Selective capture and speciated analysis of soluble inorganic mercury in high activity tank waste

Andrew J. Boggess,[1] Mark A. Jones,[1] Thomas L. White,[1] Christopher J. Bannochie,[2] Brian Looney[3]

1. Analytical Development, Science and Technology, Savannah River National Laboratory, Savannah River Site, Aiken, SC 29808, USA

2. Wasteform Processing Technology, Environmental Stewardship, Savannah River National Laboratory, Savannah River Site, Aiken, SC 29808, US

3. Environmental Restoration Technology, Environmental Stewardship, Savannah River National Laboratory, Savannah River Site, Aiken, SC 29808, US

Abstract

A method has been developed, optimized, and analytically validated using nitrogen purged samples, gold-coated bead traps, thermal desorption, and atomic fluorescence spectroscopy. Using a reduced factorial multivariate optimization method, nitrogen purge flow rate was determined to be highly correlated with increased response. Taken with total purge time and a model generated using a modified Henry's Law, a total purge gas volume of 1000 mL was determined to be sufficient to obtain optimal purgeable mercury response. Total recovery of spiked purgeable mercury from deionized water was 99.4 ±11% and 91.6 ±15% from spiked high-activity tank waste samples. Calibration, by five-point external calibration and four-point standard addition calibration, maintained a mean accuracy of 101 ±5.3% and 99.9 ±1.8%, respectively. The mean accuracies of the two calibration methods were not significantly different ($p=0.68$). The method presented here represents an increase in efficiency and decrease in sample handling and processing over currently accepted and standard methods for purgeable mercury analysis. This validated method has been applied to routine liquid waste samples from high-activity waste tanks at Savannah River Site.

Introduction

The high-level nuclear waste tanks and legacy waste processing systems at the Savannah River Site (SRS) in Aiken County, South Carolina contain over 60 metric tons of mercury in various forms and species. Mercury, in the presence of nitric acid and heat, has been used for over 50 years at SRS as a catalyst for the dissolution of aluminum alloys, aluminum-uranium cermets, and cladding from targets and fuels. The use of mercuric ions continues today in the nuclear material processing facilities for the dissolution of various aluminum-based materials.

The two tank farms at SRS house, largely, cold-war era legacy waste in the form of saltwaste and sludge. This waste is ultimately bound for remediation through the formation of cementitious grout for the saltwaste or vitrified glass for the sludge. Local, state, and federal regulations demand that this remediated wasteform comply with environmental and, specifically, leachate performance protocols for a variety of waste constituents, including mercury. Routine samples taken from Tank 50, a hold tank, in the fourth quarter of 2014 showed relatively high levels of organomercury, compared with the formation mechanisms predicted by in-house models and leachate testing. Since this finding, efforts were taken to develop the capability to quantify organic and inorganic mercury species in high-level nuclear waste at SRS.

Mercury species of interest at SRS include particulate and dissolved elemental mercury (Hg_0), ionic Hg (Hg^+) and Hg^{2+}), and organomercury (including methylmercury, ethylmercury, and dimethylmercury) in the liquid waste stream. Novel methods have been developed and optimized at SRS to separate and quantify organomercury species of interest in high-level liquid waste using direct aqueous alkyl derivatization, gas chromatography, and fluorescence spectroscopy. The remaining inorganic mercury species have been separated into soluble and insoluble inorganic mercury- being composed of a combination of species: Hg_0, Hg(I), and Hg(II).

Methods for the determination of volatile mercury species by a variety of sample preparation techniques, such as purge and trap (P&T), adsorbent trapping, and alkyl derivatization, in addition to diverse analytical ionization and detection techniques including inductively couple plasma ionization (ICP) and cold-vapor atomic fluorescence have existed in the literature for decades. While effective standard methods exist for the determination of inorganic mercury species in liquid samples, the prescribed and inherent sample handling and manipulation make many accepted and commonplace methods for inorganic mercury analysis incompatible with the As Low As Reasonably Achievable (ALARA) principals of radionuclear analytical work. For example, sample preparation that involves multiple handling and transfer steps in incompatible with nuclear work, as every analytical step introduces opportunity for a contamination event, as well as exposes the analyst to unnecessary radioactivity. Likewise, while ICP mass spectrometry (ICP-MS) would provide highly accurate mercury quantification and, when paired with an appropriate chromatographic separation, could provide high quality species information, the footprint associated with an ICP-MS is not amenable to radio-hood containment, where cost of containment estimates can range in the millions of dollars. When optimizing for nuclear work, a balance must be found between analytical optimization, the safety of the analyst and laboratory, and cost of instrumentation and containment.

Many optimized methods currently exist for the extraction and quantification of inorganic mercury; however, in the context of a nuclear facility, specific methods for radiological containment, reduction in analyst-exposure, remote operation, safety, and security must be further developed. Savannah River National Laboratory (SRNL), which is house at SRS, undertook work presented here focused on the development, optimization, and application of a fully-contained, modular, high-throughput method for the separation and species-specific analysis of soluble inorganic mercury in high activity tank waste by P&T, thermal desorption (TD), and CVAFS with and without selective stannous chloride ($SnCl_2$) reduction. For this work, it was proposed to separate and quantify “soluble inorganic mercury,” consisting of a combination of ionic mercury and purgeable mercury- a species itself composed of an equilibrium between dissolved gaseous mercury (DGM) and suspended colloidal mercury (SCM). This validated, high-throughput procedure was further applied to legacy liquid waste samples and compared, via inter-laboratory testing, with previously obtained results.

Experimental

Safety and Security

This document is not intended to provide a thorough analysis or prescription for safety and security for future work, but is intended to merely outline the context within which this work was performed. Numerous administrative controls not listed here exist within SRNL that govern the transfer, transport, storage, and analysis of nuclear materials onsite to ensure the safety of analysts, radiological protection workers, instrumentation, and structures.

All workers, scientists, and technicians were registered on appropriate Radiological Work Permits (RWP) that defined the maximum allowed radiological exposure. Likewise, all personnel had completed SRS radiological training courses, as well as an additional SRNL-specific Advanced Radiological Worker (ARW) course. The laboratory within which this work was performed was designated a Radiological Buffer Area (RBA), with the containment hood containing the instrumentation and samples designated a Contamination Area (CA). The radiological dose limits for the RBA laboratory were 0.05 mSv/h (at 30cm), with a transferable contamination limit of 0.02 Bq/100 cm^2 α radiation and 0.2 Bq/100 cm^2 β and γ radiation. The radiological dose limits for the CA working area were 0.05 mSv/h at (30 cm), with a transferable contamination limit of 3.33 Bq/100 cm^2 α radiation and 166 Bq/100 cm^2 β and γ radiation. The RWPs designated no permissible airborne contamination within the RBA or CA. Both the RBA and CA were in compliance with regular survey and certification by the Radiation Protection Department.

Instrumental Configuration

The instrumentation within the CA hood was configured to allow maximum efficiency, minimal worker exposure, and limited sample handling. The setup of instrumentation can be seen diagrammed in figure 1.

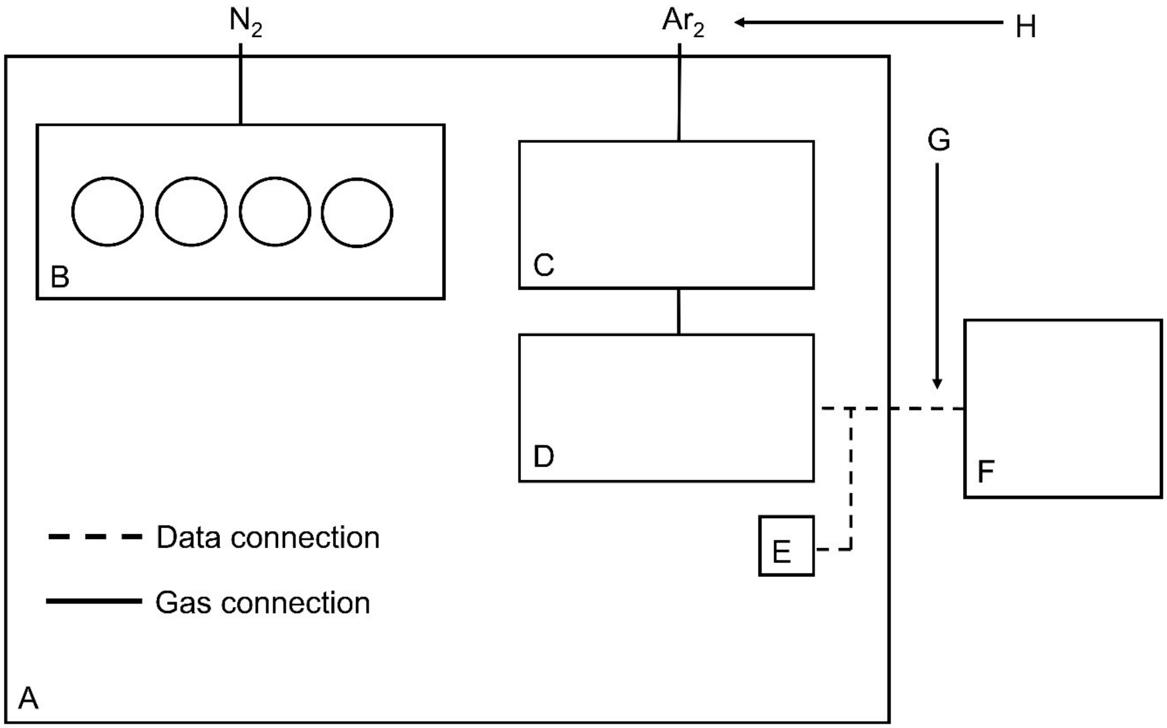

Figure 1: Schematic of the configuration of the P&T-TD-CVAFS within the contamination area

As seen in figure 1, the CA hood (A) enveloped the working area, including a 4-vessel P&T (B) system (Brooks Rand Instruments, Seattle, WA), Dual Trap TDM-II thermal desorption system (Brooks Rand Instruments) (C), and Model III (Brooks Rand Instruments) CVAFS (D). Data analysis, handling, and signal processing was performed at an external workstation PC (F) running Microsoft Excel (Microsoft Corporation, Redmond, WA) and Mercury Guru software (Brooks Rand Instruments), connected to the Model III digitally via a RS-232 communication port. Carrier and purge gas lines (ultra-high purity grade 5 argon and nitrogen, respectively, with 1/8" outer diameter [O.D] Teflon tubing) were fed through the back of the CA (H). A small control pad was installed within the CA (E), connected to the external workstation digitally (G) that enabled operation of basic functions of the instrument, as well as control over simple data processing and analysis from within the CA.

Preparation and processing of samples followed the sequence of (1) loading of sample (encompassing reagent water, air-blanks, liquid waste samples, or any other sample-type containing or not containing volatile mercury species) into glass purge vessels, (2) purging of sample with N_2 purge gas for a determined amount of time, (3) passing purge gas through a quartz tube packed with soda lime (calcium oxide and sodium hydroxide), and (4) capturing purged mercury vapor onto traps containing gold-coated glass beads. Following purging, the solid-phase trap was transferred by hand to the receptacle in the TDM-II unit where the trap was desorbed at 600 °C for a predetermined amount of time. Desorbed mercury vapor was transferred via 1/8" Teflon tubing from the TDM-II to the Model III CVAFS where atomic fluorescence spectroscopy was performed.

Initial parameters for instrumental operation, prior to any optimization, were obtained from standardized methods and vendor recommendation: N_2 purge flow rate of 25 mL/min, carrier gas flow rate of 30 mL/min Ar_2, a N_2 purge time of 17 minutes, 10.6 V for the heating coil on the flow-rate of TDM-II, TDM-II heating and cooling times of 3 minutes each.

Calibration was obtained by two methods: external calibration curve and standard addition. External calibration was performed by placing a quartz-T connector containing a septum and two openings in-line with the Argon carrier gas upstream from the TDM-II. A known amount of mercury gas was injected through the septum of the T-connector. Known amounts (ng) of mercury were calculated using the volume of mercury withdrawn using a gas-tight syringe and the ambient temperature of the room, as shown in equation 1. The argon carrier gas carried the mercury vapor to a gold-bead trap held stationary and unheated in the receptacle of the TDM-II. Following a 2 minute adsorption period, the trap was heated and peak-area data was collected.

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

Standard addition calibration, validation samples, matrix spike samples, and ongoing quality control samples were generated at the purge vessels by spiking known amounts of mercury vapor through the septum of a quartz-T connector into the N_2 purge gas flow downstream of the purge vessels. This setup allowed the mercury vapor to enter the purge vessel, flow through the sample matrix, exit the purge vessel, and retain on the gold-bead trap. Standard addition calibration was performed in a method similar to the validation, matrix spikes, and quality control samples: a varying, known amount of mercury gas was injected via T-connector into the purge stream into vessels containing unknown liquid waste sample, and the resulting purged gas was collected on gold bead traps. For development, mercury vapor was used to represent all soluble purgeable mercury.

Multivariate Development

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

Table 1: Three variable – three level multivariate optimization experiment design

	Purge Flow (mL/min)	Purge Time (min.)	Matrix Addition (%)
1	25	5	0
2	25	5	10
3	25	5	20
4	25	17.5	0
5	25	17.5	10
6	25	17.5	20
7	25	30	0
8	25	30	10
9	25	30	20
10	45	5	0
11	45	5	10
12	45	5	20
13	45	17.5	0
14	45	17.5	10
15	45	17.5	20
16	45	30	0
17	45	30	10
18	45	30	20
19	65	5	0
20	65	5	10
21	65	5	20
22	65	17.5	0
23	65	17.5	10
24	65	17.5	20
25	65	30	0
26	65	30	10
27	65	30	20

Liquid Waste Samples Collection and Storage

Quarterly waste samples were, and are, collected from one of several waste hold tanks at SRS for routine testing. Samples were collected in small, stainless steel bottles with approximately zero headspace. Stainless steel is not recommended for mercury testing; however, sampling and transport of high-level waste can only be performed with stainless steel. The bottles were transferred to the SRNL shielded cells where 1:100 dilution was performed into a Teflon bottle, prior to immediate transfer to refrigeration at 4 °C. For purgeable mercury analysis, a further 1000-fold dilution was imparted to the sample in deionized water and 100mL was transferred to the purge vessel.

Reagents and Consumable

Ultra-high purity Argon (99.999%) was used as carrier gas through 1/8” O.D Teflon tubing at 2-PSI (1.4 bar). Standard laboratory grade (grade 4.5) Nitrogen was used as purge gas, connected through 1/8” O.D Teflon tubing regulated at 300 mL/min. Soda lime-packed tubes measuring ¼” O.D. x 10 cm long (Brooks Rand Instruments) were used for water vapor removal from the purged gases prior to trapping. Gold-coated glass bead traps (Brooks Rand Instruments) measuring ¼” O.D. x 10 cm long with Teflon end plugs were used for trapping of purged gas. Each gold bead trap was heated approximately 50 times before replacement. A mercury Vapor Box with internal temperature sensor (Brooks Rand Instruments) and gas-tight syringes of volumes 10 µL and 100 µL were used for spiking of known amounts of mercury gas. Potassium chloride (>99.0%, Fisher Scientific, Pittsburgh, PA) was used for matrix ionic activity adjustment.

Validation and Statistics

Comparison testing was performed via statistical analysis at the 95% confidence interval and a standard hypothesis testing value of p=0.05. Unless indicated, all uncertainty and standard deviation was given as a percentage relative to the mean value. Methods limits of detection and quantification (LOD, LOQ, respective) were calculated using equations 2 and 3, respectively, where σ_n is the standard deviation of n samples:

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

$$\text{LOQ} = \text{LOD} \times 3.33$$

Percent recovery of purgeable mercury was determine in a Tank 50 liquid waste sample from SRS, diluted 1,000-fold. Percent recovery was calculated according to equation 3, as prescribed by EPA Method 1631. Where, A is the measured concentration of purgeable mercury after spiking, B is the measure concentration of the analyte before spiking, and T is the true concentration of the mercury vapor spike. The uncertainty of recovery is equal to the standard deviation of the mean recoveries for each sample.

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

Bias was assessed in this work and is largely treated as synonymous with recovery in many respects. When taken with calculated uncertainty, bias can, and often must, be used as an analytical correction factor. Bias, as with recovery, was calculated as an estimate from spiking studies. The assumption was made that the primary source of analytical bias in the work would likely arise in the purge and trap step. Combine bias in the purging and trapping steps was determined on 15 consecutive samples at 0.422 ng mercury vapor. Each reported measured value in this work that generated by purge and trap, was calculated as the product of the raw calculated measurement value and a bias correction of +28.9%. The uncertainty of values reported in this work that are the product of purging was calculated by the law of error propagation, as demonstrated in equation 4, where u_{sample} is the uncertainty associated with the specified sample, u_{meas} is uncertainty contributed by the original, uncorrected, measurement, and u_b is the uncertainty contributed by the original bias factor calculation. The uncertainty of the bias correct factor was determined to be 11.2%.

Equation 4: $u_{sample} = \sqrt{u_{meas}^2 + u_b^2}$

Results and Discussion

Multivariate optimization of purgeable mercury

Three independent variables were optimized simultaneously using a 3x3 reduced factorial multivariate experiment and changes in their parameters were tested for significance. No multivariate combination of parameters was predictive of response to a significant degree.

However, taken as univariate experiments, purge flow rate was significantly predictive of response. Figure 2 demonstrates the results at the low and high ends of each optimization experiment. Figure 2-A demonstrates the nonsignificant difference (p=0.23) in response between matrix solutions prepared at 0% and 20% ionic activity with KCl (n=5). Figure 2-B shows the highly trending, but nonsignificant difference (p=0.18) in response between samples purged with N_2 for 5 minutes and 30 minutes (n=5). Figure 2-C shows the significant difference (p=0.023) in samples purged at a flow rate of 25 mL/min and 65 mL/min, regardless of purge time (to a minimum of 5 minutes) (n=5). Figure 2-D demonstrates the significant (p=0.00019) decrease in peak area replicate variance as sample purge rate is increased, regardless of purge time (n=5).

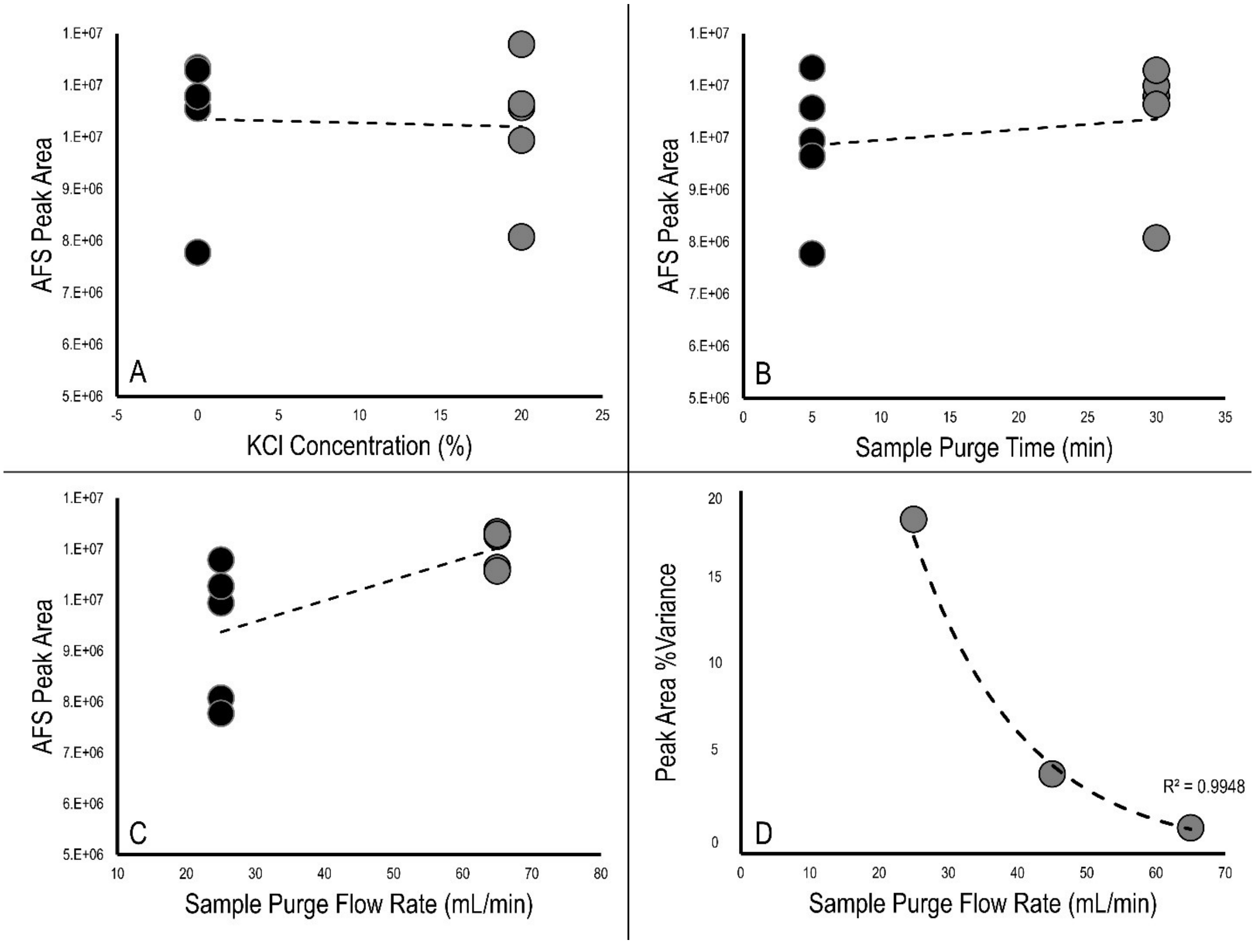

Figure 2: Univariate results of multivariate optimization experiments, showing (A) matrix ionic activity response, (B) sample purge time, (C) flow rate of nitrogen purge gas, and (D) relationship between purge flow rate and response variance

Using the optimized purge flow rate data set (65 mL/min, n=8), the total cumulative volume of nitrogen delivered was calculated, based on the varying purge times used, and computed as a phase ratio of purge volume delivered *versus* volume of sample. At each of these points, a blank-corrected and normalized peak area was calculated. Figure 3 demonstrates the increasing peak area observed with increasing phase ratio (grey dots). The optimum peak area was obtained at an approximate phase ratio of 10, representing approximately 1000 mL of purge gas delivered through the 100 mL sample. The black line in figure 3, plotted on the right-side Y-axis, represents a modified and specific form of Henry's Law that demonstrates the rate at which mercury is predicted to be sparged from an aqueous sample *versus* the volume of purge gas delivered. The observed data agrees to a reasonable degree with the predicted kinetics of mercury vapor sparging.

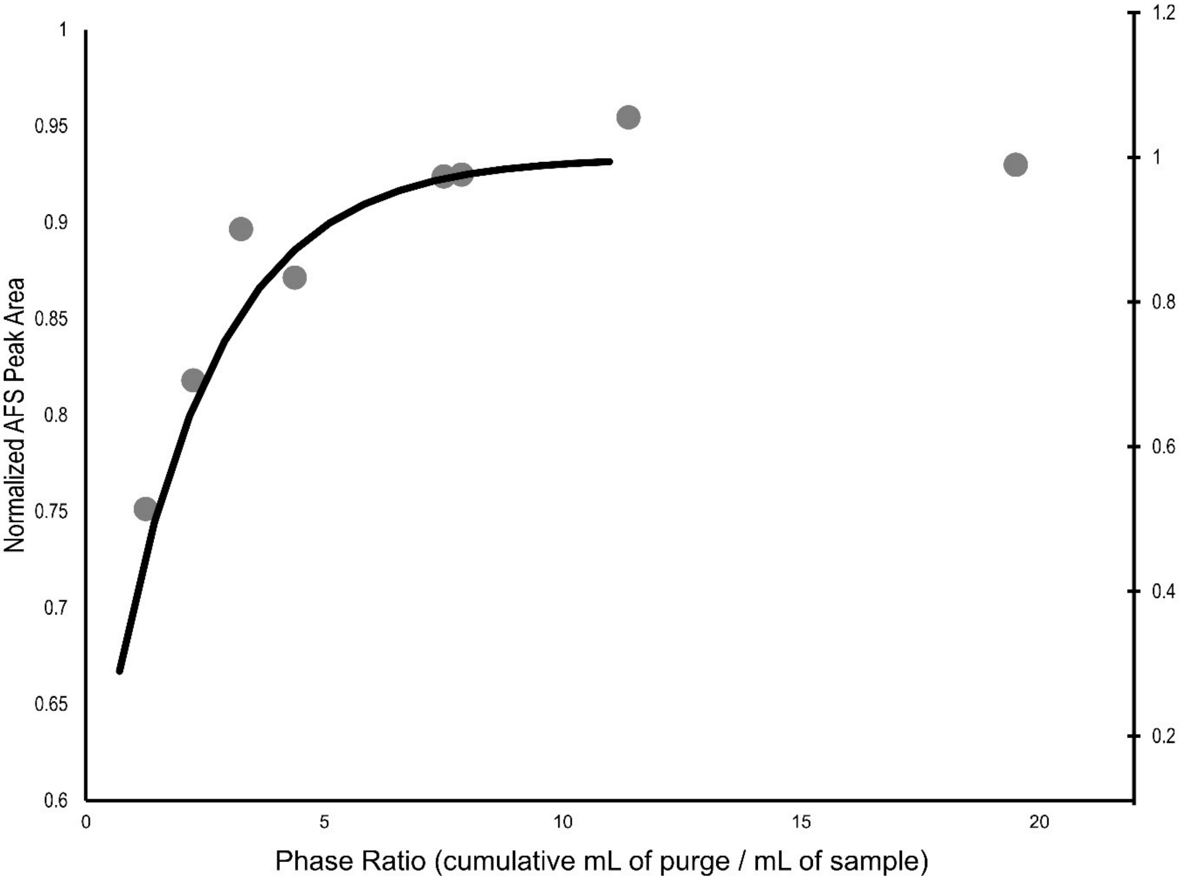

Figure 3: Normalized instrument response of spiked mercury vapor purged at 60 mL/min for variable lengths of time, relative to the ratio of volume of purge gas delivered to volume of sample purged. Black line represents a modified Henry's Law of predicted fraction of purged mercury vapor relative to the phase ratio of purge gas delivered to volume of sample.

Understanding that the observed measurements of purged mercury vapor corresponded with the predictive model provided by Henry's Law, an optimal sample purge time and rate of 15 minutes and 65 mL/min were chosen to fit the 1000 mL cumulative purge volume required for a 100 mL sample to maintain a phase ratio of approximately 10.

Total cumulative recovery was determined for mercury vapor spiked through the purge and trap system. For mercury vapor, mean percent recovery (n=5) was determined to be 100 ±7.9% when measured directly without the purge and trap system, 99.4 ±11% when purged through into deionized water, and 91.6 ±15% when purged through 1000-fold diluted and blank-corrected Tank 50 liquid waste sample. Recovery, when spiked and purged through Tank 50 samples, was not significantly lower than non-purged spikes measured directly (p=0.77) or spikes purged through deionized water (p=0.57). Spikes purged through deionized water were similarly not recovered at significantly different values (p=0.58). A comparison of recovery values, showing 95% confidence levels, can be found in figure 4.

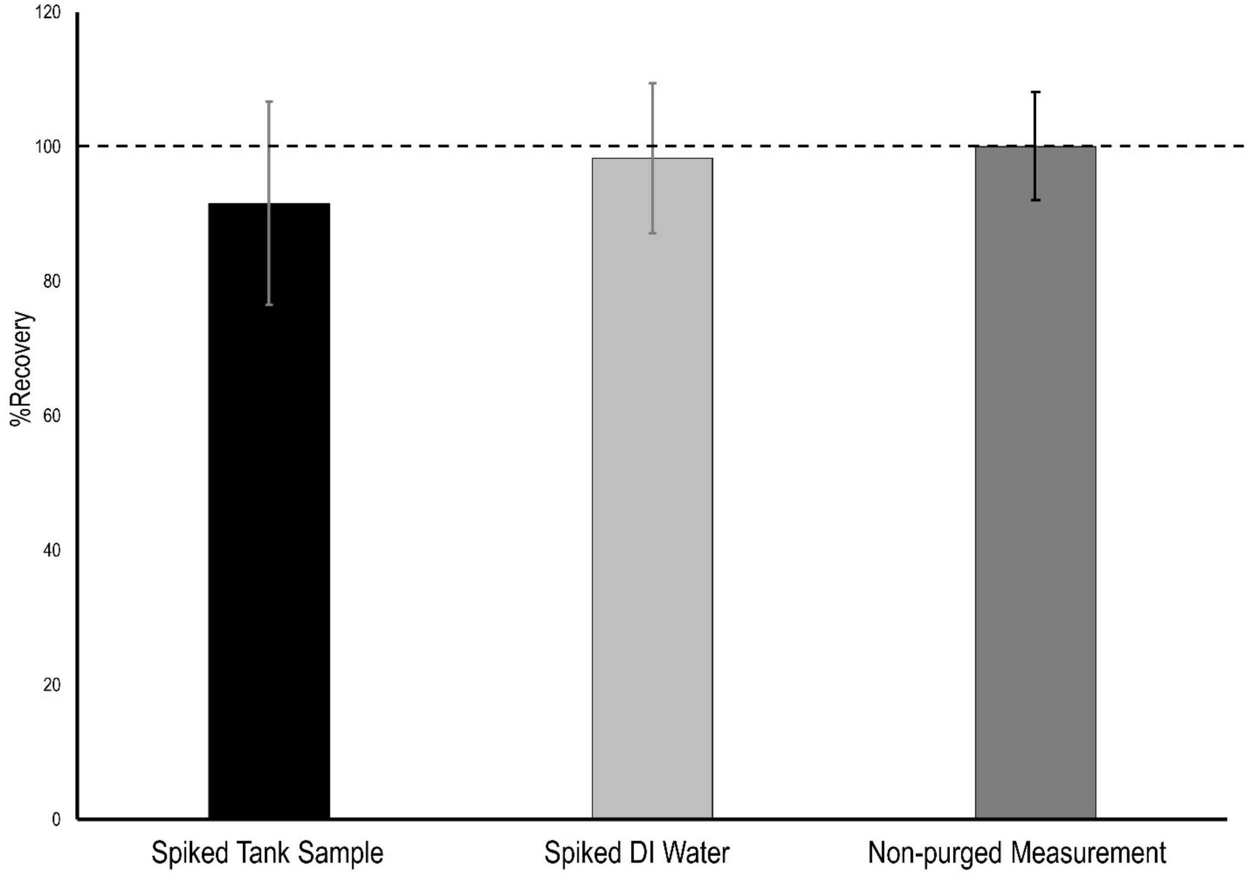

Figure 4: A comparison of analytical recovery of mercury vapor spiked and purged through liquid waste tank sample, deionized water, and measured directly without purge

Two sets of calibration data were collected: traditional 5-point external calibration and 4-point standard addition calibration. External calibration maintained linearity over the five-point curve, composed of 2.5, 5, 10, 50, and 100 µL mercury vapor spiked measured directly (non-purged), with a coefficient of determination of 0.9999. Mean accuracy over this calibration curve was determined as 101 ±5.3%. Standard addition calibration was obtained over four points, comprised of 0, 10, 25, and 50 µL mercury vapor additions spiked and purged through liquid tank waste, with a coefficient of determination of 0.9999. Mean accuracy over this calibration curve was determined as 99.9 ±1.8%. The mean accuracies of the two calibration methods were not significantly different (p=0.68). The external calibration and standard addition calibration can be seen in figure 5, where the standard addition has been blank-corrected to display only peak area associated with the spiked mercury vapor.

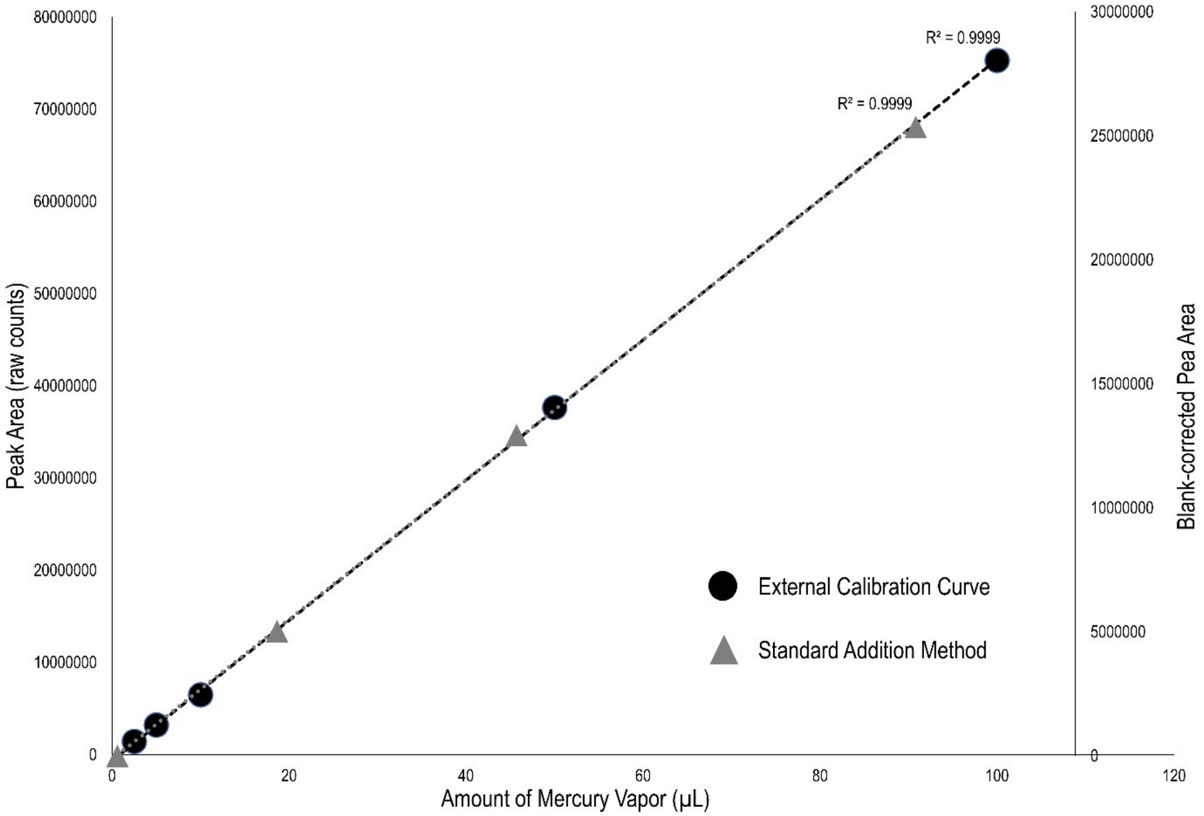

Figure 5: External and standard addition calibration techniques performed directly (non-purged), or purged through liquid tank waste (respectively) and blank-corrected

The agreement between the plateau in peak area of observed measurements and the trend predicted by Henry's Law, as seen in figure 3, implies that an optimal fraction of mercury vapor may be purged from an aqueous sample with 1000 mL of purge gas. Statistically similar recoveries achieved from spiked and purged tank samples and deionized water, as seen in figure 4, demonstrate a lack of matrix effect in the liquid tank waste samples. This absence of matrix effect is further implied by the agreement between the external calibration and standard addition in tank waste, as seen in figure 5, indicating that matrix effects are negligible in high-activity Tank 50 tank waste at SRS.

Application to Liquid Tank Waste

This developed, optimized, and analytically validated method, initially sourced from standard and accepted methods of purgeable mercury analysis, was applied to the analysis of purgeable mercury in routine samples taken in the second quarter of 2018 from Tank 50. Quantified by external calibration (ECC), the 2Q Tank 50 liquid waste samples contained 26.3 µL ± 18.2%. Quantified by standard addition method (SAM), the 2Q Tank 50 liquid waste samples contained 25.9 µL ± 15.1%. The observed measurements using ECC and SAM were not significantly different (p=0.93).

Table 2: Results obtained from calibration verification, quality control checks, and 2nd quarter Tank 50 analyzed by two calibration methods

	Amount (µL)	Uncertainty$_{95\%}$	Accuracy
Calibration Check	50.4	± 5.79%	101%
Purged QC Sample	24.8	± 2.81%	99.8%
2Q Tank 50 ECC	26.3	± 18.2%	N/A
2Q Tank 50 SAM	25.9	± 15.1%	N/A

Limitations and Considerations

The solubility limit of elemental gaseous mercury is debated, but generally agreed to be within ______. Given the large volume of elemental mercury present in the waste tanks at SRS, it is likely that dissolved gaseous mercury may be present in tank samples at the solubility point of gaseous mercury. Mercury may also likely be present in the tanks in the form of a dense separate phase or in suspended colloidal materials, as a source for the dissolved gaseous mercury. If true, these condensed-phase sources of elemental mercury in the sample could act as sources for gaseous mercury- attempting to attain equilibrium as dissolved gaseous mercury is purged from the sample. In this case, a purged liquid tank waste sample would not provide useful data for dissolved gaseous mercury, but rather (if purged to completion) all potentially purgeable mercury materials. This consideration was accounted for in this work by using the nomenclature of purgeable mercury in lieu of dissolved gaseous mercury. A limitation not addressed in this work, however, is that of non-homogenous sub-sampling. As a 1 mL aliquot was taken from the sample bottles for the 2Q Tank 50 analysis, it is impossible to determine if suspended colloids were present in the sub-sample; whereas, another aliquot may not contain an identical condensed-phase mercury composition. Given the limitation of sub-sampling, greater emphasis should be placed on attaining higher dilution and care must be taken in comparing results between laboratories and between sub-sampled aliquots.

Conclusions

A method has been developed to separate and analyze purgeable mercury from high activity tank waste samples at Savannah River Site. The species encompassed by purgeable mercury include dissolved gaseous mercury, suspended colloidal mercury, and dense separate phase mercury. The developed method was optimized using a reduced factorial multivariate experimental optimization and validated internally. Matrix effects were probed by determining the percent recovery of mercury vapor from various matrices. In addition to external calibration, matrix effects were further examined by preparation of a standard addition calibration. No significant difference in recovery or analytical performance was observed between the calibration methods or various matrices. This validated method represents a reduction in sample preparation and sample handling inherent with many standard gaseous mercury method and has been applied to routine high activity tank waste analysis.

Mercury problem at SRS

Current speciation capabilities

Plan of attack for selective DGM and inorganic

Development of extraction

- Multivariate setup
- Multivariate results
- Confirmation of previous work
- Validation results

Application and comparison

- Apply DGM and stannous chloride to tank samples
- Compare with outside lab (maybe use maybe not)

Stannous chloride tests

- Inject methylmercury standard
- Purge and measure
- Inject stannous chloride
- Purge and measure
- Calculate moles of Hg0 that should've been produced
- Calibration using gas standard
- This will let us get a percent reaction from ug that should've been produced vs ug produced
- Only one calibration ever

Results and Discussion

Optimization

Validation in-lab of dgm

Validation in-lab of inorganic

Tank samples for dgm

Tank samples for inorganic

Comparison with eurofins

Future applications and technological development

Reference other mercury papers and discuss total speciation work at srns

Conclusions

References