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Total Mercury Analysis Comparison

DEPLOYMENT OF ANALYTICAL METHOD FOR THE SAVANNAH RIVER SITE LIQUID WASTE SYSTEM

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July 2019

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EXECUTIVE SUMMARY

A direct mercury analyzer (DMA; EPA 7473) and Cold Vapor Atomic Absorption Spectroscopy (CVAAS; EPA 245.2) have been used to analyze samples high in methylmercury and other forms of mercury with oxidation states of Hg⁰ (elemental), Hg¹⁺ (mercurous), and/or Hg²⁺ (mercuric) to determine analytical data equivalency for total mercury. The DMA instrument has been determined to be the preferred method based on both simulated and radioactive sample testing due to analytical results and ease of use in a radiological hood. SRNL made a number of modifications to the DMA instrument and analysis method to limit the amount of time personnel are required to work in a radiological environment. Equivalency is based on comparative statistical evaluation of the results from: spike solutions/simulants, Tank 50 samples, Mixed Analyte Performance Evaluation Program (MAPEP) samples, and Modular Caustic-Side Solvent Extraction Unit (MCU) solvent samples. SRNL performed a cross-comparison of results using CVAAS, DMA, and Inductively Coupled Plasma Mass Spectrometer (ICP-MS), as well as independent analysis from an offsite laboratory (using cold vapor sample processing with atomic fluorescence detection, EPA 1631). All data were within the combined uncertainty ($2\sigma \pm 20\%$) of the CVAAS and DMA methods; for example:

- Triplicate second quarter 2018 Tank 50
 - CVAAS analyses – 54.1 mg/L
 - DMA analyses – 56.0 mg/L
 - % difference = 3.4%
- Triplicate fourth quarter 2018 Tank 50
 - Offsite analyses 61.7 mg/L
 - DMA analyses 61.9 mg/L
 - % difference = 0.32%
- MAPEP mercury sample with a reference value of 0.109 mg/L ($\pm 30\%$) analyzed by the CVAAS (reported to the Department of Energy (DOE)) and DMA (reported in this report)
 - CVAAS result – 0.0880 mg/L (passed)
 - MAPEP sample analyzed on the DMA by one technician after installation – 0.0784 mg/L (passed)
 - MAPEP sample analyzed (n=3) on the DMA by three different technicians and averaged – 0.103 mg/L (passed)

The remaining sample types and instrument comparisons generated similar statistical outcomes – i.e., equivalent measured values and similar RSD values. Notably, the equivalency of direct analysis of MCU solvent by DMA with analysis of MCU aqueous extracts by DMA/CVAA/ICP-MS demonstrated the matrix independence of the DMA – the initial sample pyrolysis step at elevated temperature (700 °C) is effective in releasing mercury from alternative matrices (e.g.,

aqueous or organic liquids, or solids). The capability of direct analysis of organic solvent eliminates the need to extract mercury from the MCU solvent in a pressure vessel, simplifying the method, improving safety, and reducing waste and labor.

This work also assessed the performance of alternative oxidants used in CVAAS sample preparation as described in the Task Technical and Quality Assurance Plan TTQAP¹. Environmental protection agency (EPA) methods suggest using permanganate with persulfate and heat (EPA 245.2) or bromine monochloride (EPA 1631) to oxidize all forms of mercury in a sample to the mercuric cation prior to CVAAS analysis. The baseline SRNL method is heated permanganate/persulfate. Each oxidant has been tested on samples unusually high in methylmercury, a challenging form of mercury to oxidize. Oxidant equivalency was determined for all oxidants on CVAAS using samples ranging from 50 to 100 µg/L. The results were all within the overall uncertainty of the CVAAS method ($2\sigma \pm 20\%$). More detailed statistical analysis suggested that total Hg analysis using bromine monochloride oxidant showed a bias ($\sim +6\%$) at the 5% significance level compared to the baseline CVAAS total Hg analysis using heated permanganate/persulfate oxidant. Note that the baseline CVAAS heated permanganate/persulfate total Hg analysis was statistically the same as DMA total Hg analysis for the same sample set.

Two disadvantages with the operation of the CVAAS for Hg analyses are (1) a multi-step, labor-intensive and time-consuming sample preparation protocol and (2) higher waste volume and generation of liquid high chloride radioactive waste from sample preparation that must be absorbed onto sorbent for disposal. The DMA avoids these disadvantages for the analysis of total mercury while meeting/improving the Limit of Quantitation (LOQ) compared to the CVAAS (2.5 ng Hg). Further, discontinuing CVAAS for total mercury and shifting analysis of the hydride nonmetals (selenium and arsenic) to the ICP-AES or ICP-MS allows for decommissioning of the CVAAS instrument and elimination of the use of flammable acetylene in the radiochemistry laboratory.

The data support SRNL transitioning to the DMA for determining total mercury in radioactive samples. The deployed DMA provides equivalent performance ($2\sigma \pm 20\%$) and low ppb detection limits) and provides a number of benefits in radiological service, including: reduction of waste, reduction in sample preparation/handling, and the ability to analyze organic liquids and solids.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ANOVA	Analysis of Variance
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
DMA	Direct Mercury Analyzer
DSA	Documented Safety Analysis
ELN	Electronic Laboratory Notebook
EM	Electron Multiplier
EPA	Environmental Protection Agency
ICP-AES	Inductively-Coupled Plasma Atomic Emission Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
KED	Kinetic Energy Discrimination
LCL	Lower Control Limit
LIMS	Laboratory Information Management System
LOD	Limit of Detection
LOQ	Limit of Quantitation
LWS	Liquid Waste System
MAPEP	Mixed Analyte Performance Evaluation Program
MCP	Measurement Control Plan
MCU	Modular Caustic-Side Solvent Extraction Unit
MeHg	Methylmercury
MMHg	Monomethylmercury (same as methylmercury)
ORS	Octopole Reaction System
RCRA	Resource Conservation and Recovery Act
SDU	Saltstone Disposal Unit
SREL	Savannah River Ecology Laboratory
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
QC	Quality Control
LCL	Lower Control Limit
UCL	Upper Control Limit
WAC	Waste Acceptance Criteria

1.0 Introduction

The Savannah River Site (SRS) follows the Environmental Protection Agency (EPA) regulations described in the Resource Conservation and Recovery Act (RCRA) for handling legacy waste. To date, total mercury (Hg) has been primarily analyzed by Cold Vapor Atomic Absorption Spectroscopy (CVAAS) to ensure correct hazardous waste identification and handling occurs at SRS. Some of the frequent samples analyzed at SRS by CVAAS are Tank 50 and Tank Closure samples. Table 1 lists the regulatory limit² for mercury that an analytical method needs to meet for compliance and is the basis for the Waste Acceptance Criteria (WAC) for Tank 50³. The WAC needs to be met for the Saltstone Disposal Unit (SDU) to receive waste to make grout. Additionally, information on a recent Tank 21 sample is listed⁴. Any analytical method should have a Limit of Quantitation (LOQ) that meets these WAC values⁵. The Tank 50 value of 325 mg/L is listed as the LOQ target in the Technical Task Request (TTR)⁶. To meet the Task Technical and Quality Assurance Plan (TTQAP): *Speciation of Mercury in SRS Tank Samples*¹, SRNL analyzed the total mercury content in samples containing methylmercury and other mercury compounds. These samples were tested to determine total mercury using CVAAS compared to a Direct Mercury Analyzer (DMA)⁷. Select samples were also tested using Inductively Coupled Plasma Atomic Emission (ICP-AES) and Mass Spectrometry (ICP-MS). Two separate oxidation protocols used during sample preparation for total mercury on the CVAAS instrument were also compared. The DMA and CVAAS results are compared in this report and demonstrated to be within the uncertainty of the CVAAS instrument ($2\sigma \pm 20\%$)⁸. Other data is provided where samples were analyzed by our laboratory and off-site laboratories, such as the Mixed Analyte Performance Evaluation Program (MAPEP) (Appendix E) and Tank 50 quarterly samples.

Table 1. RCRA Metal Analyzed by CVAAS

RCRA metal	RCRA Limit (mg/L)	Tank 50 WAC Limit (mg/L)	Tank 21 WAC Limit (mg/L)
Mercury (Hg)	0.2	325	325

SRNL retired the CVAAS instrument (Varian 880) in October of 2018 after 18 years of service. Operators of the instrument encountered several issues primarily due to the corrosive atmosphere in the hood generated while using hydrochloric acid during sample preparation. Mechanical parts within the instrument used to optimize the ultra-violet signal to the detector had stopped working due to corrosion from the acid. In addition, the interior hood had become discolored along with the sample preparation oven. SRNL Research Operations Department also requested we look to alternatives to the use of acetylene (flammable gas) to support revisions to the SRNL Documented Safety Analysis (DSA).

A team⁵ from SRNL began investigating total mercury methods that would eliminate corrosive and oxidative solution chemistry. A starting point was a visit to the Savannah River Ecology

Laboratory (SREL) which has been using DMA instruments for several years. Based on that visit, literature references, and discussions with DMA manufacturers, SRNL determined the DMA should be able to analyze the suite of samples currently encountered (LWS samples, environmental samples, etc.) at the sample Limit of Quantitation (LOQ) of the CVAAS. Additionally, the DMA instrument reports matrix independence, thus potentially expanding the variety of samples that may be directly analyzed (Modular Caustic-Side Solvent Extraction Unit (MCU) solvent, Saltstone Facility grout, etc.).

2.0 Experimental Procedure

Researchers analyzed mercury samples by Direct Mercury Analyzer (DMA)⁹, Cold Vapor Atomic Absorption Spectroscopy (CVAAS), and the Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Procedures for the operation of the DMA (EPA 7473¹⁰; L16.1 ADS-1580¹¹), ICP-MS (EPA 6020A¹²; L16.1 ADS-1578¹³), CVAAS (EPA 245.1¹⁴/245.2¹⁴⁻¹⁵; L16.1 ADS-1557¹⁶) are based on EPA methods and comply with Manual 1Q, Procedure 2-7, “QA Program Requirements for Analytical Measurement System.” Personnel dilute High-Purity Standards (HPS) that are NIST traceableⁱ. Data generated from this project can be found in the SRNL E-Notebook (ELN)¹⁷ and links found therein.

The International Union of Pure and Applied Chemistry (IUPAC) naming of the organomercury cation with a single methyl group bonded to mercury is methylmercury. Methylmercury is commonly called monomethyl mercury to readily distinguish it from dimethylmercury, a more volatile neurotoxin. Both terms may be found in this report.

Using JMP Pro Version 11.2.1 (Appendix F), DMA, CVAAS, and Offsite CVAFS QC data all meet the nominal uncertainty of $\pm 20\%$ at the 95% level. The DMA and the offsite CVAFS QC data were statistically similar, while the CVAAS QC data was slightly biased high.

2.1 DMA

The DMA instrument is configured to reproducibly perform the following sequential steps – sample pyrolysis, catalysis, amalgamation, de-amalgamation, and atomic absorption spectrometry (AAS) – Figure 1. As configured in SRNL, the three AAS detector cells (0, 1, and 2) within the DMA instrument have a nominal calibration range (r^2 at least 0.995) from 0.1 ng of Hg to 300 ng of Hg. Personnel analyze two opening check standards of 1.0 ng Hg (cell 0) and 10 ng Hg (cell 1 and 2) prior to analysis, and a closing check standard of 10 ng Hg after sample analysis. Technicians prepare the check standards daily by dilution from certified inorganic mercury standards with a Certificate of Analysis (COA) from High-Purity Standards (HPS)ⁱ recorded in the SRNL ELN. Check standards and samples are diluted to fall in range of the calibration curve using 2% (v/v) nitric acid. An aliquot of each standard or sample, generally 100 microliters, is transferred

ⁱ 1000 mg/L mercury standard in 2% (v/v) HNO₃ traceable to NIST SRM 3133 and certified ISO Guide 34 and 17025 with an 18 month expiration date.

to a sample boat that has been preloaded with ~200 mg of Milestone Sample Additive Bⁱⁱ, to ensure retention of methyl mercury. Analysts measure the boats with blanks to ensure a low background absorbance below 0.0015. Appendix D has the QC chart ($\pm 20\%$ 2σ) for the first three months of DMA operation in the contained hood.

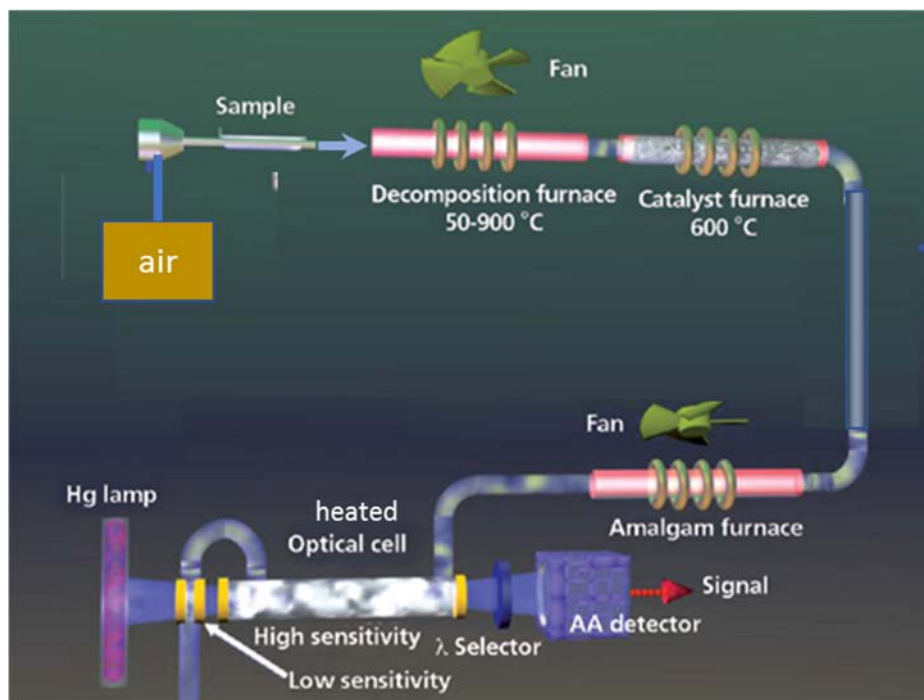


Figure 1. Schematic of DMA¹⁸.

2.2 CVAAS

Analysts generated a three-point calibration curve (r^2 at least 0.995) using 0.025 mg/L, 0.050 mg/L, and 0.075 mg/L inorganic mercury standards with COAs from High-Purity Standards (HPS)¹. A 0.050 mg/L check standard (QC target = $\pm 20\%$) is analyzed before and after each batch of samples. Researchers use one of two protocols to oxidize mercury species to the mercuric cation followed by a stannous chloride reduction to elemental mercury: 1) permanganate/persulfate oxidation in acid with heat for 2 hours (based on EPA 245.2¹⁵) or 2) bromine monochloride oxidation (based on EPA 1631, Revision E¹⁹) at room temperature for 24 hours. Analysts account for sample amounts digested from 1 to 10 mL in the dilution factor. Below are examples of sample preparation:

- 1) In a 30 mL test tube, analysts add 1 mL of sample, 0.5 mL of sulfuric acid, 0.2 mL of nitric acid, 1.5 mL of 5% (w/v) potassium permanganate; ensure the color is purple after 15 minutes; add 1.0 mL of persulfate and heat the solution at 95° C for 2 hours. The solution is allowed to cool to room temperature prior to the addition of 6% (w/v)

ⁱⁱ Milestone Sample Additive B is an inert high purity alumina powder that is placed in the sample boat to retain mercury species until they are analyzed by the DMA-80.

- sodium chloride/6% (w/v) hydroxylamine hydrochloride until the purple color disappears. Analysts then add 2 mL of conc. HNO_3 and dilute the sample to 30 mL.
- 2) In a 500 mL polyethylene bottle, 250 mL of concentrated HCl , 2.7 g KBr , and 3.8 g KBrO_3 is added with stirring. Researchers ensure the solution changes from yellow to red to orange while standing for 1 hour. To a 30 mL test tube, 0.475 mL of BrCl solution, 3.5 mL of sample, and 6.5 mL of water is added. The straw-color of the solution remains at room temperature for 24 hours. If the next day, the color remains, add 0.2 mL hydroxylamine hydrochloride solution and 2 mL of nitric acid, followed by diluting to 30 mL.

Incoming LWS samples are digested with aqua regia or peroxide fusion prior to using the permanganate/persulfate oxidation.

Figure 2 provides a general schematic¹⁸ of a CVAAS where samples are prepared by oxidizing all mercury species to Hg(II) followed by reduction with stannous chloride to Hg(0) . Argon gas sweeps the volatile mercury to the optical cell where a response is observed at 254 nm. The Varian 880 instrument is housed in a containment unit for the analysis of radiological samples.

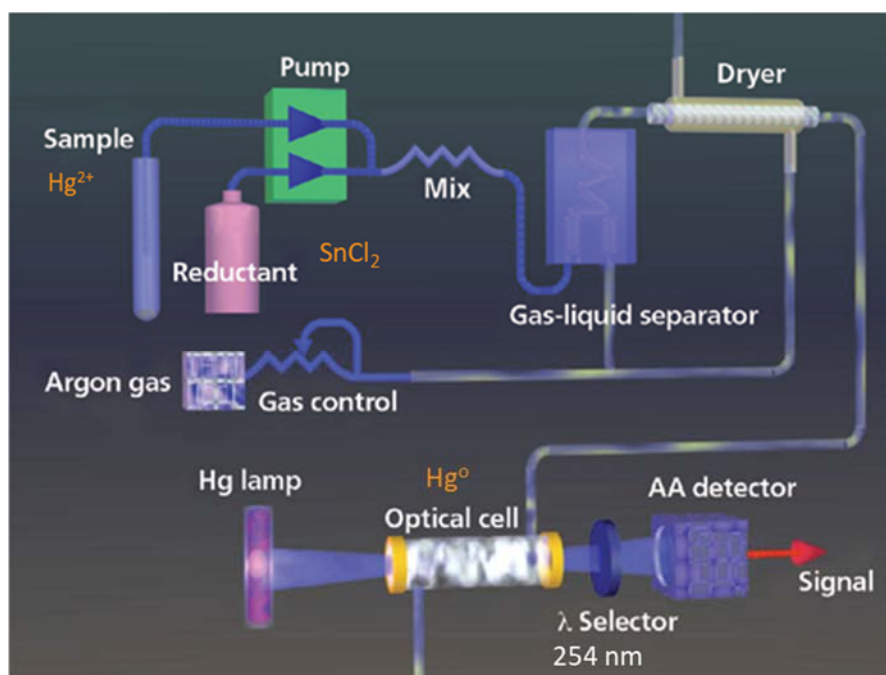


Figure 2. Schematic of CVAAS¹⁸.

2.3 ICP-MS

SRNL performed mercury analysis on an Agilent 7700x ICP-MS. The Agilent 7700x ICP-MS unit (Figure 3) is configured with a solid-state RF-generator for a high temperature ICP ion source that is positioned in line with the sampler and skimmer cones. A series of lenses are configured behind the cones to focus the ions into an Octopole Reaction System (ORS). Helium gas is supplied to the ORS and, based on the kinetic energy discrimination process; the ORS serves as a collision cell to reject the interfering polyatomic ions that have the same mass as the analyte. The ions are then separated by the quadrupole mass filter and directed to the electron multiplier (EM). The EM employs a dual mode detector that measures analog and pulse counts. The sample introduction components consist of a peristaltic pump, concentric nebulizer, and cooling spray chamber. The system is set up in a fume hood containment unit (Figure 4) for the analysis of radiological samples.

For mercury analysis, the instrument operates at 1550 W RF power, 15 L/min coolant gas, 0.9 L/min auxiliary gas, 0.8 L/min carrier gas, and 0.3 L/min makeup gas. A calibration curve (r^2 at least 0.995) consisting of blank, 0.5, 1, 5, 10 parts-per-billion (ppb) level mercury is measured at 201 and 202 m/z. Quality Control (QC) standards at 10 ppb from a different lot are measured to check the calibration. Additionally, bismuth serves as an internal standard at 5 ppb in all blanks, standards, and samples. An acid solution of 50 parts-per-million (ppm) Au in 2% (v/v) hydrochloric acid is used to dilute samples for mercury analysis.

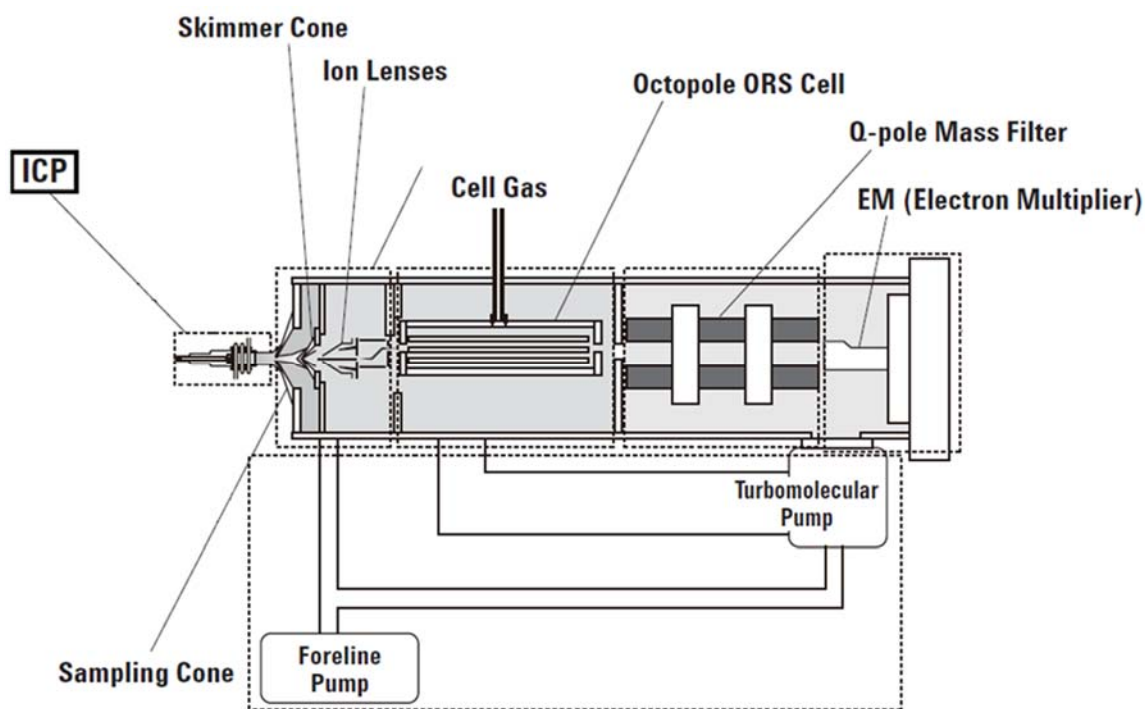


Figure 3. ICPMS Schematic.²⁰

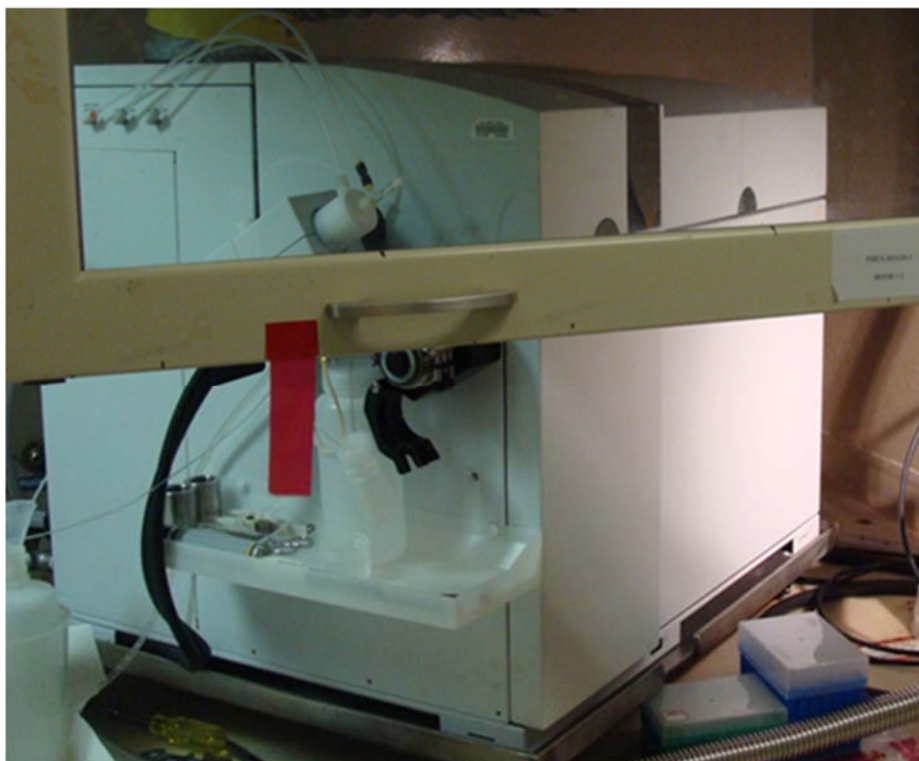


Figure 4. Contained Agilent 7700x ICPMS.

3.0 Results and Discussion

3.1 DMA Method Development

3.1.1 Instrument Layout

The DMA may be considered “hot vapor atomic absorption.” Liquid (or solid) samples that have been diluted to within the calibration range of the instrument are transferred into a quartz or nickel boat by pipette and placed onto an autosampler. Figure 5 shows a layout of the instrument with the catalyst and the amalgamator highlighted. Sample boats are automatically moved from the autosampler to an oven where the mercury containing liquid sample is vaporized. An air stream moves the gaseous species through a catalyst that converts all compounds of Hg into elemental Hg. The elemental Hg is concentrated on gold in the amalgamator. The elemental mercury is then flashed to a detector (254 nm) with three gas cells (cell 0, 1, and 2). Cell 1 (medium) and Cell 2 (short) are the principal cells used for routine samples. These cells are in line and use a single ultraviolet light source and detector; the signal from Cell 2 is time delayed from Cell 1 providing two observable/quantifiable peaks on the instrument controller. Cell 0 (long) is used when special levels of sensitivity are required; this cell uses the second ultra-violet light source and a second detector to generate a signal observed on the instrument controller.

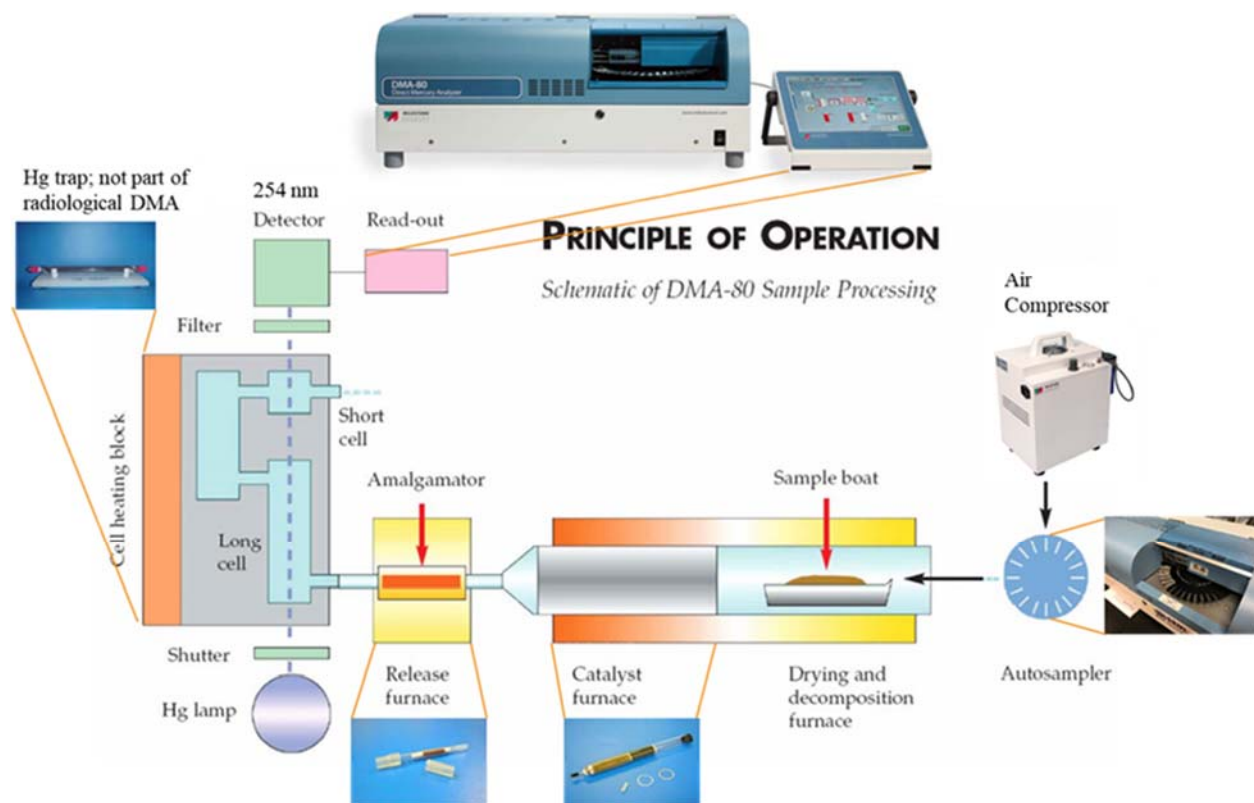


Figure 5. Principle of Direct Mercury Analyzer (DMA)²¹ or “Hot Vapor” Atomic Absorbance

The DMA response, sensitivity and operation are governed by total mercury mass in the sample boat (i.e., ng of Hg of any oxidation state in the sample). For routine operation, the nominal dynamic range (Table 2) covers more than three orders of magnitude, 0.4 ng to 200 ng, while the ideal range based on signal and operational considerations is 5 to 20 ng. The routine limit of detection is 0.4 ng. For liquid samples, the mass of Hg in the sample boat is related to both concentration and the quantity of sample placed in the boat. Thus, for typical 0.1 mL liquid aliquots, the DMA nominal dynamic range is 4 to 1000 $\mu\text{g/L}$ (ppb) and the ideal target range is 50 to 200 $\mu\text{g/L}$ (ppb).

Table 2. Operating Range for Routine Use

DMA-80 with 0.1 mL or 100 μL in the boat			
<i>ng</i>	<i>μg/L or ppb</i>	<i>μg/mL or mg/L or ppm</i>	<i>Comments</i>
0.4	4	0.004	LOD
1	10	0.01	LOQ
5	50	0.05	“sweet spot”
10	100	0.1	“sweet spot”
20	200	0.2	“sweet spot”
100	1000	1	acceptable
200	2000	2	Potential carry over
300	3000	3	Carry over

This column is the output of the DMA-80. All values are valid with a 0.1 mL aliquot.
Dilute starting mg/L sample to target range of 0.01 to 1 mg/L.

3.1.2 Control Chart for Total Hg on the DMA at ACTL

The opening and closing 100 ng/mL check standards (Appendix A) show a 2-sigma uncertainty of $\pm 12\%$. The control chart is shown in Figure 6. Each day the instrument background is reduced by running flour samples that create carbon in the gas phase, which is effective at lowering the mercury concentration still present in the DMA. Blanks and check standards are analyzed before and after sample analyses. One of the first check standards analyzed gave a result above the 2-sigma upper control limit (UCL) – we attribute this to instrument familiarization and points to the need to maintain a low mercury background. With more experience with the DMA method, we expect our uncertainties to improve.

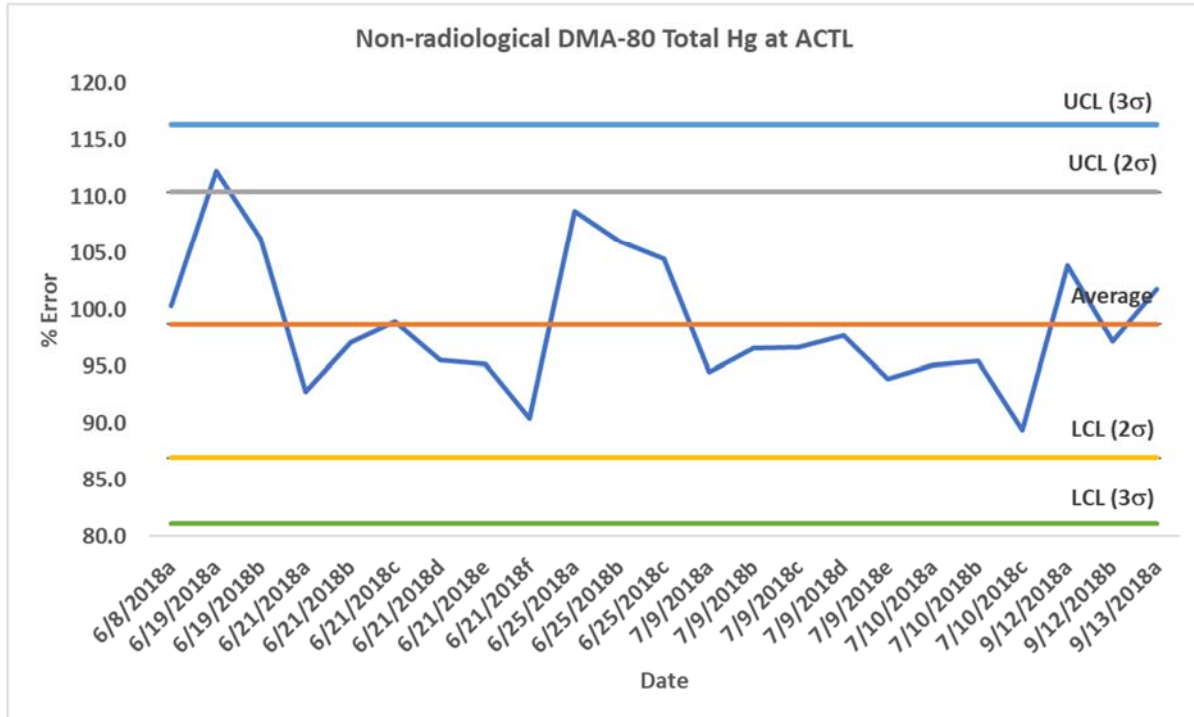


Figure 6. Total Mercury Check Standards at ACTL over 4 Months.

3.1.3 LODs and LOQs

Table 3 identifies three categories for LODs/LOQs based on the expected concentration of total mercury in the sample with the calculations listed in Appendix B. For samples from the Liquid Waste System (LWS), the initial total mercury would be in the mg/L range, typically requiring dilution. These samples would fall under “routine operation” to provide appropriate sensitivity and avoid mercury carry over issues. Note that lower LODs/LOQs are achievable through more intensive instrument preparation/cleaning and use of multiple blanks between samples. Environmental samples, for example, would fall under a special study scenario where potentially high blanks from mercury carryover would cause data issues. The LOQ and LOD were determined using linear regression²². For routine LWS samples, the LOQ was determined to be 10 µg/L for a 0.1 mL sample on the DMA, which is lower than the 25 µg/L LOQ for CVAAS. Note that lower LOQ/LOD values can be achieved on the DMA by increasing the sample size from 0.1 mL to 0.3 mL.

Table 3. LODs and LOQs of DMA-80³

	Mass (ng in DMA sample)		LOD/LOQ - liquid concentration on DMA (µg/L) using 0.1 mL aliquot		LOD/LOQ - liquid concentration on previous CVAAS system (µg/L)
	Routine Operation (cells 1 and 2)	Special Study (cell 0 to cell 2)	Routine Operation	Special Study	Routine Operation
Sample Type	Liquid Waste System (LWS)	e.g., Environmental	Liquid Waste System (LWS)	e.g., Environmental	Liquid Waste System (LWS)
Limit of Detection (LOD)	0.4 ng	0.1 ng to 0.2 ng	4.0 µg/L	1.0 ng to 2.0 µg/L	10 µg/L
Limit of Quantification (LOQ)	1.0 ng	0.4 ng to 0.6 ng	10 µg/L	4.0 ng to 6.0 µg/L	25 µg/L

³ Calculations in Appendix B.

3.1.4 Loss of MeHg on the Autosampler of the DMA

SRNL research documented that when using standard configuration sample boats, some species of mercury decrease in concentration over time while waiting on the autosampler for analysis. For instance, inorganic ionic mercury is stable in sample boats on the autosampler while methylmercury (MeHg) decreases in concentration over time ($t_{1/2} = 0.79$ h). Figure 7 summarizes the results of MeHg and ionic mercury over a six-hour period. Each boat contained 0.1 mL of sample containing either inorganic Hg or MeHg. Nearly all the MeHg (>90%) was lost after three hrs. We suggest the small aliquot of liquid in the sampling boat has a relatively high surface area leading to a measurable evaporation/sublimation rate over time²³ for the semi-volatile methylmercury. Thus, sampling bottles should be filled, i.e. limiting headspace, to avoid analyte loss.

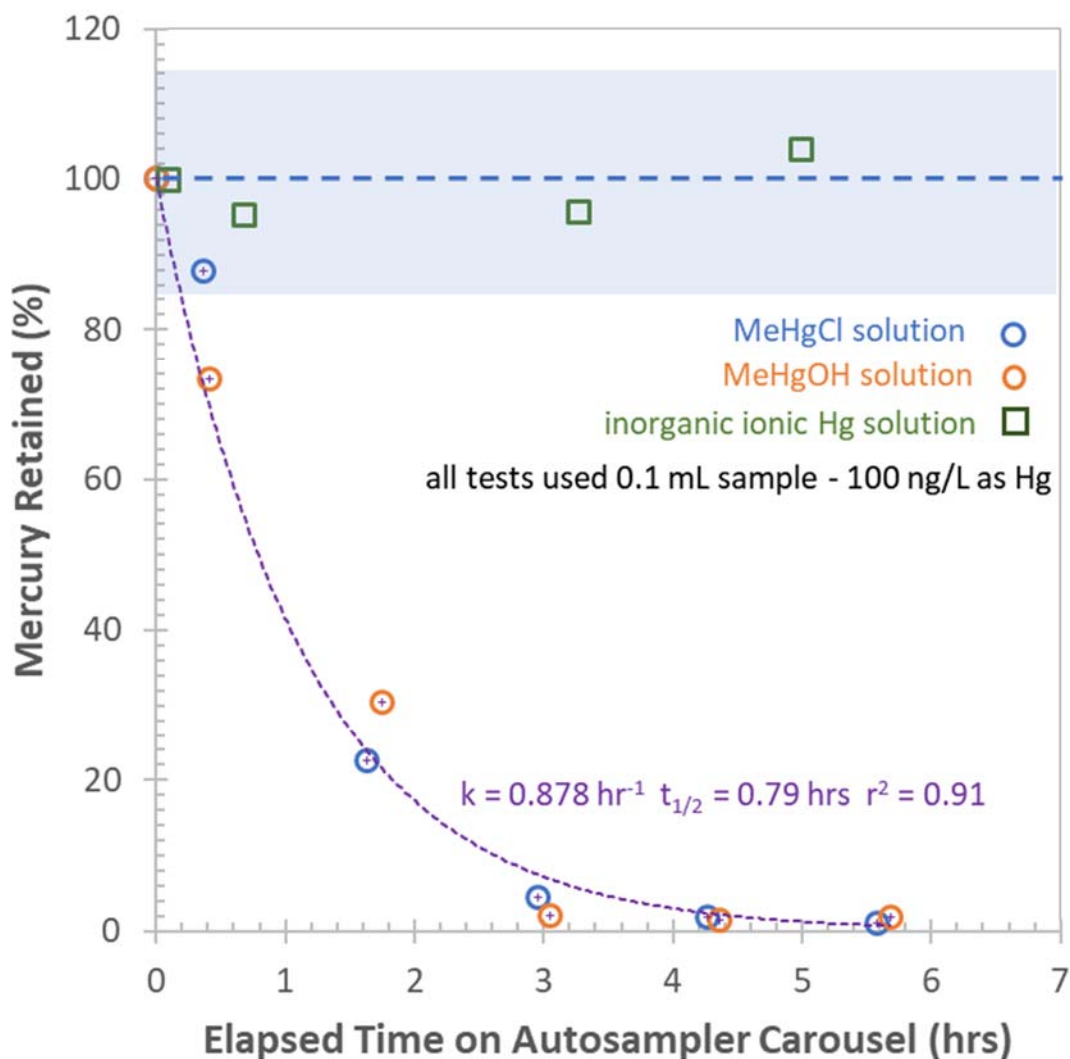


Figure 7. Loss of MeHg Over Time on the DMA Autosampler.

3.1.5 Best Practices for Sampling

Based on EPA recommendation²⁴, sampling bottles should be filled and made of glass, Teflon[®], or plastic. If significant fraction of the total mercury is expected to be MeHg, Teflon[®] containers should be utilized. Contact with stainless steel should be avoided or limited²⁵. In addition, it is recommended samples be diluted with nitric acid solution to less than pH 2 for preservation of total Hg. For low level mercury in water, fluoropolymer bottles are recommended with HCl preservation²⁶. Samples containing methylmercury, such as many of SRS site samples should be collected in fluoropolymer bottles, filled to the top with no headspace, capped tightly and maintained cool (0-4) °C²⁷. For prolonged storage, our group recommends preservation by acidifying in 2% (v/v) nitric acid in glass or Teflon[®] bottles and filled to the top with no headspace. For special studies (environmental analyses or upper ppt analyses), we recommend the use of 4 mL/L (0.048 M) of HCl as a preservative. SRNL requires information on arriving samples for waste handling purposes.

3.1.6 Retaining Mercury Species in the Boat

Three solid materials were examined to fix mercury in samples waiting for DMA analysis in sample boats (Figure 8). Biotage ISOLUTE[®] Si-Thiol in boat B^{iv}, Milestone AdsoQUICK in boat C^v, and Milestone Additive B^{vi} in boat D and E are visually shown below in the amounts used. A sample diluted to fall within the calibration curve is pipetted in a 0.1 mL aliquot onto the solid material, the boat is placed into the autosampler well, and each boat is analyzed in seven minutes with a blank (empty slot) between each sample. After each run, the ash residue is disposed, and the boat cleaned (Appendix C).

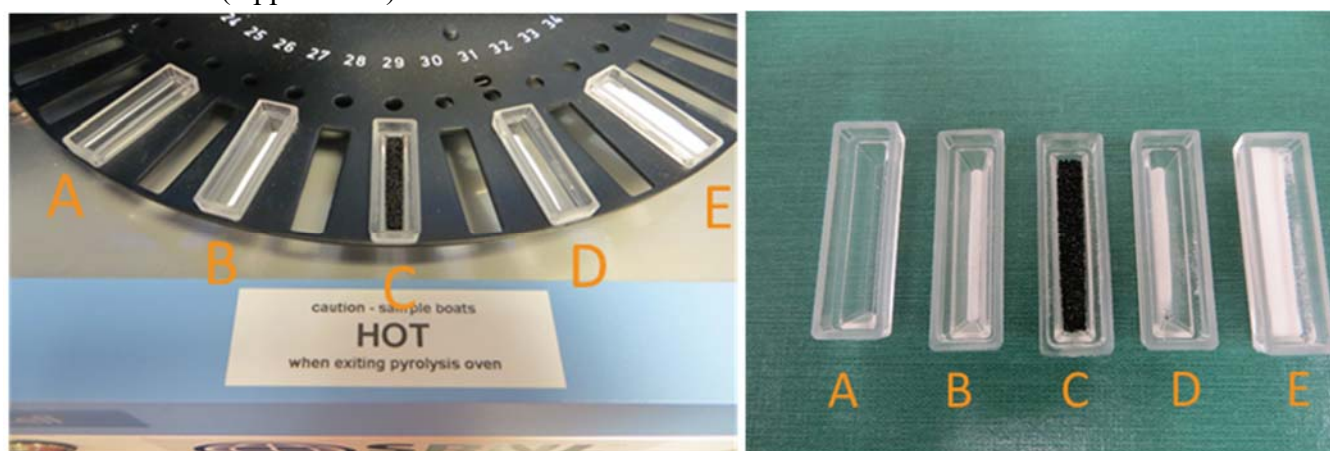


Figure 8. Boats Containing Solid Materials for Mercury Species Stabilization.

^{iv} Biotage ISOLUTE[®] Si-Thiol is a commercially available silica 1-propanethiol or 3-mercaptopropyl silica gel. The off-white powder is used as a metal (Pd, Pt, Cu, Hg, Ag, Pb, etc.) scavenger with a stoichiometry of 1:1, a particle size of 63 μm, and a capacity of 1.3 mmol/g. One area where researchers use the material successfully is removing transition metals from coupling reactions (S resulting in metal free product).

^v Milestone AdsoQUICK is a commercially available activated charcoal product known to retain various forms of mercury.

^{vi} Milestone Sample Additive B is an inert high purity alumina powder that is placed in the sample boat to retain mercury species until they are analyzed by the DMA-80.

As depicted in Figure 9, use of the solid mercury fixatives stabilized MeHg in the sample boats during the wait time on the autosampler carousel. One of the materials, Milestone Additive B, was partially effective at 5 mg (light brown dots) and fully effective when used in larger quantity (e.g., 400 mg, dark brown dots). A full autosampler requires about 4 hours to analyze all the boats, thus setting the 5-hour testing time for the solid materials. All solid materials in the correct amounts effectively stabilized MeHg.

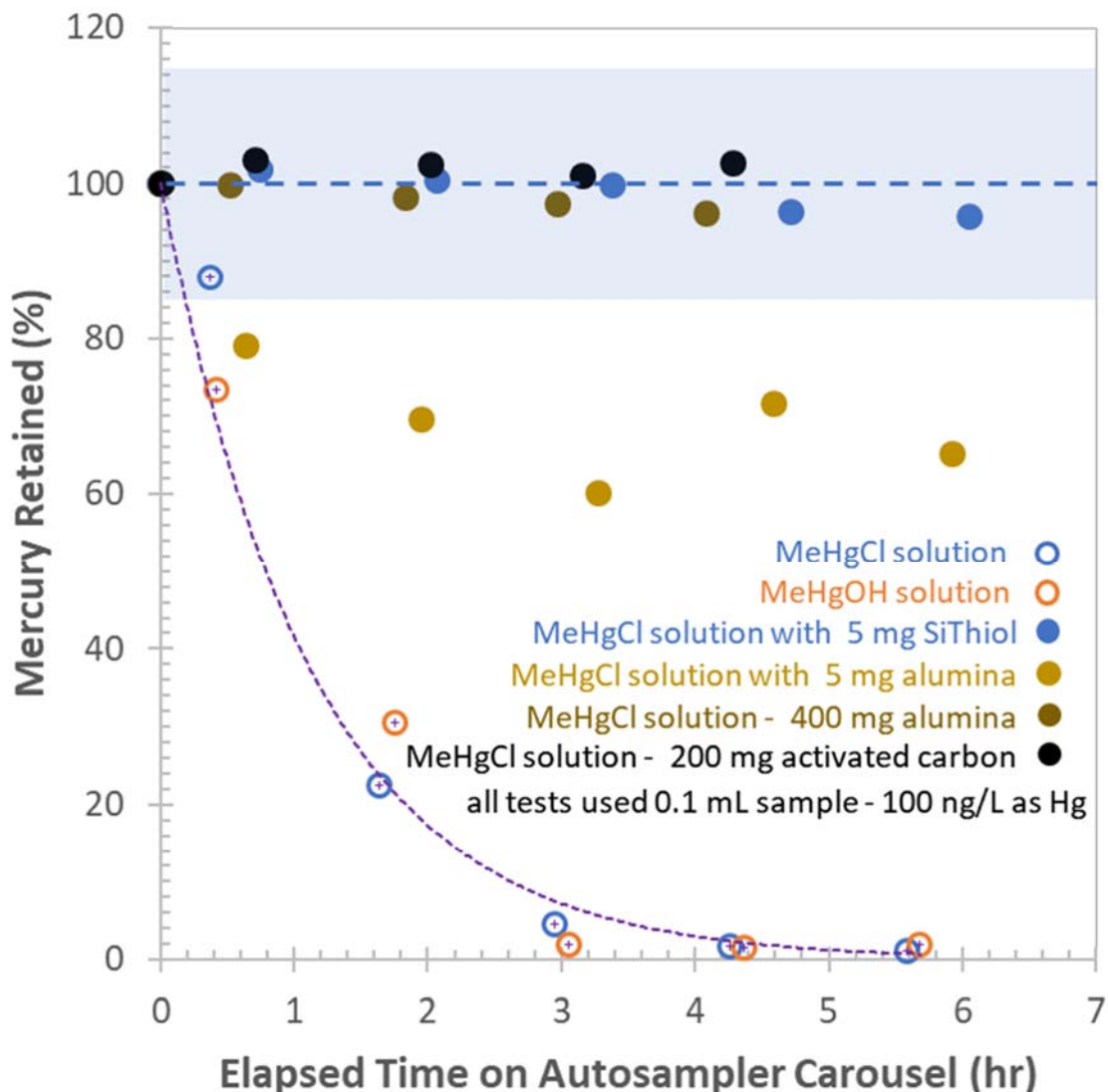


Figure 9. Solid Mercury Fixatives Biotage ISOLUTE® Si-Thiol (blue dot), Milestone AdsoQUICK (black dot), Milestone Additive B (light/dark brown dots)

Based on the results, Milestone Additive B, a zeolite, was identified for routine use based on cost, ease of use, and inertness to the catalyst. Figure 10 summarizes these results where green is the best option and red is the least desirable.

		solid material / stabilizing mechanism(s)	sample stability	sample handling (loading)	sample handling (disposal)	Notes		
Methylmercury	A	inorganic ionic mercury (aqueous solution in empty boats)	none / NA	good	liquid pipetted	rinse/bake boat	none	⊗
	A	Methylmercury (aqueous solution in empty boats)	none / NA	poor >95% loss in 4 hours	liquid pipetted	rinse/bake boat	none	
	B	Methylmercury (aqueous solution in boat preloaded with 5 mg SiThiol)	Biotage SiThiol / strong Hg sorbent	good	preload well behaved powder - liquid pipetted	discard well behaved powder rinse/bake boat	SiThiol irritating to eyes - sulfur impacts DMA catalyst life	←
	C	Methylmercury (aqueous solution in boat preloaded with 200 mg activated carbon)	Milestone Adsoquick / Hg sorbent - high porosity and surface area	good	preload poorly behaved beads - liquid pipetted	discard beads (or bake out beads) rinse/bake boat	small beads difficult to control	▽
	D	Methylmercury (aqueous solution in boat preloaded with 5 mg alumina)	Milestone Additive B / high porosity and surface area	poor 30 to 40% loss in 4 hours	preload well behaved powder - liquid pipetted	scrape/discard powder residue rinse/bake boat	boat cleaning more difficult	⊗
	E	Methylmercury (aqueous solution in boat preloaded with 400 mg alumina)	Milestone Additive B / high porosity and surface area	good	preload well behaved powder - liquid pipetted	discard well behaved powder rinse/bake boat	requires more stabilizer than SiThiol	←

Codes - overall assessment for samples that may contain both inorganic and monomethylmercury:

- ← Effective Protocol
- ▽ Acceptable Protocol
- ⊗ Ineffective Protocol

Figure 10. Summary of Solid Mercury Fixative

3.2 Simulant Tests Using DMA and CVAAS Instruments with Two Different Oxidation Methods

The CVAAS protocol for total mercury requires all mercury species in a sample solution to be oxidized to the mercuric ion followed by reduction to elemental mercury prior to analysis. Researchers²⁸ have shown organic mercury compounds tend to degrade readily using bromine monochloride as an oxidizer, although permanganate/persulfate with a heat step is often used. Our work examined Tank 50²⁹ and Tank 38³⁰ simulated waste to show analytical equivalency between the DMA protocol based on EPA 7473³¹ and the CVAAS protocol using permanganate/persulfate oxidation based on EPA 245.2¹⁵ or the bromine monochloride oxidation based on EPA 1631, Revision E¹⁹. Table 4 shows the testing outline where samples were generated using two waste simulants and varying concentration levels of MeHg or mercuric ion.

Table 4. Mercury Spikes into Simulated Waste for CVAAS and DMA Testing

#	LWS simulated waste	Spike Amounts	Total Hg, ng/mL
1	Tank 50	Spike A = 60 ng/mL Hg ²⁺	60
2	Tank 50	Spike B = 60 ng/mL Hg ²⁺ and 20 ng/mL MeHg	80
3	Tank 50	Spike C = 50 ng/mL Hg ²⁺	50
4	Tank 50	Spike D = 50 ng/mL Hg ²⁺ and 50 ng/mL MeHg	100
5	Tank 38	Spike E = 50 ng/mL Hg ²⁺	50

Figure 11 shows that the three methods reasonably fall within the uncertainty band ($\pm 20\% 2\sigma$) and that the main difference lies in analysis time and analysis residue volume. Of the two oxidation methods, the bromine monochloride method is a simpler protocol that does not require a heat step and should be more effective on organomercury compounds as indicated by the literature². In-house, LWS samples are digested by aqua regia before analyzing with the CVAAS protocol to ensure high recoveries for total mercury. This comparison on simulated waste was done without the aqua regia digestion step and good mercury recoveries were observed for samples containing MeHg at ng/mL (ppb) levels. At mg/L levels of MeHg, aqua regia should be used to facilitate high recoveries of mercury. The DMA instrument analysis and sample preparation time are more rapid since no oxidation/reduction step is required. Additionally, significantly less sample residue requiring disposal is generated with no the solution chemistry step.

More subtle statistical details emerge by examining and comparing each small population total Hg data set using JMP Pro Version 11.2.1 (Appendix F). CVAAS total Hg analysis at the 5% significance level using bromine monochloride showed a high bias (~6%) that is statically different ($p = 0.0001$) from CVAAS total Hg analysis using permanganate/persulfate oxidant. Additionally, the CVAAS-permanganate/persulfate total Hg analysis was statistically the same as DMA total Hg analysis for the same sample set. The slight bias observed using bromine monochloride is not unexpected for a new sample preparation protocol and would likely decrease with increased sample population and familiarity with the method.

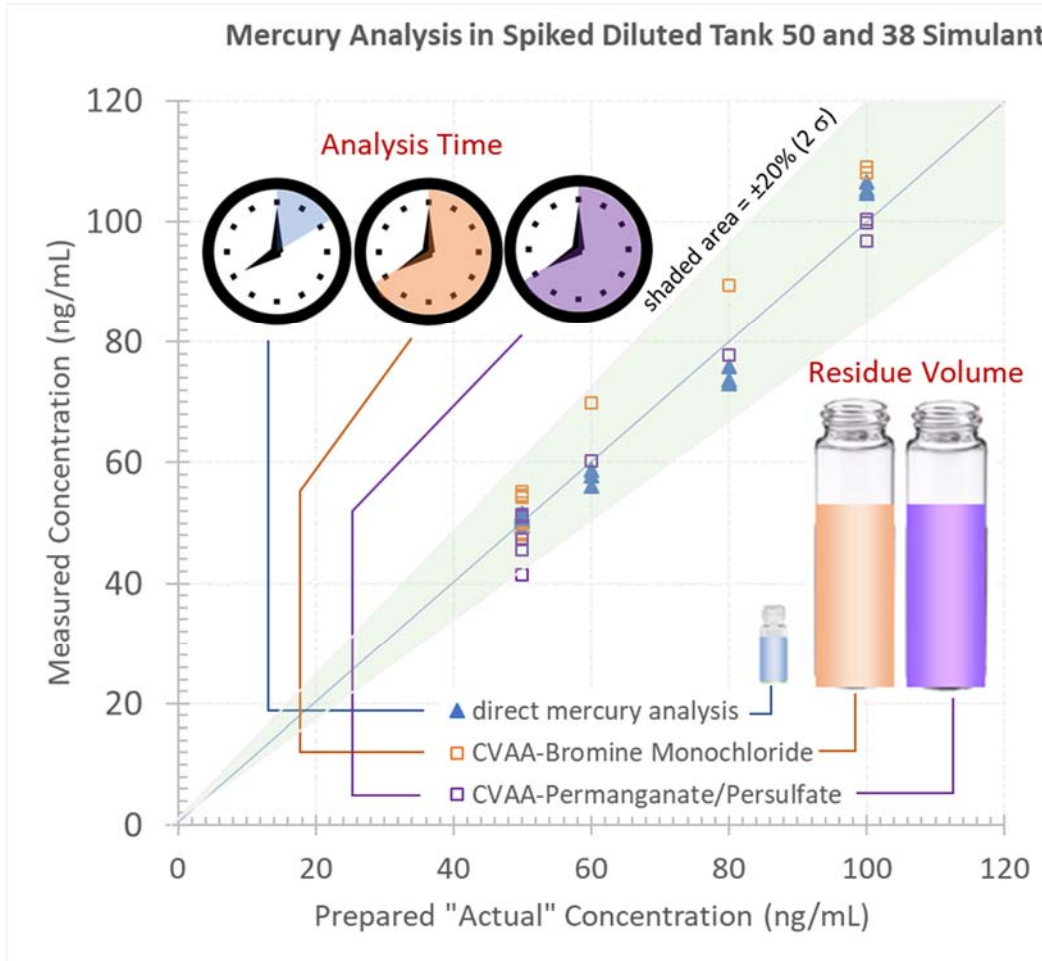


Figure 11. Summary of CVAAS and DMA Analyses of Simulated Tank Waste for Total Hg

3.3 Performance on the DMA and CVAAS using the Mixed Analyte Performance Evaluation Program (MAPEP)

As an initial comparison, SRNL analyzed two samples from the Department of Energy’s (DOE) Mixed Analyte Performance Evaluation Program (MAPEP), MAPEP-37 and MAPEP-39, as undigested samples. The results from the CVAAS analysis have been reported to DOE and the same sample has been analyzed by the DMA. For MAPEP-37, there was no mercury present thus CVAAS reported <0.01 (mg/L) while the DMA found <0.003 mg/L. For MAPEP-39, the CVAAS found 0.0880 mg/L ($2\sigma \pm 20\%$) of mercury with a percent difference $((\text{Actual} - \text{Reference})/\text{Reference} * 100)$ from the target value of 19.2 % (CVAAS). This value was lower than the reference value of 0.109 mg/L but within the acceptable range of 0.076 to 0.142 for the study and considered passing. Three separate analysts examined the MAPEP 39 sample on the DMA and found passing total mercury values (0.103 mg/L; Appendix E). These MDA results were not reported to DOE since only the CVAAS was enrolled in the performance test. Using JMP Pro Version 11.2.1 (Appendix F) on this small population data, the likelihood of SRNL’s DMA total Hg measurement falling outside the acceptable range for MAPEP is statistically improbable.

In 2019, our laboratory participated in the MAPEP Series 40 using the DMA instrument instead of the CVAAS. Our result of 0.158 mg/L was flagged acceptable when compared to the reference of 0.175 mg/L with a bias of -9.7%. This value is closer to the performance test reference value than the -19.3% bias value reported on the MAPEP Series 39 performance test for total mercury by CVAAS.

3.4 Radioactive Material Tests

3.4.1 *Nuclearization*

Personnel set up the instrument controller and air compressor on the laboratory bench beside a contamination area (CA) chemical hood. Power, ethernet, and gas lines were connected through a custom manifold mounted at the side of the hood, shown in Figure 12, and to the instrument residing in the hood. This manifold configuration ensures cabling remains static and will not move into or out of the hood boundary. The DMA instrument rests on a platform³² with low profile locking wheels giving researchers the option of moving the instrument to any location on the hood floor. Personnel modified the top cover to fit into scaffolding (metal bars in Figure 12) equipped with spring loaded cable spools allowing for the weightless raising and lowering of the top cover for maintenance and repair. Technicians simply removed knobbed screws by hand from the base of the cover and the entire top portion raises up with the cables slowly spooling onto the reel. Our group has installed bumpers to the top of the instrument to rest the blue hinged portion of the cover when it is open for internal access to the instrument (Figure 12).



Figure 12: DMA-80 in Laboratory Containment Unit.

Researchers also created a rack to hold the sampling boats while in the hood. Once all sample handling within the boat is finished, technicians use tweezers to move the boats from the rack to the autosampler. Figure 13 shows the slotted holder.



Figure 13: DMA sample boat rack.

3.4.2 Analysis of Tank 12 by CVAAS and DMA

Our group analyzed Tank 12³³ digested by peroxide fusion with the CVAAS (58400 µg/g) and DMA (60400 µg/g). Similar total Hg concentrations were observed with a small percent difference $((CVAAS - DMA)/(CVAAS + DMA)/2 * 100)$ of 3.3 %.

3.4.3 Analysis of Tank 50 by CVAAS, DMA, and ICPMS

Quarterly, SRNL analyzes Tank 50 samples digested by aqua regia in triplicate for total mercury. Archived second and third quarter Tank 50 samples were used to cross compare in-house total mercury analysis between DMA, CVAAS, and ICP-MS instruments. Each sample underwent aqua regia digestion to help stabilize all forms of mercury compounds for CVAAS and ICP-MS analysis. This step is not required for the DMA analysis. Table 5 summarizes the results for two quarters which are in keeping with historical data. For CVAAS, DMA, and ICP-MS, the total Hg results are similar and no statistical difference was observed between instruments using JMP Pro Version 11.2.1 software analysis on this small population (Appendix F).

Table 5. Tank 50 Total Hg Results

Sample	DMA (mg/L)	CVAAS (mg/L)	ICPMS (mg/L)
Tk 50 2Q18-1 (aqua regia)	57.6	54.1	56.3
Tk 50 2Q18-2 (aqua regia)	54.7	53.5	54.2
Tk 50 2Q18-3 (aqua regia)	56.0	54.4	56.1
Mean	56.0	54.1	55.5
Tk 50 3Q18-1 (aqua regia)	54.7	Out of Service	54.2
Tk 50 3Q18-2 (aqua regia)	50.9	Out of Service	54.9
Tk 50 3Q18-3 (aqua regia)	55.3	Out of Service	54.6
Mean	53.6		54.6

Figure 14 shows the triplicate analyses for total Hg by all three instruments with a 2σ uncertainty of $\pm 20\%$. The results of each replicate were normalized by averaging the sample result of each instrument and dividing into the instrument result. The results are similar regardless of instrument,

but the DMA has the shortest analysis time, does not require aqua regia digestion, and has the shortest sample preparation requirements.

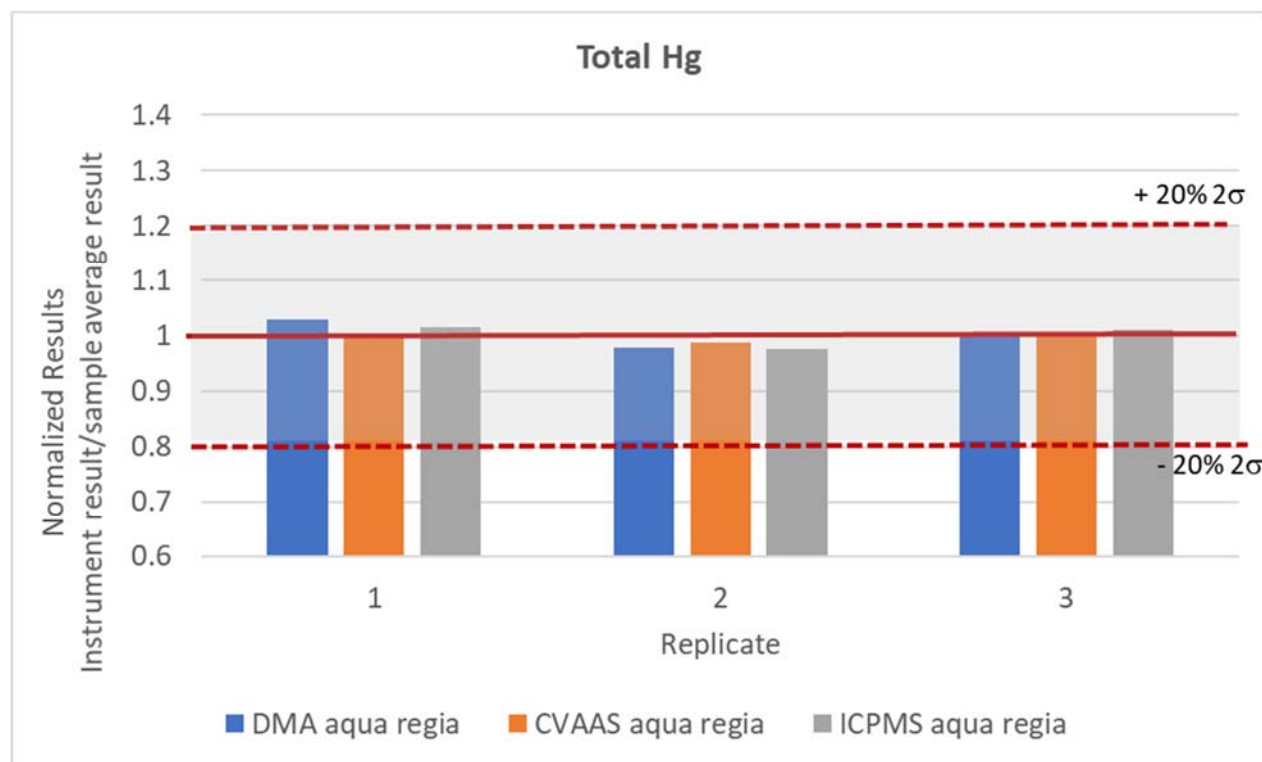


Figure 14. Tank 50 Second Quarter Sample

After DMA containment in December, fourth quarter 2018 tank 50 samples were the first set analyzed in-house by the DMA instead of the CVAAS and reported to the Laboratory Information Management System (LIMS). These results compared to an offsite laboratory³⁴ (61.7 mg/L %RSD 4.6 for n = 3) and to our facility¹⁷ (61.9 mg/L %RSD 0.28 for n = 3) found a % difference $\left(\frac{\text{outside lab} - \text{DMA}}{\text{outside lab} + \text{DMA}} \div 2 \times 100\right)$ of 0.32%. The first quarter 2019 tank 50 analytical total Hg result (59.8 mg Hg/L %RSD 0.580 n = 3) from our MDA instrument and an offsite laboratory³⁵ (67.4 mg Hg/L %RSD 5.6 n = 3) also were within our $\pm 20\%$ (2σ) uncertainty band with a % difference of 11.9 %.

3.4.4 Analysis of MCU Solvent by CVAAS, DMA, and ICP-MS

Monthly, SRNL analyzes MCU samples³⁶ digested by aqua regia in triplicate for total mercury. The MCU solvent is a four component solution containing Isopar™ L (hydrocarbon diluent, nominally 6.11 mg/L), 1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-secbutylphenoxy)-2-propanol (modifier, nominally 169,000 mg/L), *N,N',N''*-tris(3,7-dimethyloctyl)guanidine (Suppressor, nominally 1440 mg/L), and 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arenebenzocrown-6 (Extractant, nominally 47,800 mg/L). Table 6 summarizes the results for four quarters in *YEAR*. The total Hg results are similar, and all three instruments showed similar results for July and August.

Table 6. MCU Solvent Total Hg Results

Total Hg				
Sample	DMA (Solvent)	DMA (digested)	CVAAS (digested)	ICPMS (digested)
MCU (April)	24.4 µg/g	Not Analyzed	28.5 µg/g	Not Analyzed
MCU (May)	19.9 µg/g	Not Analyzed	22.1 µg/g	Not Analyzed
MCU (July)	28.6 µg/g	23.5 µg/g	21.9 µg/g	30.5 µg/g
MCU (Aug)	26.2 µg/g	26.1 µg/g	25.9 µg/g	23.8 µg/g

All three instruments give similar results as shown in Figure 15 ($2\sigma \pm 20\%$) but the DMA can also analyze the solvent directly without the Parr[®] bomb digestion step. The results from each month were averaged to get a nominal value as shown on the graph. The average was divided into that month's sample result to get the normalized value. Using JMP Pro Version 11.2.1 on this small population (Appendix F), no method preference was observed and the DMA method was considered in keeping with CVAAS and ICP-MS.

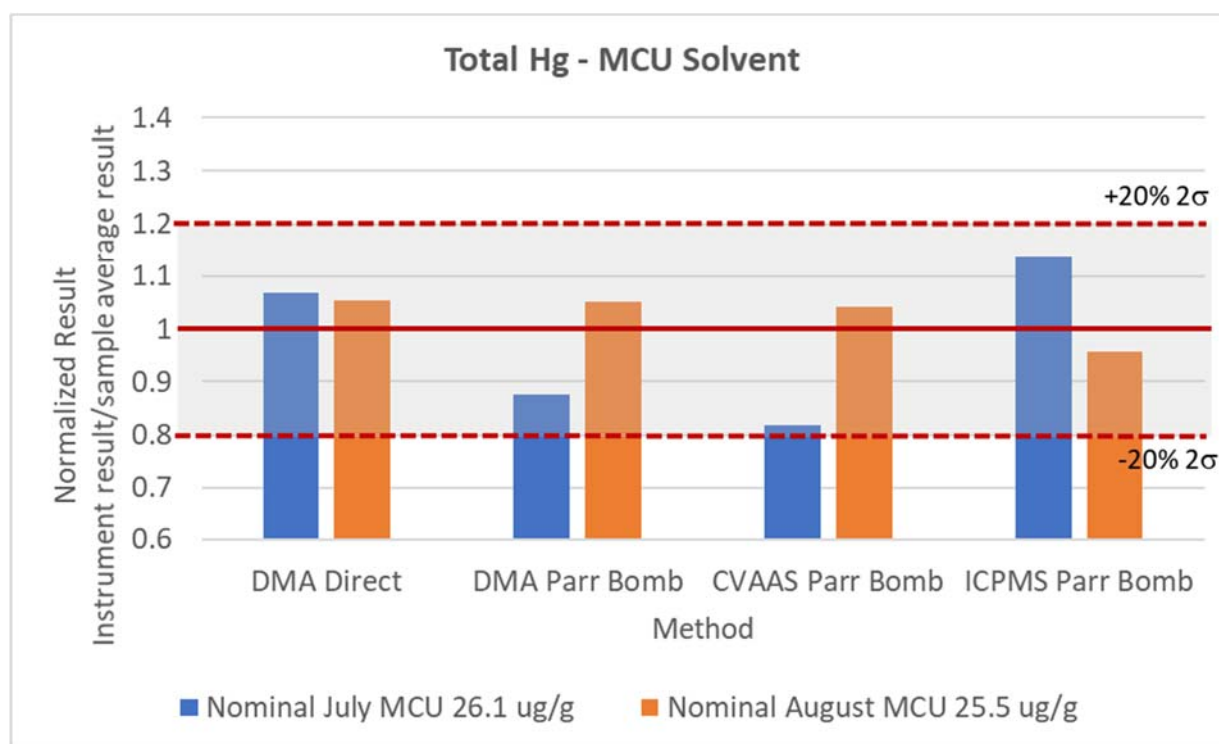


Figure 15. Total Hg Results on July and August MCU Solvents

4.0 Conclusions

The goal of this work was to demonstrate that total mercury analysis on the DMA would match the more involved total mercury analysis on the CVAAS within the uncertainty of the method ($2\sigma \pm 20\%$). SRNL believes the objective of this work has been met for the following reasons: 1)

analysis of Tank 50 samples on the contained DMA (56.0 mg/L) gave results that were within the uncertainty band of the CVAAS (54.1 mg/L) for the total mercury, 2) analysis of Tank 50 samples sent to an off-site laboratory for total mercury (61.7 mg/L) and analyzed by our DMA (61.9 mg/L) were also within the uncertainty of the CVAAS method ($2\sigma \pm 20\%$), 3) analysis of Tank 12 gave results within the uncertainty of the CVAAS method ($2\sigma \pm 20\%$), 4) analysis of MCU samples gave results within the uncertainty of the CVAAS method ($2\sigma \pm 20\%$) and 5) Tank 50 and Tank 38 simulated waste standards demonstrated good recoveries (within $2\sigma \pm 20\%$ uncertainty band) for mercury spikes.

5.0 Acknowledgements

The authors of this report wish to acknowledge the efforts of Sharon Gleaton and Lawrence Cheatham for performing the analyses of samples on the DMA instrument. Additionally, we would like to thank Don Pak for modifying the DMA instrument for ease of use in a contamination area and manufacturing the sample boat rack. We also are grateful to Tommy Edwards for providing the statistical evaluations using JMP Pro Version 11.2.1 and follow on analysis.

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Appendix A: Non-radioactive Control Chart for DMA-80 at Aiken County Technology Laboratory (ACTL) with Data

QC sample #	Date	Ck Std Recovery	Average	UCL (2 σ)	LCL (2 σ)	UCL (3 σ)	LCL (3 σ)
1	6/8/2018a	100.4	98.7	110	87.0	116	81
2	6/19/2018a	112.3	98.7	110	87.0	116	81
3	6/19/2018b	106.3	98.7	110	87.0	116	81
4	6/21/2018a	92.8	98.7	110	87.0	116	81
5	6/21/2018b	97.1	98.7	110	87.0	116	81
6	6/21/2018c	98.9	98.7	110	87.0	116	81
7	6/21/2018d	95.6	98.7	110	87.0	116	81
8	6/21/2018e	95.2	98.7	110	87.0	116	81
9	6/21/2018f	90.5	98.7	110	87.0	116	81
10	6/25/2018a	108.7	98.7	110	87.0	116	81
11	6/25/2018b	106.0	98.7	110	87.0	116	81
12	6/25/2018c	104.5	98.7	110	87.0	116	81
13	7/9/2018a	94.5	98.7	110	87.0	116	81
14	7/9/2018b	96.6	98.7	110	87.0	116	81
15	7/9/2018c	96.7	98.7	110	87.0	116	81
16	7/9/2018d	97.7	98.7	110	87.0	116	81
17	7/9/2018e	93.9	98.7	110	87.0	116	81
18	7/10/2018a	95.1	98.7	110	87.0	116	81
19	7/10/2018b	95.5	98.7	110	87.0	116	81
20	7/10/2018c	89.4	98.7	110	87.0	116	81
21	9/12/2018a	103.84	98.7	110	87.0	116	81
22	9/12/2018b	97.24	98.7	110	87.0	116	81
23	9/13/2018a	101.8	98.7	110	87.0	116	81
	Average		98.7				
	RSD		5.87				

Appendix B: Calculated LOQ/LOD

Special Study - Cell 1 (tabulated LOD = 0.2 ng, LOQ = 0.6 ng):

measured	calculated							
cell 1	quadratic equation							
absorbance	instrument	response	actual	perform regression of instrument response in ng (x) to actual ng (y)				
(AU)	(ng)	(ng)	(ng)	see associated spreadsheet for results				
0.001	0.05216	0	0	the LOQ = 10 x (Std error on intercept / slope)				
0.0032	0.12182	0.1	0.1	the LOD = 3.3 x (Std error on intercept / slope)				
0.0052	0.18521	0.2	0.2	LOQ	LOD			
0.0154	0.50959	0.5	0.5	0.56	0.19			
0.0279	0.90958	1	1					
0.0558	1.81246	2	2					
0.0871	2.84267	3	3					
0.1519	5.03803	5	5					
0.2965	10.2929	10	10					
0.4088	14.8034	15	15					
0.5254	20.0362	20	20					

Associated spreadsheet

SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.999796							
R Square	0.999592							
Adjusted R Square	0.999546							
Standard Error	0.146543							
Observations	11							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	472.9538	472.9538	22023.66	1.46E-16			
Residual	9	0.193273	0.021475					
Total	10	473.1471						
	<i>Coefficient</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-0.02848	0.056284	-0.50607	0.62497	-0.15581	0.09884	-0.15581	0.09884
X Variable	1.002066	0.006752	148.4037	1.46E-16	0.986791	1.017341	0.986791	1.017341
<i>RESIDUAL OUTPUT</i>								
<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>	<i>Standard Residuals</i>					
1	-0.02848	0.080647	0.580096					
2	0.071723	0.050094	0.360328					
3	0.171929	0.013281	0.095528					
4	0.472549	0.037037	0.266408					
5	0.973582	-0.064	-0.46039					
6	1.975648	-0.16319	-1.17381					
7	2.977715	-0.13505	-0.9714					
8	4.981847	0.056186	0.404152					
9	9.992178	0.300686	2.162857					
10	15.00251	-0.19908	-1.43197					
11	20.01284	0.023385	0.168208					

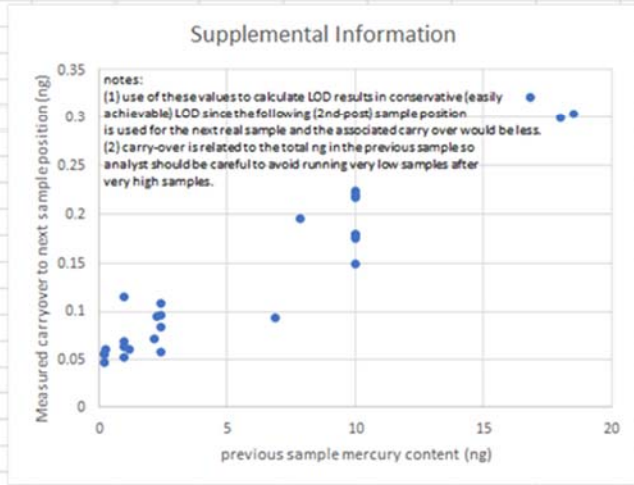
Special Study - Cell 0 (tabulated LOD = 0.1 ng, LOQ = 0.4 ng):

cell 0	quadratic equation	instrument	actual		
absorbance (AU)	response (ng)		(ng)	perform regression of instrument response in ng (x) to actual ng (y) see associated spreadsheet for results the LOQ = 10 x (Std error on intercept / slope) the LOD = 3.3 x (Std error on intercept / slope)	
0.0008	0.02638634		0		
0.0062	0.11417215		0.1		
0.0106	0.18584178		0.2	LOQ	LOD
0.0154	0.26417152		0.5	0.39	0.130
0.0574	0.95613243		1		
0.1117	1.86898554		2		
0.173	2.92598003		3		
0.5382	9.9662374		10		

Associated Spreadsheet

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999671							
R Square	0.999342							
Adjusted R Square	0.999232							
Standard Error	0.093116							
Observations	8							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	78.96798	78.96798	9107.609	8.92E-11			
Residual	6	0.052023	0.008671					
Total	7	79.02						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.064103	0.039229	1.634064	0.153364	-0.03189	0.160093	-0.03189	0.160093
X Variable	0.998729	0.010465	95.43379	8.92E-11	0.973122	1.024336	0.973122	1.024336
RESIDUAL OUTPUT								
<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>	<i>Standard Residuals</i>					
1	0.090456	-0.09046	-1.04927					
2	0.17813	-0.07813	-0.90629					
3	0.249708	-0.04971	-0.57661					
4	0.327939	0.172061	1.995877					
5	1.01902	-0.01902	-0.22063					
6	1.930713	0.069287	0.803719					
7	2.986364	0.013636	0.15818					
8	10.01767	-0.01767	-0.20499					

Develop practical LOD based on updated EPA method* - using real-world blanks between samples during routine operation			
mean "blank"	0.136		
sd	0.085		
number of "blanks"	27		
calculated LOD	0.39	99th confidence interval for blank using t test	
calculated LOQ	1.0		
Date	position	previous sample (ng)	blank value (ng)
11/7/2018	6	1	0.116
11/7/2018	8	10	0.225
11/7/2018	10	2.4	0.1095
11/7/2018	12	2.26	0.0949
11/7/2018	14	2.41	0.0966
11/7/2018	16	2.42	0.059
11/7/2018	18	2.4033	0.084
11/7/2018	20	1.18	0.0611
11/7/2018	22	2.14	0.073
11/7/2018	24	0.23	0.048
11/7/2018	26	10	0.179
11/7/2018	28	10	0.179
11/12/2018	6	1	0.0645
11/12/2018	8	10	0.1752
11/12/2018	11	0.29	0.0614
11/12/2018	13	18.52	0.3046
11/12/2018	15	16.83	0.3224
11/12/2018	17	17.99	0.3002
11/12/2018	19	0.2143	0.0554
11/12/2018	21	7.84	0.1956
11/12/2018	23	10	0.2178
11/13/2018	6	1	0.069
11/13/2018	8	10	0.15
11/13/2018	11	0.219	0.057
11/13/2018	14	1	0.053
11/13/2018	16	6.895	0.0937
11/13/2018	19	10	0.22



* EPA guidance updated in Federal Register /Vol. 82, No. 165 /Monday, August 28, 2017 effective September 27, 2017

Routine Operation- all cells (tabulated LOD = 0.4 ng, LOQ = 1.0 ng):

Appendix C: DMA-80 Sample Boat Cleaning

R&D Directions	Reference: PS PL-AP-4006
---------------------------	---------------------------------

1. PI: Brian Looney/Leigh Brown
2. Task Title: Cleaning boats
3. Date: _____ Customer Name: _____ Analyst: _____ Speed Chart:0203LAT81
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B143
5. Applicable Reference Documents: L1 Manual, AD procedure L16.1 ADS-1580, HAS SRNL-ACT-0677

Boat Cleaning

There are two protocols for boat cleaning:

- Protocol 1 uses a programmed Milestone Direct Mercury Analyzer (DMA 80) for heating/cleaning; this is the normal cleaning method that should be used if a DMA 80 is available.
- Protocol 2 uses a muffle furnace for heating/cleaning

Protocol 1 – using the DMA 80

- _____ Identify DMA 80 for use to clean sample boats [e.g., SRNL Aiken County Technology Laboratory (ACTL) room 109] and confirm instrument availability with laboratory custodian.
- _____ Obtain new (or empty) boats for cleaning
- _____ Place boats to be cleaned in the DMA 80 autosampler carousel
- _____ In the “Data”-“Results” menu, add a run for the first boat position
- _____ For that first boat position, go to the “Data”-“Links” menu and select the boat cleaning method (e.g., “SRNL Boat Cleaning.M80” – see instrument setting below
- _____ Return to the “Data”-“Results” menu and add runs for all the other boats to be cleaned
- _____ Enter “1” in the volume cell for all runs and click “Start”
- _____ When complete repeat runs to assure boats are adequately cleaned; In the “Data”-“Results” menu add a run for each boat cleaning position and enter “1” for the volume cell for all runs.
- _____ Check to make sure boats are low (target average < 0.006 ng, max = 0.01 ng)
- _____ Place cleaned boats in ziplock bag or poly bottle for storage until use
- _____ Label storage bag/bottle with cleaning date, name and cleaning protocol used

DMA Method - Boat Cleaning	
Temperature Profile:	
350C	maximum start
start to 300C	10 seconds
300C	30 seconds
300C to 750C	90 seconds
750C	180 seconds
Sample Processing:	
Purge time	60 seconds
amalgamator time	60 seconds
signal record time	30 seconds

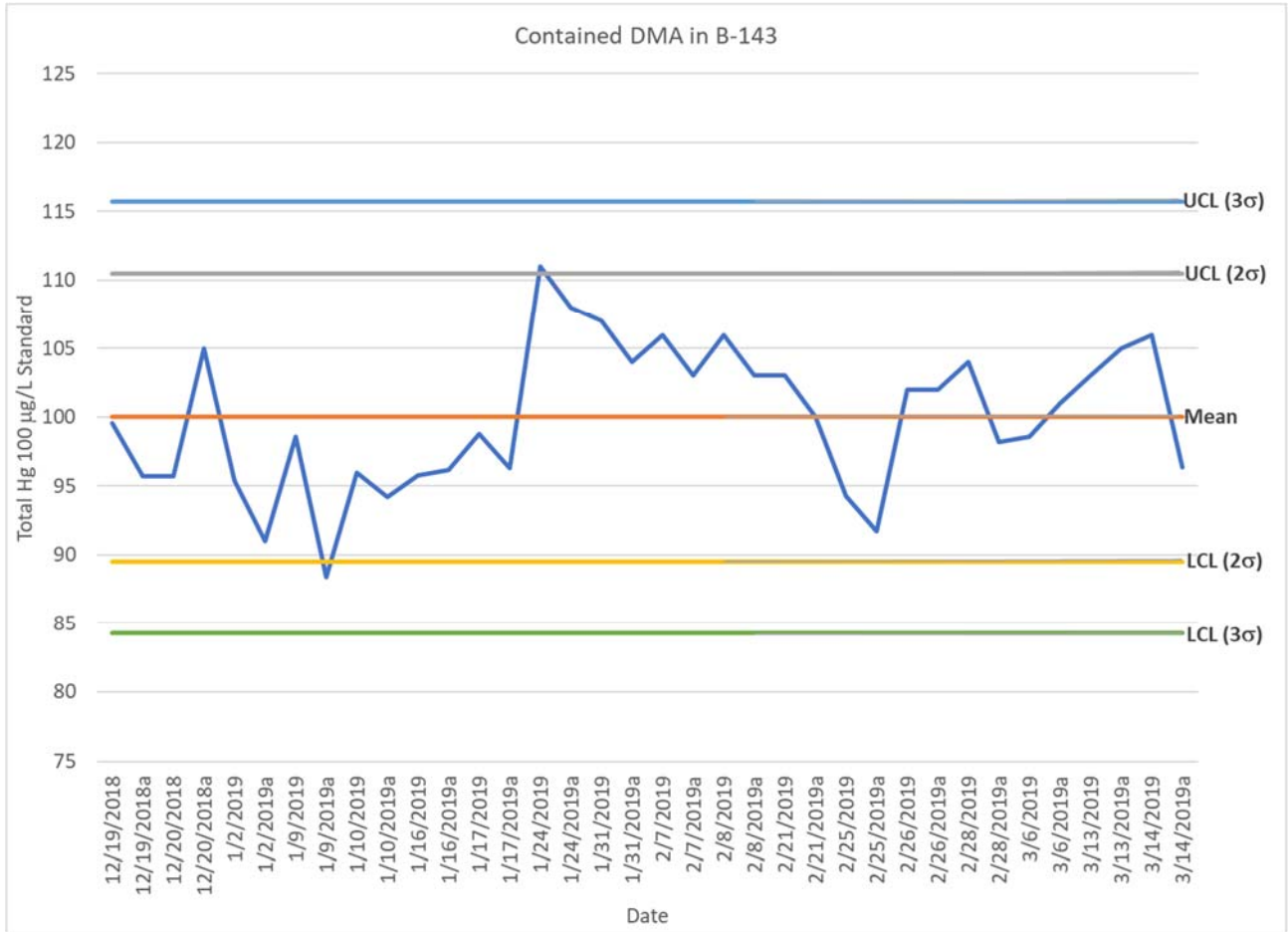
Protocol 2 – using a muffle furnace

- ___ Identify muffle furnace and confirm availability with laboratory custodian.
- ___ Obtain new (or empty) boats for cleaning
- ___ Place boats to be cleaned in a heatproof (quartz or ceramic) container
- ___ Place boats in muffle furnace and heat to 750C – note follow procedures, operating instructions and safety protocols for the muffle furnace
- ___ Maintain temperature at 750C for at least 10 minutes
- ___ Allow muffle furnace to cool
- ___ After cleaned boats have cooled completely, place in ziplock bag or poly bottle for storage until use
- ___ Label storage bag/bottle with cleaning date, name and cleaning protocol used

Appendix D: First Quarter QC chart for Contained DMA-80 in B-143 with data

**Table 1
Hg Analyzer Data**

Row	Date	10 ng or 100 ug/L Std	Mean	UCL (2 σ)	LCL (2 σ)	UCL (3 σ)	LCL (3 σ)	QC
1	12/19/2018	99.6	100.0	110	89.5	116	84.3	Open
2	12/19/2018a	95.7	100.0	110	89.5	116	84.3	Close
3	12/20/2018	95.7	100.0	110	89.5	116	84.3	Open
4	12/20/2018a	105	100.0	110	89.5	116	84.3	Close
5	1/2/2019	95.4	100.0	110	89.5	116	84.3	Open
6	1/2/2019a	91	100.0	110	89.5	116	84.3	Close
7	1/9/2019	98.6	100.0	110	89.5	116	84.3	Open
8	1/9/2019a	88.4	100.0	110	89.5	116	84.3	Close
9	1/10/2019	96	100.0	110	89.5	116	84.3	Open
10	1/10/2019a	94.2	100.0	110	89.5	116	84.3	Close
11	1/16/2019	95.8	100.0	110	89.5	116	84.3	Open
12	1/16/2019a	96.2	100.0	110	89.5	116	84.3	Close
13	1/17/2019	98.8	100.0	110	89.5	116	84.3	Open
14	1/17/2019a	96.3	100.0	110	89.5	116	84.3	Close
15	1/24/2019	111	100.0	110	89.5	116	84.3	Open
16	1/24/2019a	108	100.0	110	89.5	116	84.3	Close
17	1/31/2019	107	100.0	110	89.5	116	84.3	Open
18	1/31/2019a	104	100.0	110	89.5	116	84.3	Close
19	2/7/2019	106	100.0	110	89.5	116	84.3	Open
20	2/7/2019a	103	100.0	110	89.5	116	84.3	Close
21	2/8/2019	106	100.0	110	89.5	116	84.3	Open
22	2/8/2019a	103	100.0	110	89.5	116	84.3	Close
23	2/21/2019	103	100.0	110	89.5	116	84.3	Open
24	2/21/2019a	100	100.0	110	89.5	116	84.3	Close
25	2/25/2019	94.3	100.0	110	89.5	116	84.3	Open
26	2/25/2019a	91.7	100.0	110	89.5	116	84.3	Close
27	2/26/2019	102	100.0	110	89.5	116	84.3	Open
28	2/26/2019a	102	100.0	110	89.5	116	84.3	Close
29	2/28/2019	104	100.0	110	89.5	116	84.3	Open
30	2/28/2019a	98.2	100.0	110	89.5	116	84.3	Close
31	3/6/2019	98.6	100.0	110	89.5	116	84.3	Open
32	3/6/2019a	101	100.0	110	89.5	116	84.3	Close
33	3/13/2019	103	100.0	110	89.5	116	84.3	Open
34	3/13/2019a	105	100.0	110	89.5	116	84.3	Close
35	3/14/2019	106	100.0	110	89.5	116	84.3	Open
36	3/14/2019a	96.4	100.0	110	89.5	116	84.3	Close
	Mean	100						



Appendix E: MAPEP-39 Analysis on DMA-80 by Three Technicians

Tech	Date	MAPEP-39	mg/L
Analyst 1	1/9/2019	LW11668	0.108
Analyst 2	1/10/2019	LW11668	0.105
Analyst 3	1/17/2019	LW11668	0.096

Target 0.109
mean 0.103
Std. Dev. 0.00510


12/3/2018

MAPEP: Mixed Analyte Performance Evaluation Program

Current Series Performance Results

Study: MAPEP Series 39 (entire series) ▼ ?

Lab: SAVANNAH RIVER NUCLEAR SOLUTIONS (SRNS)

SRNL (non-purchased material receipt)  [Generate as pdf](#)
AIKEN, SC 29808-0000

Show Expanded Results

MAPEP-18-MaW39: Radiological and inorganic combined water standard

Inorganic

Units: (mg/L)

Analyte	Result	Ref Value	Flag	Notes	Bias (%)	Acceptance Range	Unc Value	Unc Flag
Antimony	15.2	15.8 A			-3.8	11.1 -20.5	1.5 A	
Arsenic	0.981	1.08 A			-9.2	0.76 -1.40	0.098 A	
Barium	19.1	19.3 A			-1.0	13.5 -25.1	1.9 A	
Beryllium	5.00	5.18 A			-3.5	3.63 -6.73	0.5 A	
Cadmium	0.848	0.873 A			-2.9	0.611 -1.135	0.085 A	
Chromium	3.26	3.33 A			-2.1	2.33 -4.33	0.326 A	
Cobalt	5.07	5.31 A			-4.5	3.72 -6.90	0.507 A	
Copper	4.76	5.19 A			-8.3	3.63 -6.75	0.476 A	
Lead	2.81	2.83 A			-0.7	1.98 -3.68	0.28 A	
Mercury	0.088	0.109 A			-19.3	0.076 -0.142	0.017 W	
Nickel	14.4	15.8 A			-8.9	11.1 -20.5	1.44 A	
Selenium	0.865	0.875 A			-1.1	0.613 -1.138	0.087 A	
Technetium-99	NR	5.37E-6				3.76E-6 -6.98E-6		
Thallium	4.16	4.26 A			-2.3	2.98 -5.54	0.42 A	
Uranium-235	NR	0.00125				0.00088 -0.00163		
Uranium-238	NR	0.176				0.123 -0.229		
Uranium-Total	0.176	0.177 A			-0.6	0.124 -0.230	0.018 A	
Vanadium	17.8	18.5 A			-3.8	13.0 -24.1	1.78 A	
Zinc	18.5	19.3 A			-4.1	13.5 -25.1	1.85 A	

Appendix F: Statistical Evaluations using JMP Pro Version 11.2.1

Several methods for total mercury (Hg) measurements are evaluated in the sections that follow; JMP Pro Version 11.2.1 was used to conduct these evaluations [1]; and while little data are available for direct comparison of the methods, statistical conclusions are pursued as part of this investigation with the caveat of their reliance on small numbers of observations in most cases.

Main points

- CVAAS, DMA, and ICP-MS behave statistically the same on a small sample set in regard to simulated waste test samples, MAPEP samples, and Tank 50 samples falling within the method uncertainty ($\pm 20\% 2\sigma$).
- Bromine monochloride oxidant used for CVAAS analysis of total Hg gave a slightly high bias on a small sample set of simulated waste samples. Permanganate/Persulfate oxidant with CVAAS matched the DMA analysis and both methods were closest to the expected total Hg value.

Comparisons of Quality Control (QC) Check Standards

For the DMA and CVAAS methods the available QC data are comprised of daily measurements of opening and closing standards (with reference values of 100 $\mu\text{g/L}$ of total Hg) while for the outside laboratory the data are in groups of daily percent recovery values for total Hg standards measured at that laboratory. Figure F1 provides a graphic of these results (open symbol for opening standard and closed symbol for closing standard for DMA and CVAAS) with the orange horizontal line representing the average of each method's measurements.

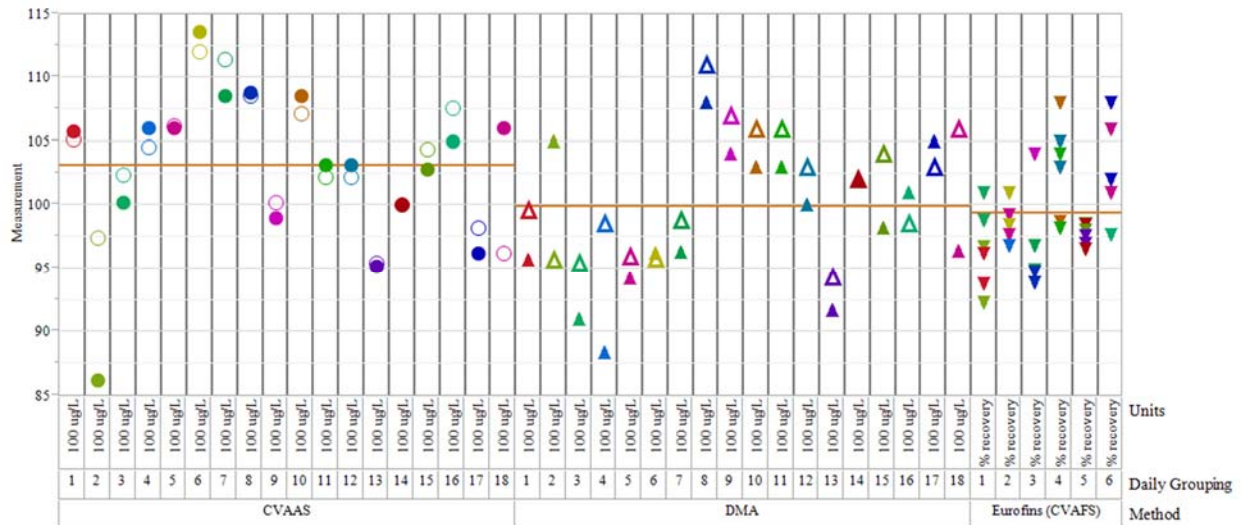


Figure F1. QC Results by Method

Since the target value for each method is 100, the measurements were re-expressed as % relative differences around this target value as additional evaluations were conducted. Exhibit FA1 in Appendix FA provides

the results of a random effects analysis of variance (ANOVA) of the % relative difference values. While the day-to-day variation seen in these measurements for all three methods accounts for about 64% of the total variance, there does not appear to be a statistical difference (at the 5% significance level) in the method averages (i.e., the p-value for a significant effect due to method is 0.0856).

Exhibit FA2 in Appendix FA continues the investigation into the QC results. In this exhibit, the averages of the % relative difference values for the daily groupings are determined and compared across the three methods. Two statistical tests are of interest for the three methods: equality of variances and equality of means. Levene’s test is utilized to judge the results of the equal variance test, and its p-value of 0.3351 indicates that the null hypothesis of equality of variance cannot be rejected at the 5% significance level. The ANOVA’s F-test with a p-value of 0.0908 leads to the conclusion that the null hypothesis of mean equality for the methods cannot be rejected at the 5% significance level.

Summary statistics for these data are provided in Table F1, which includes the mean and standard deviation as well as a 95% confidence interval (CI) for the mean of each method. While there is overlap in the confidence intervals for the means of the results for these methods, the CVAAS method is slightly biased high while the other two methods yield unbiased results over the course of these QC measurements.

Table F1. Summary Statistics for Daily Averages of QCs by Method

Method	Number of Observations	Mean	Std Dev	Lower 95% CI Mean	Upper 95% CI Mean
CVAAS	18	3.217	5.307	0.578	5.856
DMA	18	-0.003	4.697	-2.339	2.333
Offsite Lab (CVAFS)	6	-0.519	2.701	-3.353	2.315

MAPEP-39 Sample by DMA

SRNL analyzed a Mixed Analyte Performance Evaluation Program (MAPEP) sample, MAPEP-39, with a reference value of 0.109 mg/L total Hg and an acceptable range for measurements of 0.076 to 0.142 mg/L. Three separate SRNL analysts examined this sample on the DMA; the resulting values were 0.108, 0.105, and 0.096 mg/L. All these results were acceptable, and even though the number of analyses is limited (only three) a closer evaluation of the results was considered. Exhibit FA.3 in Appendix FA provides summary statistics of this sample of three results. Included in the exhibit is a statistical test for normality for the data. The null hypothesis of normality was not rejected at the 5% significance level (with such a limited set of data, there was not much power brought to bear for this evaluation). With the assumption of normality for the distribution of SRNL’s DMA measurements of MAPEP-39 samples, a capability analysis of the DMA method was evaluated that included an estimate of the percent of future SRNL values likely to fall outside of the acceptability range for MAPEP-39 measurements. These results suggest that if future SRNL DMA measurements of MAPEP-39 follow the pattern seen in the three current measurements, there is little chance of SRNL’s measurements falling outside of the acceptability range.

Simulant Tests Using DMA and CVAAS Instruments

Samples of simulant waste spiked with mercury were prepared for analysis by DMA and CVAAS. Two CVAAS oxidation protocols were used: permanganate/persulfate and bromine monochloride. Figure F2

provides a graphical display of the sample information along with the resulting measurements expressed as percent relative differences: $100\% \times (\text{Measurement} - \text{Reference Value}) / [\text{Reference Value}]$.

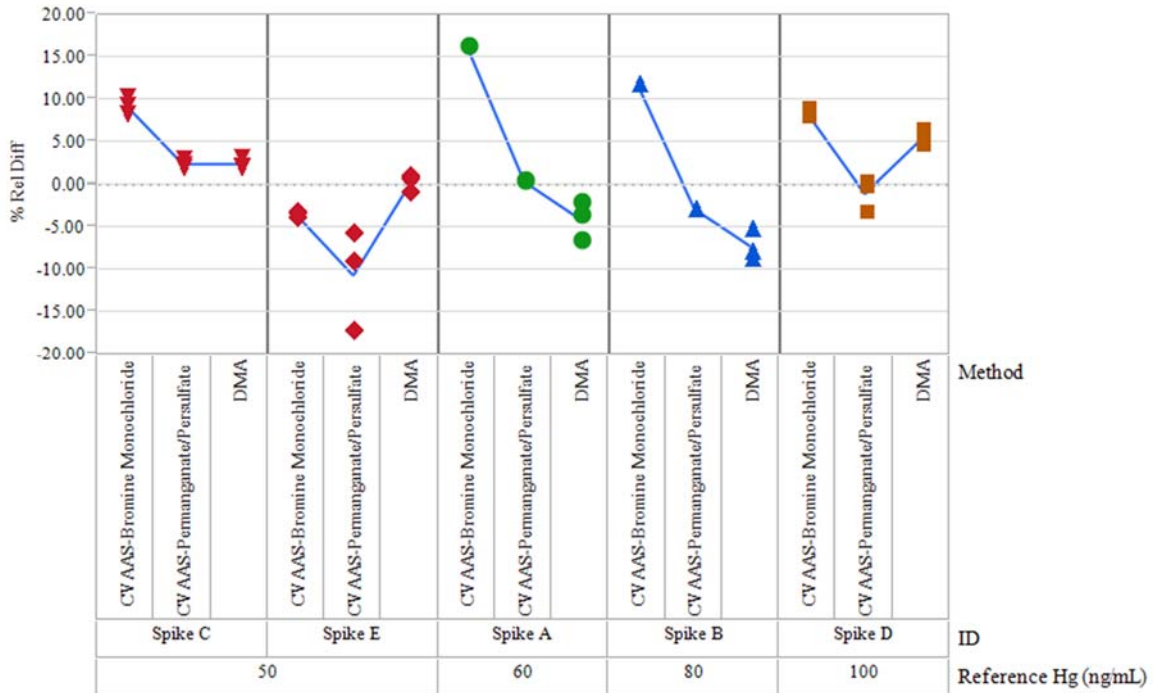


Figure F2. Simulant Test Results Expressed as % Relative Differences (% Rel Diff)

Exhibit FA4 in Appendix FA provides an ANOVA investigating for effects on these results due to the method employed for the analysis as well as the sample ID. The results indicate that the effects for both terms are statistically significant at the 5% significance level: the p-value for ID is 0.0005 and the p-value for method is 0.0001. A closer look at the method effects is provided by the results from the Tukey Honestly Significance Difference (HSD) test, which indicate that the average % relative difference (6.1%) for the CVAAS-Bromine Monochloride measurements is statistically different from (larger than) the average (-0.6%) for DMA and from the average (-3.1%) for CVAAS-permanganate/persulfate while the averages for DMA and CVAAS-permanganate/persulfate are not statistically different.

Tank 50 Samples by Method

Two quarterly samples from Tank 50 digested by aqua regia in triplicate were analyzed by DMA for total mercury. The first sample was also analyzed by CVAAS and ICP-MS, while the second sample was analyzed only by ICP-MS. Figure F3 provides a graphical display of the mg/L measurements.

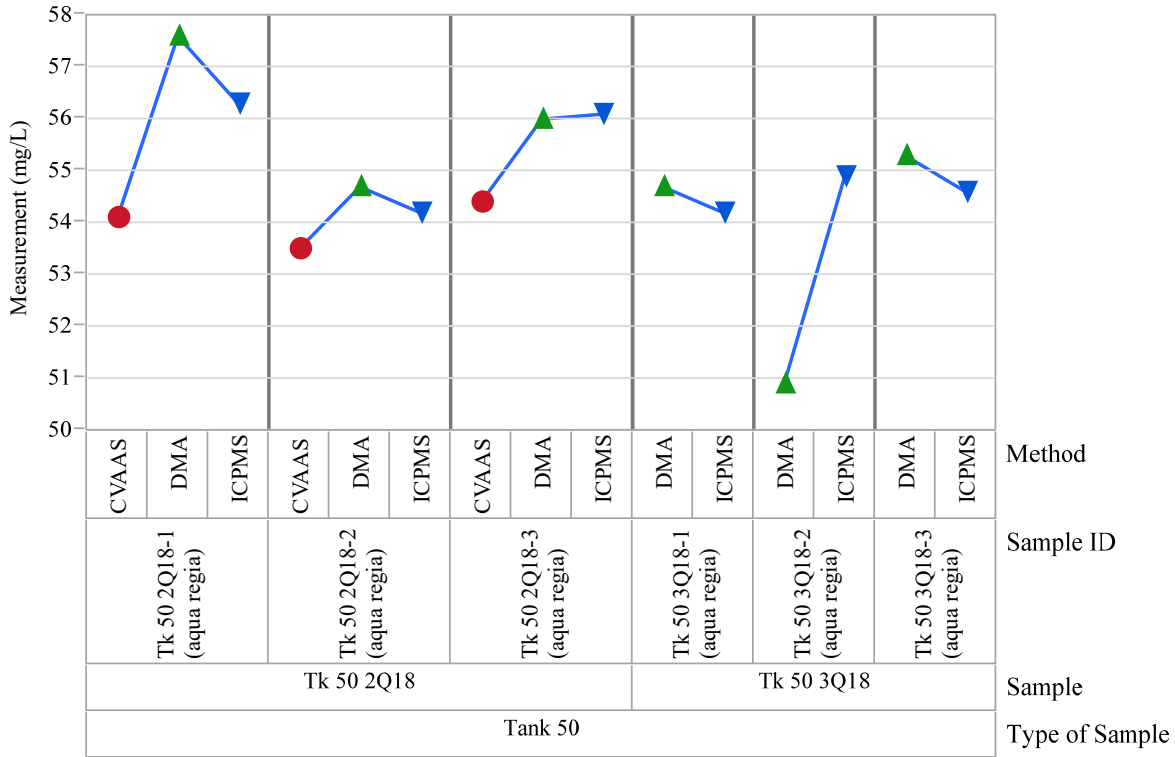


Figure F3. Tank 50 Total Hg Results in mg/L

Exhibit FA5 in Appendix FA provides a pair of ANOVAs investigating for effects on these results due to the method employed for the analysis. On the left side of this exhibit, comparisons of the CVAAS, DMA, and ICP-MS results from the sampling of Tank 50 for the second quarter of 2018 are made. The Levine test is utilized to test the null hypothesis that the variances of these methods are equal (with the identified caveat of the need for caution due to the small number of samples). The p-value resulting from this test is 0.3138 indicating that the null hypothesis cannot be rejected at the 5% significance level. The p-value for the ANOVA F-test of 0.1315 indicates that the null hypothesis of no effect on the means of these data due to method cannot be rejected at 5% significance level. Thus, there is no indication of differing means or variances across the three methods for this very limited data set.

The right side of Exhibit FA5 provides comparisons between DMA and ICP-MS results from the sampling of Tank 50 for the third quarter of 2018. Once again, the Levine test is utilized to test the null hypothesis that the variances of these methods are equal (with the identified caveat of the need for caution due to the small number of samples). The p-value resulting from this test is 0.0341 indicating that the null hypothesis is rejected at the 5% significance level. Under the assumption of differing variances for the two methods, Welch’s test is utilized to test the null hypothesis of equal means. The resulting p-value is 0.5692, indicating that the null hypothesis cannot be rejected at 5% significance level. Thus, there is no indication of differing means but there is an indication that the variances of the two methods may differ for this very limited data set.

MCU Samples by Method

Several recent monthly samples from the MCU process were analyzed by DMA for total mercury. For some cases, the sample was also analyzed by CVAAS and ICP-MS. Figure F4 provides a graphical display of the measurements in micrograms of total Hg per gram of sample ($\mu\text{g/g}$)[▲].

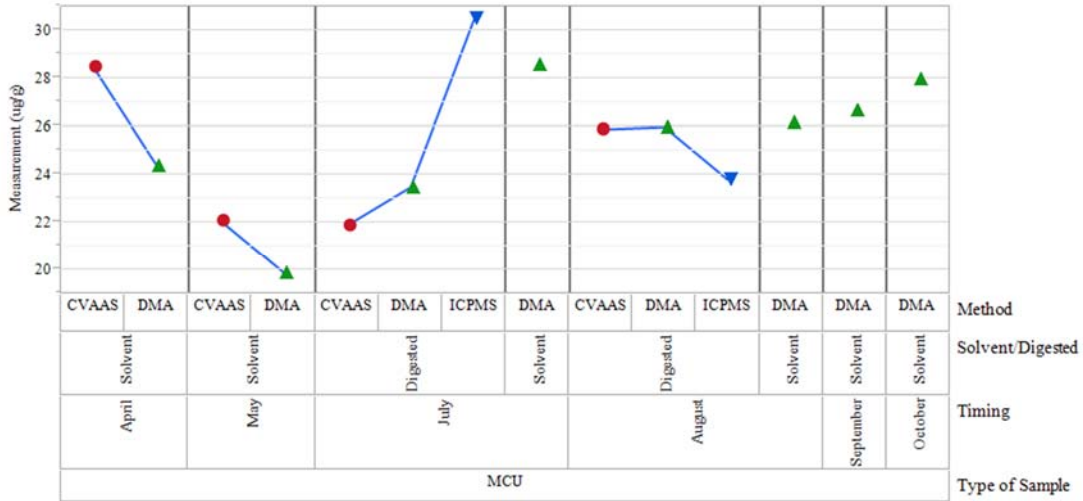


Figure F4. MCU Sample Measurements of Total Hg in $\mu\text{g/g}$

While there are limited data to support the evaluations of interest for these measurements, attempts were made to look for effects due to month, solvent/digested preparation, and method. Exhibit FA6 in Appendix FA provides the results of two ANOVA evaluations conducted using the JMP software. On the left side of the exhibit is an initial evaluation investigating for all three effects: month, solvent/digested preparation, and method. None of these effects is statistically significant at the 5% significance level; their p-values are: 0.3758 for Timing; 0.2478 for sample preparation (i.e., solvent/digested), and 0.5205 for method. With the conclusion that the total Hg content of the MCU process did not change over the months sampled for this evaluation, the effects on the total Hg measurements of a single factor that combined method and preparation were evaluated. The results appear on the right side of Exhibit FA6. The p-value from Leven’s test (0.5738) and the p-value from the F-test (0.8996) lead to the conclusion that the null hypotheses of equal variances and equal means for these groupings of the total Hg measurements cannot be rejected at the 5% significance level. Once again, the conclusions are offered with the caveat of the need for caution given the small number of samples available to support these evaluations.

Reference

[1] JMP® Pro Version 11.2.1, SAS Institute, Inc., Cary, NC, 2014.

[▲] Note in the use of the JMP software this metric was indicated by $\mu\text{g/g}$.

Appendix FA. Supporting Exhibits

Exhibit FA1. Random Effects Analysis of Variance for Quality Control Check Standard Data

Response % Relative Difference Whole Model

Summary of Fit

RSquare	0.74159
RSquare Adj	0.736668
Root Mean Square Error	3.171794
Mean of Response	0.898148
Observations (or Sum Wgts)	108

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Pct of Total
Daily Grouping[Method]	1.7539405	17.645129	5.1750412	7.502235	27.788024	63.688
Residual		10.060278	1.7663067	7.3308448	14.6664	36.312
Total		27.705408	5.166473	19.828698	41.446084	100.000

-2 LogLikelihood = 616.74745861

Note: Total is the sum of the positive variance components.

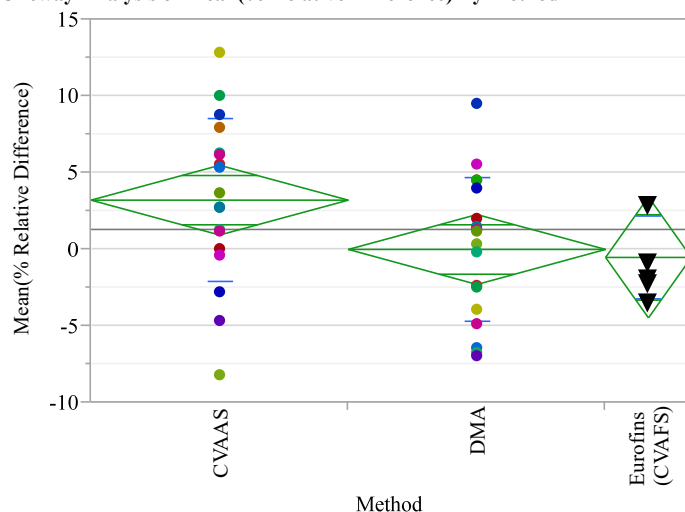
Total including negative estimates = 27.705408

Fixed Effect Tests

Source	Nparm	DF	DFDen	F Ratio	Prob > F
Method	2	2	34.19	2.6436	0.0856

Exhibit F2. Analysis of Variance for Daily Averages of the Quality Control Check Standard Data

Oneway Analysis of Mean(% Relative Difference) By Method



**Oneway Anova
Summary of Fit**

Rsquare	0.115751
Adj Rsquare	0.070404
Root Mean Square Error	4.777772
Mean of Response	1.303175
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Method	2	116.5370	58.2685	2.5526	0.0908
Error	39	890.2570	22.8271		
C. Total	41	1006.7940			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
CVAAS	18	3.2167	1.1261	0.939	5.4945
DMA	18	-0.0028	1.1261	-2.281	2.2750
Eurofins (CVAFS)	6	-0.5194	1.9505	-4.465	3.4258

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

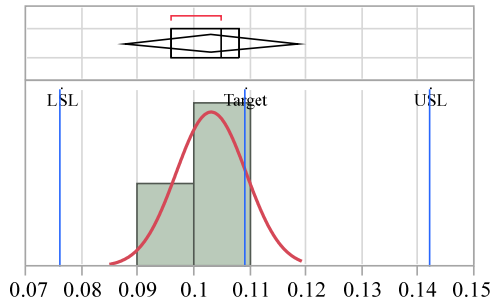
Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
CVAAS	18	5.306517	4.138889	4.138889
DMA	18	4.697229	3.797531	3.758333
Eurofins (CVAFS)	6	2.700543	2.212963	2.069444

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	1.0150	2	39	0.3718
Brown-Forsythe	1.1982	2	39	0.3126
Levene	1.1245	2	39	0.3351
Bartlett	1.2943	2	.	0.2741

Exhibit FA3. Summary Statistics of DMA Measurements of MAPEP-39

Distributions

MAPEp-39 w DMA



Normal(0.103,0.00624)

Quantiles

100.0%	maximum	0.108
99.5%		0.108
97.5%		0.108
90.0%		0.108
75.0%	quartile	0.108
50.0%	median	0.105
25.0%	quartile	0.096
10.0%		0.096
2.5%		0.096
0.5%		0.096
0.0%	minimum	0.096

Summary Statistics

Mean	0.103
Std Dev	0.006245
Std Err Mean	0.0036056
Upper 95% Mean	0.1185134
Lower 95% Mean	0.0874866
N	3

Fitted Normal

Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	0.103	0.0874866	0.1185134
Dispersion	σ	0.006245	0.0032515	0.0392482

-2log(Likelihood) = -22.9422155362758

Goodness-of-Fit Test

Shapiro-Wilk W Test

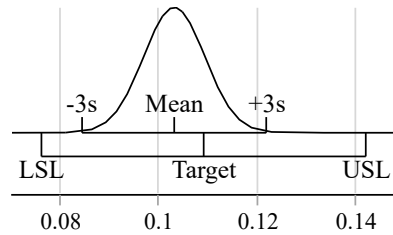
W	Prob<W
0.923077	0.4633

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

Capability Analysis

Specification	Value	Portion	% Actual
Lower Spec Limit	0.076	Below LSL	0.0000
Spec Target	0.109	Above USL	0.0000
Upper Spec Limit	0.142	Total Outside	0.0000

Long Term Sigma



Sigma = 0.00624

Capability Index Lower CI Upper CI

CP	1.761	0.280	3.383
CPK	1.441	-0.021	2.903
CPM	1.270	0.476	2.343
CPL	1.441	0.147	2.810
CPU	2.082	0.274	4.028

Portion Percent PPM Sigma Quality

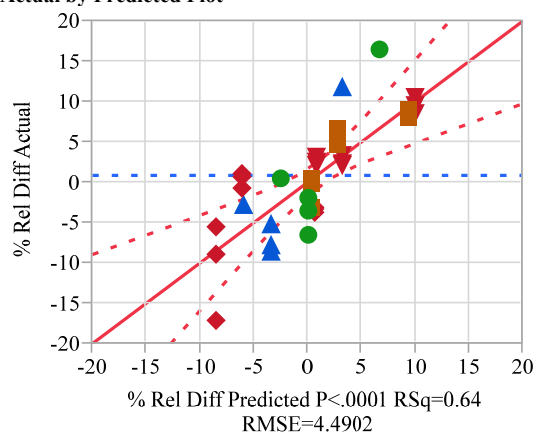
Below LSL	0.0008	7.6800	5.823
Above USL	0.0000	0.0002	7.745
Total Outside	0.0008	7.6803	5.823

Exhibit FA4. Analysis of Variance of Spiked Simulant Sample Results

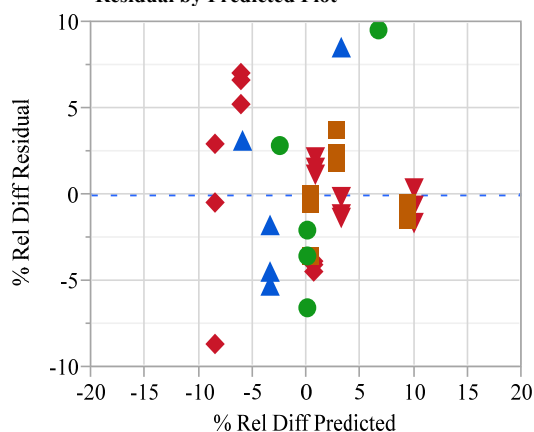
Response % Relative Difference (% Rel Diff)

Whole Model

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

RSquare	0.637798
RSquare Adj	0.565358
Root Mean Square Error	4.490205
Mean of Response	0.871171
Observations (or Sum Wgts)	37

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	1065.0888	177.515	8.8044
Error	30	604.8583	20.162	Prob > F
C. Total	36	1669.9470		<.0001*

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	8	501.14659	62.6433	13.2883
Pure Error	22	103.71167	4.7142	Prob > F
Total Error	30	604.85826		<.0001*

Max RSq

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
ID	4	4	549.31794	6.8113	0.0005*
Method	2	2	498.37508	12.3593	0.0001*

Method

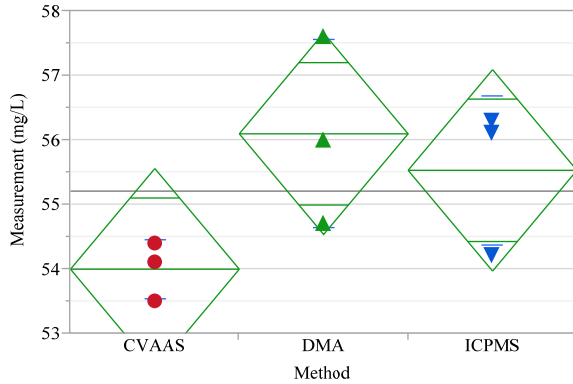
LSMeans Differences Tukey HSD

Level	Least Sq Mean
CVAAS-Bromine Monochloride A	6.089069
DMA B	-0.608333
CVAAS-Permanganate/Persulfate B	-3.061688

Levels not connected by same letter are significantly different.

Exhibit FA5. Analysis of Variance Evaluations of Tank 50 Sample Results

Oneway Analysis of Measurement (mg/L) By Method Type of Sample=Tank 50, Sample=Tk 50 2Q18



Oneway Anova Summary of Fit

Rsquare	0.491518
Adj Rsquare	0.322023
Root Mean Square Error	1.105039
Mean of Response	55.21111
Observations (or Sum Wgts)	9

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Method	2	7.082222	3.54111	2.8999	0.1315
Error	6	7.326667	1.22111		
C. Total	8	14.408889			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
CVAAS	3	54.0000	0.63799	52.439	55.561
DMA	3	56.1000	0.63799	54.539	57.661
ICPMS	3	55.5333	0.63799	53.972	57.094

Std Error uses a pooled estimate of error variance

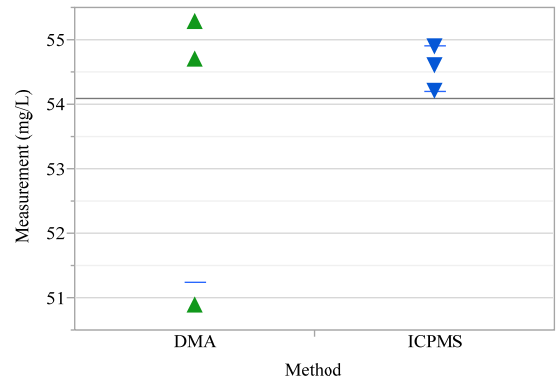
Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
CVAAS	3	0.458258	0.333333	0.300000
DMA	3	1.452584	1.000000	0.966667
ICPMS	3	1.159023	0.888889	0.700000

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	0.7734	2	6	0.5025
Brown-Forsythe	0.5324	2	6	0.6126
Levene	1.4149	2	6	0.3138
Bartlett	0.9148	2	.	0.4006

Warning: Small sample sizes. Use Caution.

Oneway Analysis of Measurement (mg/L) By Method Type of Sample=Tank 50, Sample=Tk 50 3Q18



Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
DMA	3	2.386071	1.822222	1.466667
ICPMS	3	0.351188	0.244444	0.233333

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	1.7008	1	4	0.2622
Brown-Forsythe	1.0822	1	4	0.3569
Levene	10.0069	1	4	0.0341
Bartlett	3.9820	1	.	0.0460
F Test 2-sided	46.1622	2	2	0.0424

Warning: Small sample sizes. Use Caution.

Welch's Test

Welch Anova testing Means Equal, allowing Std Devs Not Equal

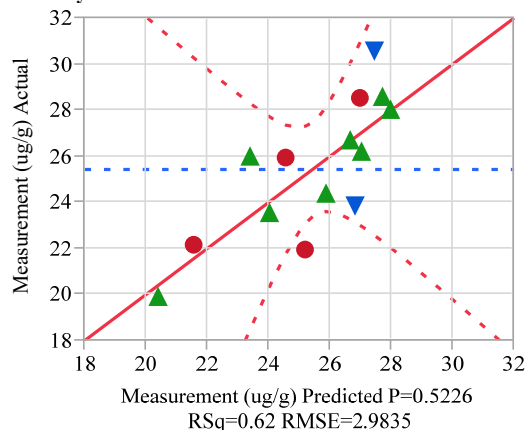
F Ratio	DFNum	DFDen	Prob > F
0.4493	1	2.0866	0.5692

Exhibit FA6. Analysis of Variance Evaluations of MCU Sample Results

Response Measurement (ug/g)

Whole Model

Actual by Predicted Plot



Summary of Fit

RSquare	0.616673
RSquare Adj	0.003351
Root Mean Square Error	2.983538
Mean of Response	25.42857
Observations (or Sum Wgts)	14

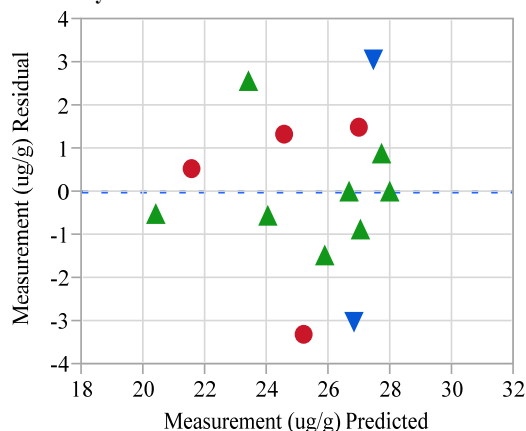
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Model	8	71.60107	8.95013	1.0055	
Error	5	44.50750	8.90150	Prob > F	
C. Total	13	116.10857		0.5226	

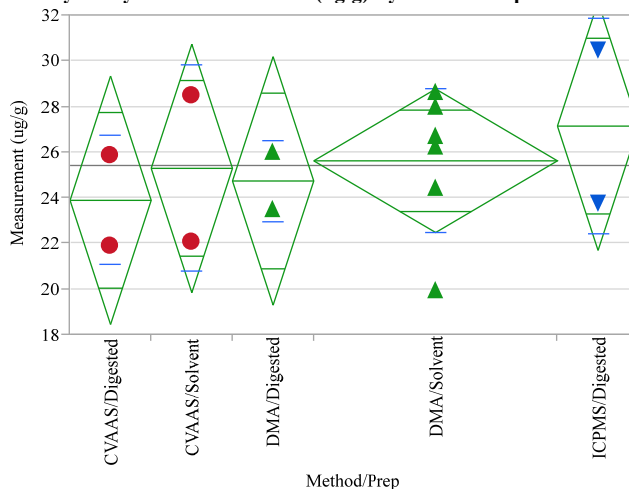
Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Timing	5	5	59.956000	1.3471	0.3758
Solvent/Digested	1	1	15.225714	1.7105	0.2478
Method	2	2	13.285833	0.7463	0.5205

Residual by Predicted Plot



Oneway Analysis of Measurement (ug/g) By Method/Prep



Oneway Anova Summary of Fit

Rsquare	0.101674
Adj Rsquare	-0.29758
Root Mean Square Error	3.4043
Mean of Response	25.42857
Observations (or Sum Wgts)	14

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Method/Prep	4	11.80524	2.9513	0.2547	0.8996
Error	9	104.30333	11.5893		
C. Total	13	116.10857			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
CVAAS/Digested	2	23.9000	2.4072	18.455	29.345
CVAAS/Solvent	2	25.3000	2.4072	19.855	30.745
DMA/Digested	2	24.7500	2.4072	19.305	30.195
DMA/Solvent	6	25.6333	1.3898	22.489	28.777
ICPMS/Digested	2	27.1500	2.4072	21.705	32.595

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
CVAAS/Digested	2	2.828427	2.000000	2.000000
CVAAS/Solvent	2	4.525483	3.200000	3.200000
DMA/Digested	2	1.767767	1.250000	1.250000
DMA/Solvent	6	3.170279	2.322222	2.133333
ICPMS/Digested	2	4.737615	3.350000	3.350000

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	.	0	5	.
Brown-Forsythe	0.5322	4	9	0.7158
Levene	0.7651	4	9	0.5738
Bartlett	0.2169	4	.	0.9292

Warning: Small sample sizes. Use Caution.

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