Methylmercury and Ethylmercury Analytical Performance in SRR Samples Measured by SRNL and Eurofins Frontier Global Sciences

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July 2019
SRNL-STI-2018-00250

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Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2018-00250
Revision 0

Keywords: Mercury, Methylmercury, Ethylmercury, Analysis, Tank Samples

Retention: *Permanent*

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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EXECUTIVE SUMMARY

Existing models and simulants of tank disposition media at the Savannah River Site (SRS) have presumed the presence of high concentrations of inorganic mercury. However, quarterly Tank 50 analyses have shown that mercury is present as organomercurial species at concentrations that may present challenges to its remediation and disposition and may challenge the Waste Acceptance Criteria (WAC) for Saltstone. To-date, methylmercury analyses for Savannah River Remediation (SRR) have been performed at an off-site laboratory by Eurofins Frontier Global Sciences (FGS) in Bothell, WA.

Savannah River Remediation requested the development of methylmercury and ethylmercury determination capabilities at the Savannah River National Laboratory (SRNL) to support the Liquid Waste Operations at SRS. 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 FGS. This document reports on this method development work as well as the comparative analyses conducted between the two laboratories.

A series of optimization and validation experiments has been performed at SRNL, which has resulted in the development of on-site methylmercury and ethylmercury speciation capabilities using purge and trap (P&T) gas chromatography (GC) coupled with thermal desorption (TD) cold vapor – atomic fluorescence spectroscopy (CVAFS). Speciation has been achieved for both species, with a methylmercury method reporting limit (MRL) value of 1.13 pg and an overall uncertainty (1σ) of 5.1%. An ethylmercury MRL of 11.5 pg and an overall uncertainty (1σ) of 4.8% were obtained. These analytical parameters compare favorably with Eurofins FGS, which demonstrates uncertainties (1σ) for methylmercury and ethylmercury of 13% and 9.1%, respectively. Results obtained by SRNL from the routine analysis of Tanks 21, 40, 50, and 51 samples have provided statistically indistinguishable results compared with Eurofins FGS.

Based upon the work performed by SRNL-AD and the data currently available, the following recommendations can be made:

- Further work should be performed to determine a “best practices” for sample holding time prior to analysis (both preserved and non-preserved samples), as well as any detrimental effects sample age may have on data quality.
- Analysis of ethylmercury is only recommended for tank samples that are reasonably expected to have significant quantities of ethylmercury, such as from the DWPF SMECT. Trace levels of ethylmercury in the presence of large quantities of methylmercury can be difficult or impossible to quantify.

SRNL-AD development of methods for total mercury, purgeable mercury (which includes Hg(0) and dimethylmercury), inorganic mercury (Hg(I) and Hg(II)), dissolved mercury, and particulate mercury are underway and will be reported upon separately.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
FGS	(Eurofins) Frontier Global Sciences
GC	Gas Chromatography
LLC	Limited Liability Corporation
LOQ	Limit of Quantification
MDL	Method Detection Limit
MRL	Method Reporting Limit
P&T	Purge & Trap
pg	picogram
RSD	Relative Standard Deviation
SaB	Salt Batch
SB	Sludge Batch
SMECT	Slurry Mix Evaporator Condensate Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TD	Thermal Desorption
WAC	Waste Acceptance Criteria

1.0 Introduction

Existing models and simulants of tank disposition media at the Savannah River Site (SRS) have presumed the presence of high concentrations of inorganic mercury. However, a variety of work over the past four years has demonstrated that there is a much greater variety of mercury species in the SRS liquid waste system.[1-6] Quarterly analyses of Tank 50 samples were the first to show that mercury is present as organomercurial species. Methylmercury has been shown to leach from the saltstone waste form at concentrations that may present challenges to its remediation and disposition.[5] To-date, methylmercury analyses for Savannah River Remediation (SRR) have been performed at an off-site laboratory by Eurofins Frontier Global Sciences (FGS) in Bothell, WA.

Savannah River Remediation requested the development of methylmercury and ethylmercury determination capabilities at the Savannah River National Laboratory (SRNL) to support the Liquid Waste Operations at SRS.[7] 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 FGS. This document reports on this method development work as well as the comparative analyses conducted between the two laboratories.

A series of optimization and validation experiments have been performed at SRNL, which have resulted in the development of on-site organomercury speciation capabilities using purge and trap (P&T) gas chromatography (GC) coupled with thermal desorption (TD) cold vapor – atomic fluorescence spectroscopy (CVAFS).[8] Speciation has been achieved for methylmercury and ethylmercury, with reporting sensitivities of 1.13 pg and 11.5 pg, respectively. Results obtained by SRNL from the analysis of past samples from Tanks 21, 40, 50, and 51 have demonstrated statistically indistinguishable concentration values compared with the concentration data obtained from Eurofins FGS.

2.0 Experimental Procedure

2.1 Reagents and Consumables

Helium carrier gas was used as carrier gas (99.99% purity) and argon was used as the purging gas (99.99% purity). All reagent water was deionized water or HPLC grade reagent water from Fisher Scientific (Hampton, NH). Buffering of samples was performed with 0.3 mL of 2M acetate buffer (Brooks Rand Instruments, Seattle, WA), certified free of mercury and suitable for application to EPA Method 1630. Preservation of samples was performed using 1.2 mL of 12.1 molar hydrochloric acid (Fisher Scientific). Sodium tetraethylborate and sodium tetra-n-propyl borate required potassium hydroxide (KOH, Fisher Scientific) and were prepared following vendor instructions. Ethylmercury chloride was purchased from

AccuStandard (New Haven, CT) at 100 µg/mL in methanol, methylmercury chloride (Brooks Rand Instruments) was purchased at 1 µg/mL in 0.5% (v/v) acetic acid and 0.2% (v/v) hydrochloric acid, and methylmercury hydroxide (Brooks Rand Instruments) was purchased at 1 µg/mL in 0.5% (v/v) acetic acid and 0.2% (v/v) hydrochloric acid. Methylmercury hydroxide (MeHgOH) and methylmercury chloride (MeHgCl) were certified and traceable to NIST 1641D, and ethylmercury chloride (EtHgCl) was certified by ISO/IEC 17025:2005 (Brooks Rand Instruments). Non-radioactive tank waste simulant was used for development purposes, consisting of a mixture of components that are generally representative of the SRS Tank Waste Decontaminated Salt Solution in pH, ionic strength, and (non-radioactive) elemental composition. Further salt solution simulant composition information can be found in Exhibit C-1 in Appendix C.

The derivatizing agents were mixed, gently inverted, and distributed into separate 4 mL Teflon bottles before being transferred to a -20 °C freezer. One Teflon bottle was removed from the freezer at the start of sample preparation for each batch of samples. The bottle and any remaining derivatizing agent were discarded following a single use. This solution has a vendor-listed expiration of 3 hours once thawed.

2.2 Sample Collection and Storage

Prior to arrival at SRNL, 250 mL variable depth samples were collected by Savannah River Remediation (SRR, Aiken, SC) from a selected tank following approved collection protocols.[4-5] Typical waste samples are highly caustic (pH > 12) aqueous solutions containing high concentrations of salts and various known and unknown organic and inorganic compounds. Each sample was transported to SRNL high-activity shielded cells for apportionment and dilution. Using remote-operated arms, one 30 mL aliquot was transferred to a Teflon bottle without headspace. The samples were stored in the dark. The 30 mL aliquot underwent a 1:2500 dilution with deionized water and 1.2 mL concentrated HCl preservative in a chemical fume hood rated for radioactive work. Amber glass bottle containing 250 mL portions of this diluted sample were stored in SRNL refrigerators at 4 – 6 °C until analysis. [9-14]

2.3 Sample Analysis and Quality Control

Following SRNL method L16.1-ADS-2659, standards were prepared from certified stock solutions. A 10 µg/mL calibration standard containing methylmercury and/or ethylmercury was prepared using 0.1 mL of 1 mg/mL MeHgOH and/or 1 mg/mL EtHgCl stock solutions and 9.9 mL of HPLC reagent water into an acid-washed glass vial. The vial was capped and shaken thoroughly. A 1 µg/mL working standard was then prepared by pipetting 1 mL of the calibration standard and 9.0 mL of reagent water into an acid-washed glass vial. Calibration standards were prepared at levels 10, 50 250, 500, and 1000 pg from the 1 µg/mL working standard. Blanks were prepared using 0.3 mL of 2M acetate buffer and 39.7 mL reagent water. Calibration verification samples were prepared at 250 pg using 0.3 mL of 2M acetate buffer, 0.25 mL of the 1 μg/mL working standard prepared as described above with MeHgCl and EtHgCl, and 39.45 mL of reagent water. [15]

Tank samples attained a dilution factor before introduction into the MERX-M. An aliquot was taken from each refrigerated 250 mL tank sample and a 1x – 1,00,000x serial dilution factor was applied prior to analysis, dependent upon anticipated mercury content. The diluted tank samples were spiked with 0.3 mL of 2M acetate buffer, 0.05 mL of derivatizing agent, filled to the top with reagent water to eliminate headspace, and sealed with a Teflon-lined cap before being inverted to effect mixing. All calibration vials, calibration verification vials, blanks, matrix spikes, and tank samples were spiked with 0.3 mL of 2M acetate buffer, 0.05 mL of derivatizing agent, filled to the top with reagent water to eliminate headspace, and sealed with a Teflon-lined cap before being inverted to effect mixing.[11, 15]

All vials underwent analysis as part of a MERX-M analytical system (Brooks Rand Instruments). The analytical method used for this analysis was based on Methods 1630 and 1631 from the U.S. Environmental Protection Agency (EPA), with modifications primarily focused on leveraging the advantage of the high mercury concentration present in tank solution.[16-17]

The CVAFS detector was calibrated to achieve maximum peak height by adjusting the photomultiplier tube voltage such that a 25 pg standard of methylmercury produced a peak height of approximately 12,000 counts. Before the start of each batch of samples, the detector was "zeroed." A recommended, non-binding, quality assurance / quality control (QA/QC) template was typically used as part of an SRNL measurement control system for each batch of sample to ensure the proper rinses, blanks, calibrants, calibration verifications, sample sets, and closing blanks were run with each batch, with modification present where necessary.[15] This measurement control system was designed to monitor the performance of the GC-CVAFS measurement system and to provide a graded approach to establish appropriate quality of data for the task requirements. This general template can be found in Table 2-1.

Table 2-1 Typical waste tank sample batch template to ensure QA/QC

Vial Number	Vial Type	Sample Description	Matrix
1	3x Rinse	Non-analytical opening blank to flush system	Deionized water
2	3x Blank	Reagent blank to establish baseline	Deionized water
3	5x Calibration	Calibration curve standards	Deionized water
4	3x Calibration verification	Prepared as the mid-point calibration standard	Deionized water
5	3x Blank	Reagent blank to establish baseline	Deionized water
6	Sample	1,000,000- fold dilution of the received sample	Tank sample
7	Sample 2x dilution	2,000,000-fold dilution of the received sample	Tank sample
8	Matrix spike	Tank sample spiked with calibrant standard	Tank sample
9	3x Calibration verification	Prepared as the mid-point calibration standard	Deionized water
10	3x Closing blank	Reagent blank to establish baseline	Deionized water

Instrumentation and Analytical Parameters

The analytical instrument consisted of a 72-position MERX Autosampler tray, a Hg Speciation P&T module, three Tenax TA (Buchem BV, Apeldoorn, The Netherlands) traps, a Hg Speciation GC and Pyrolysis module containing a mini-column GC (operated isothermally at 36 °C) and pyrolysis trap (held at a stable temperature of 700 °C), and Model III CVAFS photomultiplier tube detector (peak emission wavelength of 253.7 nm). For testing and optimization, a 10-position Methylmercury Distillation System (Brooks Rand Instruments), including a heated sample-holding block rack and chilled Teflon tube disposition reservoir rack with accompanying 10 rotameters to control gas flow, was used to isolate methylmercury from matrix and potential interferences. Mercury Guru Software was used for instrument control and data analysis. Derivatizing agent-dependent analytical parameters can be found in Table 2-2. The purging gas, drying gas, and GC carrier gas flow rates were 50, 40, and 35 PSI, respectively. Gas flow rates were controlled using instrument rotameters.

Table 2-2 Derivatization agent-dependent instrumental parameters

Ethylation Batch		**Propylation Batch**	
Parameter	*Time (minutes)*	*Parameter*	*Time (minutes)*
Run Duration	5.0	Run Duration	10
Heat Duration	9.9	Heat Duration	9.9
Retention Start Time	1.1	Retention Start Time	4.0
Retention Stop Time	1.5	Retention Stop Time	5.0
Drying Duration	3.0	Drying Duration	4.0
Purge Duration	5.0	Purge Duration	9.0

2.5 Ethylmercury Analytical Method Modification

For speciation and quantification of ethylmercury, several method parameters were modified. Notably, the derivatizing agent tetraethylborate used for methylmercury speciation was exchanged for the derivatizing agent tetra-*n*-propylborate.[18] This derivatizing agent enabled purging of both methyl- and ethylmercury from solution, as well as chromatographic resolution of ethylmercury from Hg^{2+} by the addition of a propyl functional ground to the charged alkylmercury species. The optimized and modified instrumental parameters used for ethylmercury speciation can be found in Table 2-3 (right), compared with the analytical parameters used for methylmercury analysis (left).

Table 2-3 Analytical parameters used in two derivatization schemes for the speciation of methylmercury and ethylmercury

Ethylation Batch		**Propylation Batch**	
Parameter	*Time (minutes)*	*Parameter*	*Time (minutes)*
Run Duration	5.0	Run Duration	10
Heat Duration	9.9	Heat Duration	9.9
Retention Start Time	1.1	Retention Start Time	4.0
Retention Stop Time	1.5	Retention Stop Time	5.0
Drying Duration	3.0	Drying Duration	4.0
Purge Duration	5.0	Purge Duration	9.0

2.6 Contaminants and Interferents

To separate alkylmercury from possible interferences and contaminants, distillation is often required for the analysis of environmentally sourced samples. In particular, many ionic metals are known interferences, causing a reduction in mercury recovery with increasing interferent concentration.[19] Another known, but under-studied, interferent is sulfur-containing compounds (particularly from organic sources) that may be present in municipal water supplies in areas with highly humic soil. [16]

Contamination of the sample with laboratory mercury or interferents, and contamination of the environment or laboratory with mercury from the sample were the primary concerns in contamination control. The use of metal-free laboratory apparatus and sampling equipment, performing sample preparation and analysis in environments known to be free of contamination, using disposable apparatus or covering and cleaning non-disposable apparatus, and avoiding sources of contamination, were part of the guiding philosophy of cross-contamination prevention, where possible. Wide-mouth fluorinated polyethylene bottles (Brooks Rand Instruments) certified for use in EPA Methods 1630 and 1631 were used for storage of reagent water. Sources of contamination were avoided by assessing carryover, removing unused samples and waste, and preventing airborne contamination as dust or aerosol.

2.7 Validation, Optimization, and Inter-laboratory Assessment

Calibration of methylmercury and/or ethylmercury was performed using increasing concentrations of MeHgOH and/or EtHgCl spiked into deionized water to produce a linear calibration curve over three orders of magnitude between 10 pg and 1000 pg.[15]

The primary modification present in this method relative to EPA Method 1630 is the absence of a distillation sample preparation step. It was proposed that, due to the high concentration of methylmercury present in the SRR tank waste samples, that sample dilution could be used to impart a similar effect of decreasing the effects of potential interferents (i.e. high chloride). For this reason, an experiment was performed to determine the impact of the distillation step on analyte recovery. Duplicate analyses were performed in deionized water at spiked methylmercury levels of 20 pg, 40 pg, 80 pg, and 40 pg spiked in salt solution simulant (see: Appendix C). The same analyses were repeated without distillation, so-named "direct analysis." Simulant was used in place of radioactive tank waste to avoid unnecessary fouling of laboratory equipment with contamination.

Further testing was performed to determine the recovery of methylmercury from simulant. This testing was performed following the distillation testing; therefore, distillation was not performed in the simulant recovery experiments. Methylmercury was spiked into deionized water or simulant at 10 pg and statistical comparisons were performed on analyte recovery.

2.8 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.

2.9 Statistical Evaluation

The data available for statistical evaluation included measurements of Quality Control (QC) standards analyzed by Analytical Development (AD) and of QC standards analyzed by Eurofins (EF) as well as results from tank samples that were analyzed by both AD and EF. QCs for both ethylmercury and methylmercury were measured by both laboratories, while only methylmercury results from both laboratories are available for the tank samples. JMP Pro Version 11.2.1 was used to conduct these evaluations.[20]

All SRR tank samples required dilution prior to analysis in SRNL. Often, two or more dilution levels were utilized to ensure that at least one dilution set was quantified within the established calibration curve. If more than one set of dilution levels were quantified within the calibration curve, then an average of the dilutions was submitted to Process Technology Programs for reporting of concentration values to SRR. For the purposes of this document, however, only the dilution level that produced quantitation data within the calibration curve was used for comparison, to more accurately compare with the single-replicate data provided by Eurofins FGS. If both dilution levels produced results within the calibration curve, then both dilution values are provided (see: N8940-00267-02 for further explanation).

3.0 Results and Discussion

Chromatographic resolution of derivatized methylmercury was achieved using sodium tetraethylborate; while, derivatized methylmercury and ethylmercury were resolved using sodium tetra-*n*-propylborate. As seen in Figure 3-1 (left), the ethylating agent produced resolved peaks for volatile elemental mercury (peak 1), ethylated methylmercury (peak 2), and a combined peak containing derivatized ethylmercury and Hg^{2+} (peak 3). Figure 3-1 (right) shows the propylating agent effected separation for volatile elemental mercury (peak 1), propylated methylmercury (peak 2), propylated ethylmercury (peak 3), and propylated Hg^{2+} (peak 4, not shown).

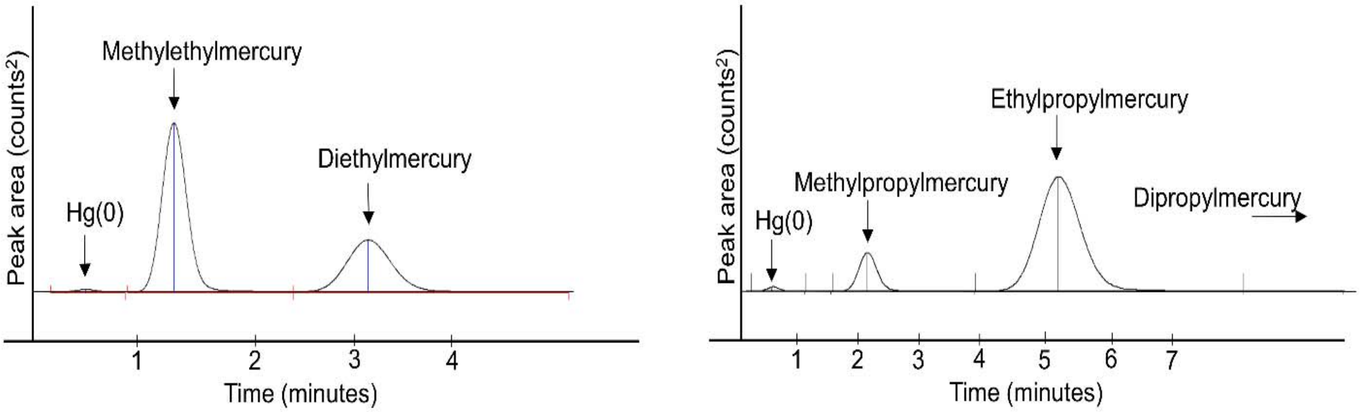

Figure 3-1 Demonstrating chromatographic resolution of methylmercury cation achieved using tetraethylborate derivatizing agent (left), and resolution of methylmercury and ethylmercury using tetra-n-propylborate (right)

3.1 Development and optimization

Data from two options for the analytical protocol in AD's methylmercury measurement process are considered in this section. A comparison is made between two treatments: distillation sample preparation (as recommended by EPA 1630) versus non-distilled (so-called "direct analysis"); and a comparison is made between two types of solution matrix: water versus simulant (see: Appendix C).

Figure 3-2 provides plots of the results as measured by AD for the two treatment types: sample preparation by distillation and "direct analysis" without distillation. Both plots display on the y-axis the percent relative difference (computed as measured minus reference value with the difference expressed as a percent of the corresponding reference value). In Exhibit A-1 in Appendix A, the groupings of the results are primarily by treatment and then by reference value; for Figure 3-2, the groupings are reversed. In general, there appears to be slightly more scatter in the results from the direct treatment but a more substantial negative bias in the measurements from the distillation treatment.

Exhibit A-2 in Appendix A provides the results of an Analysis of Variance (ANOVA) investigation into the effects of reference material and treatment. Both factors are determined to be statistically significant at the 5% significance level, and the table of estimates for treatment effects indicates a -10.4% bias from the direct measurements of these standards with a statistically different, -22.4% bias, from the distillation treatment. Thus, the direct treatment leads to a more accurate result than that from the distillation treatment.

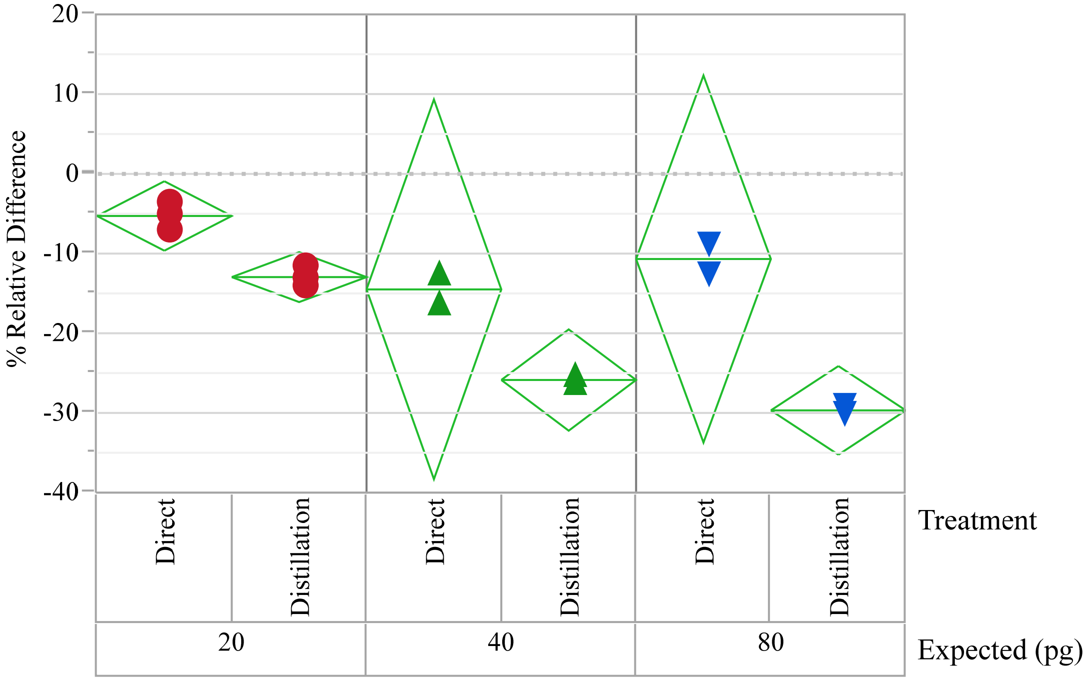

Figure 3-2 Results of investigation into the effects of two sample preparation treatments at various methylmercury spike level, showing 95% diamonds and mean response as horizontal dashes.

Given the differences in the results due to treatment, Exhibit A.3 in Appendix A provides the output from ANOVA investigations of the data separated into treatment groups. There are limited data for each group, so some caution in the interpretation of these results is warranted. The results from the direct treatment are provided in the upper portion of the exhibit. The estimate of the bias, -9.97%, is not statistically significant at the 5% level, and the 95% confidence interval for the bias is -21.40% to 1.45%. The estimate of the overall variance of these data is 24.5 leading to an estimate of the standard deviation of 4.95%.

The lower portion Exhibit A-3 provides the results for the distillation treatment. The estimate of the bias, -22.71%, is statistically significant at the 5% level, and the 95% confidence interval for the slightly negative bias is -44.48% to -0.94%. The estimate of the overall variance of these data is 77.5 leading to an estimate of the standard deviation of 8.81%. Thus, for this limited amount of data from the measurement of methylmercury standards, the direct treatment provides measurements with accuracy and precision comparable to those provided by the distillation treatment.

Figure 3-3 and Exhibit A-4 in Appendix A provide the results of an ANOVA investigation into the effect of solution matrix on methylmercury measurements of 10 pg methylmercury standards as well as a variability chart of the results. As in the discussions above, the measurements are expressed as % relative differences. The means and standard deviations of the results for each matrix are provided in the exhibit as well as 95% confidence intervals for the means. Figure 3-3 provides a plot of these confidence intervals as green diamonds. In addition, a box plot, shown in red, is also provided for each group of results. A box plot is a descriptive display used for continuous data. The lower edge of the box is the 25th percentile, the upper edge the 75th percentile, and the horizontal line within the box the 50th percentile, or median of the data set. Any points that fall beyond the lines extended from the boxes (i.e., points not connected to the box) of the box plot may be considered as potential outliers for the data set. Note that the most negative value (i.e., ~-40%) for the simulant treatment results may be an outlier for that set of results.

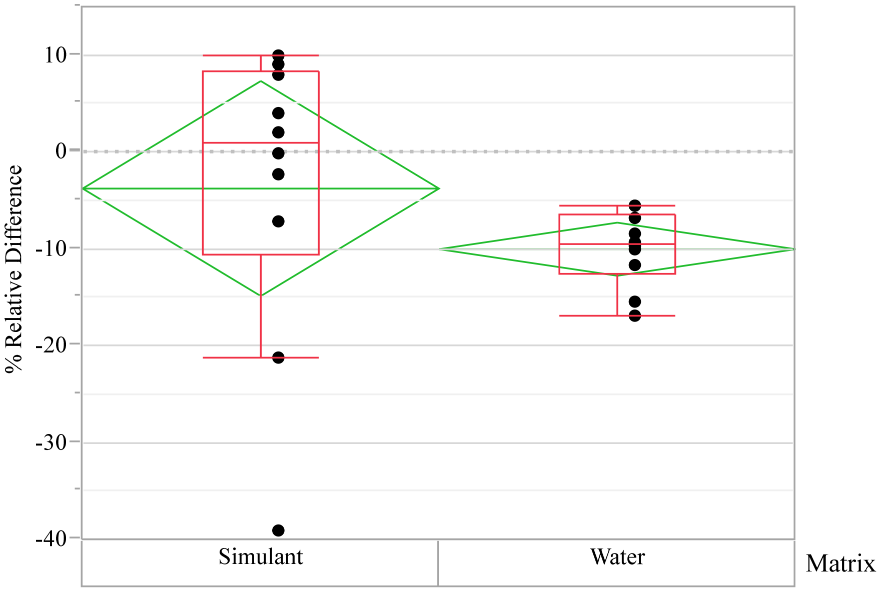

Figure 3-3 Plot of relative difference of each measurement of 10 pg of methylmercury performed in one of two matrices. Provided are 95% confidence diamonds with horizontal line means, as well as traditional box-and-whisker plots.

Relying on Levine's test for equality of variance for the measurements shows that the variance test rejects the null hypothesis of equality (i.e., the p-value for the test is less than 0.05, indicating statistical significance at a 5% level) as part of the ANOVA results. Welch's test for equal means for the measurements has a p-value of greater than 0.05, suggesting no statistically significant difference in the means due to solution matrix. Thus, the methylmercury results from the simulant matrix have a smaller, yet not statistically different, negative bias as compared to the water matrix results, while the simulant matrix does yield results with a statistically larger variability as compared to the results from a water matrix. The summary statistics from the exhibit are provided in Table 3-1.

Table 3-1 Means and Std Deviations of % Relative Differences by Matrix

Matrix	**Number of Observations**	**Mean**	**Std Dev**	**Lower 95%**	**Upper 95%**
Simulant	10	-3.7000	15.5147	-14.80	7.399
Water	10	-9.9600	3.8399	-12.71	-7.213

The result of direct analysis providing greater efficiency of recovery is reflective of previous work performed in this field. Prior research has noted, similarly, that direct analysis imparts the added benefit of improving the sensitivity of the mercury analysis without sacrificing analytical quality.[21] The wider uncertainty observed in the spiked simulant work, relative to spiked water, is likely an artifact of the significantly increased complexity of the matrix. This may be related to the so-called "salting out" effect, wherein nonpolar, volatile analytes (e.g. derivatized forms of methylmercury) may be driven from a solution at a greater efficiency with a corresponding increase in matrix ionic activity.

3.2 SRNL Measurement of Blanks

A closer look at the measurement of blanks (non-spiked deionized water containing acetate buffer and derivatizing agent) grouped by sampling event is provided in Figure 3-4. Each of the green diamonds on these plots provides a 95% confidence interval for the mean of the corresponding grouping of these measurements. The methylmercury results exhibit less variation as well as less short-term bias as compared to the ethylmercury measurements. Exhibit B-3 in Appendix B provides statistical comparisons of these grouped results for each of the two analytes. Relying on the Levine test for equality of variance and Welch's test for equal means for the ethylmercury measurements shows that both tests reject the null hypothesis of equality (i.e., the p-value for each test is less than 0.05, indicating statistical significance at a 5% level). Thus, for the ethylmercury data, there is a statistically significant difference in the means and in the variances of these groupings of measurements. For the methylmercury, Levine' test, with a p-value of 0.1533, indicates no statistically significant difference in the variances of these data groupings, and the analysis of variance (ANOVA) results yield a p-value of 0.0512, just above the significance level of 0.05. Thus, the methylmercury results reveal more consistent variability and central tendency for the measurements of blanks over these groupings as compared to the results for ethylmercury.

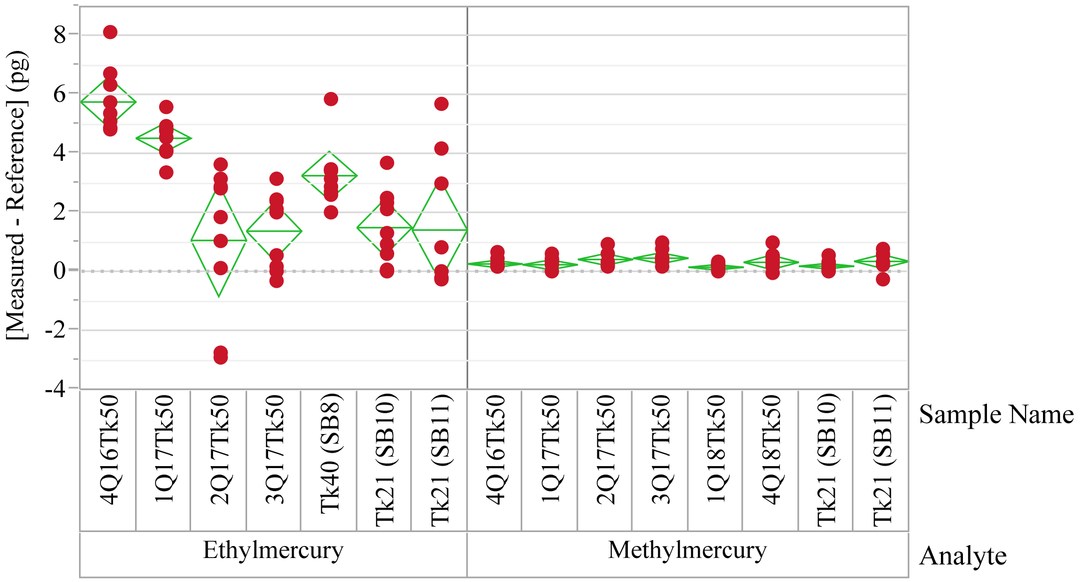

Figure 3-4 Results of blank measurements performed over time by SRNL-AD, showing obtained value (pg), and a 95% confidence interval for the mean of each group of blanks. The horizontal axis shows the sequence within which the set of blanks was performed.

Another way to evaluate AD's measurements of blanks is through a random effects model. In this model, the average values for the data groups can vary and estimating that variance is one of the goals of the modeling effort. Exhibit B-4 in Appendix B provides the results generated by this approach for both analytes. For the ethylmercury results, there is a statistically significant positive bias; the interval of 1.01 to 4.44 pg provides a 95% confidence interval for the bias in the measurements of the ethylmercury blanks. The total variance of these measurement is 5.615 yielding a standard deviation of 2.37 pg. These results imply that measurements of $4.44 + (3 \times 2.37) = 11.5$ pg or more are above those likely to be generated from the analyses of blanks. For the methylmercury, there is also a statistically significant positive bias; however, the 95% confidence interval for the bias is smaller at 0.225 to 0.408 pg. The total variance of these measurement is 0.0585 yielding a standard deviation of 0.242 pg. These results imply that measurements of $0.408 + (3 \times 0.242) = 1.13$ pg or more are above those likely to be generated from the analyses of blanks.

Exhibit B-5 in Appendix B provides a final evaluation of AD's measurements of these blanks; one that does not utilize groupings of these data. In this exhibit histograms and summary statistics are displayed for the complete set of ethylmercury and methylmercury data. This evaluation provides similar results (i.e., ethylmercury bias interval of 2.15 to 3.30 pg and standard deviation of 2.28; and methylmercury bias interval of 0.259 to 0. 369 pg and standard deviation of 0.240 pg) to those of the earlier investigations of these data.

These calculated reporting limits of 11.5 pg and 1.13 pg for ethylmercury and methylmercury, respectively, represent the sensitivity of the analytical system and do not account for any dilution factors that were applied to the sample prior to introduction into the system. For example, with a dilution factor of 10,000x (i.e. 1 µL of sample diluted to 10 mL), methylmercury analysis would produce a concentration reporting limit of $[(1.13 \text{ pg} / 1 \text{ mL}) \times 10{,}000]$, or 0.0113 mg/L. As the tank samples are known to contain large concentration of methylmercury, any analysis for ethylmercury must be diluted as to prevent the large methylmercury concentrations from damaging the instrumentation. This means that, even if relatively low ethylmercury concentration are expected in a given sample, the methylmercury concentration will drive the determination of a dilution factor- and, thus, the concentration reporting limit will likely be a function of the high methylmercury concentration, not ethylmercury.

The bias observed in the analysis of non-spiked blank samples yielded a positive bias, in comparison with the small negative bias observed in section 3.1. Negative bias cannot exist for the analysis of blanks. Therefore, only the positive portion of bias is reported in this section.

3.3 Quality Control Assessment in SRNL and Eurofins

Exhibit B-1 in Appendix B provides a plot of the QC results as measured by AD. For each batch of samples analysis, QC data for SRNL-AD was composed of all calibration points, calibration verification, and independent-vendor calibration verifications. For Eurofins FGS, QC results were calculated using all available data supplied by Eurofins FGS: calibration verifications, matrix spikes, and duplicates of each. For each of the two analytes (ethylmercury and methylmercury), two plots are shown. The first displays the difference between the reference value for the standard and the measured value (expressed as measured minus reference). The second expresses each difference as a percent of the corresponding reference value. For the ethylmercury, all the values (except for 3) fall within 10% of the reference value. The results for methylmercury are even better, with only 1 value falling outside of the 10% band.

EF's QC results were also available for these evaluations. While no measurements of blanks were available, for the non-blank QCs, EF expressed the results as a % recovery of the expected measurement for the standard. For the analyses presented here, these 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 % relative difference, and this metric will also be determined for each of AD's measurements of a non-blank QCs. Figure 3-5 provides an initial look at these results from both laboratories for both analytes. Once again, the green diamond plots provide 95% confidence intervals for the means of the data groupings. These plots reveal that the performance of AD in the measurement of its non-blank QCs is comparable to, if not better than, the performance demonstrated by EF.

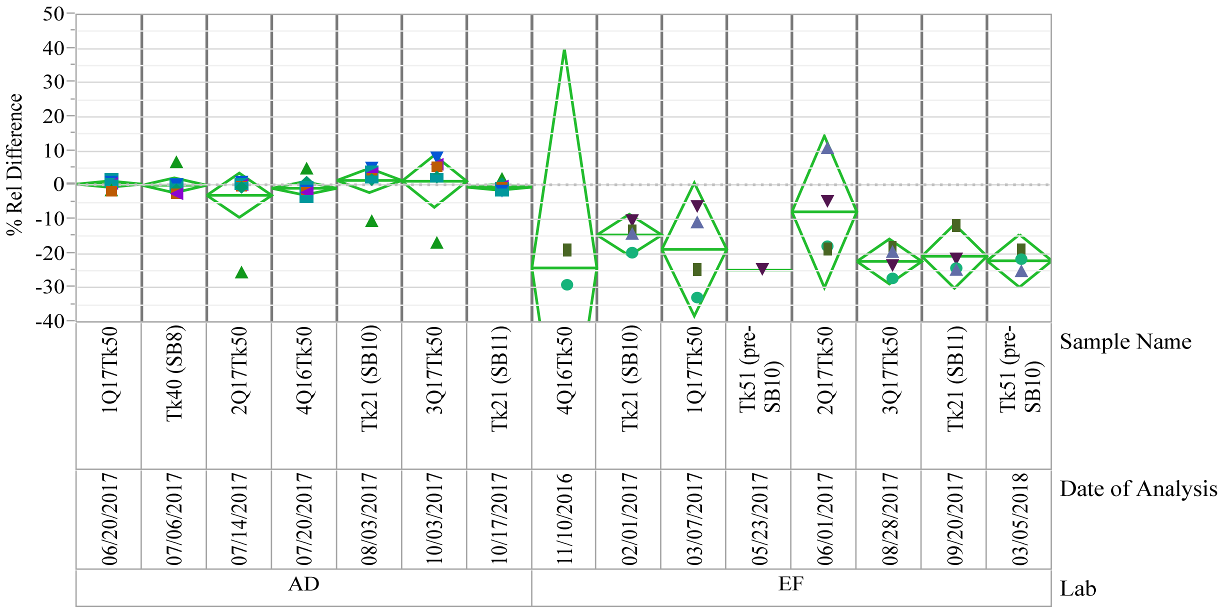

Figure 3-5 Relative percent difference of all QC data obtained in the given sample sequence, pooling calibration levels, verifications, and independent verification for ethylmercury (top) and methylmercury (bottom) by SRNL-AD and Eurofins.

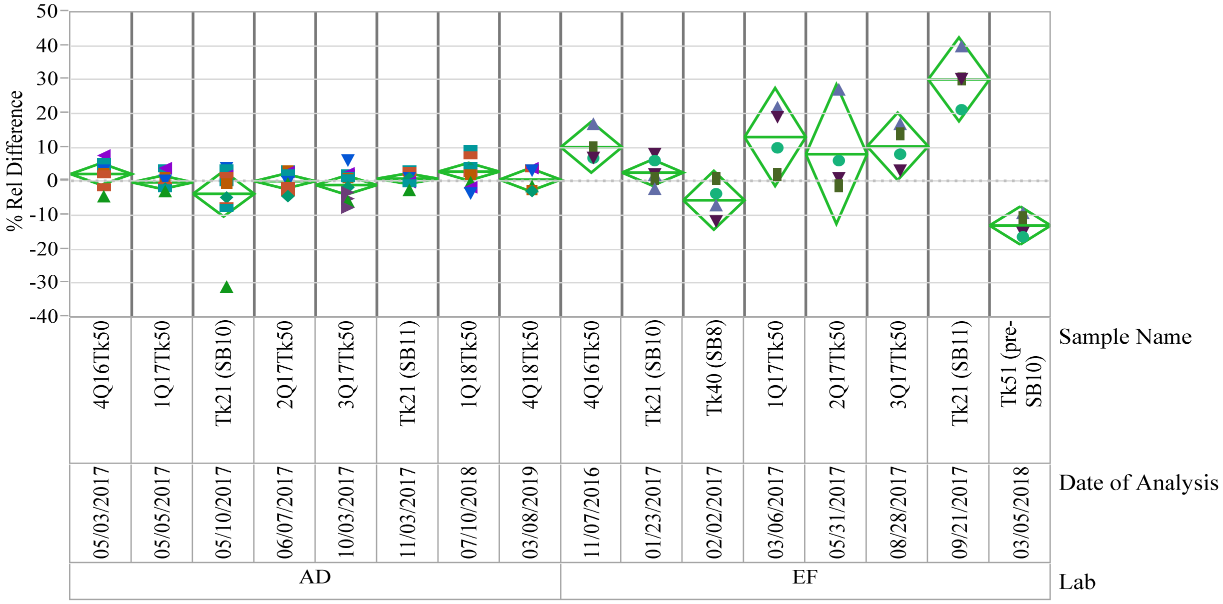

Figure 3-5 (continued) Relative percent difference of all QC data obtained in the given sample sequence, pooling calibration levels, verifications, and independent verification for ethylmercury (top) and methylmercury (bottom) by SRNL-AD and Eurofins.

Exhibit B-7 in Appendix B provides an ANOVA of these results for each analyte for each laboratory. The data from each laboratory are grouped by Sample Name and the results of a statistical test for equal means across the groups are provided. For AD's ethylmercury data, the p-value of this test is 0.5884 indicating that the null hypothesis of equal means cannot be rejected at a 5% significance level. The result of the test for EF's measurements for the same analyte yields a p-value of 0.1540, which also indicates that the null hypothesis of equal means cannot be rejected at a 5% significance level. For methylmercury, the results for AD (with a p-value of 0.1243) conclude that the null hypothesis of equal means cannot be rejected at a 5% significance level, while the EF results (with a p-value <0.0001) do indicate that the null hypothesis is to be rejected at the 5% significance level. Thus, there is an indication that the methylmercury results for EF's QCs yield statistically different averages (i.e., different short-term biases) over the time periods reviewed here.

Exhibit B-8 in Appendix B provides the results of a random effects ANOVA, where the impact of the time period effects on the QC measurements are evaluated as a random effect and the variance contribution from this effect is one of the parameters estimated as part of the analysis. However, the primary interest from each of the analyses is the estimate of the "Intercept" parameter, which represents the long-term, relative bias of these results.

For AD's ethylmercury data, the estimate is -0.095% with a 95% confidence interval for this estimate of -1.46% to 1.27%. Thus, the bias seen in these results is not statistically significant, and an immediate bound on the bias at 95% confidence would be the larger, in the absolute value, of the two end-points of this interval, 1.46%. Following the same approach for AD's methylmercury results leads to the conclusions of no statistically significant bias and a bound on the bias at 95% confidence of 2.05%.

For EF's ethylmercury data, the estimate is -18.3% with a 95% confidence interval for this estimate of -23.7% to -12.9%. Thus, the negative bias seen in these results is statistically significant, and an immediate bound on the bias at 95% confidence would be the larger, in the absolute value, of the two end-points of this interval, 23.7%. Following the same approach for EF's methylmercury results leads to the conclusions of no statistically significant bias and a bound on the bias at 95% confidence of 17.9%.

Thus, the results from Exhibit B-8 demonstrate that the AD measurements for these non-blank QCs are as good as, if not better than, the measurements provided by EF for their QCs.

Exhibit B-9 in Appendix B provides one last, the most straight-forward, evaluation of these results for each analyte for each laboratory: histograms and summary statistics for each. The primary comparisons between the two laboratories are the standard deviations and the 95% confidence intervals for the means (i.e., the relative bias of these results). As seen in Table 3-2, compared to Eurofins FGS, SRNL-AD demonstrated low percent relative standard deviation in the analysis of ethylmercury and methylmercury QC standards (4.8% and 5.1%, respectively). At the 95% level, the analysis of QC standards in SRNL-AD is non-biased for either analyte, where Eurofins FGS may be biased low for ethylmercury and high for methylmercury. These results demonstrate that the AD measurements for the non-blank QCs are as good as, if not better than, the measurements provided by EF of their QCs. For further statistical analysis, please see Exhibit B-2 and Exhibit B-6 in Appendix B.

Table 3-2 Summary Statistics for the AD and EF Measurements of Non-Blank QCs

Analyte	Lab	N Obs	Std Dev (% RSD)	Lower 95% Bias	Upper 95% Bias
Ethylmercury	AD	61	4.831	-1.32	1.15
Ethylmercury	EF	26	9.059	-21.8	-14.5
Methylmercury	AD	74	5.146	-0.96	1.43
Methylmercury	EF	34	13.500	2.16	11.6

3.4 Results of Tank Sample Comparison

In this section, the measurements from tank samples that were analyzed for methylmercury by both AD and EF are evaluated. No tank samples included in the study contained quantifiable amounts of ethylmercury, which has only been measured in Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Condensate Tank (SMECT) samples. Figure 3-6 provides an initial plot of these data. Tthe results are expressed in parts per million (ppm), and the data are grouped by the type of sampling event: sampling of

Tank 50 or sampling of other tanks, with more detail identifiers (including the laboratory) provided on the x-axis of each of the plots. The horizontal line segments provide the average measurement by laboratory for each sample name. In Exhibit B-10 in Appendix B, with the data grouped in a slightly different manner, the line segments connect the results for the two laboratories (with AD first) for each individual sample analyzed. Note the mix of upward slopes and downward slopes for these line segments, indicating that some of the AD results were smaller than the corresponding EF values while others were larger. Reported values from SRNL-AD and Eurofins are provided in Table 3-3, where NR represents non-reported values that fell below the quantitative reporting limit or were eliminated due to analyst error.

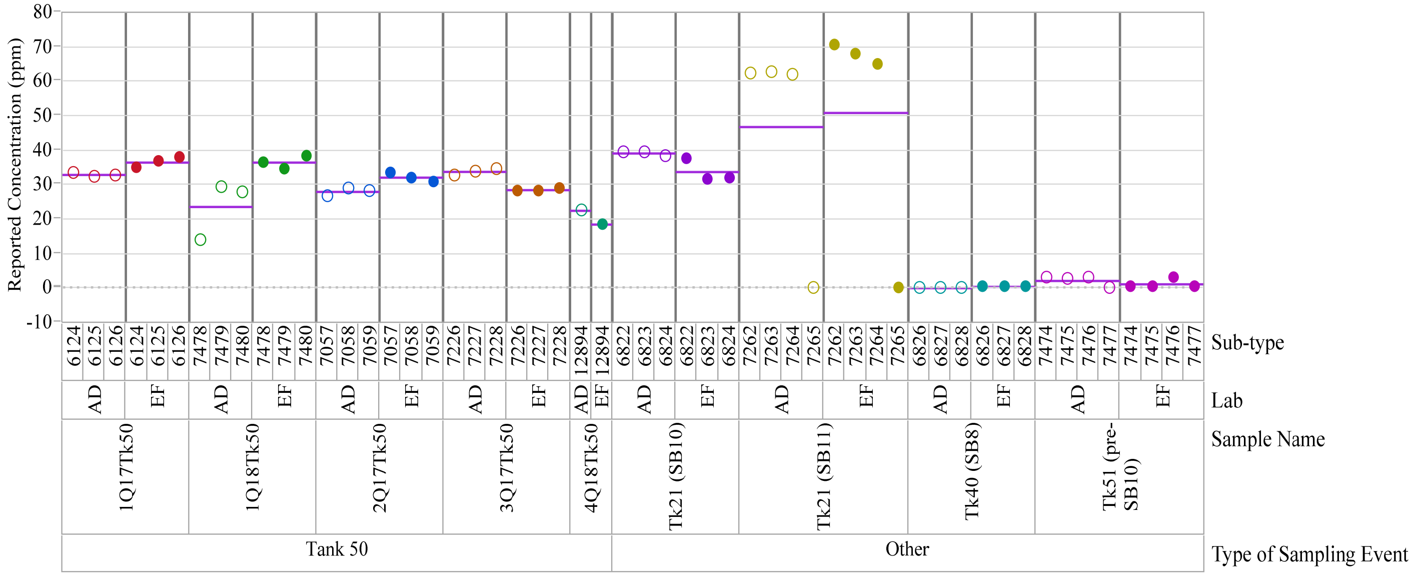

Figure 3-6 Reported methylmercury results (ppm) from SRNL-AD (open dots) and Eurofins (filled dots) for each of the given tank samples. Average value for each lab per tank sample is shown as a horizontal bar. Results separated by tank-type

Table 3-3 Results of tank sample analysis by SRNL-AD and Eurofins

Sample Name	AD Concentration (ppm)	Eurofins FGS Concentration (ppm)	Date Sampled	Date AD Analysis	Date Eurofins Analysis
4Q16Tk50	44.0	56.8	10/4/2016	5/3/2017	11/11/2016
4Q16Tk50	43.3	59.6	10/4/2016	5/3/2017	11/11/2016
4Q16Tk50	43.6	68.4	10/4/2016	5/3/2017	11/11/2016
Tk21 (SB10)	39.1	31.6	11/21/2016	5/10/2017	2/9/2017
Tk21 (SB10)	37.8	32.0	11/21/2016	5/10/2017	2/9/2017
Tk21 (SB10)	38.1	37.8	11/21/2016	5/10/2017	2/9/2017
Tk40 (SB8)	0.150	<0.491	11/21/2016	5/25/2017	2/9/2017
Tk40 (SB8)	NR	<0.492	11/21/2016	5/25/2017	2/9/2017
Tk40 (SB8)	0.150	<0.493	11/21/2016	5/25/2017	2/9/2017
1Q17Tk50	32.0	35.1	1/16/2017	5/5/2017	3/20/2017
1Q17Tk50	33.0	36.7	1/16/2017	5/5/2017	3/20/2017
1Q17Tk50	34.4	37.9	1/16/2017	5/5/2017	3/20/2017
2Q17Tk50	28.7	31.0	4/19/2017	6/7/2017	6/26/2017
2Q17Tk50	29.0	32.0	4/19/2017	6/7/2017	6/26/2017
2Q17Tk50	25.2	33.5	4/19/2017	6/7/2017	6/26/2017
3Q17Tk50	33.8	28.3	7/27/2017	10/3/2017	9/21/2017
3Q17Tk50	32.9	28.4	7/27/2017	10/3/2017	9/21/2017
3Q17Tk50	34.8	29.0	7/27/2017	10/3/2017	9/21/2017
Tk21 (SB11)	62.5	65.1	8/1/2017	11/3/2017	10/12/2017
Tk21 (SB11)	62.3	68.1	8/1/2017	11/3/2017	10/12/2017
Tk21 (SB11)	62.5	70.7	8/1/2017	11/3/2017	10/12/2017
Tk21 (SB11)	0.000912	<5.55E-03	8/1/2017	11/3/2017	10/12/2017
Tk21 (SB11)	0.000247	<5.55E-03	8/1/2017	11/3/2017	10/12/2017
1Q18Tk50	29.4	34.8	2/6/2018	7/10/2018	4/6/2018
1Q18Tk50*	14.0*	36.4	2/6/2018	7/10/2018	4/6/2018
1Q18Tk50	27.9	38.5	2/6/2018	7/10/2018	4/6/2018
Tk51 (pre-SB10)	2.98	3.10	2/6/2018	7/10/2018	4/6/2018
Tk51 (pre-SB10)	NR	<5.72E-01	2/6/2018	7/10/2018	4/6/2018
Tk51 (pre-SB10)	3.14	<5.75E-01	2/6/2018	7/10/2018	4/6/2018
Tk51 (pre-SB10)	3.07	<5.77E-01	2/6/2018	7/10/2018	4/6/2018
4Q18Tk50	23.6	18.2	11/16/2018	3/8/2019	1/18/2019
4Q18Tk50	21.5	18.9	11/16/2018	3/8/2019	1/18/2019

NR: Sample data not reported due to falling below reporting limit or analyst error

*Analyst error was suspected. The analyst recalled potentially adding only ½ of the required amount of sample. The data has been included for completeness, but the fidelity of this data point is in question.

A review of the results in Exhibit B-10 reveals that some of the samples submitted along with the tank samples were "unknown" (to the receiving laboratory) blanks. In Exhibit B-11 in Appendix B, those samples have been removed and the plots of Exhibit B-10 repeated. In the first plot, the laboratory averages for each sample name are indicated by the horizontal line segments, and in the second, the line segment connects the results for the two laboratories (with AD first) for each individual sample analyzed. In both plots, the AD result is sometimes smaller than the corresponding EF result and sometimes larger.

Exhibit B-12 in Appendix B provides an initial investigation into statistically significant effects on the measurements for the tank samples. In this evaluation, the terms introduced into the analysis were the type of sampling event, sample name within each type, and laboratory. The first two terms were seen to be statistically effects (both have p-values <0.0001), while the p-value for laboratory in this model was 0.1317, indicating that there did not appear to be a statistical difference in the results due to laboratory.

Exhibit B-13 in Appendix B repeated the investigation of Exhibit B-12 with an additional term, the age of the sample at the time of analysis. Once again, type of sampling event and sample name within each type were seen to be statistically significant effects (both have p-values <0.0001). However, in this analysis neither laboratory nor sample age was statistically significant (p-values of 0.5461 and 0.5309, respectively)

Exhibit B-14 in Appendix B provides an investigation into significant effects on the measurement of samples just from Tank 50. In this evaluation, the terms introduced into the analysis were sample name and laboratory. Sample name was found to be statistically significant at the 5% significance level (with a p-value of 0.0243), while laboratory was not (p-value 0.0941).

Figure 3-7 provides a closer look at the effects of sample age on the measurement of Tank 50 samples. The horizontal line segments represent the average of the measurements at the sample age indicated on the x-axis. No sustained pattern is revealed in these results. A mix of results, where the older sample measurements are larger than the younger measurements and vice versa, is seen. For further statistical analysis, please see Exhibit B-14 in Appendix B.

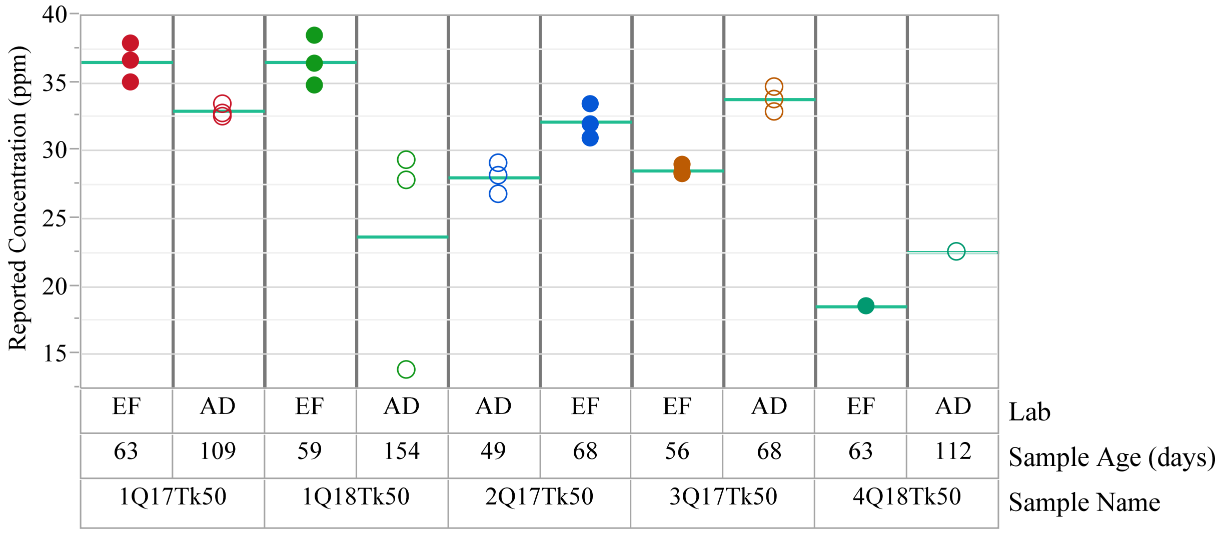

Figure 3-7 Reported tank concentration (ppm) per lab shown as a function of sample age

3.5 Statistical Conclusions

The statistical evaluations presented in this document support the following conclusions. For AD's analyses of blanks: for ethylmercury, measurements of 11.5 pg or more are above those likely to be generated from the analyses of blanks for this analyte, and for the methylmercury, measurements of 1.13 pg or more are above those likely to be generated from the analyses of blanks for this analyte.

Several ways of comparing the ethylmercury and methylmercury measurements from both laboratories of non-blank QCs demonstrate that AD's measurements of its QCs are as good as, if not better than, EF's measurements, relative to bias and precision.

Several comparisons of methylmercury results for tank samples analyzed by both laboratories, when the true values for these measurements are unknown, were also conducted as part of this investigation. While statistically significant effects where discerned in these results, the analytical laboratory was not a statistically significant effect, at a 5% significance level, in the outcomes of these measurements.[♣] Thus, while it is impossible to discern which laboratory's result may be closer to the true methylmercury value for a given tank sample (that value being an unknown), with AD values being larger than their EF counterparts for some samples and smaller for others, and with the results seen from the comparisons of the QCs from both laboratories, the conclusion from this evaluation is that the AD results for these tank samples is as reliable as those from EF.

[♣] For all statistical tests conducted as part of this evaluation, a 5% significance level was utilized to identify statistically significant outcomes.

4.0 Conclusions

A method for methylmercury speciation and quantification has been developed, optimized, and validated by inter-laboratory comparison at SRNL. A simultaneous method for ethylmercury analysis has been developed, as a modified variant of the reported methylmercury method, optimized and internally validated. This developed method demonstrates a non-biased method uncertainty for methylmercury of 5.1% (n=74), compared to 13% (n=34) with a positive bias from Eurofins FGS. A nonbiased method uncertainty of 4.8% (n=61) was observed in the analysis of ethylmercury in SRNL-AD, compared with 9.1% (n=26) with a negative bias from Eurofins FGS. The analytical quality achieved by these method affords high precision and accuracy required by existing and future WAC limits, and allows for high dilution of tank samples to comply with ALARA practices sample preparation best practices. As requested by SRR, SRNL-AD has produced a method for the analysis of methylmercury and ethylmercury of quality equal to or greater than that provided by the existing external commercial laboratory, Eurofins FGS.

5.0 Recommendations and Future Work

Based upon the work performed by SRNL AD and the data currently available, the following recommendations can be made:

- Further work should be performed to determine a "best practices" for sample holding time prior to analysis (both preserved and non-preserved samples), as well as any detrimental effects sample age may have on data quality.
- Separate analysis of ethylmercury from methylmercury is only recommended for tank samples that are reasonably expected to have more significant quantities of ethylmercury, such as from the DWPF SMECT. Trace levels of ethylmercury in the presence of large quantities of methylmercury can be difficult or impossible to quantify. There is a significant time, and hence cost, savings analyzing the two species of mercury together.

SRNL AD development of methods for total mercury, purgeable mercury (which includes both Hg(0) and dimethylmercury),[22] inorganic mercury (Hg(I) and Hg(II)), dissolved mercury, and particulate mercury are underway and will be reported upon separately.[23]

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Appendix A

Exhibit A-1 Initial Plots of the Results from the Direct versus Distillation Treatments

Variability Chart for % Relative Difference
Grouping 1

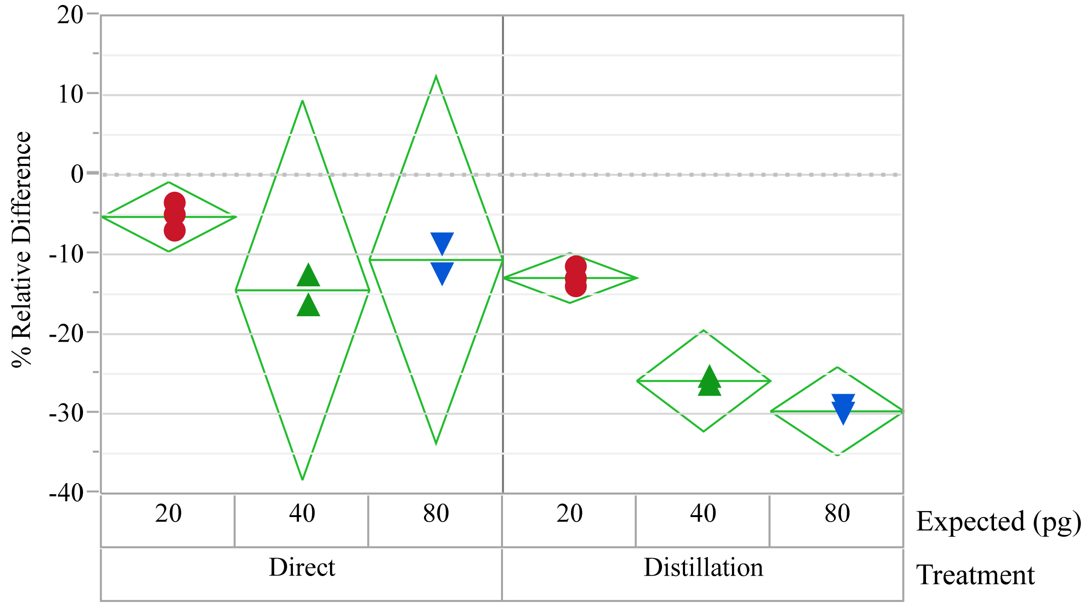


Exhibit A.1 Initial Plots of the Results from the Direct versus Distillation Treatments (*continued)*

Grouping 2

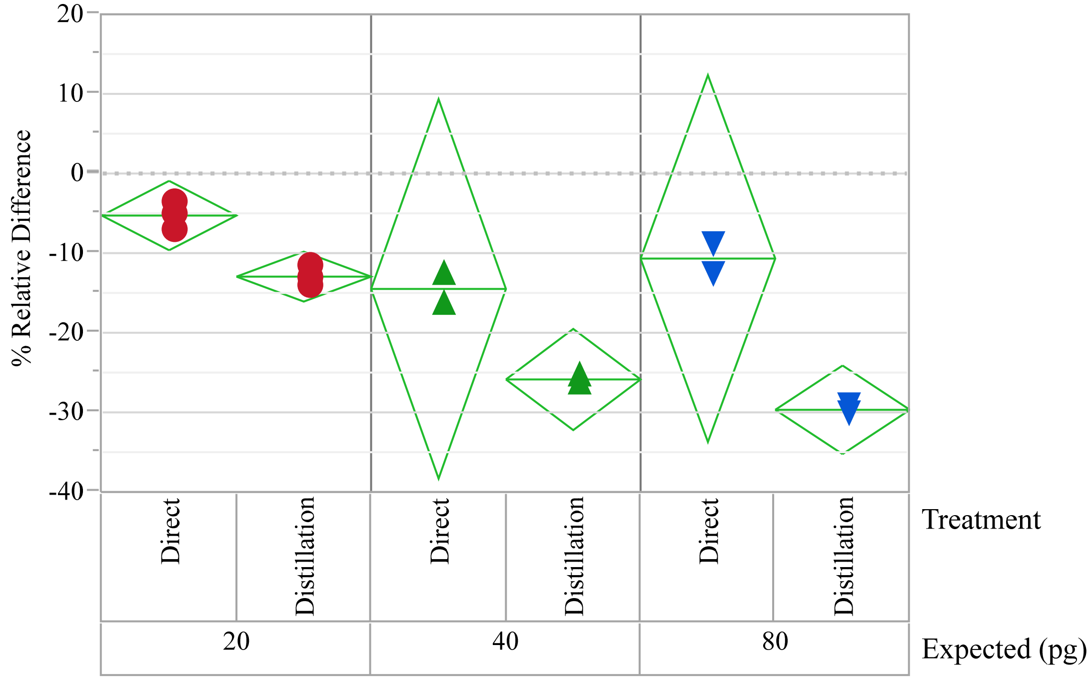
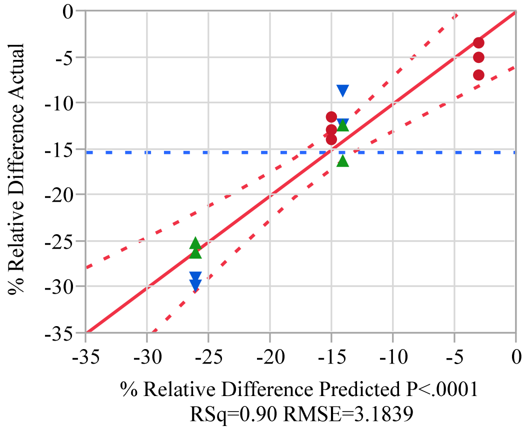


Exhibit A-2 Analysis of Variance Results of Direct versus Distillation Treatments

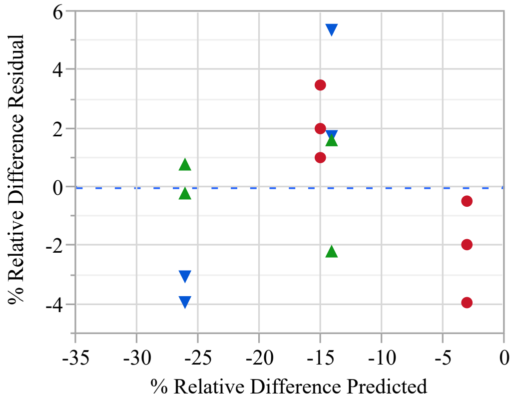
Response % Relative Difference

Whole Model

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.900808
RSquare Adj	0.87105
Root Mean Square Error	3.183874
Mean of Response	-15.3214
Observations (or Sum Wgts)	14

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	920.5893	306.863	30.2714
Error	10	101.3705	10.137	**Prob > F**
C. Total	13	1021.9598		<.0001*

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	2	77.55283	38.7764	13.0244
Pure Error	8	23.81771	2.9772	**Prob > F**
Total Error	10	101.37054		0.0030*
				Max RSq

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-16.375	0.866541	-18.90	<.0001*
Expected (pg)[20]	7.375	1.146326	6.43	<.0001*
Expected (pg)[40]	-3.6875	1.263189	-2.92	0.0153*
Treatment[Direct]	5.9821429	0.850926	7.03	<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Expected (pg)	2	2	419.58482	20.6956	0.0003*
Treatment	1	1	501.00446	49.4231	<.0001*

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
Direct	-10.39286	1.2144827	-9.339
Distillation	-22.35714	1.2144827	-21.304

Exhibit A-3Analysis of Variance Results for Each Treatment

Response % Relative Difference Treatment=Direct
Whole Model

Summary of Fit

RSquare	0.835542
RSquare Adj	0.835542
Root Mean Square Error	2.218467
Mean of Response	-9.33929
Observations (or Sum Wgts)	7

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	-9.972802	2.694635	2.031	-3.70	0.0643	-21.39717	1.451571

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Expected (pg)	3.9787649	19.58188	21.623635	-22.79967	61.963426	79.915
Residual		4.9215977	3.4658219	1.772142	40.119585	20.085
Total		24.503478	21.695318	7.3610208	491.1193	100.000

-2 LogLikelihood = 33.146153921
Note: Total is the sum of the positive variance components.

Total including negative estimates = 24.503478

Response % Relative Difference Treatment=Distillation
Whole Model

Summary of Fit

RSquare	0.989728
RSquare Adj	0.989728
Root Mean Square Error	1.006
Mean of Response	-21.3036
Observations (or Sum Wgts)	7

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	-22.70805	5.065417	2.003	-4.48	0.0462*	-44.4753	-0.940807

REML Variance Component Estimates

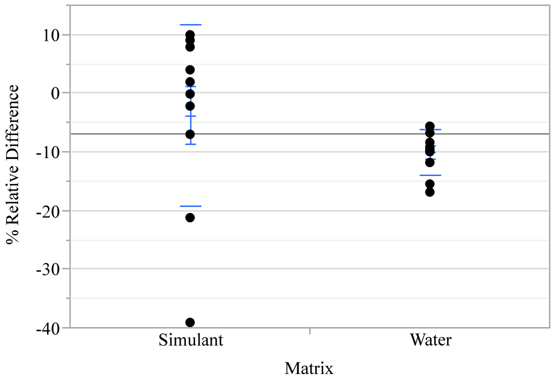
Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Expected (pg)	75.615321	76.525376	76.924665	-74.2442	227.29495	98.695
Residual		1.0120353	0.7153809	0.3633712	8.3480375	1.305
Total		77.537411	76.925704	21.162662	2914.3513	100.000

-2 LogLikelihood = 29.345600513
Note: Total is the sum of the positive variance components.

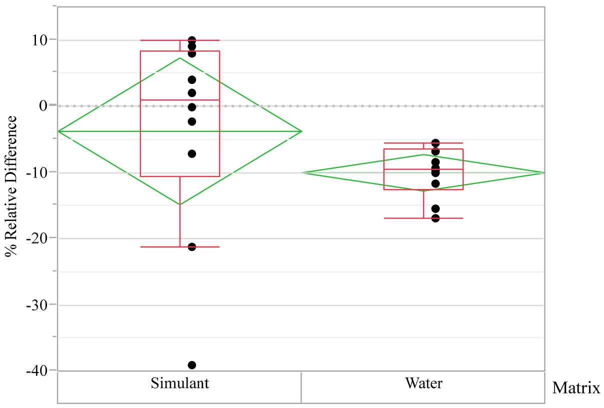
Total including negative estimates = 77.537411

Exhibit A-4 Analysis of Variance Results of Simulant versus Water Solution Matrix

Oneway Analysis of % Relative Difference By Matrix



Variability Chart for % Relative Difference



Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Simulant	10	-3.7000	15.5147	4.9062	-14.80	7.399
Water	10	-9.9600	3.8399	1.2143	-12.71	-7.213

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Simulant	10	15.51465	11.28000	10.30000
Water	10	3.83991	2.85200	2.80000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	2.5674	1	18	0.1265
Brown-Forsythe	3.6871	1	18	0.0708
Levene	6.7626	1	18	0.0181
Bartlett	13.0051	1	.	0.0003
F Test 2-sided	16.3246	9	9	0.0003

Welch's Test

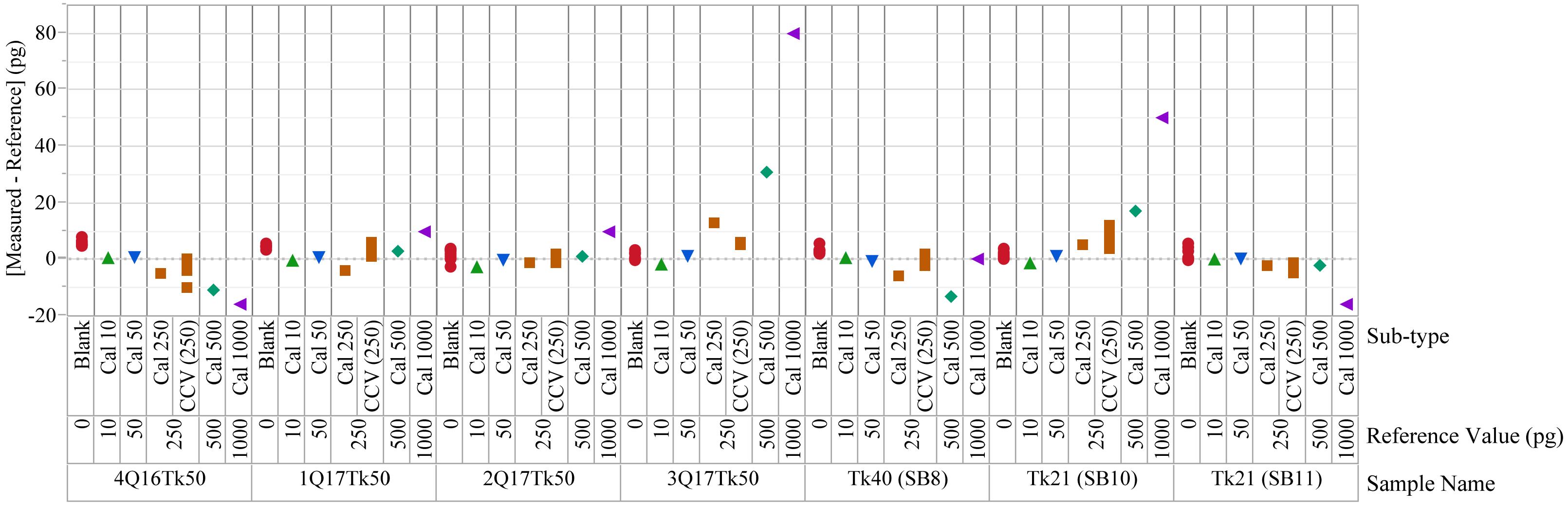
Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob > F
1.5341	1	10.099	0.2435

Appendix B

Exhibit B-1 Results for the AD QC Standards

Type=standard, Analyte=Ethylmercury
Variability Chart for [Measured - Reference] (pg)



Variability Gauge Type=standard, Analyte=Ethylmercury
Variability Chart for % Relative Difference [100% (M-R)/R]

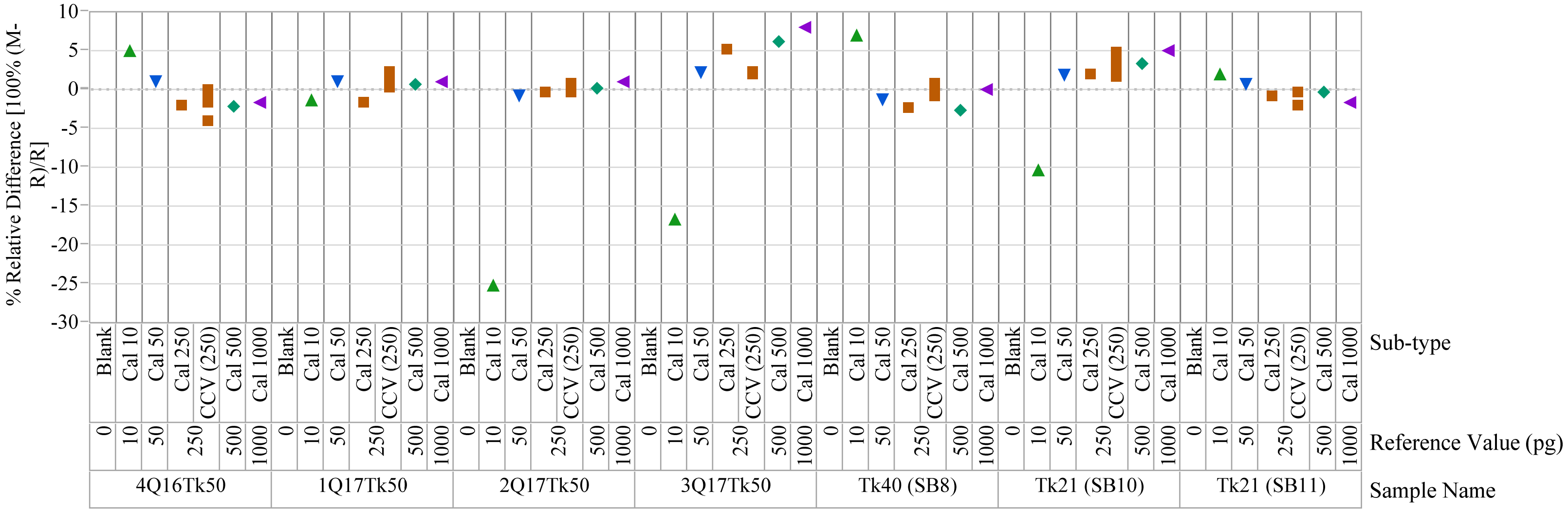
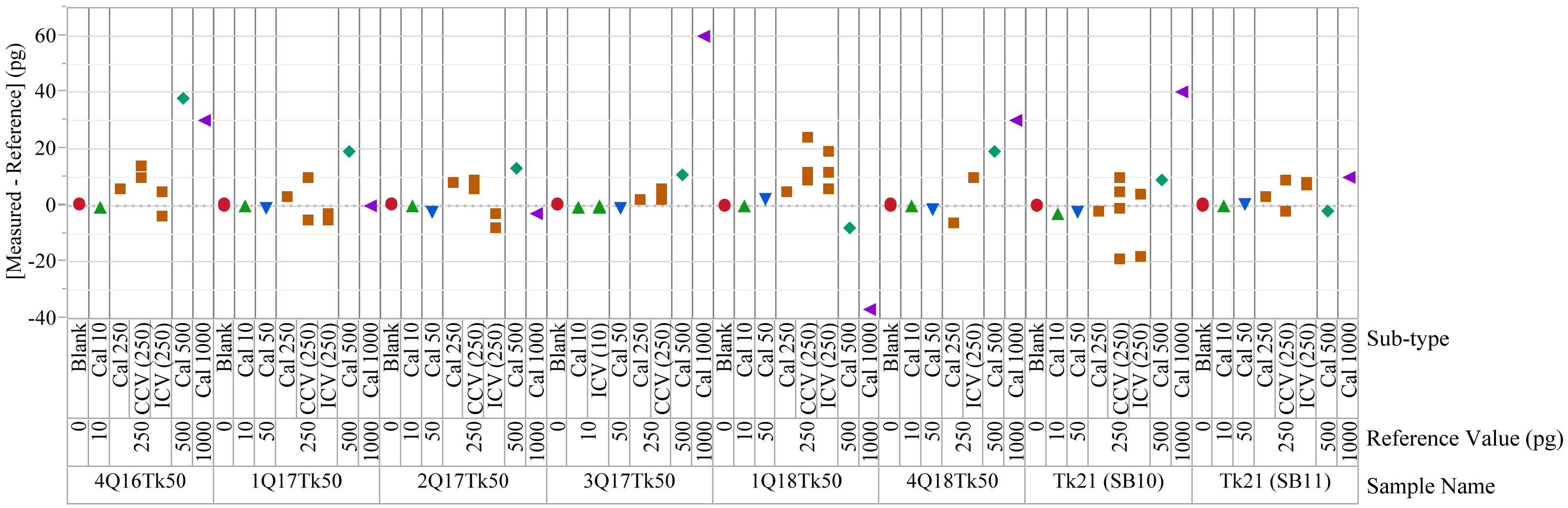


Exhibit B.1 Results for the AD QC Standards *(continued)*

Variability Gauge Type=standard, Analyte=Methylmercury
Variability Chart for [Measured - Reference] (pg)



Variability Gauge Type=standard, Analyte=Methylmercury
Variability Chart for % Relative Difference [100% (M-R)/R]

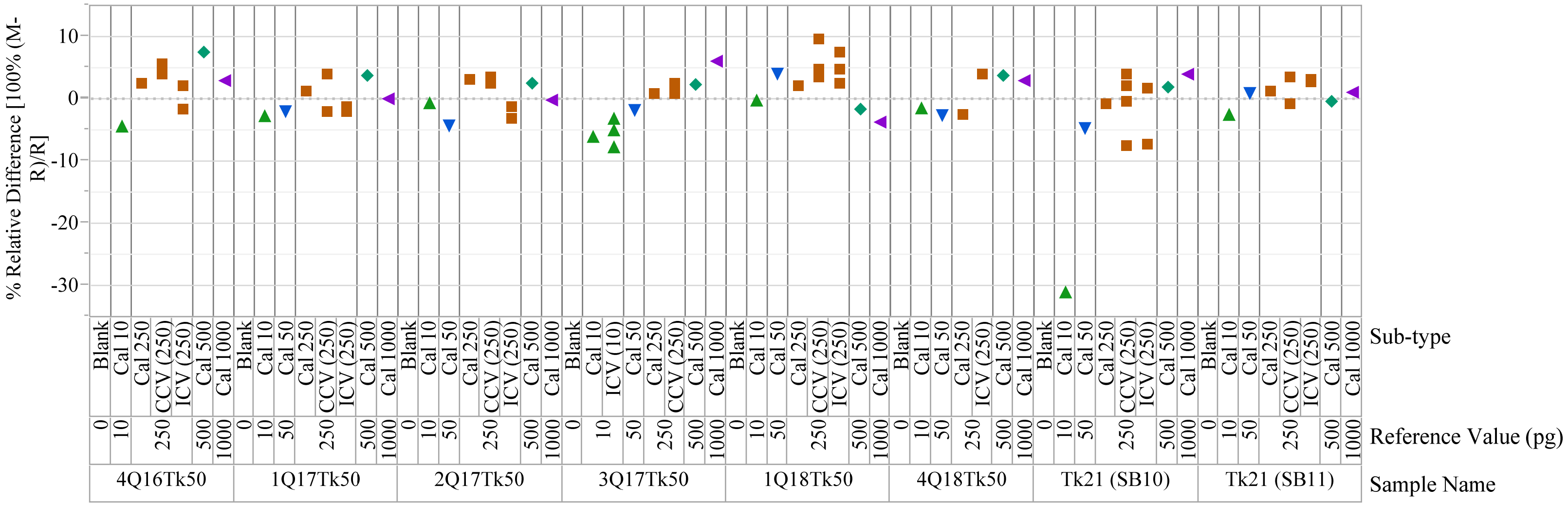


Exhibit B-2 Results for the AD QC Blanks

Type=standard, Sub-type=Blank
Variability Chart for [Measured - Reference] (pg)

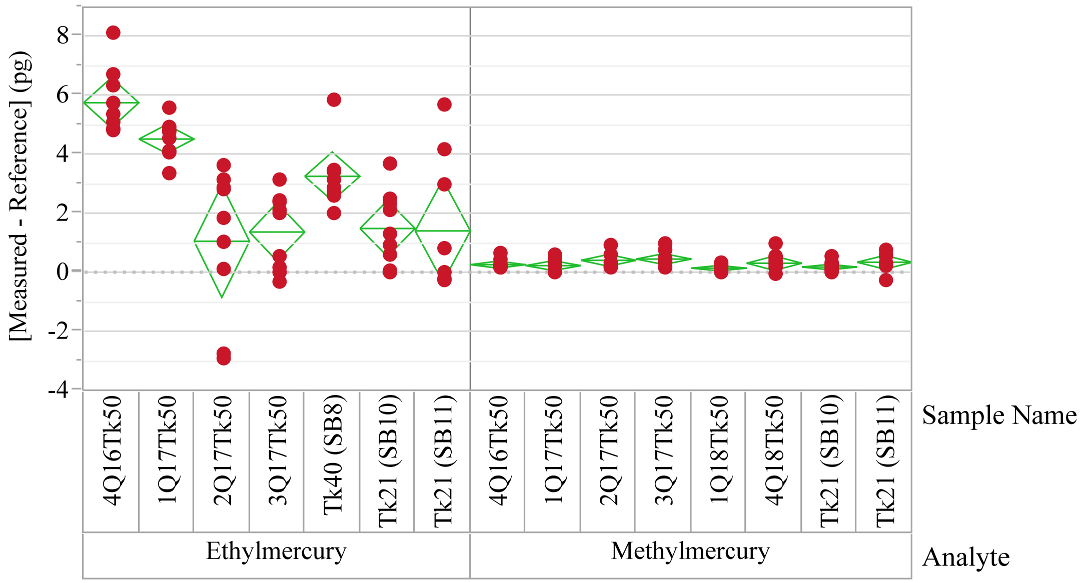
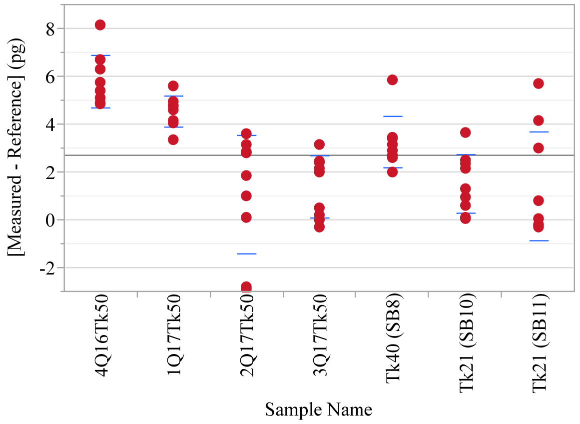


Exhibit B-3 Statistical Comparisons of the Results for the AD QC Blanks

Oneway Analysis of [Measured - Reference] (pg) By Sample Name Type=standard, Sub-type=Blank, Analyte=Ethylmercury



Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
4Q16Tk50	9	1.105158	0.851111	0.794444
1Q17Tk50	9	0.634094	0.466667	0.438889
2Q17Tk50	9	2.480852	1.974074	1.890000
3Q17Tk50	9	1.281066	1.146272	1.077200
Tk40 (SB8)	9	1.072883	0.673827	0.660000
Tk21 (SB10)	9	1.233760	1.023546	1.001489
Tk21 (SB11)	9	2.261454	1.898178	1.601078

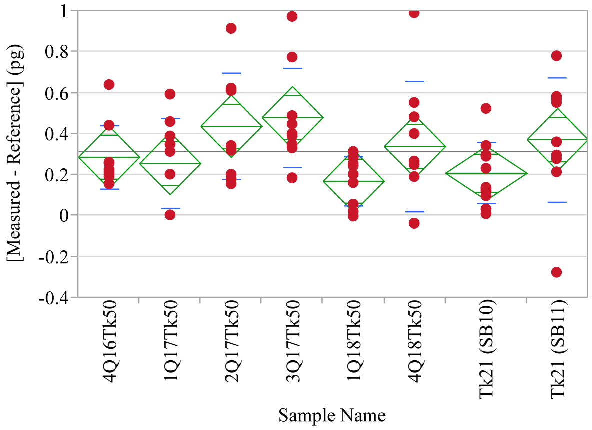
Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	2.8426	6	56	0.0173
Brown-Forsythe	1.6752	6	56	0.1442
Levene	4.7115	6	56	0.0006
Bartlett	3.1836	6	.	0.0040

Welch's Test

Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob > F
18.4392	6	24.371	<.0001*

Oneway Analysis of [Measured - Reference] (pg) By Sample Name Type=standard, Sub-type=Blank, Analyte=Methylmercury



Oneway Anova

Summary of Fit

Rsquare	0.181996
Adj Rsquare	0.096533
Root Mean Square Error	0.228548
Mean of Response	0.313891
Observations (or Sum Wgts)	75

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Sample Name	7	0.7786377	0.111234	2.1295	0.0521
Error	67	3.4996858	0.052234		
C. Total	74	4.2783235			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
4Q16Tk50	9	0.286556	0.07618	0.13449	0.43862
1Q17Tk50	9	0.255222	0.07618	0.10316	0.40728
2Q17Tk50	9	0.437222	0.07618	0.28516	0.58928
3Q17Tk50	9	0.479444	0.07618	0.32738	0.63151
1Q18Tk50	9	0.169452	0.07618	0.01739	0.32151
4Q18Tk50	9	0.338189	0.07618	0.18613	0.49025
Tk21 (SB10)	12	0.208258	0.06598	0.07657	0.33995
Tk21 (SB11)	9	0.372000	0.07618	0.21994	0.52406

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
4Q16Tk50	9	0.1552056	0.1124198	0.0930000
1Q17Tk50	9	0.2183133	0.1817531	0.1756667
2Q17Tk50	9	0.2612613	0.2222469	0.2115556
3Q17Tk50	9	0.2429301	0.1754815	0.1585556
1Q18Tk50	9	0.1187714	0.0990531	0.0953256
4Q18Tk50	9	0.3192421	0.2373877	0.2291444
Tk21 (SB10)	12	0.1483517	0.1207425	0.1207425
Tk21 (SB11)	9	0.3035708	0.2195556	0.2180000

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	1.1218	7	67	0.3601
Brown-Forsythe	1.1525	7	67	0.3418
Levene	1.5908	7	67	0.1533
Bartlett	1.8996	7	.	0.0652

Exhibit B-4 Random Effects Model Applied to the Measurements by AD of the QC Blanks

Response [Measured - Reference] (pg) Type=standard, Sub-type=Blank, Analyte=Ethylmercury
Whole Model

Summary of Fit

RSquare	0.570039
RSquare Adj	0.570039
Root Mean Square Error	1.567829
Mean of Response	2.722483
Observations (or Sum Wgts)	63

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	2.7224825	0.70002	6	3.89	0.0081*	1.009596	4.4353691

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Sample Name	1.2843605	3.1570722	1.9810954	-0.725804	7.0399478	56.224
Residual		2.4580887	0.4645351	1.7520419	3.6991958	43.776
Total		5.6151609	2.0230121	3.0851735	13.261141	100.000

-2 LogLikelihood = 251.03606969
Note: Total is the sum of the positive variance components.

Total including negative estimates = 5.6151609

Response [Measured - Reference] (pg) Type=standard, Sub-type=Blank, Analyte=Methylmercury
Whole Model

Summary of Fit

RSquare	0.142165
RSquare Adj	0.142165
Root Mean Square Error	0.228492
Mean of Response	0.313891
Observations (or Sum Wgts)	75

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	0.3164502	0.03858	7.05	8.20	<.0001*	0.2253542	0.4075461

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Sample Name	0.1205346	0.006293	0.0063912	-0.006233	0.0188194	10.757
Residual		0.0522087	0.0090148	0.0382279	0.0755955	89.243
Total		0.0585017	0.010252	0.042653	0.0852207	100.000

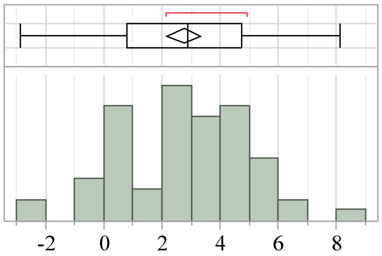
-2 LogLikelihood = 1.1136925224
Note: Total is the sum of the positive variance components.

Total including negative estimates = 0.0585017

Exhibit B-5 Histograms and Summary Statistics of the Measurements by AD of the QC Blanks

Distributions Type=standard, Sub-type=Blank, Analyte=Ethylmercury

[Measured - Reference] (pg)



Quantiles

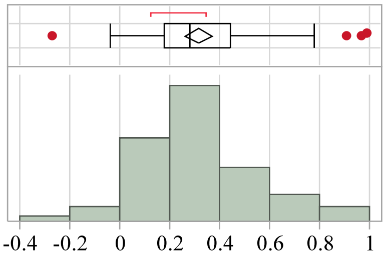
100.0%	maximum	8.14
99.5%		8.14
97.5%		7.288
90.0%		5.64
75.0%	quartile	4.75
50.0%	median	2.87
25.0%	quartile	0.801
10.0%		-0.1197
2.5%		-2.828
0.5%		-2.9
0.0%	minimum	-2.9

Summary Statistics

Mean	2.7224825
Std Dev	2.2820598
Std Err Mean	0.2875125
Upper 95% Mean	3.2972118
Lower 95% Mean	2.1477532
N	63

Distributions Type=standard, Sub-type=Blank, Analyte=Methylmercury

[Measured - Reference] (pg)



Quantiles

100.0%	maximum	0.991
99.5%		0.991
97.5%		0.9721
90.0%		0.6144
75.0%	quartile	0.443
50.0%	median	0.282
25.0%	quartile	0.177
10.0%		0.00347
2.5%		-0.0642
0.5%		-0.275
0.0%	minimum	-0.275

Summary Statistics

Mean	0.3138915
Std Dev	0.2404479
Std Err Mean	0.0277645
Upper 95% Mean	0.3692135
Lower 95% Mean	0.2585694
N	75

Exhibit B-6 AD and EF Results of Non-Blank QCs

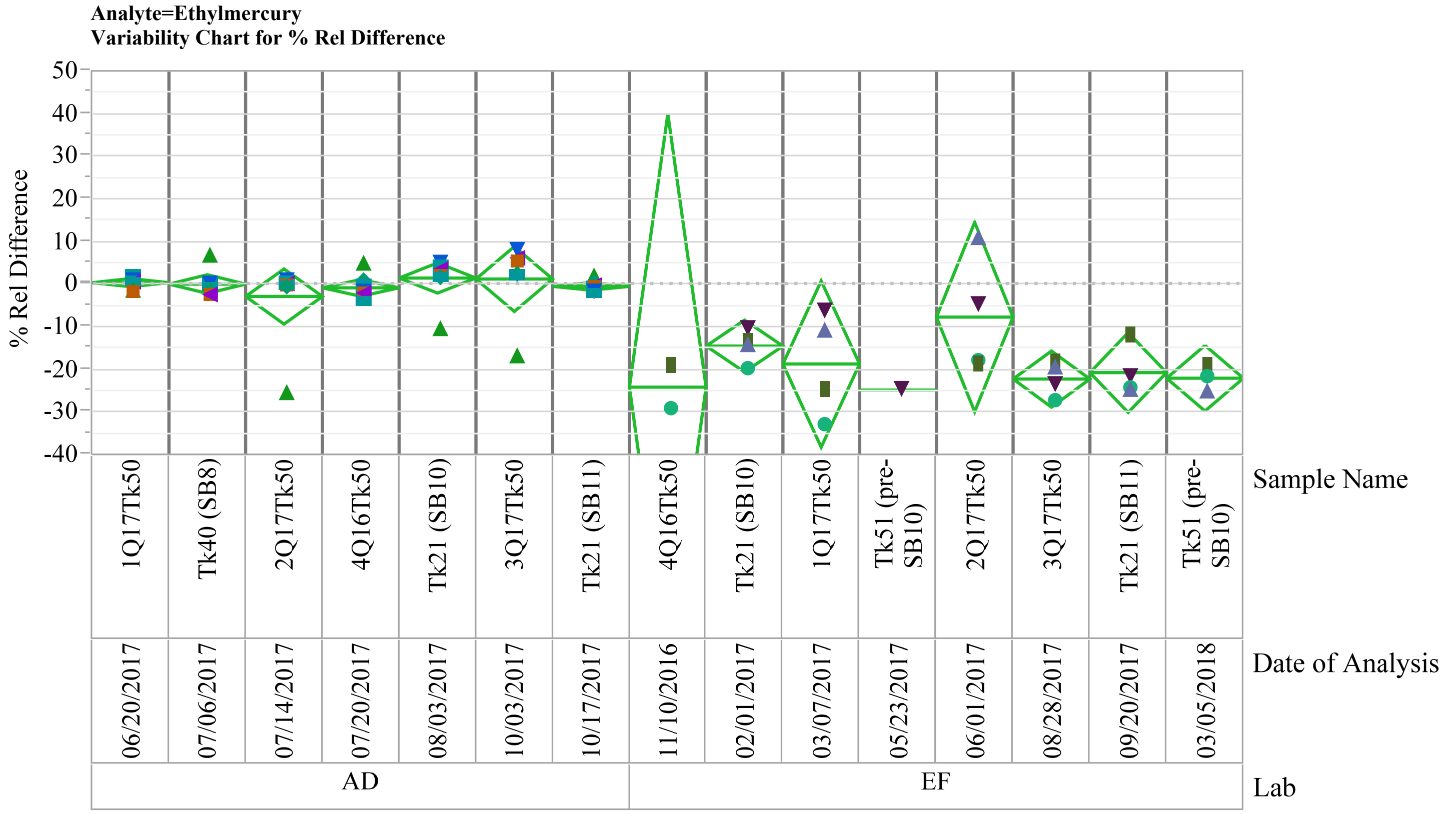

Analyte=Ethylmercury
Variability Chart for % Rel Difference

Exhibit B.6 AD and EF Results of Non-Blank QCs *(continued)*

Analyte=Methylmercury
Variability Chart for % Rel Difference

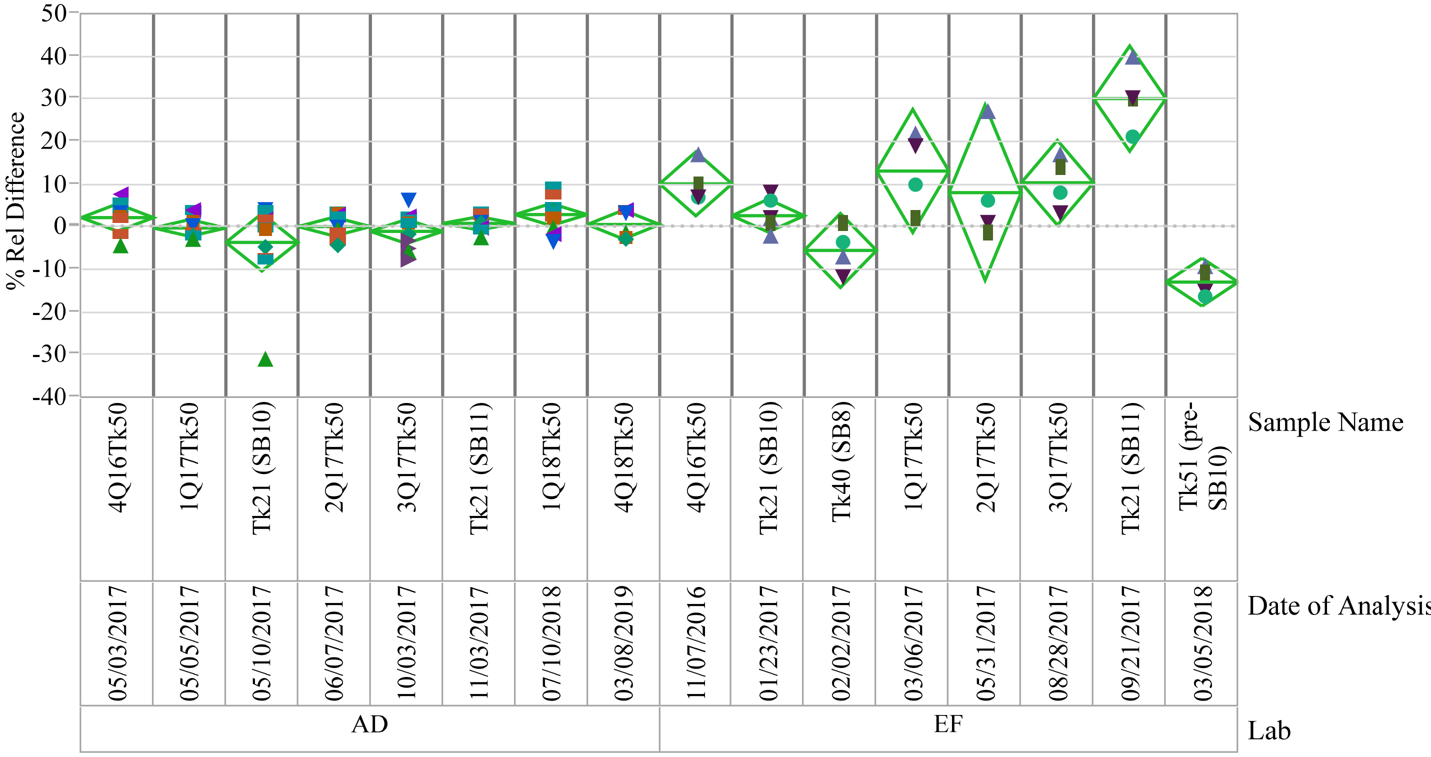
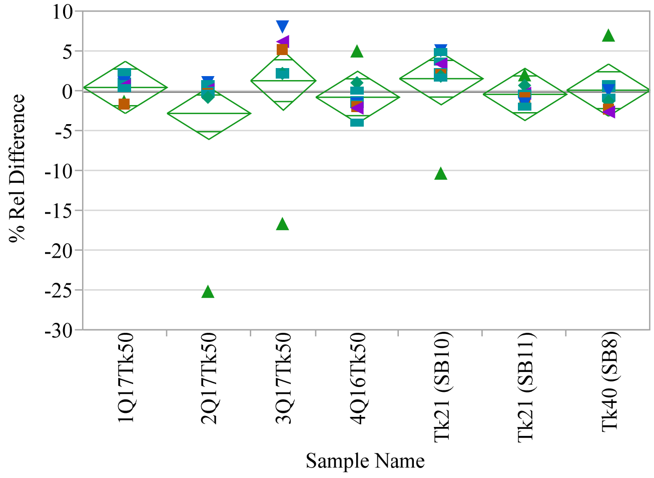


Exhibit B-7 Analysis of Variance for the AD and EF Results of Non-Blank QCs

Oneway Analysis of % Rel Difference By Sample Name Analyte=Ethylmercury, Lab=AD



Oneway Anova
Summary of Fit

Rsquare	0.079858
Adj Rsquare	-0.02238
Root Mean Square Error	4.884871
Mean of Response	-0.08525
Observations (or Sum Wgts)	61

Analysis of Variance

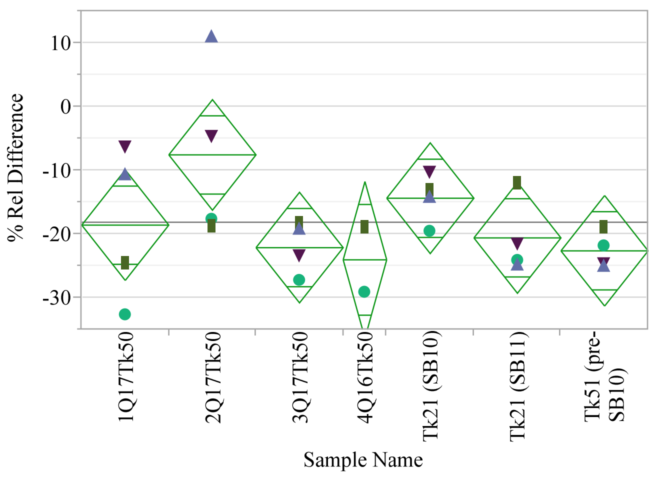
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Sample Name	6	111.8307	18.6384	0.7811	0.5884
Error	54	1288.5460	23.8620		
C. Total	60	1400.3767			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1Q17Tk50	9	0.5000	1.6283	-2.765	3.7645
2Q17Tk50	9	-2.7556	1.6283	-6.020	0.5090
3Q17Tk50	7	1.3429	1.8463	-2.359	5.0445
4Q16Tk50	9	-0.7333	1.6283	-3.998	2.5312
Tk21 (SB10)	9	1.5889	1.6283	-1.676	4.8534
Tk21 (SB11)	9	-0.3778	1.6283	-3.642	2.8867
Tk40 (SB8)	9	0.1556	1.6283	-3.109	3.4201

Std Error uses a pooled estimate of error variance

Oneway Analysis of % Rel Difference By Sample Name Analyte=Ethylmercury, Lab=EF



Oneway Anova
Summary of Fit

Rsquare	0.361716
Adj Rsquare	0.160152
Root Mean Square Error	8.301728
Mean of Response	-18.1423
Observations (or Sum Wgts)	26

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Sample Name	6	742.0685	123.678	1.7946	0.1540
Error	19	1309.4550	68.919		
C. Total	25	2051.5235			

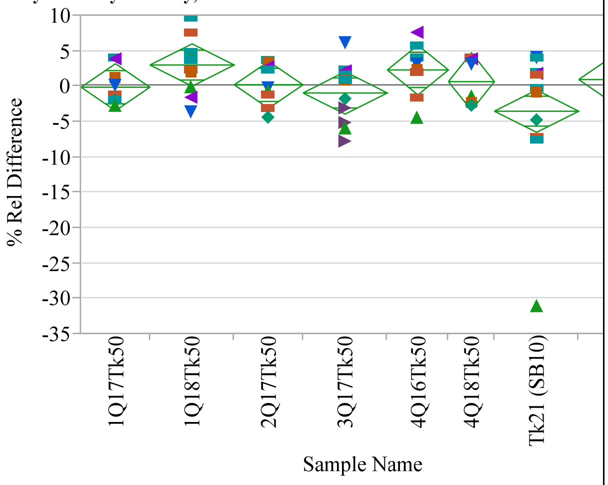
Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1Q17Tk50	4	-18.600	4.1509	-27.29	-9.91
2Q17Tk50	4	-7.575	4.1509	-16.26	1.11
3Q17Tk50	4	-22.125	4.1509	-30.81	-13.44
4Q16Tk50	2	-24.050	5.8702	-36.34	-11.76
Tk21 (SB10)	4	-14.375	4.1509	-23.06	-5.69
Tk21 (SB11)	4	-20.600	4.1509	-29.29	-11.91
Tk51 (pre-SB10)	4	-22.625	4.1509	-31.31	-13.94

Std Error uses a pooled estimate of error variance

Exhibit B.7 Analysis of Variance for the AD and EF Results of Non-Blank QCs *(continued)*

Oneway Analysis of % Rel Difference By Sample Name Analyte=Methylmercury, Lab=AD



Oneway Anova
Summary of Fit

Rsquare	0.152746
Adj Rsquare	0.062885
Root Mean Square Error	4.98171
Mean of Response	0.233784
Observations (or Sum Wgts)	74

Analysis of Variance

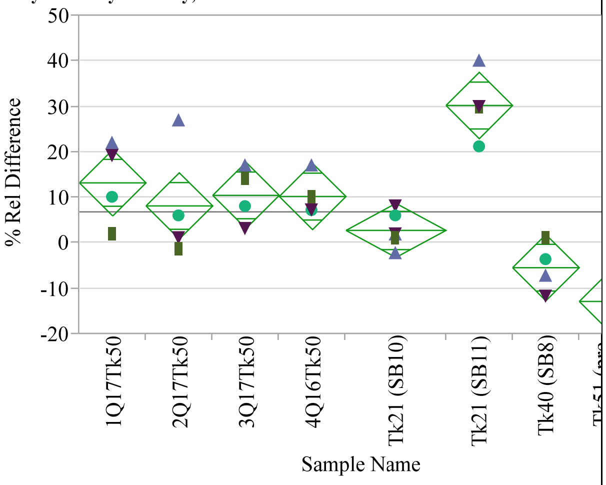
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Sample Name	7	295.2949	42.1850	1.6998	0.1243
Error	66	1637.9506	24.8174		
C. Total	73	1933.2455			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1Q17Tk50	9	-0.1111	1.6606	-3.427	3.204
1Q18Tk50	11	3.0273	1.5020	0.028	6.026
2Q17Tk50	9	0.2222	1.6606	-3.093	3.538
3Q17Tk50	11	-0.9182	1.5020	-3.917	2.081
4Q16Tk50	8	2.3250	1.7613	-1.192	5.842
4Q18Tk50	6	0.6833	2.0338	-3.377	4.744
Tk21 (SB10)	11	-3.4909	1.5020	-6.490	-0.492
Tk21 (SB11)	9	0.9778	1.6606	-2.338	4.293

Std Error uses a pooled estimate of error variance

Oneway Analysis of % Rel Difference By Sample Name Analyte=Methylmercury, Lab=EF



Oneway Anova
Summary of Fit

Rsquare	0.782857
Adj Rsquare	0.724396
Root Mean Square Error	7.087403
Mean of Response	6.867647
Observations (or Sum Wgts)	34

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Sample Name	7	4708.5211	672.646	13.3910	<.0001*
Error	26	1306.0133	50.231		
C. Total	33	6014.5344			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1Q17Tk50	4	13.250	3.5437	5.97	20.53
2Q17Tk50	4	8.175	3.5437	0.89	15.46
3Q17Tk50	4	10.500	3.5437	3.22	17.78
4Q16Tk50	4	10.250	3.5437	2.97	17.53
Tk21 (SB10)	6	2.783	2.8934	-3.16	8.73
Tk21 (SB11)	4	30.250	3.5437	22.97	37.53
Tk40 (SB8)	4	-5.400	3.5437	-12.68	1.88
Tk51 (pre-SB10)	4	-12.825	3.5437	-20.11	-5.54

Std Error uses a pooled estimate of error variance

Exhibit B-8 Random Effects Analysis of Variance for the AD and EF Results of Non-Blank QCs

Response % Rel Difference Analyte=Ethylmercury, Lab=AD
Whole Model
Summary of Fit

RSquare	-0.04901
RSquare Adj	-0.04901
Root Mean Square Error	4.882934
Mean of Response	-0.08525
Observations (or Sum Wgts)	61

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	-0.094902	0.556035	5.989	-0.17	0.8701	-1.456098	1.2662942

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Sample Name	-0.024287	-0.579082	1.3364666	-3.198509	2.040344	0.000
Residual		23.843045	4.5835154	16.90429	36.161839	100.000
Total		23.843045	4.5835154	16.90429	36.161839	100.000

-2 LogLikelihood = 363.24672324
Note: Total is the sum of the positive variance components.

Total including negative estimates = 23.263963

Response % Rel Difference Analyte=Ethylmercury, Lab=EF
Whole Model
Summary of Fit

RSquare	0.252523
RSquare Adj	0.252523
Root Mean Square Error	8.284545
Mean of Response	-18.1423
Observations (or Sum Wgts)	26

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	-18.27768	2.211342	5.98	-8.27	0.0002*	-23.69304	-12.86232

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Sample Name	0.2192948	15.051011	20.118995	-24.38149	54.483516	17.985
Residual		68.633688	22.148804	39.794118	145.71152	82.015
Total		83.684698	25.322692	49.974733	168.13225	100.000

-2 LogLikelihood = 183.46030585
Note: Total is the sum of the positive variance components.

Total including negative estimates = 83.684698

Exhibit B.8 Random Effects Analysis of Variance for the AD and EF Results of Non-Blank QCs *(continued)*

Response % Rel Difference Analyte=Methylmercury, Lab=AD
Whole Model
Summary of Fit

RSquare	0.108356
RSquare Adj	0.108356
Root Mean Square Error	4.961477
Mean of Response	0.233784
Observations (or Sum Wgts)	74

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	0.2783423	0.76866	7.909	0.36	0.7268	-1.497754	2.0544386

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Sample Name	0.0812684	2.0005226	2.3604691	-2.625912	6.626957	7.516
Residual		24.61625	4.2536834	18.020418	35.653976	92.484
Total		26.616773	4.5446863	19.55163	38.366451	100.000

-2 LogLikelihood = 449.20984387
Note: Total is the sum of the positive variance components.

Total including negative estimates = 26.616773

Response % Rel Difference Analyte=Methylmercury, Lab=EF
Whole Model
Summary of Fit

RSquare	0.778452
RSquare Adj	0.778452
Root Mean Square Error	7.090067
Mean of Response	6.867647
Observations (or Sum Wgts)	34

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	7.1089616	4.554853	6.96	1.56	0.1628	-3.674264	17.892187

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Sample Name	3.0621759	153.93269	89.035311	-20.57331	328.43869	75.383
Residual		50.269056	13.952726	31.166022	94.461881	24.617
Total		204.20175	89.562879	100.8283	611.80253	100.000

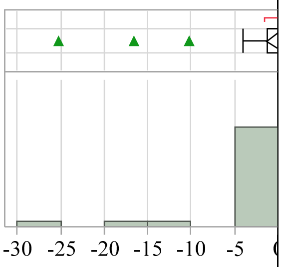
-2 LogLikelihood = 244.86004141
Note: Total is the sum of the positive variance components.

Total including negative estimates = 204.20175

Exhibit B-9 Histograms and Summary Statistics for the AD and EF Results of Non-Blank QCs

Distributions
Analyte=Ethylmercury, Lab=AD

% Rel Difference



Quantiles

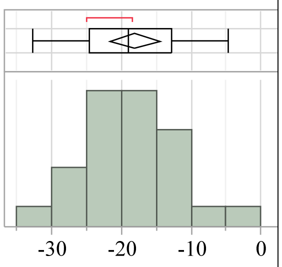
100.0%	maximum	8
99.5%		8
97.5%		7.45
90.0%		4.96
75.0%	quartile	2
50.0%	median	0.4
25.0%	quartile	-1.25
10.0%		-2.36
2.5%		-20.47
0.5%		-25.2
0.0%	minimum	-25.2

Summary Statistics

Mean	-0.085246
Std Dev	4.8311088
Std Err Mean	0.6185601
Upper 95% Mean	1.1520585
Lower 95% Mean	-1.32255
N	61

Distributions
Analyte=Ethylmercury, Lab=EF

% Rel Difference



Quantiles

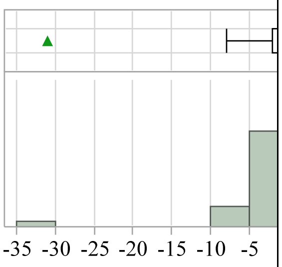
100.0%	maximum	11
99.5%		11
97.5%		11
90.0%		-5.89
75.0%	quartile	-12.9
50.0%	median	-19.1
25.0%	quartile	-24.625
10.0%		-27.84
2.5%		-32.8
0.5%		-32.8
0.0%	minimum	-32.8

Summary Statistics

Mean	-18.14231
Std Dev	9.0587493
Std Err Mean	1.7765669
Upper 95% Mean	-14.4834
Lower 95% Mean	-21.80122
N	26

Distributions
Analyte=Methylmercury, Lab=AD

% Rel Difference



Quantiles

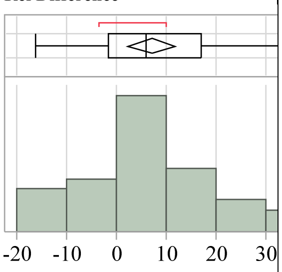
100.0%	maximum	9.6
99.5%		9.6
97.5%		7.85
90.0%		4.4
75.0%	quartile	3.3
50.0%	median	1.1
25.0%	quartile	-2
10.0%		-4.6
2.5%		-10.7
0.5%		-31
0.0%	minimum	-31

Summary Statistics

Mean	0.2337838
Std Dev	5.1461457
Std Err Mean	0.5982273
Upper 95% Mean	1.426049
Lower 95% Mean	-0.958481
N	74

Distributions
Analyte=Methylmercury, Lab=EF

% Rel Difference



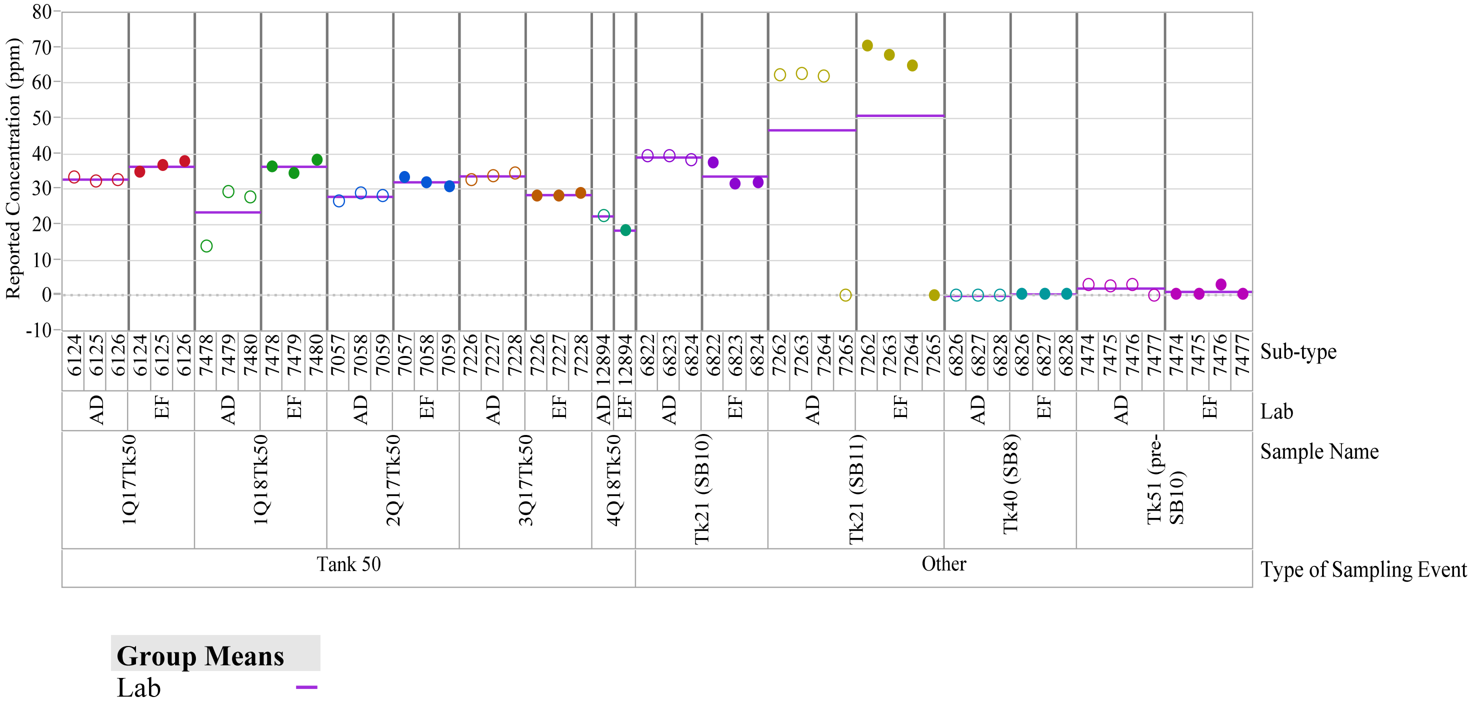
Quantiles

100.0%	maximum	40
99.5%		40
97.5%		40
90.0%		28.5
75.0%	quartile	17
50.0%	median	6
25.0%	quartile	-1.55
10.0%		-11.25
2.5%		-16.4
0.5%		-16.4
0.0%	minimum	-16.4

Summary Statistics

Mean	6.8676471
Std Dev	13.500319
Std Err Mean	2.3152856
Upper 95% Mean	11.578131
Lower 95% Mean	2.157163
N	34

Exhibit B-10 Complete Set of AD and EF Methylmercury Results for Samples Submitted with Tank Samples



Analyte=Methylmercury
Variability Chart for Reported Concentration (ppm)

Exhibit B.10 Complete Set of AD and EF Methylmercury Results for Samples Submitted with Tank Samples *(continued)*

Analyte=Methylmercury
Variability Chart for Reported Concentration (ppm)

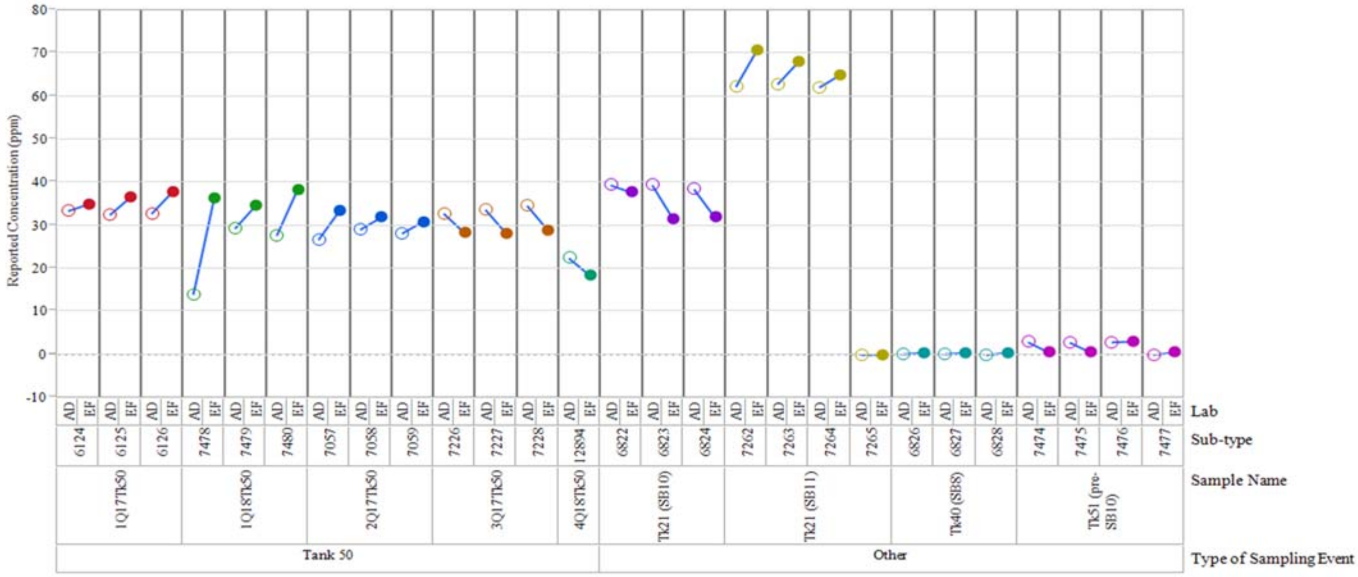


Exhibit B-11 AD and EF Methylmercury Results for Tank Samples Only

Analyte=Methylmercury
Variability Chart for Reported Concentration (ppm)

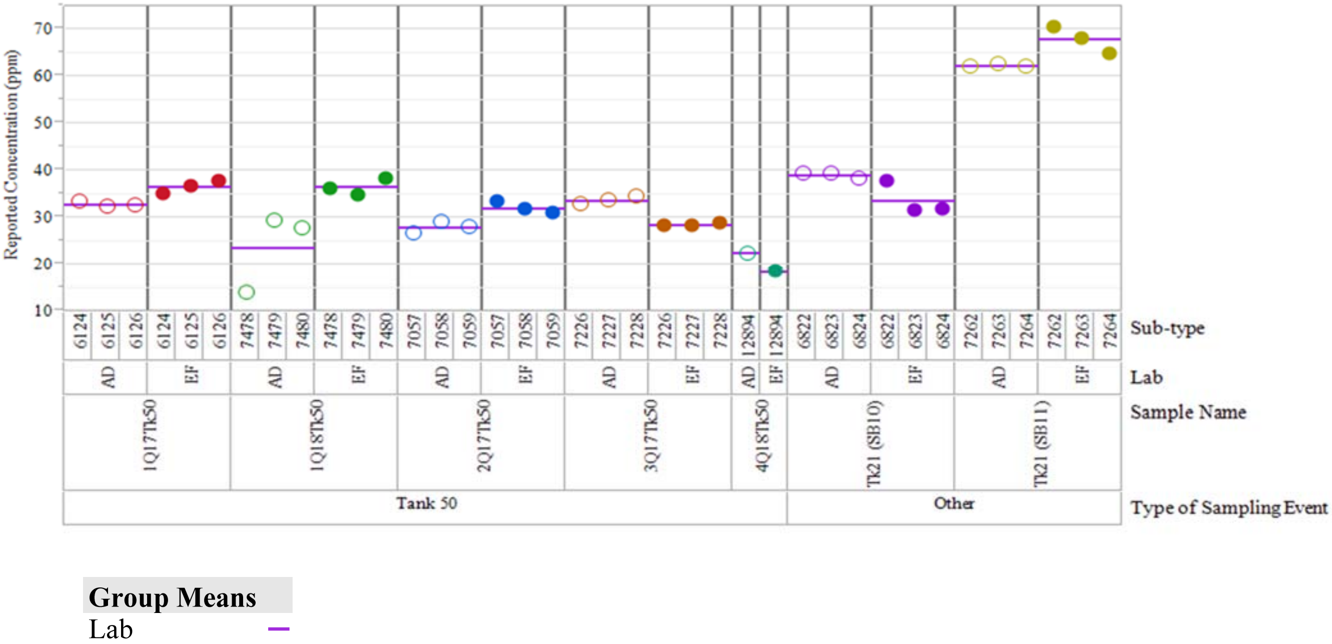


Exhibit B.11 AD and EF Methylmercury Results for Tank Samples Only *(continued)*

Analyte=Methylmercury
Variability Chart for Reported Concentration (ppm)

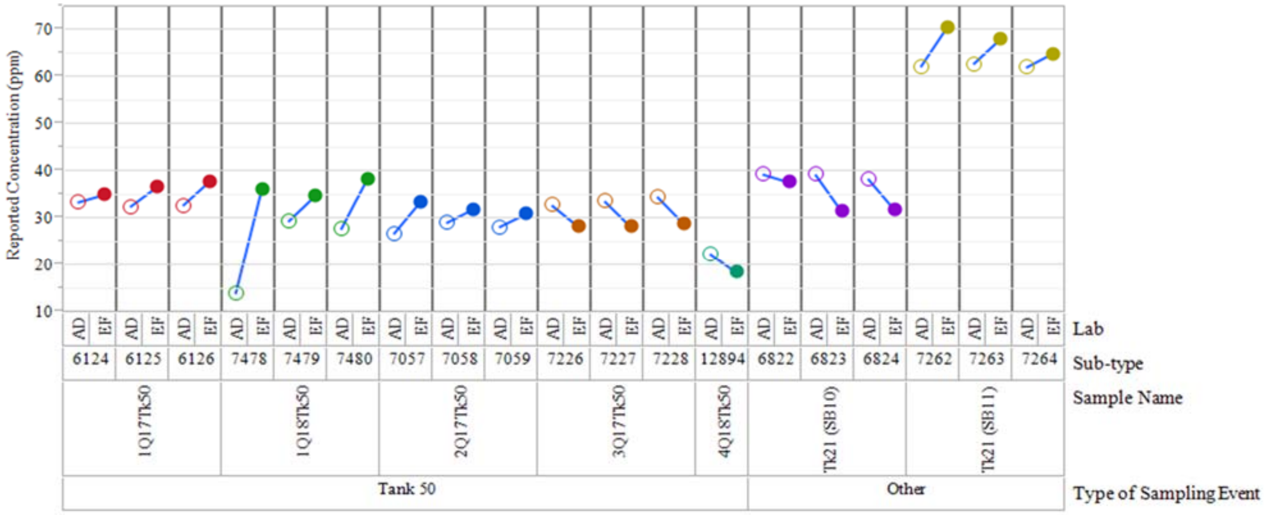
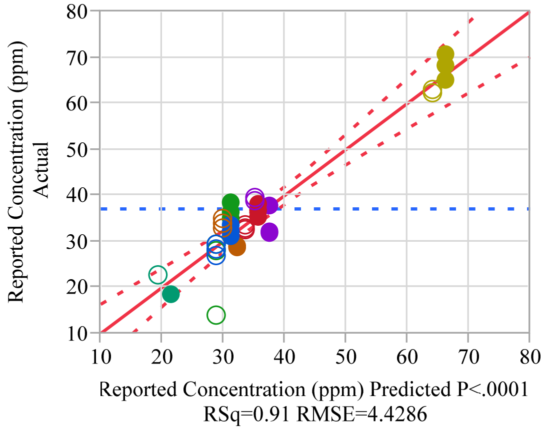


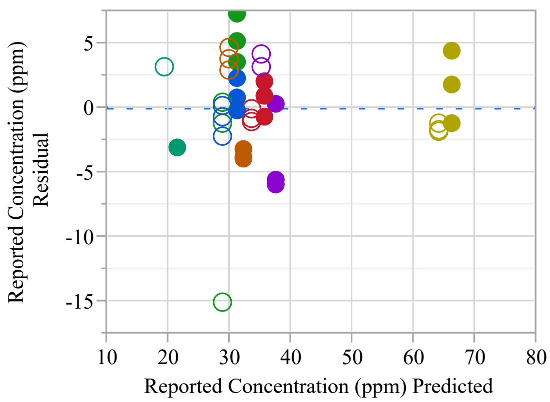
Exhibit B-12 Evaluation of Significant Effects for the Measurements from Tank Samples (part 1)

Response Reported Concentration (ppm)
Whole Model

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.912884
RSquare Adj	0.892557
Root Mean Square Error	4.428579
Mean of Response	37.06814
Observations (or Sum Wgts)	38

Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	7	6165.5282	880.790	44.9100
Error	30	588.3694	19.612	**Prob > F**
C. Total	37	6753.8976		<.0001*

Lack Of Fit

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Lack Of Fit	6	384.35581	64.0593	7.5359
Pure Error	24	204.01364	8.5006	**Prob > F**
Total Error	30	588.36945		0.0001*
				Max RSq

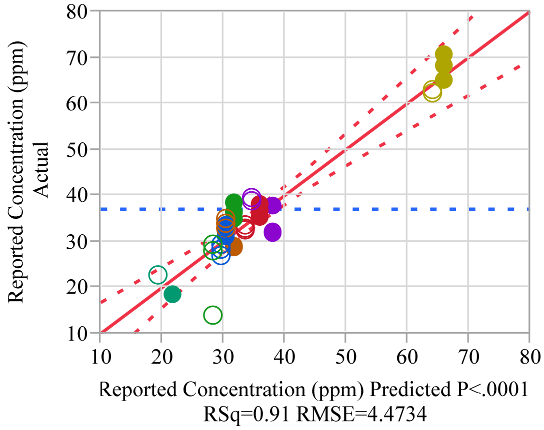
Effect Tests

Source	**Nparm**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
Type of Sampling Event	1	1	3556.2756	181.3287	<.0001*
Sample Name[Type of Sampling Event]	5	5	2785.6111	28.4068	<.0001*
Lab	1	1	47.1106	2.4021	0.1317

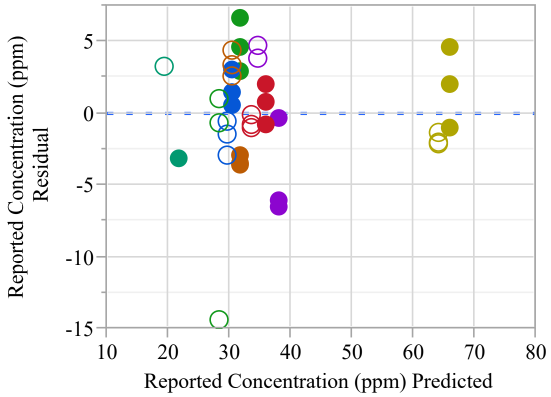
Exhibit B-13 Evaluation of Significant Effects for the Measurements from Tank Samples (part 2)

Response Reported Concentration (ppm)
Whole Model

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.914076
RSquare Adj	0.890373
Root Mean Square Error	4.473365
Mean of Response	37.06814
Observations (or Sum Wgts)	38

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	8	6173.5788	771.697	38.5637
Error	29	580.3188	20.011	**Prob > F**
C. Total	37	6753.8976		<.0001*

Lack Of Fit

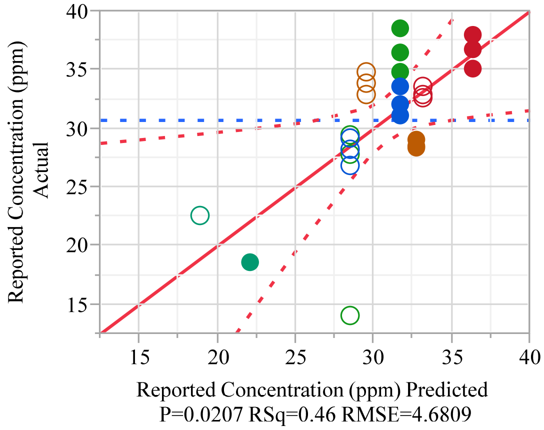
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	5	376.30514	75.2610	8.8536
Pure Error	24	204.01364	8.5006	**Prob > F**
Total Error	29	580.31879		<.0001*
				Max RSq

Effect Tests

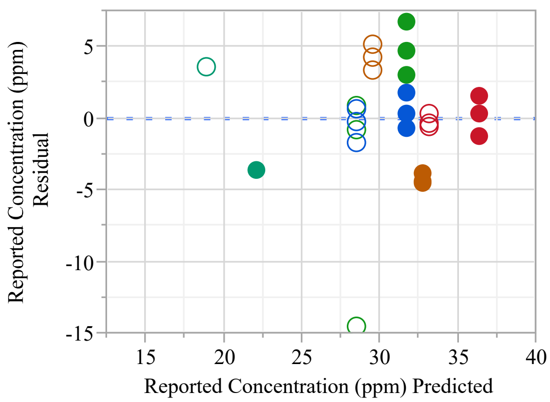
Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Type of Sampling Event	1	1	2903.4931	145.0949	<.0001*
Sample Name[Type of Sampling Event]	5	5	2244.6394	22.4341	<.0001*
Sample Age (days)	1	1	8.0507	0.4023	0.5309
Lab	1	1	7.4648	0.3730	0.5461

Exhibit B-14 Evaluation of Significant Effects for the Measurements from Tank 50 Samples

Response Reported Concentration (ppm)
Whole Model
Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.463292
RSquare Adj	0.329115
Root Mean Square Error	4.680901
Mean of Response	30.70579
Observations (or Sum Wgts)	26

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	378.27349	75.6547	3.4528
Error	20	438.21662	21.9108	**Prob > F**
C. Total	25	816.49012		0.0207*

Lack Of Fit

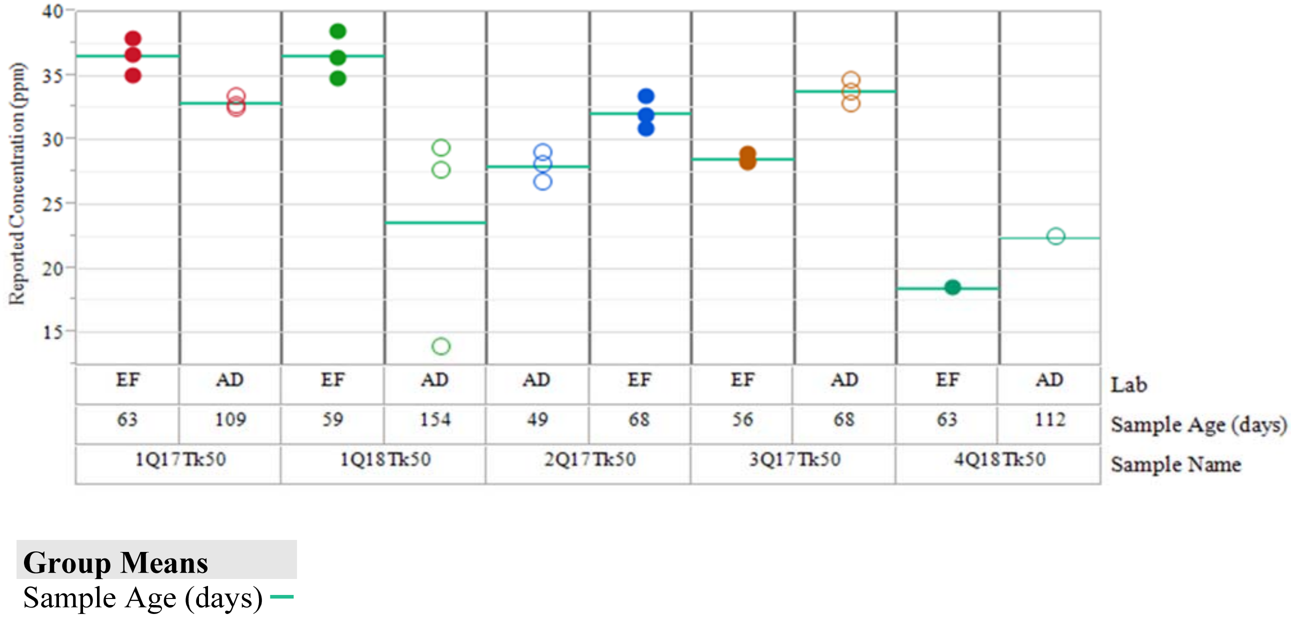
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	4	274.86999	68.7175	6.7310
Pure Error	16	163.34663	10.2092	**Prob > F**
Total Error	20	438.21662		0.0022*
				Max RSq

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sample Name	4	4	310.59072	3.5438	0.0243*
Lab	1	1	67.68278	3.0890	0.0941

Exhibit B-15 A Closer Look at the Effects of Sample Age on the Measurements from Tank 50 Samples

Variability Chart for Reported Concentration (ppm)



Appendix C

R&D Direction — Environmental Stewardship Directorate
Principal Investigator: Brian Looney
Preparation of Decontaminated Salt Solution Simulants (DSS)

Project: Scoping Studies for Advanced Oxidation Reactions for Transformation of Methylmercury in Alkaline Liquid Waste Simulants
Date: 06-27-2016
ELN Experiment ID: T6751-00178-02
Correspondence Number: SRNL-L3200-2016-00009

Description and Objectives of R&D Direction

The objective of this R&D Direction is to prepare simulant recipe that is generally representative of Savannah River Site (SRS) Tank Waste Decontaminated Salt Solution (DSS). This simulant will be used to evaluate various options for modifying and/or controlling mercury speciation and provide data for developing future waste treatment strategies. In particular, the research will focus on various oxidation, and reduction reactions to convert methylmercury, predominant mercury specie in the Tank Farm, into inorganic ionic and elemental mercury forms that are amenable to removal with existing Tank Farm mercury treatment systems.

To meet the objectives of the R&D Direction, a standard SRS simulant recipe for decontaminated salt solution (see Peterson, 2000; Zamecnik et al., 2005) was selected with the following notes/modifications. Cesium was eliminated from the standard SRS recipe (Peterson, 2000) — to better represent DSS per Zamecnik et al. (2005). Inorganic mercury was eliminated from the standard recipe — methylmercury will be spiked into small subsamples of the primary and secondary simulants immediately prior to each set of experiments. Stannous [tin (Il)] chloride (because of its reactivity with inorganic ionic mercury) was eliminated from the standard recipe for the primary simulant. A secondary simulant solution with the tin (Il) chloride added back will also be prepared to assess the potential significance of Sn-Hg reactions. If possible, the simulant will be used unfiltered for the experiments. The primary and secondary simulants and the recommended nomenclature are described below:

Primarv Simulant

DSS-NC-NM-NT (decontaminated salt solution — no cesium — no mercury — no tin). Labeling shall also: a) briefly describe simulant/modifications and reference Peterson (2000) and Zamecnik et al. (2005), b) list the person preparing simulant, c) provide the preparation date, and d) list the hazards ("corrosive — high pH", "contains toxic elements")

Secondary Simulant

DSS-NC-NM-ST (decontaminated salt solution — no cesium — no mercury — standard tin). Labeling shall also: a) briefly describe simulant/modifications and reference Peterson (2000) and Zamecnik et al. (2005), b) list the person preparing simulant, c) provide the preparation date, and d) list the hazards ("corrosive — high pH", "contains toxic elements")

Safety

Perform all work with chemicals according to eHAP Hazards and Control Summary.

Follow standard chemical laboratory safety protocols when performing these tasks. Use the following personal protective equipment (PPE): splash proof lab coat, nitrile gloves, safety glasses.

Mix the solutions in a chemical hood using a magnetic stirrer. Do not use a hot plate or externally heat the solutions. When mixing the sodium hydroxide into water, the solution will heat up. After mixing in the sodium hydroxide, allow to cool and use caution to avoid pressure build or similar issues. Exercise caution when adding NH4NOJ as poisonous and flammable ammonia gas may evolve from solution.

Instructions for Simulant Preparation

General Considerations

All vessels must be washed and thoroughly rinsed to remove all traces of contaminants. (e.g. oils, surfactants, etc.). The weights and volumes of all chemicals used and each step of the procedure should be recorded in a lab notebook (e.g., the electronic lab notebook).

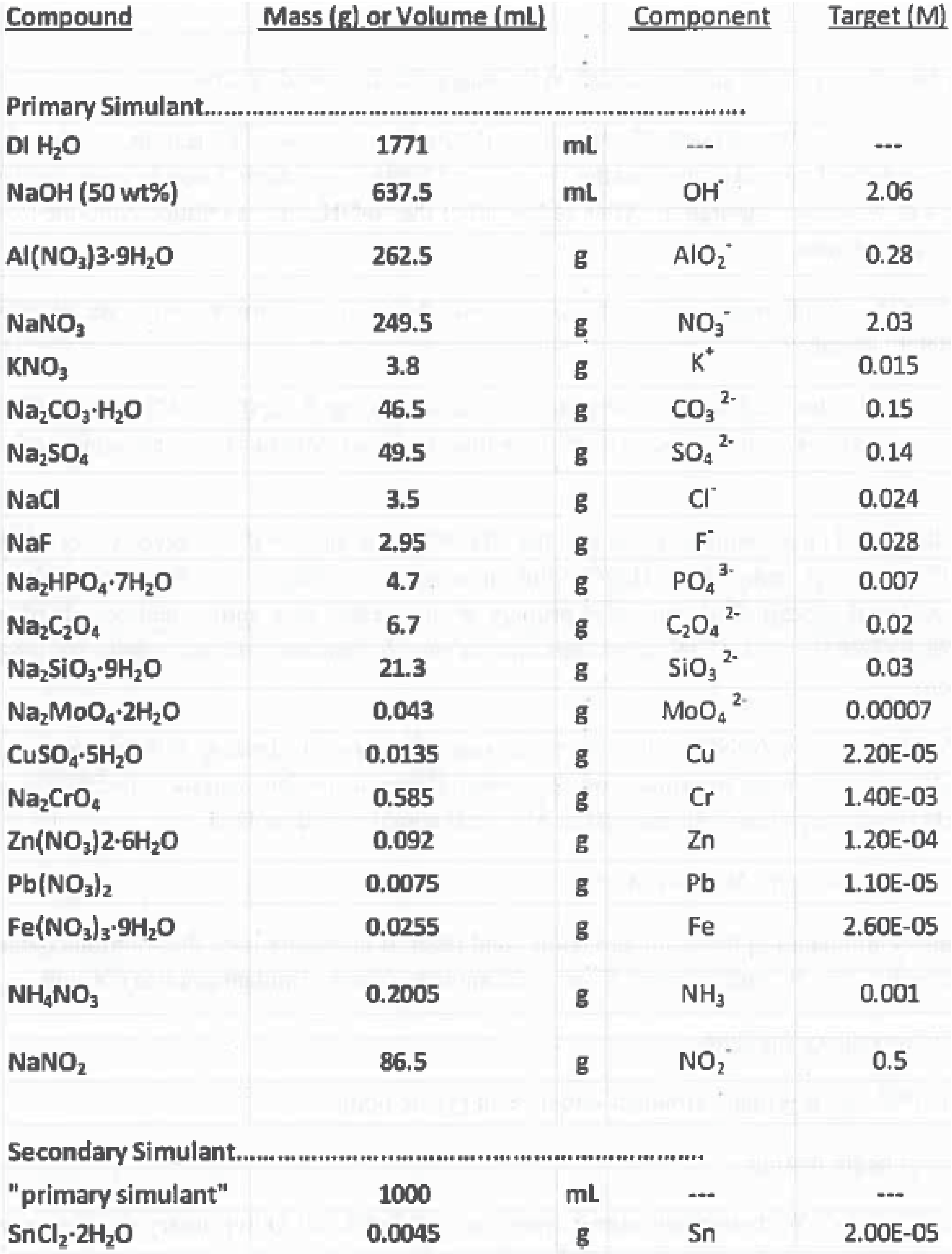
Equipment and Chemicals:

Primary Mixing Vessel — Identify a 4L (approximate) plastic container (bottle, flask or carboy) for the primary mixing. Do not use a glass mixing vessel so as to avoid leaching of elements from glass by the alkaline solution. When mixing, loosely cover the mixing vessel with plastic, that is taped to the outside of the mixing vessel — this will allow condensed water vapor to collect near the center of the plastic cover and return to the mixing vessel.

Mixer — identify a magnetic stirrer and stir bar to perform the mixing operation. Identify a retriever to remove the stir bar after the mixing is completed.

Chemicals — Obtain the chemicals for preparing the simulant that are listed in Exhibit C-1. This table includes the form of each chemical to add, the target mass used to prepare the simulant, the desired simulant solution component, and the target molarity in the final simulant solution

Exhibit C-1 Chemicals Used in DSS Recipe for Mercury Research



Compound	Mass (g) or Volume (mL)		Component	Target (M)
Primary Simulant…………………………………………………				
DI H_2O	1771	mL	---	---
NaOH (50 wt%)	637.5	mL	OH^-	2.06
$Al(NO_3)3{\cdot}9H_2O$	262.5	g	AlO_2^-	0.28
$NaNO_3$	249.5	g	NO_3^-	2.03
KNO_3	3.8	g	K^+	0.015
$Na_2CO_3{\cdot}H_2O$	46.5	g	CO_3^{2-}	0.15
Na_2SO_4	49.5	g	SO_4^{2-}	0.14
NaCl	3.5	g	Cl^-	0.024
NaF	2.95	g	F^-	0.028
$Na_2HPO_4{\cdot}7H_2O$	4.7	g	PO_4^{3-}	0.007
$Na_2C_2O_4$	6.7	g	$C_2O_4^{2-}$	0.02
$Na_2SiO_3{\cdot}9H_2O$	21.3	g	SiO_3^{2-}	0.03
$Na_2MoO_4{\cdot}2H_2O$	0.043	g	MoO_4^{2-}	0.00007
$CuSO_4{\cdot}5H_2O$	0.0135	g	Cu	2.20E-05
Na_2CrO_4	0.585	g	Cr	1.40E-03
$Zn(NO_3)2{\cdot}6H_2O$	0.092	g	Zn	1.20E-04
$Pb(NO_3)_2$	0.0075	g	Pb	1.10E-05
$Fe(NO_3)_3{\cdot}9H_2O$	0.0255	g	Fe	2.60E-05
NH_4NO_3	0.2005	g	NH_3	0.001
$NaNO_2$	86.5	g	NO_2^-	0.5
Secondary Simulant………………………………………………				
"primary simulant"	1000	mL	---	---
$SnCl_2{\cdot}2H_2O$	0.0045	g	Sn	2.00E-05

Preparation of the primary simulant

Add the correct mass of DI water to the primary mixing vessel. Pour off and reserve a few hundred mL for premixing chemical components in later steps. Place primary mixing vessel in a secondary containment.

Add stirring bar, place primary mixing vessel on the magnetic stirrer and turn on.

While stirring, slowly add the 50 wt% NaOH solution — the mixing vessel will heat up, so add the NaOH in increments and check to make sure that the vessel is not heating too much. Loosely cover the vessel to minimize loss of water by evaporation. After adding all of the NaOH, let the solution continue to mix and cool to room temperature.

Weigh out With magnetic stirrer operating, add $Al(NO_3)_3$ to primary mixing vessel. Mix until salt is completely dissolved. Weigh out remaining chemical salts for the primary simulant (except NH4NCh and $NaNO_2$). With magnetic stirrer operating, add these salts to primary mixing vessel. Mix until salts are completely dissolved.

Weigh out NH4N03. In the chemical hood, mix the NH4N03 with some of the reserved water in a beaker. With magnetic stirrer operating, add NH4N03 solution to primary mixing vessel. Rinse the beaker with some of the reserved water and add rinsate to primary mixing vessel. Mix until completely dissolved. (EXCERCISE EXTREME CAUTION: poisonous and flammable ammonia gas may evolve from solution upon addition).

Weigh out NaN02. Mix the NaN02 with some of the reserved water in a beaker. With magnetic stirrer operating, add NaN02 solution to primary mixing vessel. Rinse the beaker with the remaining reserved water and add rinsate to primary mixing vessel. Mix until completely dissolved.

Continue to mix for 24 hours. Remove stir bar. Transfer primary simulant to plastic storage bottles and label. If necessary (i.e., the solution contains a significant quantity of solid precipitates), filter or decant the primary simulant prior to bottling.

Preparation of secondary simulant

Measure out 1000 mL of primary simulant into a clean plastic bottle.

Add stir bar and begin mixing.

Weigh out SnCl•2H20. With magnetic stirrer operating, add SnC12•2H20 to primary mixing vessel. Mix until salt is completely dissolved. Label secondary simulant.

PI Name: Brian B. Looney

Employee Name: Charlyne Smith

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