol/L (0.07 mg/L as Hg) in aqueous solution; literature suggests that solubility may be influenced by temperature and the ionic activity of solution. [7] It is reasonable to presume that tank-waste and sub-sample aliquots taken from large-volume solutions may contain dense-phase or suspended colloidal mercury forms. As a given aliquot is to be diluted with deionized water, a shift is equilibrium may have the potential to dissolve some previously non-solubilized mercury.

For these reasons, the term purgeable mercury will be used in this work to refer to the sum of all potentially purgeable mercury species. Quantitatively, the result will provide a reasonable estimate of volatile mercury species. When considering the original sample, this would include dissolved gaseous mercury and dense phase or colloidal mercury that may dissolve in the diluted sample.

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.[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, 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. 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.[4]

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 soluble organomercury species in high activity waste by leveraging volatility and the affinity between purged 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.

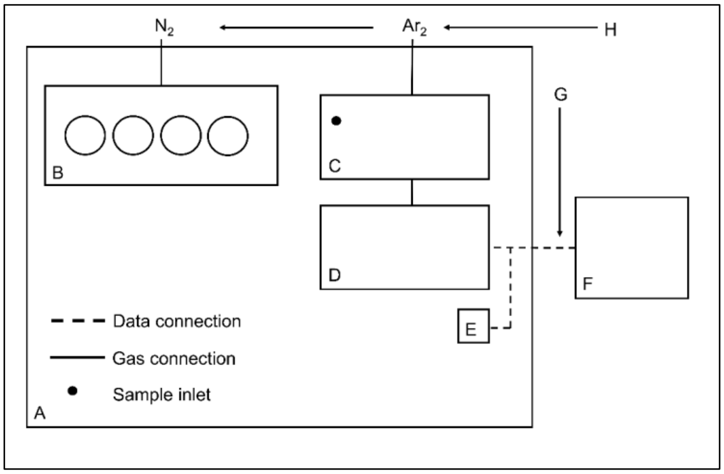

Figure 2-1: Schematic of the configuration of the P&T-TD-CVAFS within the contamination area demonstrating (A) the radiological hood, (B) purge and trap system, (C) thermal desorption device and sample inlet, (D) atomic fluorescence detector, (E) digital instrumental control pad, (F) instrumental control 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. For optimization purposes, purge flow rate, purge time, and matrix modification will be investigated.

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.[14] 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]

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

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.

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 typically 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 design limitation should be noted.

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. A QC was considered “failed” if it fell outside of ±50% of the expected value.

2.2 Multivariate Development

To detect large effects in the optimization of this method, an central composite design with 3 levels was used for variable optimization. [16] For each of levels designated for each variable, a mid-point was selected representing the standard method variable setting, and low / high levels representing reasonable extreme parameters.[17] Table 2-1 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. Of note, the parameters of purge flow rate and purge time are often combined into a single variable called "air: water phase ratio," with the intent of investigating the effects of varying the ratio between solution (water) and the volume of purge gas exposed to the solution (air). [20]

Table 2-1. Three variable – three level central composite experimental design

Pattern	Purge time (min.)	Purge flow (mL/min.)	Matrix addition (%KCl)
−−−	5	25	0
−−+	5	25	20
−+−	5	65	0
−++	5	65	20
+−−	30	25	0
+−+	30	25	20
++−	30	65	0
+++	30	65	20
a00	5	45	10
A00	30	45	10
0a0	17.5	25	10
0A0	17.5	65	10
00a	17.5	45	0
00A	17.5	45	20
0	17.5	45	10

2.3 Sample Processing and Data Handling

Quarterly samples were collected in small, stainless steel bottles with zero headspace. The bottles were transferred to 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. [1]

Percent recovery of purgeable mercury was determine 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).[13]

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. [13, 21]

2.4 Quality Assurance

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.

Unless otherwise stated, reported variance in this work is at the 95% confidence intervals. The elemental 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. JMP Pro Version 11.2.1 was used to conduct these evaluations [1].

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 were discovered. Figure 3-1 demonstrates the significant variable, purge flow rate (p=0.012) and the AFS response of replicate mercury vapor injections as a function of nitrogen purge flow rate. No linear correlation was discovered for KCl addition or sample purge time. Further statistical evaluation of purge flow rate can be found in Exhibit A-1 in Appendix A.

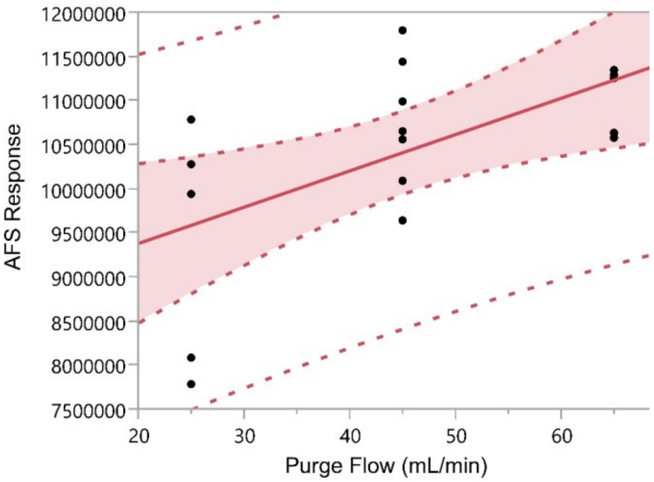

Figure 3-1: Linear relationship between increasing nitrogen purge flow rate and analyte recovery, as measured by increasing detector response

Figure 3-2 demonstrates the results at the low and high ends of each optimization experiment. Figure 3-2A demonstrates the nonsignificant difference in response between matrix solutions prepared at 0% and 20% ionic activity with potassium chloride (n=9). Figure 3-2B shows the nonsignificant difference in response between samples purged with N_2 for 5 minutes and 30 minutes (n=9). Figure 3-2C shows the significant difference in samples purged at a flow rate of 25 mL/min and 65 mL/min (n=9). Figure 3-2D demonstrates the decrease in replicate variance as sample purge rate is increased. The observed data provides a reasonable match with theoretically optimal performance. [20] This suggests that the kinetics of the described sparging system are relatively fast, and not the rate-limiting step. A comparison of the data collected in this optimization experiment with the theoretical maximum recovery can be found in Appendix A, Exhibit A-2.

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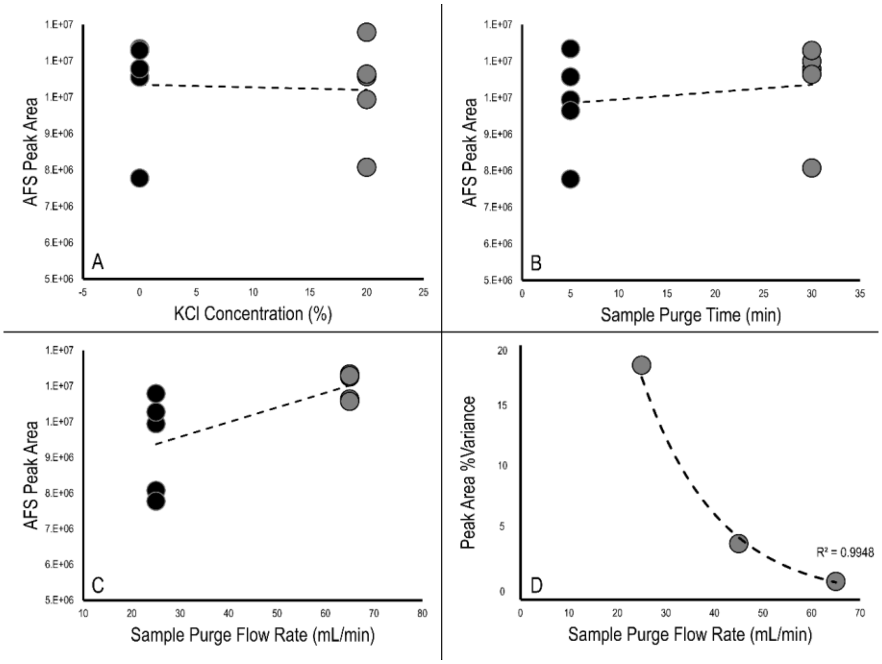

Figure 3-2: Univariate results of multivariate optimization experiments, showing (A) matrix ionic activity response, (B) sample purge time, (C) flow rate of nitrogen purge gas, and (D) relationship between purge flow rate and response variance, showing a polynomial regression and coefficient of determination (R2). 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. ±7% (n=5) when measured directly 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 3-3. 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.

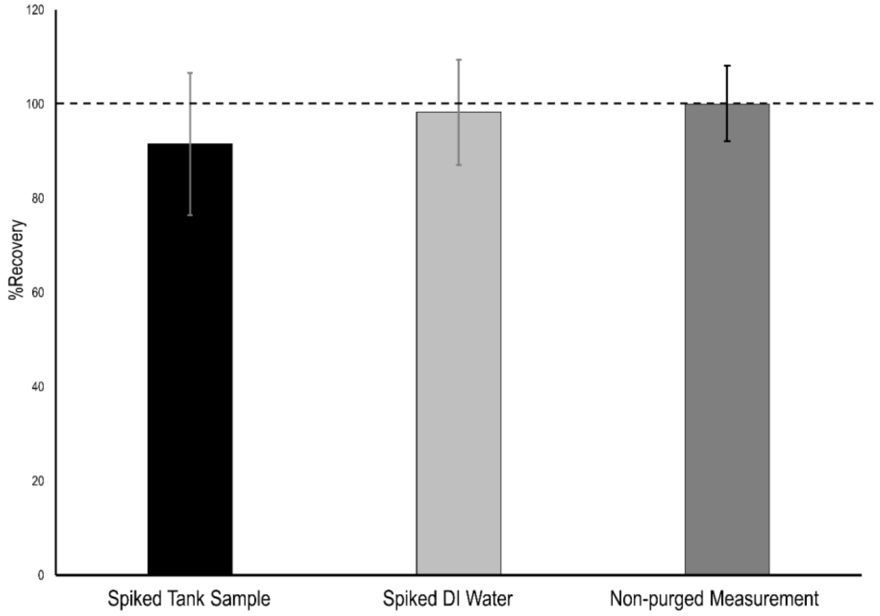

Figure 3-3: A comparison of analytical recovery of mercury vapor spiked and purged through SRR waste sample, deionized water, and measured directly without purge

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 3-4, 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.

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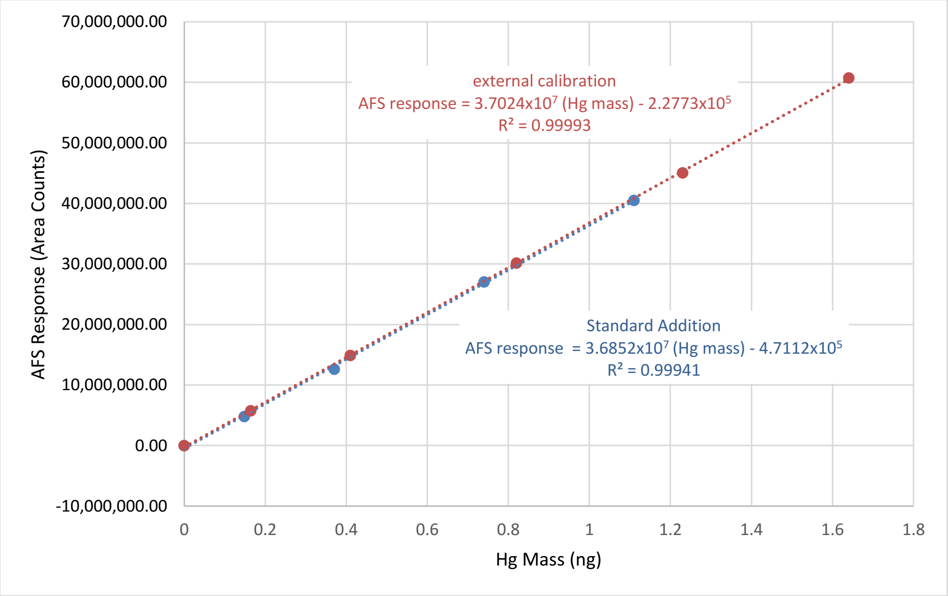

Figure 3-4: Calibration techniques performed directly (external calibration) or *via* purge through SRR samples (standard addition)

3.2 Quality Control and Validation

Given the results of optimization, the parameters of purge flow rate and purge time were modified from previously reported manufacturer recommendations. Purge time was decreased from 35 minutes to 17 minutes (equal to the midpoint of the AD optimization schema) and purge flow rate was increased from 25 mL/min to 65 mL/min to attain optimal air: water phase ratio. 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.

Table 3-1: Performance of SRNL-AD method quality control replicates for elemental mercury matrix spike samples

Sample Name	Sub-type	Expected Result (pg)	Analyzed Result (pg)	% Recovery
SRNL-AD QC	QC	0.409	0.459	112
SRNL-AD QC	QC	0.409	0.453	111
SRNL-AD QC	QC	0.409	0.425	104
SRNL-AD QC	QC	0.409	0.540	132
SRNL-AD QC	QC	0.409	0.421	103
SRNL-AD QC	QC	0.409	0.364	88.9
SRNL-AD QC	QC	0.409	0.237	58.0
SRNL-AD QC	QC	0.409	0.399	97.6
SRNL-AD QC	QC	0.409	0.382	93.5
SRNL-AD QC	QC	0.409	0.247	60.3
SRNL-AD QC	QC	0.409	0.443	108
SRNL-AD QC	QC	0.409	0.327	80.0

3.3 Comparison between SRNL-AD and Eurofins FGS in Quality Control samples

EF reports QC data obtained for total mercury, methylmercury, dimethylmercury, ethylmercury, and inorganic mercury; however, no QC or recovery data is reported by EF for elemental mercury. Therefore, for comparison purposes, this report will compare the QC data obtained from AD from direct matrix spike experiments of elemental mercury with EF recovery data obtained from matrix spikes and laboratory control spikes of inorganic mercury (Hg^{2+}). This comparison is not ideal, as inorganic mercury is not susceptible to many of the analytical challenges of measuring elemental mercury- particularly volatilization low solubility. The EF QC data used for this comparison can be found in Table 3-2.

Table 3-2: Performance of Eurofins FGS method quality control replicates for inorganic mercury matrix spike and laboratory control 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

For the following evaluations, each of AD’s QC results is presented as the relative difference between the measured value for the standard and the reference value (i.e., measured minus reference as a percent of the reference value). EF QC results were also available; each of these results was provided as a percent recovery of the expected measurement for the standard. For the analyses presented here, the EF results will be expressed as a difference relative to the 100% target recovery. This will allow for the EF values to be expressed as a percent relative differences as were the AD measurements.

Figure 3-5 provides statistical comparisons between the QC results for the two laboratories. 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-3. 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.

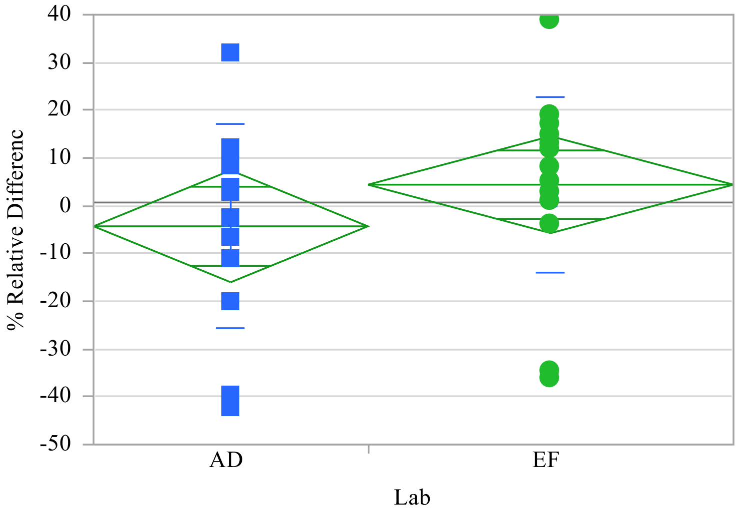

Figure 3-5: One-way analysis of Percent Relative Difference by Lab for the replicate analysis of Quality Control samples

Summary statistics are also provided for the two laboratories. The results include a 95% confidence interval for the bias (i.e., the average relative difference) for each laboratory. A review of the confidence interval for each laboratory indicates that the biases seen (i.e., -4.3% for AD and 4.4% for EF) are not statistically significant at the 5% level (i.e., each confidence interval includes 0). It should also be noted that the percent relative standard deviation for each of the laboratories is rather large (i.e., 21.5% for AD and 18.4% for EF).

Table 3-3: Summary Statistics for the SRNL-AD and Eurofins FGS Measurements of Elemental Mercury QCs

Laboratory	AD	EF
# Observations	12	16
% Bias	-4.299	4.419
% Relative Standard Deviation (% Relative Difference)	21.474	18.369
Lower 95% Confidence Limit for Bias	6.20	4.59
Upper 95% Confidence Limit for Bias	-17.94	-5.37

3.4 Comparison between SRNL-AD and Eurofins FGS in SRR Tank samples

The measurements (in nanograms, ng) of tank samples that were analyzed for purgeable mercury by both AD and EF are evaluated. Data obtained for three quarterly Tank 50 samples from AD and EF can be found in Table 3-4. Exhibit A-4 in Appendix A provides a histogram and summary statistics for the differences in these measurements (AD minus EF) for each of these tank samples. The average difference is -0.27 ng and the standard deviation of the differences is 0.386 ng. There is no indication of a statistically significant bias (at the 5% significance level) since the 95% confidence interval for the mean is -0.563 to 0.030, which includes zero. A comparison of relative standard deviation between same-sample replicates over time obtained by AD and EF can be found in Exhibit A-5 in Appendix A.

Table 3-4: Quarterly Tank 50 results obtained by SRNL-AD and Eurofins FGS

Sample Name	Sub-type	AD Analyzed Result (ng/L)	Eurofins FGS Concentration (ng/L)
Tk501Q18	7936	0.397	0.673
Tk501Q18	7937	0.276	0.682
Tk501Q18	7938	0.283	0.676
Tk503Q18	8305	0.645	0.877
Tk503Q18	8306	0.593	1.6
Tk503Q18	8307	1.19	1.67
Tk504Q18	8478	0.661	0.292
Tk504Q18	8480	0.09	0.0907
Tk504Q18	8477	0.711	0.683

3.5 Conclusions from Statistical Evaluations

The statistical evaluations presented in this document support the following conclusions. For the QC data, the biases for the two laboratories are -4.3% for AD and 4.4% for EF, and neither are statistically significant at the 5% level. While the percent relative standard deviation for each of the laboratories is rather large (i.e., 21.5% for AD and 18.4% for EF), there is no indication of a statistically significant difference between the two laboratories in the precision of these results.

For both QC standards and tank samples, there is no indication of a relative bias between the two laboratories at the 5% significance level.

4.0 Recommendations

Both AD and EF have demonstrated robust, high-quality laboratory methods that produce reliable and reproducible data. While no statistical bias was observed between the two laboratories in measuring the SRR tank samples, relatively high variability was observed in the analysis of these samples, particularly in the analysis of same-sample different-bottle analyses. Specifically, note should be taken of the large between-bottle variance in Tk504Q18 in table 3-4. Qualitatively, strong agreement can be seen between AD and EF results for each bottle, though high variance is observed between bottles. It should be stated that the three bottles (samples 8477, 8478, and 8480) represent aliquots of the same parent sample.

Given the challenges present in collecting these samples from the tanks, the difficulty of the matrix (particularly for radioactive samples requiring remote manipulation), and the probable presence of dissolved gases and colloidal elemental mercury solids, the variability observed by both AD and EF is unsurprising. To the extent practical, this report highlights the necessity to limit sample handling and to give specific attention to challenges specific to purgeable mercury: limiting bottle headspace, ensuring homogenous mixing before sample aliquots are taken, as well as limiting sample hold and ship times.

5.0 References

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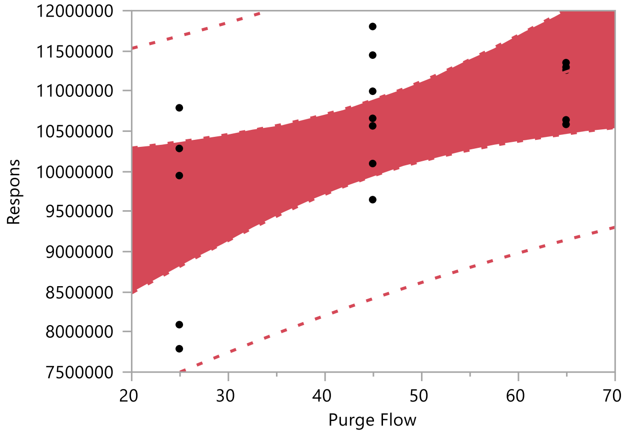
Appendix A

Exhibit A-1: Statistical Analysis of Purge Flow Rate

Study Variables: Purge Time, Purge Flow, and Matrix
Only significant variable is: Purge Flow, but is a weak predictor of Response

Response By Purge Flow



Linear Fit

Response = 8563878.9 + 41184.28*Purge Flow

Summary of Fit

RSquare	0.352134
RSquare Adj	0.308943
Root Mean Square Error	912230.2
Mean of Response	10417171
Observations	17

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	6.7846e+12	6.785e+12	8.1529
Error	15	1.2482e+13	8.322e+11	**Prob > F**
C. Total	16	1.9267e+13		0.0120*

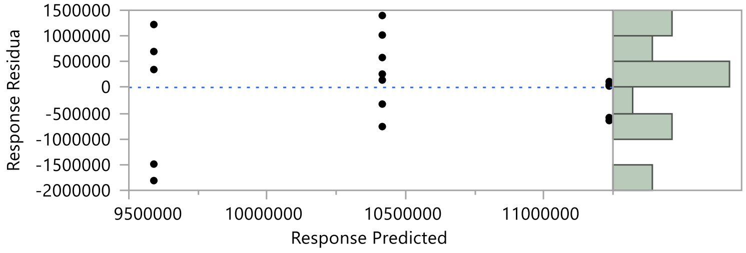
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	8563878.9	685736	12.49	<.0001*
Purge Flow	41184.28	14423.63	2.86	0.0120*

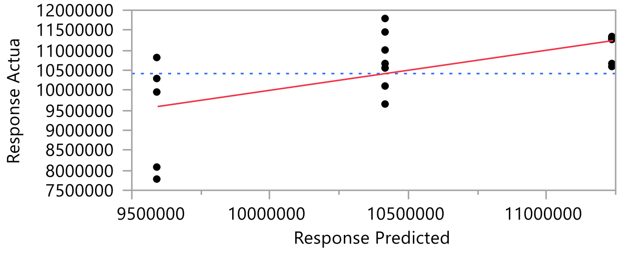
Exhibit A-1: Statistical Analysis of Purge Flow Rate (*continued*)

Diagnostics Plots

Residual by Predicted Plot



Actual by Predicted Plot



Residual by Row Plot

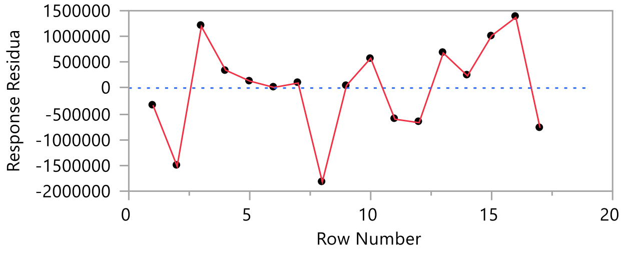
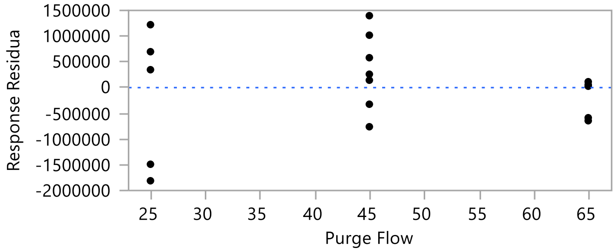
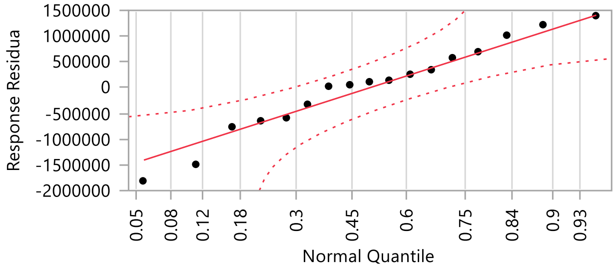


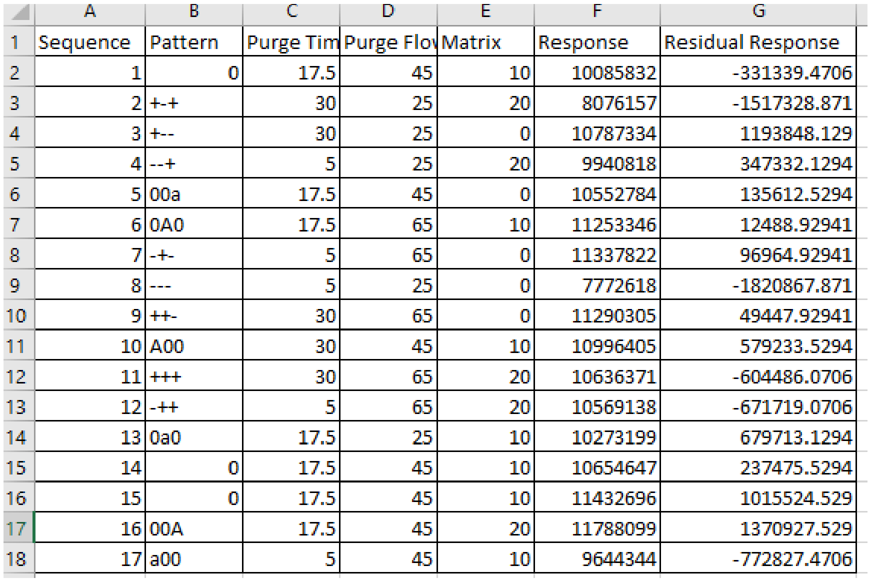
Exhibit A-1: Statistical Analysis of Purge Flow Rate (*continued*)

Residual by X Plot



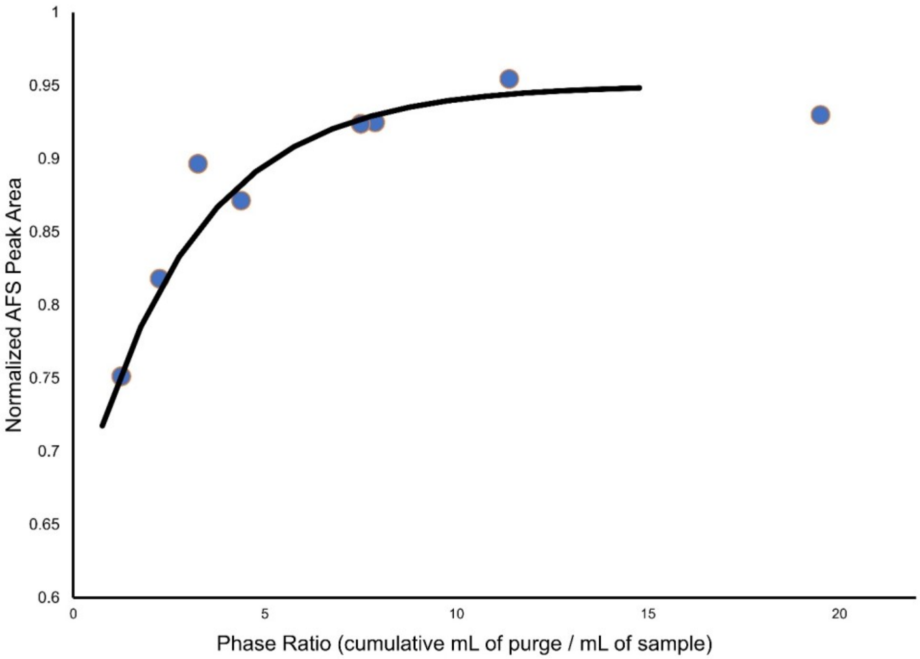
Residual Normal Quantile Plot





	A	B	C	D	E	F	G
1	Sequence	Pattern	Purge Tim	Purge Flo	Matrix	Response	Residual Response
2	1	0	17.5	45	10	10085832	-331339.4706
3	2	+-+	30	25	20	8076157	-1517328.871
4	3	+--	30	25	0	10787334	1193848.129
5	4	--+	5	25	20	9940818	347332.1294
6	5	00a	17.5	45	0	10552784	135612.5294
7	6	0A0	17.5	65	10	11253346	12488.92941
8	7	-+-	5	65	0	11337822	96964.92941
9	8	---	5	25	0	7772618	-1820867.871
10	9	++-	30	65	0	11290305	49447.92941
11	10	A00	30	45	10	10996405	579233.5294
12	11	+++	30	65	20	10636371	-604486.0706
13	12	-++	5	65	20	10569138	-671719.0706
14	13	0a0	17.5	25	10	10273199	679713.1294
15	14	0	17.5	45	10	10654647	237475.5294
16	15	0	17.5	45	10	11432696	1015524.529
17	16	00A	17.5	45	20	11788099	1370927.529
18	17	a00	5	45	10	9644344	-772827.4706

Exhibit A-2: Comparison of combined optimization purge flow volume/time data with Henry's Law predicted purge fraction



Normalized instrument response of spiked mercury vapor purged at 60 mL/min for variable lengths of time, relative to the ratio of volume-of-purge-gas-delivered to volume-of-sample-purged. Black line represents a modified Hendry's Law of the predicted fraction of purged mercury vapor relative to the phase ratio of purge-gas-delivered to volume-of-sample.

Exhibit A-3: 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

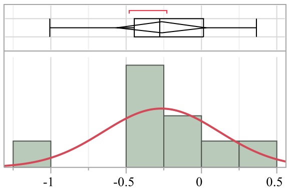
Exhibit A-3: Further Statistical Analysis of QC Precision and Means from SRNL-AD and Eurofins FGS (*continued*)

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

Exhibit A-4: Histogram and Summary Statistics of AD and EF Tank Sample Results

Distributions

[AD - EF] (pg)



— Normal(-0.2664,0.38599)

Quantiles

100.0%	maximum	0.369
99.5%		0.369
97.5%		0.369
90.0%		0.369
75.0%	quartile	0.01365
50.0%	median	-0.276
25.0%	quartile	-0.443
10.0%		-1.007
2.5%		-1.007
0.5%		-1.007
0.0%	minimum	-1.007

Summary Statistics

Mean	-0.266411
Std Dev	0.3859899
Std Err Mean	0.1286633
Upper 95% Mean	0.030287
Lower 95% Mean	-0.563109
N	9

Fitted Normal

Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	-0.266411	-0.563109	0.030287
Dispersion	σ	0.3859899	0.2607196	0.7394682

-2log(Likelihood) = 7.40589982553368

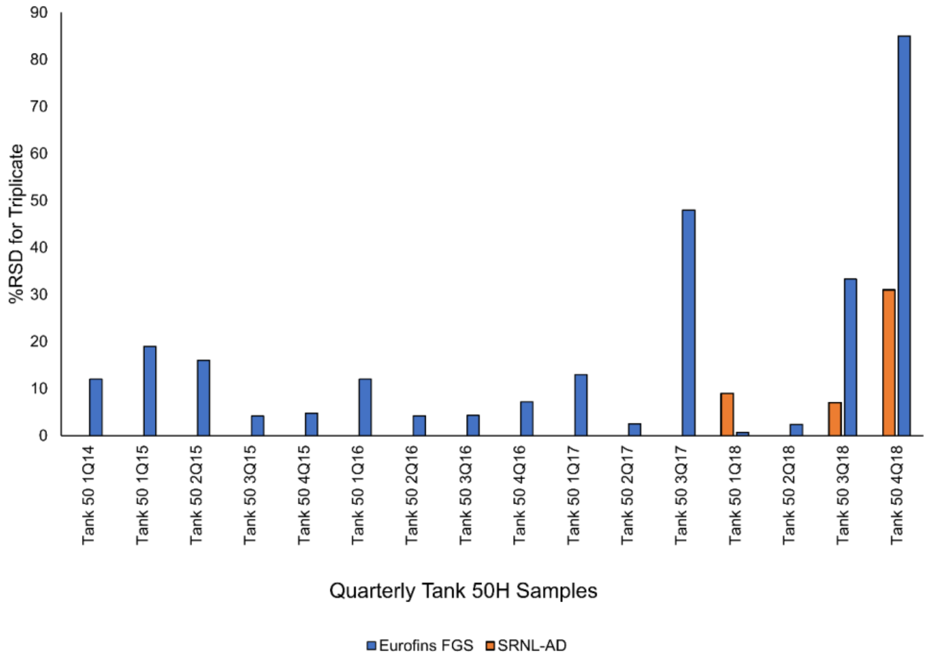
Goodness-of-Fit Test

Shapiro-Wilk W Test

W	Prob<W
0.961219	0.8110

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

Exhibit A-5: Relative Standard Deviation Observed for SRNL-AD and Eurofins FGS in SRR Tank 50 Quarterly Tank Samples



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