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# Mercury Speciation and Quantification of Hanford 241-AP-107 Tank Waste Feed and Treated Samples

December 2019

CLH Bottenus
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JR Wood

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

# Summary

This report describes the second phase of a multi-year project to adapt and develop an analytical technique for the low-level determination of total mercury (HgT), elemental mercury ($Hg^0$), and monomethyl mercury (MeHg, hereafter referred to as methyl mercury) in Hanford tank waste[1]. The focus of Phase II was to quantify the mercury (Hg) species – total, elemental, and methyl mercury – from a raw sample and treated (i.e., filtered and cesium-decontaminated) waste samples originating from Hanford waste tank 241-AP-107. The focus of Phase I[2] work was to determine if mercury species can be preconcentrated from aqueous Hanford tank waste solution onto a solid adsorbent while simultaneously eliminating or very significantly reducing the parent radionuclide activity. This was demonstrated by developing protocols for the preparation, separation, and collection of total mercury and methyl mercury onto solid adsorbents, then measuring the adsorbents for radiological content at Pacific Northwest National Laboratory's (PNNL's) Radiochemical Processing Laboratory (RPL) on the Hanford Site. During Phase II, the Hanford tank waste material was preserved, separated (through distillation or digestion), then collected as either solid adsorbents or into liquid distillate form at the RPL and transferred to the PNNL Marine Sciences Laboratory (MSL) in Sequim, Washington, for analysis and quantification. Quantification of total, elemental, and methyl mercury was conducted under radiological control at the MSL using the ultra-trace analytical capabilities available there.

The logistical separation of the RPL facility and the MSL facility required sample shipping protocols and inherently extra waiting time between sample preconcentration and analysis. Prior to tank waste sample measurements, investigations were conducted to address the concerns of methyl mercury sample stability during an extended time. The two options for transferring methyl mercury samples to the MSL for analysis are (1) as a distillate (liquid solution) sample derived from the parent sample, or (2) as methyl mercury stripped from solution followed by ethylation to methylethyl mercury and capture on a Carbotrap®[3]-filled trap. The stability of these two matrices was investigated by studying their respective time course stability. Methylethyl mercury captured on Carbotrap® adsorbent was observed to decrease an average of 4.6% per day over a 9-day waiting period. Methyl mercury in a distillate sample was observed to have a slower loss rate of 0.55% per day over a 9-day observation period. Given the anticipated waiting time between sample separation/collection and analysis of 5-7 days, the methyl mercury recovery would be >96% if the sample is transported as a distillate versus ~68% recovery if transported on the Carbotrap®-filled trap. The total and elemental mercury samples, which were transported to the MSL on gold-coated sand traps, are not known to suffer from the same stability challenges. Past experience of environmental mercury research indicates that mercury collected on gold-coated sand traps remains stable (no loss of mercury) for periods of weeks to months.

Three additional quality assurance investigations were conducted to verify that the environmental mercury analytical methods employed at the MSL could be used for application to mercury speciation of Hanford tank waste and that the comparative performance of these methods was quantified for both facilities. These studies verified acceptable distillation recovery factor for determination of methyl mercury with the distillation system established at the RPL, quantified the performance of the gold-coated

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[1] The determination of mercury species concentration in tank waste is specifically referring to tank waste supernatant.

[2] Fountain MS, SD Branch, and GA Gill. 2018. *Separation and Speciation of Mercury from Hanford 241-AP-107 Tank Waste Supernatant*. PNNL-28067 Rev. 0 (RPT-OSIF-004 Rev. 0). Pacific Northwest National Laboratory, Richland, Washington.

[3] Carbotrap is a registered trademark of Sigma Aldrich Co. LLC.

sand traps between the two facilities, and quantified the performance of the Carbotrap®-filled traps between the two facilities.

Total mercury was determined, in replicate, in the raw, filtrate, and post ion exchange samples of AP-107 Hanford tank waste; concentrations averaged 1534 ± 115, 1050 ± 64.8, and 745 ± 56.5 ng/L, respectively. The total mercury concentration of the raw feed sample, 1534 ng/L, is well supported by a method detection limit of 20 ng/L. This is comparable in magnitude to the < 2200 ng/L reported by 222-S Laboratory based on detection limits[1] and indicates that total mercury inventory basis for AP-107 supernatant is conservative and could be reduced.

Processing of the waste feed sample (via filtration and cesium ion exchange) results in removal of significant amounts of mercury from the waste stream; of the mercury present in the raw AP-107 supernatant, 32% was removed by 5-µm filtration, and a further 20% by passing the filtrate through cesium ion exchange using crystalline silicotitanate media. The current flowsheet modeling gives no credit to the filtration and ion exchange unit operations for mercury removal and should consider an update with respect to mercury mass behavior during pretreatment.

Elemental mercury concentrations were significantly lower than total mercury levels while showing more replicate analytical variability. Unlike in the total mercury measurements, there was no clear concentration trend related to tank waste treatments. The raw sample had an elemental mercury concentration of 37 ng/L (one of the raw sample determinations was below the detection limit of 19 ng/L and was not included in the average), the filtrate averaged 19 ng/L, and the post ion exchange averaged 32 ng/L. Analyzing a slightly larger sample volume (~5 mL) for the elemental mercury determinations would boost the analytical signal farther above the detection limit, which would likely help to reduce replicate variability and provide an even more accurate and reliable result. On average, based on the fraction of $Hg^0$/HgT for each of the three tank waste forms, 2.8% of the total mercury was associated with elemental mercury species.

The determination of methyl mercury in Hanford tank waste was not demonstrated due to unusual and unexpected analytical difficulties during the methyl mercury measurement. Nevertheless, all preliminary quality control checks and earlier testing for methyl mercury in the system indicated that the measurement will be successful in future investigations. There is evidence that the issue was related to a flow stoppage that prevented the sample from reaching the analysis column. Test procedures for future work will contain flow tests and coordinated efforts will be made to have multiple samples available for analysis so that backup samples will be available if this or other unforeseen issues arise.

Application of ultra-trace environmental mercury speciation techniques to the analysis of mercury speciation in Hanford tank waste has been clearly demonstrated for total and elemental mercury. Moreover, the ultra-trace techniques have positively demonstrated achievable detectable signals even while working with small parent sample volumes (0.26 and 0.6 mL, volume of parent sample contained in analyzed sample). This work has demonstrated that despite relatively low dilution factors – between 8.3 and 17.5, compared to previous approaches at other U.S. Department of Energy sites that used dilution factors on the order of 100,000-fold or greater – the application of ultra-trace analytical techniques can be quantified in low-level radiological facilities once isolated from parent tank waste.

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[1] Rasmussen, JH. 2019. *Derivation of Best-Basis Inventory for Tank 241-AP-107 as of January 1, 2019.* RPP-RPT-48103, Rev. 11, Washington River Protection Solutions, LLC, Richland, Washington.

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# Acronyms and Abbreviations

| | |
|---|---|
| AFS | atomic fluorescence spectrometer |
| CA | contamination area |
| CST | crystalline silicotitanate |
| CVAF | cold vapor atomic fluorescence |
| DFLAW | direct feed low-activity waste |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| FMP | flowsheet maturation plan |
| FY | fiscal year |
| GC | gas chromatography |
| IPR | initial precision and recovery |
| IX | ion exchange |
| LAW | low-activity waste |
| LAWPS | Low-Activity Waste Pretreatment System |
| MDL | method detection limit |
| MSL | Marine Sciences Laboratory |
| OPR | ongoing precision and recovery |
| PNNL | Pacific Northwest National Laboratory |
| QA | quality assurance |
| R&D | research and development |
| RPL | Radiochemical Processing Laboratory |
| RPP | River Protection Project |
| RTP | Radioactive Test Platform |
| SAL | Shielded Analytical Laboratory |
| SOP | Standard Operating Procedure |
| SRNL | Savannah River National Laboratory |
| SRS | Savannah River Site |
| WAC | waste acceptance criteria |
| WRPS | Washington River Protection Solutions, LLC |
| WTP | Hanford Waste Treatment and Immobilization Plant |
| WWFTP | WRPS Waste Form Testing Program |

# Symbols

| | |
|---|---|
| Au | symbol for gold |
| BrCl | bromine chloride |
| HCl | hydrochloric acid |
| Hg | symbol for mercury |
| $Hg^0$ | elemental mercury species |
| HgT | total mercury species |
| MeHg | monomethyl mercury species (referred to as methyl mercury) |
| $NH_2OH \cdot HCl$ | hydroxylamine hydrochloride |
| $SnCl_2$ | stannous chloride |

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# 1.0 Introduction

## 1.1 Background

The U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State stores 56 million gallons of chemical and radioactive waste stored in underground tanks. DOE's River Protection Project (RPP) mission is scoped to retrieve the tank waste from single-shell tanks, pretreat the waste, and then immobilize it for long-term near-surface geologic disposal. An initial phase of the RPP mission is the Direct Feed Low-Activity Waste (DFLAW) phase, which involves the filtration and cesium decontamination of decanted supernatant liquid before vitrifying the treated low-activity waste (LAW) with glass formers into a glass waste form. The DFLAW flowsheet represents a tracking of mass and concentration of chemicals and radionuclides in the tank waste during retrieval, storage, feed staging, pretreatment, immobilization, and final disposal operations, and includes accounting for all secondary waste streams.

Mercuric nitrate, $Hg(NO_3)_2$, was introduced into the Hanford flowsheet when it was used to catalyze nitric acid dissolution of certain aluminum alloy fuels and to suppress radioiodine volatilization during nitric acid dissolution of short-cooled uranium metal fuel (Kupfer et al. 1999). Inventory estimates, based primarily on Hanford process knowledge, suggest a total mercury inventory of 2100 kg (Kupfer et al. 1999) in the Hanford tank farms. Aside from the obvious human exposure concerns via tank vapors, mercury species in the tank waste liquid and solid fraction pose significant risk to the implementation and execution of the RPP mission due to mercury limits imposed under waste acceptance criteria (WAC), toxicity characteristic leaching procedure restrictions for secondary waste disposal, and air emission permits.

## 1.2 Technical Drivers and Solution Approach

A recent DFLAW feed composition uncertainty evaluation indicated the mercury-to-sodium molarity criterion apparently exceeding the Low-Activity Waste Pretreatment System (LAWPS) WAC for 32 months of the 12-year DFLAW operations phase (Britton 2017). Secondary solid waste disposal considerations and approvals for items such as spherical resorcinol formaldehyde, grouted Effluent Management Facility overheads, and the Hanford Waste Treatment and Immobilization Plant (WTP) LAW melters are highly dependent on identification of retained mercury species, retention characteristics, and the associated impact on discharge and disposal permits. Although no tank waste is currently being processed at Hanford, waste processing is imminent and representative mercury inventory tracking is desired to anticipate and mitigate stack emission and secondary liquid waste disposal issues like those experienced at the Savannah River Site (SRS) (Bannochie et al. 2016, 2017).

Metallic mercury is in dynamic equilibrium with mercuric (i.e., valence state of 2) and mercurous (i.e., valence state of 1) ions under the waste storage conditions at Hanford. The mercury species in the waste solids are unknown and may be waste-specific. The liquid phase mercury is believed to be in the mercury (II) ion form ($Hg^{2+}$). However, mercury detection in supernate has been negligible based on limited aqueous sample data. For example, tank AY-102 sample data showed about 2% of the total mercury inventory coming from the supernate (Cramer 2001) compared to the sludge.

Closure of this mercury inventory and speciation gap can improve the confidence in the WAC-affecting feed mercury inventories during waste processing operations and the conclusions drawn in previous testing of the high-level waste melter and melter off-gas abatement system (Goles et al. 2004) and in the WTP mercury pathway and treatment assessment (Cramer 2001).

A methodology to determine mercury speciation and accurately quantify concentrations while maintaining low mercury detection limits currently does not exist at Pacific Northwest National Laboratory (PNNL) or Hanford. Moreover, the mercury species in the waste solids are unknown and may be waste-specific. Commercial laboratories such as Brooks Applied Laboratories and Eurofins Frontier Global Sciences, Inc. have successfully completed analyses for seven species of mercury for the SRS, but "[t]he species fraction of total mercury measured has ranged broadly from a low of 32% to a high of 146%" (Bannochie and Wilmarth 2016). This uncertainty in speciation and recovery is primarily driven by large sample dilutions to reduce radiological dose and by the separation techniques employed.

The development of an analytical method to separate and speciate mercury from tank waste[1] was undertaken by PNNL while leveraging an existing non-radiological, trace mercury detection technique frequently performed at PNNL's Marine Sciences Laboratory (MSL) in Sequim, Washington. The MSL has developed this mercury analytical method for trace detection of non-radiological mercury in air, water, tissues, and sediments. The ultimate goal of this work is to develop an analytical method to obtain detailed mercury speciation information and update flowsheet modeling assumptions related to mercury partitioning at Hanford.

## 1.3 Previous Phase I Work

In fiscal year (FY) 2018, the first phase of this project was completed to adapt and develop an analytical technique for the low-level determination of total mercury, elemental mercury, and methyl mercury in Hanford tank waste. The focus of Phase I was to determine whether mercury species can be preconcentrated from aqueous Hanford tank waste solution onto a solid adsorbent while simultaneously eliminating or very significantly reducing the parent radionuclide activity. This was demonstrated by developing protocols for the separation and preconcentration of total mercury and methyl mercury onto solid adsorbents, then measuring the adsorbents for radiological content at PNNL's Radiochemical Processing Laboratory (RPL) on the Hanford Site. Detailed discussion and results of the Phase I work are available in Fountain et al. (2018) and summarized below.

Total alpha, beta, and gamma activity were determined for the liquid distillate, Carbotrap®[2]-filled traps used to separate methyl mercury, soda lime trap used to scrub acidic moisture, gold-coated sand traps used to separate total mercury, and glass wool plugs used to retain the adsorbents in the collection columns. The mercury separation techniques significantly reduced the radiological background, enabling more efficient and safer handling with subsequent analyses while maintaining maximum mercury detectability. Decontamination factors for $^{137}$Cs, the only detectible gamma-emitting radionuclide, ranged from $1.79 \times 10^4$ for the liquid distillate, to as high as $2.34 \times 10^8$ for the Carbotrap®-filled trap used to collect methyl mercury. Decontamination factors for total activity showed similar radiological reductions, ranging from $1.70 \times 10^4$ for the liquid distillate to $1.88 \times 10^6$ for the gold-coated sand trap adsorbent used for total (and elemental) Hg analysis. These results demonstrate $^{137}$Cs to be the primary contributor to radiological dose of the separated samples, with very little measured contribution from alpha- and beta-emitting radionuclides.

The mercury content was successfully separated onto stable adsorbents and the radionuclide activity reduction was significant enough that the preconcentrated samples could be subjected to quantification using far less restrictive handling and radiological controls than would be required for the parent sample [i.e., contamination area (CA) fume hood vs. hot cell]. Furthermore, the mercury separation method

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[1] The determination of mercury species concentration in tank waste is specifically referring to tank waste supernatant.

[2] Carbotrap is a registered trademark of Sigma Aldrich Co. LLC.

required no sample dilution, which enabled maximum mercury detectability, while still allowing mercury speciation.

## 1.4 Current Phase II Objectives

The primary goal of Phase II was to quantify the mercury species: total (HgT), elemental ($Hg^0$), and monomethyl mercury (MeHg, hereafter referred to as methyl mercury) from raw feed and treated (i.e., filtered and cesium-decontaminated) tank waste samples originating from Hanford tank 241-AP-107. Multiple supporting test objectives were necessary to ensures that reliable separation and quantification results were obtained.

### 1.4.1 Determination of System Performance

It was necessary to verify that the efficiency/performance of the separation process (distillation and digestion) and collection process (purging) developed for environmental mercury analytical methods and employed at the MSL are translatable to the new systems implemented and used at the RPL to handle the Hanford tank waste samples. Total mercury measurements rely on chemical aided digestion of all Hg species to $Hg^{2+}$, a process independent of facility systems. Both total and elemental samples depend on purging of the elemental mercury form ($Hg^0$) onto gold-coated sand traps using an inert gas for collection. Determining and confirming the efficiency of this collection was essential to validate measurements of mercury concentration in actual tank waste samples. Methyl mercury samples require both a separation step (distillation) of samples where the methyl mercury recovered in the distillate can vary between distillation systems and a purging (collection) step of methylethyl mercury after ethylation of the methyl mercury in the distillate (solution) form onto a Carbotrap®-filled trap. Determination of the distillation efficiency factor for the RPL methyl mercury separation system was necessary to appropriately quantify the analyzed samples at the MSL. Determining and confirming the efficiency of this collection was essential to validate measurements of mercury concentration in actual tank waste samples.

Performance of the two RPL purging processes from solution form to solid adsorbent (i.e. gold-coated sand trap for total and elemental species and Carbotrap®-filled trap for methyl mercury species) was determined using mercury standards purged onto the respective traps using the RPL systems, then transporting the traps to the MSL for analysis and quantification. Performance of the MSL purging process, but using the two MSL systems, was repeated with the same mercury standards and the same gold-coated sand traps and Carbotrap®-filled traps, respectively, again followed by analysis and quantification at the MSL. The normal distillation process uses approximately 50 mL of acidified sample with approximately 40 mL of the sample being recovered into the distillate form. The distillation efficiency (also referred to as distillation recovery factor) was determined through analysis of numerous samples spiked with methyl mercury standard and then distilled using the normal process. At the RPL this was conducted on ten spiked solutions while at the MSL this was determined from an ongoing running average.

### 1.4.2 Determination of Methyl Mercury Stability

The analytical method being developed provides sample preservation, separation and preconcentration/collection in Richland, Washington, and analysis and quantification at the MSL in Sequim, Washington. The wait time (or storage time) between sample preconcentration/collection at the RPL and analysis at the MSL due to transportation was anticipated to be 2-4 days. In a typical methyl mercury analysis at the MSL, the time between purging a sample onto a Carbotrap®-filled trap and analysis was usually less than 3 hours. Due to the longer wait time in this effort there was concern about the stability of methyl mercury (in the form of methylethyl mercury) collected on a Carbotrap®-filled trap. U.S. Environmental Protection Agency (EPA) Method 1630 indicates that the methylethyl mercury collected on a Carbotrap®-filled trap is quantitatively stable for up to 6 hours and must be analyzed within that period (EPA 1998). More recent work by Baya et al. (2013) indicates that methylethyl mercury collected onto solid adsorbents can be stable for up to several months if the sample is kept in the dark and cold (<4 °C). The authors specifically found that methylethyl mercury collected on Carbotrap®-filled trap lost almost 50% of its original amount of methylethyl mercury after storage for 90 days in the dark at -20 °C. It was unclear what, if any, measurable loss of methylethyl mercury would occur during shorter storage periods. The recovery of spiked methyl mercury concentrations on both the Carbotrap®-filled trap and in the distillate form (a proposed alternative option to the solid adsorbent form) was investigated for waiting/ storage times of up to 13 days after separation/preconcentration to assess methyl mercury stability.

### 1.4.3 Determination of Appropriate Sample Size to Avoid Adsorbent Saturation and Determination of Appropriate Calibration Ranges

The concentrations of HgT, $Hg^0$, and MeHg in the Hanford tank waste are currently unknown. This creates two concerns with conducting mercury speciation measurements. First, it was difficult to determine the most appropriate mass or volume of sample to be collected for analysis, such that the signal produced would be within a typical calibration range and the instrument sensitivity adjustment, thereby providing a reliable quantification. Second, there was concern that if the mass of mercury recovered was significantly above the levels normally collected on a solid adsorbent for analysis, it was possible that the solid adsorbents would become saturated, resulting in a biased measurement. To address this concern, three different mercury mass samples were analyzed for total mercury content by using different volumes, nominally 0.01, 0.1, and 1 mL, each with the same mercury concentration. This approach assessed whether saturation was occurring based on maximum mercury concentration (i.e., total mercury). If no saturation was observed, all three sample volumes would yield identical results within experimental error. Once initial determinations of the concentrations of the various Hg species were made, the volume taken for subsequent analyses could be adjusted to an appropriate sample size.

### 1.4.4 Determination of Total, Elemental, and Methyl Mercury in Hanford Tank Waste Feed and Treated Samples

In future work, Hanford tank waste samples originating from AP-107 will be analyzed for total, elemental, and methyl mercury content. Samples for total and elemental mercury will be purged onto gold-coated sand traps and measured using cold vapor atomic fluorescence (CVAF) spectrometry. Samples for methyl mercury will be evaluated for measurement in solution or purged onto Carbotrap®-filled traps, then measured using CVAF. New equipment performance assessments were conducted for the separation systems in Richland, Washington, at the RPL.

This current work scope completes proposed activities described in the flowsheet maturation plan (FMP), FMP-WASTE-16, "Mercury Speciation and Inventory in Tank Farms During Storage, Waste Treatment, and Secondary Waste Abatement," which is provided as an attachment to the *One System River Protection Project Integrated Flowsheet Maturation Plan* (Britton et al. 2018). FMP-WASTE-16 highlights PNNL's continued efforts to provide Washington River Protection Solutions, LLC (WRPS) baseline technical support to the One System RPP Mission Integration team and illustrates PNNL's broader mission to help identify and close flowsheet model and operations gaps and realize opportunities to reduce the waste treatment mission cost, schedule, and technical risk associated with the One System RPP Integrated Flowsheet. Gaps and opportunities are documented in Britton et al. (2018) and solution approaches are proposed and declared in associated FMPs contained in its appendices.

## 2.0 Quality Assurance

This work was conducted with funding from WRPS under PNNL project 71351, contract 36437-239, with the title “Tank Waste Disposition Integrated Flowsheet Support.”

All research and development (R&D) work at PNNL is performed in accordance with PNNL’s Laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level “Applied Research” and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received appropriate technical and QA training prior to performing quality-affecting work.

# 3.0 Hanford Raw and Treated Tank Waste Samples

This project used raw and treated (i.e., filtered and cesium-decontaminated) samples of 241-AP-107 (hereafter referred to as AP-107) tank waste obtained for and treated by PNNL's Radioactive Test Platform (RTP), located in the Shielded Analytical Laboratory (SAL) hot cells within the Radiochemical Processing Laboratory (RPL). The RTP provides representative lab-scale waste processing unit operations to demonstrate filtration, cesium decontamination by ion exchange (IX), and immobilization by vitrification. In the current RTP configuration, the composited AP-107 supernatant liquid was filtered using a Mott grade 5 (i.e., ~5 μm pore size) sintered metal dead-end filter and cesium-decontaminated via IX using crystalline silicotitanate (CST) media. Three sample types (forms) were obtained and designated as raw, filtered, and cesium-decontaminated samples for subsequent analytical separation and quantification of total mercury, elemental mercury, and methyl mercury content. The following sections detail the origin, handling, preservation, separation, analysis, and quantification of each waste sample form. Furthermore, recommended changes/improvements for future sample handling and preservation are captured, and Savannah River National Laboratory (SRNL) sample handling techniques are referenced for comparison.

## 3.1 AP-107 Raw Tank Waste Sample

The AP-107 tank waste supernatant samples were shipped directly to the RPL from AP Tank Farm during December 2018 and January 2019 in two shipments of 18 glass sample bottles for a total of 36 bottles, nominally 270 mL each (Fiskum et al. 2019; Geeting et al. 2019). The samples were removed from their shielded transportation packages and transferred into SAL on January 3, 2019, and stored in flint glass jars with polytetrafluoroethylene-lined thermoset screw caps.[1] Due to the volatility of elemental mercury ($Hg^0$), loss to the gas phase was mitigated as much as is feasible by handling samples in tightly capped clear glass containers and reducing headspace in storage vessels prior to subsequent sample aliquots and preservations. Physical, chemical, and radionuclide properties of the AP-107 supernatant were measured and reported in Fiskum et al. (2019) and Geeting et al. (2019).

On March 18, 2019, a 2-mL volume was transferred from one of the raw AP-107 sample bottles (source label: 7AP-18-36; $\rho = 1.2586$ g/mL) into a scintillation vial (labeled OG-01) within the SAL hot cell and subsequently transferred to a radiological CA fume hood in the RPL 309. The OG-01 sample was a clear, intense yellow solution with no precipitates observed. After moving into the CA fume hood, the sample was immediately subsampled for preservation and analyses of mercury species, described in the subsequent section.

### 3.1.1 Subsampling and Preservation

The raw AP-107 tank waste sample, labeled OG-01, was subsampled in three 0.6-mL parent sample aliquots into borosilicate vials with polypropylene cone lined cap, each containing 5 mL of high-purity deionized water (>18 MΩ of known low mercury content). The subsamples were labeled UF-01 (designated for separation of total mercury), UF-02 (designated for separation of elemental mercury), and UF-03 (designated for separation of methyl mercury). The subsamples were treated to preserve mercury content and optimize separation of the desired mercury species.

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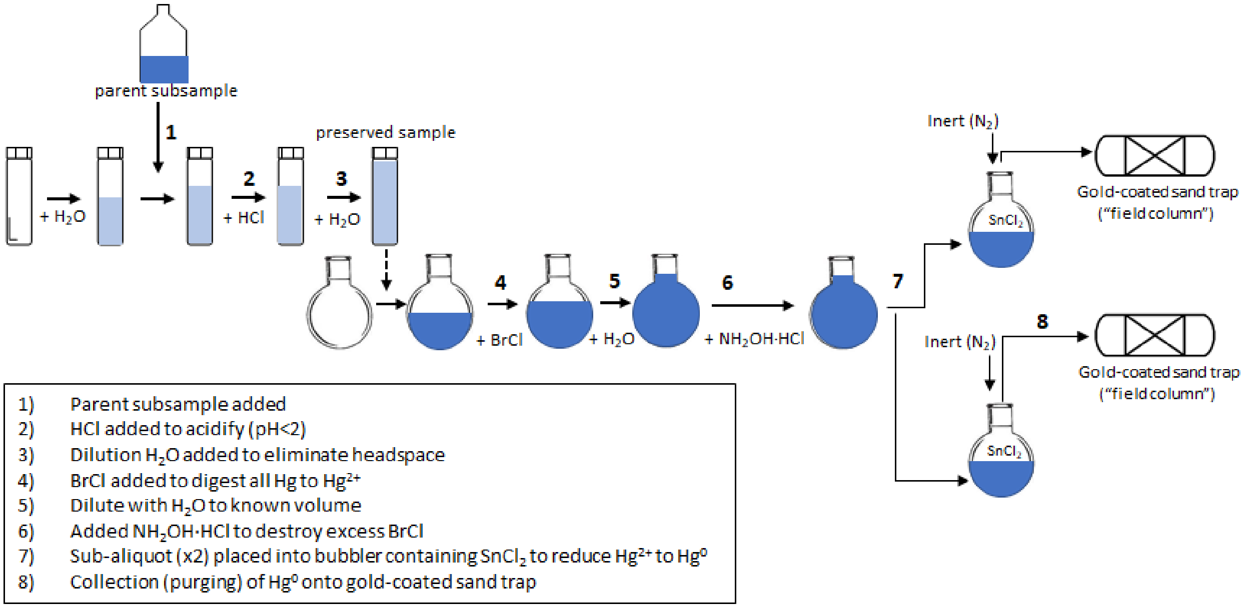
[1] Volume of flint glass jars was not documented. Procedures will be changed such that all volumes are tracked in future work.

#### 3.1.1.1 Total Mercury Preservation and Preparation (UF-01)

Environmental samples for which total mercury analyses are desired need to be treated with a strong oxidant to liberate mercury from organic complexes and particulates prior to preconcentration. Though there are several methods for sample preservation, the method to preserve total mercury used for this work was acidification to pH ~2[1] using concentrated hydrochloric acid (HCl). After acidification, the sample can be stored at room temperature for up to 6 months per EPA Method 1631 guidance (EPA 2002). Figure 1 depicts a flowchart of the total mercury sample preservation and preparation. The figure also demonstrates the follow-on mercury species separation protocols that are discussed later in Section 5.0.



1) Parent subsample added
2) HCl added to acidify (pH<2)
3) Dilution $H_2O$ added to eliminate headspace
4) BrCl added to digest all Hg to $Hg^{2+}$
5) Dilute with $H_2O$ to known volume
6) Added $NH_2OH·HCl$ to destroy excess BrCl
7) Sub-aliquot (x2) placed into bubbler containing $SnCl_2$ to reduce $Hg^{2+}$ to $Hg^0$
8) Collection (purging) of $Hg^0$ onto gold-coated sand trap

Figure 1. Total mercury sample preservation, preparation, and separation flowchart at the RPL.

The AP-107 raw tank waste sample (UF-01) received 0.104 mL concentrated HCl to neutralize the strong base of the parent solution. The sample immediately formed an off-white precipitate that appeared to float at the top of the solution. The sample was left to equilibrate completely. After ~72 hours, the precipitate had dissolved, resulting in a clear, colorless solution. The sample was measured to have a pH of ~2, then received enough deionized water to reduce headspace in the sample vial (~2.3 mL), bringing the overall volume to ~8 mL. The preserved sample was then stored at ambient CA fume hood conditions for 3 months until time of digestion using BrCl.

Approximately 24 hours before isolation of total mercury, the sample UF-01 was transferred to a 10-mL volumetric flask to obtain a known volume. A BrCl reagent [2.5% (w/v), Brooks Rand Instruments, Seattle, Washington, USA] was added in 0.5-mL aliquots and allowed to react until a yellow color persisted after a minimum of 12 hours – indicative of all mercury species in the sample having been oxidized to inorganic $Hg^{2+}$, with a leftover of unreacted BrCl. The sample required 1.75 mL BrCl reagent

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[1] Because the tank waste samples are highly basic ($[OH^-]$ ~1 M), excess acid will be needed to first neutralize the strong base, prior to acidification, to the level needed for preservation. To neutralize 1 mL of tank waste, containing 0.001 mol of strong base (1 M = 0.001 mol/mL), requires addition of 0.0862 mL (86.2 µL) of concentrated hydrochloric acid (HCl): x mL of conc. acid = [(0.001 mol of strong base) (1 mL of conc HCl)] / (0.0116 mol of $H^+$ per mL of conc. HCl) = 0.0862 mL or 86 µL of conc. HCl.

to fully oxidize all mercury species present. Once fully oxidized, the sample was again brought to volume with high-purity deionized water (>18 MΩ of known low mercury content) to eliminate headspace in the vial. In preparation for mercury separation, the sample was transferred to a clean vial and received 0.25 mL hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$, 30% w/v) to destroy any unreacted BrCl, bringing the solution back to a clear, colorless appearance. A 0.25-mL aliquot of stannous chloride[1] ($SnCl_2$; 20% w/v) solution was then added to the sample to reduce inorganic $Hg^{2+}$ to gaseous elemental $Hg^0$, bringing the overall volume to ~10.5 mL, with a dilution factor of ~17.5. The sample was then used as described in Section 5.1 for analytical separation of total mercury onto a gold-coated sand adsorbent.

### 3.1.1.2 Elemental Mercury Preservation (UF-02)

The major concern with sample preservation for the analysis of elemental mercury is to prevent the elemental mercury from de-gassing during extended sample storage. De-gassing is minimized by completely filling the sample storage bottle so that there is no or minimal headspace. Glass is the best storage container to prevent de-gassing. Plastic, and to a lesser extent Teflon, storage bottles are not suitable as storage containers as they will permit gas exchange, albeit only very slowly. Figure 2 is a flowchart of the elemental mercury sample preservation and preparation. The figure also demonstrates the follow-on mercury species separation protocols that are discussed later in Section 5.0.

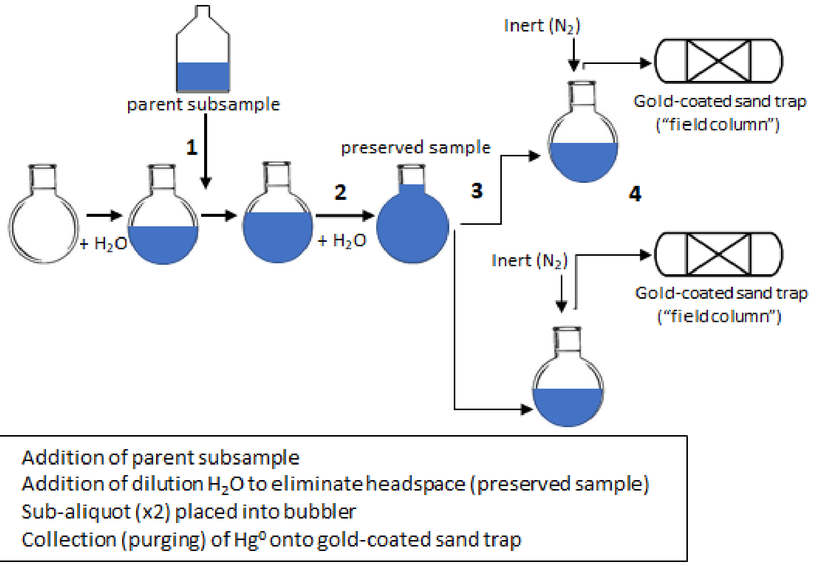

Figure 2. Elemental mercury sample preservation, preparation, and separation flowchart at the RPL.

The AP-107 raw tank waste sample (UF-02) received enough high-purity deionized water (>18 MΩ of known low mercury content) to eliminate as much headspace as was feasible (~2.4 mL). The vial was capped tightly to avoid gaseous diffusion of mercury out of the remaining headspace. The preserved sample was then stored (April 15 – July 16, 2019) prior to use for separation. For analytical separation of elemental mercury onto a solid adsorbent, the sample was brought to known volume in a 10-mL volumetric flask with high-purity deionized water (>18 MΩ of known low mercury content) to bring the dilution factor to ~16.7. The sample was then used as described in Section 5.1 for analytical separation of total mercury onto a solid adsorbent.

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[1] During preservation, 0.25 mL of $SnCl_2$ was mistakenly added directly to the sample; standard procedure was to add the $SnCl_2$ to the bubbler just prior to analysis (which was followed, as discussed in Section 5.0).

#### 3.1.1.3 Methyl Mercury Preservation (UF-03)

Aqueous environmental sample preservation for methyl mercury analysis requires the addition of concentrated HCl (trace metal grade) within 48 hours of sample collection to stabilize the methyl mercury in solution (EPA 1998). While Hanford tank waste samples are clearly not environmental samples, adding HCl as a preservative was prudent to be consistent with established environmental sampling and analysis protocols. Acidification of the sample is also necessary for the distillation step of the analytical separation procedure (Section 4.0). The procedure used for preserving environmental samples for methyl mercury analysis is to add 5 mL of trace metal grade HCl per liter of sample to achieve a 0.5% solution.[1] The pH of a 0.5% HCl[2] solution should be approximately 1.2. Based on the MSL experience, the pH of the solution for isolation of methyl mercury can be ≤2. Figure 3 is a flowchart of the methyl mercury sample preservation and preparation. The figure also demonstrates the follow-on mercury species separation protocols that are discussed later in Section 5.0.

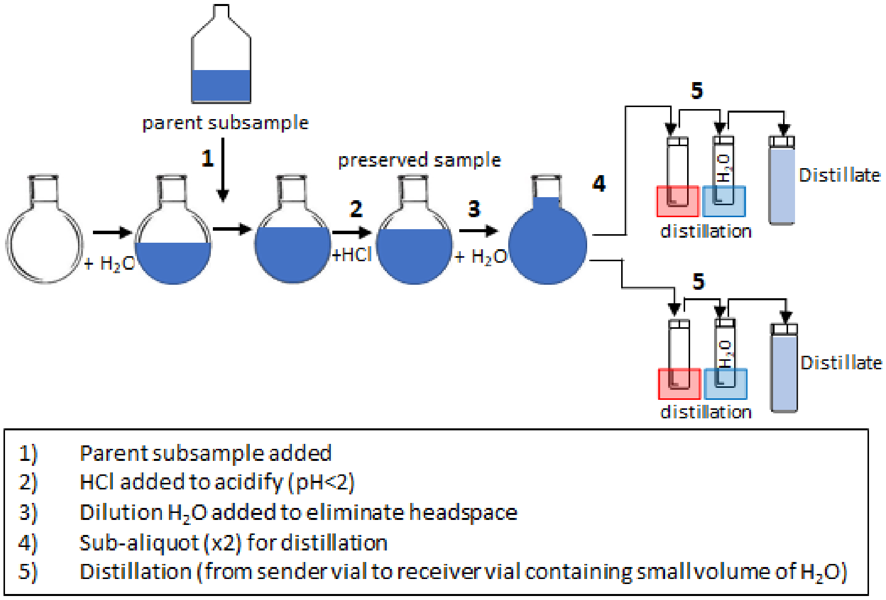

Figure 3. Methyl mercury sample preservation, preparation, and separation flowchart at the RPL.

The sample UF-03 received 0.104 mL of concentrated HCl to acidify the tank waste[3]. The sample immediately formed an off-white precipitate that appeared to float at the top of the solution. The sample was left to equilibrate for ~72 hours, after which a clear, colorless solution remained. The sample was measured to have a pH of ~2 (checked using pH paper). The sample received enough deionized water to eliminate headspace in the vial (~2.3 mL), was capped tightly to avoid gaseous diffusion of mercury out of the headspace, and was then stored (April 15 – July 15, 2019) in light conditions (i.e., not in the dark).

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[1] MSL-I-014. *Methylmercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-014, Rev 09. 2011. Document is not publicly available.

[2] Thirty-six percent hydrochloric acid (concentrated HCl) has a molarity of 11.65 mol of $H^+$/L of acid or 0.0116 mol of $H^+$ per mL of conc. HCl. Hence, adding 5 mL of acid to 1 L of pure water has a molarity of 0.0582 and a pH of 1.23; (11.65 mol/L) (0.005 L) = 0.0582 M; -log (0.0582 ) = 1.23 pH.

[3] Because the tank waste samples are highly basic ([$OH^-$] ~1 M), excess acid will be needed to first neutralize the strong base, prior to acidification, to the level needed for preservation. To neutralize 1 mL of tank waste, containing 0.001 mol of strong base (1 M = 0.001 mol/mL), requires addition of 0.0862 mL (86.2 µL) of concentrated hydrochloric acid (HCl): x mL of conc. acid = [(0.001 mol of strong base) (1 mL of conc HCl)] / (0.0116 mol of $H^+$ per mL of conc. HCl) = 0.0862 mL or 86 µL of conc. HCl.

For analytical separation of methyl mercury, the sample was brought to a known volume in a 10-mL volumetric flask with high-purity deionized water (>18 MΩ of known low mercury content) bringing the DF to ~16.7, and used as described in Section 5.2.

## 3.2 AP-107 Filtered Tank Waste Sample

The RTP in SAL was configured to filter suspended solids from the raw AP-107 tank waste using a dead-end Mott grade 5 (~5-µm pore size) sintered metal filter. The RTP filtration work was completed in the first week of April 2019. A 10-mL sample volume of the filtrate (source label: DEF-3; ρ = 1.264 g/mL) from the RTP testing was obtained on April 11, 2019, and transferred to a 20-mL glass vial (labeled OG-02) before removal from the SAL hot cells into the RPL 309. The sample was an intense yellow, clear solution with no precipitates observed. The sample was stored in secondary containment for contamination control until the time of subsampling and preservation.

### 3.2.1 Subsampling and Preservation

The AP-107 filtered tank waste sample (OG-02) was subsampled as three 3.0-mL aliquots into 20-mL scintillation vials on April 15, 2019, each containing 15 mL of high-purity deionized water (>18 MΩ of known low mercury content). The subsamples were labeled MF-01 (designated for separation of total mercury), MF-02 (designated for separation of elemental mercury), and MF-03 (designated for separation of methyl mercury).

#### 3.2.1.1 Total Mercury Preservation and Preparation (MF-01)

The AP-107 filtered tank waste supernatant sample (MF-01) received 0.259 mL of HCl[1] solution to acidify the tank waste to pH~2. After ~72 hours, the sample formed an off-white precipitate in yellow solution. Additional HCl was added, dropwise (additional 10 drops), and allowed to equilibrate, though the sample remained yellow with white precipitates and solution was still extremely basic. To prevent further dilution, the sample was stored (April 15 – June 24, 2019) in light conditions at ambient CA fume hood conditions prior to digestion using BrCl as an oxidant. Refer to Figure 1 for details of the sample preservation and preparation implemented.

To digest the sample in preparation for analytical separation, 3 mL BrCl was added (in 0.5-mL aliquots) to the solution before transferring to a larger glass vessel to accommodate additional volume. An additional 3.5 mL BrCl (in 0.5-mL aliquots) was added to the vessel. During the incremental additions of BrCl, the sample turned into a faint yellow opaque solution with intense bubbling. The sample needed to be transferred to a larger vessel, resulting in a small loss of solution. After the bubbling ceased, the sample had formed fine-white precipitates. At the conclusion of BrCl addition, the final solution was an intense yellow, slightly opaque solution, indicating the oxidation of all mercury species to inorganic $Hg^{2+}$. The sample was then transferred to a 25-mL volumetric flask and brought to volume with high-purity deionized water (>18 MΩ of known low mercury content), bringing the dilution factor to ~8.6. The sample was stored in the volumetric flask until preparation for mercury separation, in which 0.25 mL $NH_2OH \cdot HCl$ was added to the sample and mixed to destroy any unreacted BrCl. The resulting solution was a clear, colorless solution. The sample was then used as described in Section 5.1 for analytical separation of total mercury onto a solid adsorbent.

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[1] Because the tank waste samples are highly basic ($[OH^-]$ ~1 M), excess acid will be needed to first neutralize the strong base, prior to acidification, to the level needed for preservation. To neutralize 1 mL of tank waste, containing 0.001 mol of strong base (1 M = 0.001 mol/mL), requires addition of 0.0862 mL (86.2 µL) of concentrated hydrochloric acid (HCl): x mL of conc. acid = [(0.001 mol of strong base) (1 mL of conc HCl)] / (0.0116 mol of $H^+$ per mL of conc. HCl) = 0.0862 mL or 86 µL of conc. HCl.

#### 3.2.1.2 Elemental Mercury Preservation and Preparation (MF-02)

The AP-107 filtered tank waste supernatant sample (MF-02) received enough high-purity deionized water (>18 MΩ of known low mercury content) to eliminate as much headspace as was feasible (~2 mL). The vial was capped tightly to avoid gaseous diffusion of mercury out of solution and into the remaining headspace. The sample was then stored (April 15 – July 16, 2019) in light conditions at ambient CA fume hood conditions. For analytical separation of elemental mercury onto a solid adsorbent, the sample was transferred to a 25-mL volumetric flask and brought to a known volume with high-purity deionized water (>18 MΩ of known low mercury content), bringing the dilution factor to ~8.3. The sample was then used as described in Section 5.1 for analytical separation of total mercury onto a solid adsorbent. Refer to Figure 2 for details of the sample preservation and preparation implemented.

#### 3.2.1.3 Methyl Mercury Preservation and Preparation (MF-03)

The AP-107 filtered tank waste supernatant sample (MF-03) received 0.259 mL of concentrated HCl[1] to acidify the tank waste and was left to equilibrate. After ~72 hours, the sample was observed to be a strong yellow with white precipitates. Additional HCl was added, dropwise (additional 10 drops), and allowed to equilibrate, though the sample remained yellow with white precipitates. The sample was then stored (April 18 – June 24, 2019) until further actions could be considered. Refer to Figure 3 for details of the sample preservation and preparation implemented.

On June 25, 2019, the pH of the sample solution was checked and found to be too basic (pH ~14); therefore, HCl was added dropwise until the sample reached a pH of ~2. The sample then had the appearance of an off-white, opaque solution. The sample was then stored (June 25 – July 17, 2019) in light conditions at ambient CA fume hood conditions prior to distillation. For analytical separation of methyl mercury, the sample was brought to known volume in a 25-mL volumetric flask with high-purity deionized water (>18 MΩ of known low mercury content), bringing the DF to ~8.3, and used as described in Section 5.2.

## 3.3 AP-107 Cesium-Decontaminated Tank Waste Sample

After the lab-scale filtration unit operations via the RTP, cesium IX using CST media was performed and a ~15 mL cesium-decontaminated AP-107 supernatant sample volume was obtained. On July 3, 2019, the cesium-decontaminated (hereafter referred to as “post-IX”) sample (source label: EEF-7; ρ = 1.26 g/mL) was transferred into a 20-mL glass vial (labeled OG-03). The post-IX sample was an intense yellow, clear solution with no precipitates observed. The sample was immediately subsampled and preserved as described in the following sections.

### 3.3.1 Subsampling and Preservation

The post-IX sample (OG-03) was subsampled on July 3, 2019, into three 3.0-mL aliquots and transferred into 8-mL borosilicate vials, each containing 2 mL of high-purity deionized water (>18 MΩ of known low mercury content). The subsamples were labeled IX-01 (designated for separation of total mercury), IX-02 (designated for separation of elemental mercury), and IX-03 (designated for separation of methyl mercury).

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[1] Because the tank waste samples are highly basic ([OH$^-$] ~1 M), excess acid will be needed to first neutralize the strong base, prior to acidification, to the level needed for preservation. To neutralize 1 mL of tank waste, containing 0.001 mol of strong base (1 M = 0.001 mol/mL), requires addition of 0.0862 mL (86.2 µL) of concentrated hydrochloric acid (HCl): x mL of conc. acid = [(0.001 mol of strong base) (1 mL of conc HCl)] / (0.0116 mol of H$^+$ per mL of conc. HCl) = 0.0862 mL or 86 µL of conc. HCl.

#### 3.3.1.1 Total Mercury Preservation and Preparation (IX-01)

The AP-107 post-IX sample (IX-01) received 0.259 mL concentrated HCl, to acidify the waste sample and was left to equilibrate. After ~2 hours the sample turned to a clear colorless solution. The preserved sample was then stored in light conditions (July 3 – July 15, 2019) until time of digestion using BrCl as the oxidant. Refer to Figure 1 for details of the sample preservation and preparation implemented.

Prior to digestion, the sample reverted to a clear, intense yellow solution and formed flaky green solids that collected at the bottom of the vial. A total of 5 mL BrCl was added in 0.5-mL increments to digest and acidify the sample. During the second 0.5-mL BrCl addition, the sample began bubbling intensely and was transferred to a 25-mL volumetric flask to prevent the sample from bubbling over and out of the sample vial. After the addition of 2 mL BrCl, the bubbling stopped, leaving a colorless solution with no observed solids. At 5 mL BrCl added, a clear, intense yellow solution with a light green tint persisted, indicating all mercury in the sample had been oxidized to inorganic $Hg^{2+}$, leaving unreacted BrCl in the solution. After ~24 hours, the greenish-yellow color persisted, and the sample was brought to volume with high-purity deionized water (>18 MΩ of known low mercury content), bringing the DF to ~8.4. In preparation for mercury separation, 0.25 mL $NH_2OH \cdot HCl$ was added to the sample and mixed to destroy any unreacted BrCl. The resulting solution was a clear, colorless solution with a light green tint. The sample was then used as described in Section 5.1 for analytical separation of total mercury onto a solid adsorbent.

#### 3.3.1.2 Elemental Mercury Preservation and Preparation (IX-02)

The AP-107 post-IX (IX-02) received enough high-purity deionized water (>18 MΩ of known low mercury content) to eliminate as much headspace as was feasible (~3 mL). The vial was capped tightly to avoid gaseous diffusion of mercury out of the remaining headspace. The sample was then stored (July 3 – July 16, 2019) in light conditions at ambient CA fume hood conditions. For analytical separation of elemental mercury onto a solid adsorbent, the sample was brought to known volume in a 25-mL volumetric flask with high-purity deionized water, bringing the DF to ~8.3. The sample was then used as described in Section 5.1 for analytical separation of elemental mercury onto a solid adsorbent. Refer to Figure 2 for details of the sample preservation and preparation implemented.

#### 3.3.1.3 Methyl Mercury Preservation and Preparation (IX-03)

The AP-107 post-IX sample (IX-03) received 0.259 mL of HCl solution to acidify the waste sample and was left to equilibrate. After ~2 hours, the sample turned to a clear, colorless solution. The preserved sample was then stored (July 3 – July 15, 2019) in light conditions until time of distillation. Refer to Figure 3 for details of the sample preservation and preparation implemented.

Upon returning to the preserved sample, it was observed to be a clear, intense yellow solution with flaky green solids collecting at the bottom of the vial. It was observed that the sample was too basic and thus concentrated HCl was added, dropwise, until the pH was ~2. During HCl addition, the solution started bubbling intensely, and the sample needed to be transferred to a larger sample vial. The bubbling stopped as the pH approached ~2. The final solution was a clear solution with a (pale or barely visible) light green tint. For analytical separation of methyl mercury, the sample was brought to known volume in a 25-mL volumetric flask with high-purity deionized water (>18 MΩ of known low mercury content), bringing the final dilution factor to ~8.3. The sample was then used as described in Section 5.2 for analytical separation of methyl mercury onto a solid adsorbent.

## 3.4 Savannah River Preservation Procedure

Researchers at SRNL are also concerned about mercury levels and mercury speciation in the tank waste at the SRS in Aiken County, South Carolina. The SRNL approach to preserving tank waste samples for organo-mercury speciation analysis is to dilute 0.1 mL of raw tank waste into 250 mL[1] of deionized water and then add 1.2 mL of concentrated HCl as a preservative (Boggess et al. 2018). The samples are then stored prior to analysis in a refrigerator at 4 – 6 °C. This procedure results in an initial dilution of 1:2500 and a final HCl concentration of 0.20%. All subsequent mercury speciation measurements are made from this initial preserved sample following additional dilution between 2 and $4 \times 10^6$-fold with deionized water primarily to reduce radiologic dose to meet acceptance limits for radiological operating licenses at commercial facilities conducting the mercury analyses for SRNL. The preservation approach used by PNNL is consistent with SRNL methods, but PNNL uses significantly less dilution and is not constrained by radiological license limits of a commercial facility.

## 3.5 Recommended Changes/Improvements to Sample Handling

The raw AP-107 sample material received from tank farms was opportunistically used in this mercury speciation study and no timing or container requirements were imposed. Target conditions for future sample analyses of mercury consist of the following:

- Request all samples for mercury analysis be collected and stored in glass containers, under minimal headspace, and with Teflon or Teflon-lined caps.
- Immediately transfer bulk tank sample container in the hot cell, obtain subsamples within 48 hours, minimize sample exposure to light, immediately start preservation techniques, and minimize headspace in all samples or stabilize samples such that there are minimum losses of elemental mercury.
- Within the CA fume hood, store samples and subsamples so that light exposure is minimized (i.e., in covered metal cans, boxes, wrapped in aluminum foil, or other).
- Use volumetric flasks to maintain accurate accounting of parent sample dilution.

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[1] Boggess, A. Personal communication, email from A. Boggess (SRNL) to M. Fountain (PNNL), February 25, 2019.

# 4.0 Stability of Mercury Species Collected on Solid Adsorbents or in Distilled Solutions

EPA Method 1631 (EPA 2002), for total and elemental mercury measurements, and Method 1630 (EPA 1998), for methyl mercury, both anticipate and assume separation and quantification activities are co-located and completed within a limited time frame (typically < 1 day). Application of the environmental techniques to determine mercury species in radioactive tank waste required delays between sample separation and sample analyses of several days to a week. The major time constraint was that the initial separation was conducted under radiological control at the RPL in Richland, Washington, followed by shipment of a radiological sample to the MSL in Sequim, Washington, for subsequent mercury quantification. This significant delay can be removed by purchasing new analytical quantification equipment for installation at the RPL, but significant cost savings were realized by using existing equipment and expertise at the MSL. The expected delay due to shipping time between the two facilities is estimated to be 2 – 4 days; however, the time delay from separation until actual quantification could be as long as a week. Therefore, since the samples will be transferred between facilities, it was necessary to demonstrate the stability of the mercury species in their associated forms (i.e., Carbotrap®-filled trap or distillate) to ensure minimal loss or degradation over an extended time. The rest of this section presents the results of the investigation conducted to determine whether there was any loss in mercury signal associated with the analysis delay after separation.

## 4.1 Total and Elemental Mercury Stability

Total (via conversion of all species to elemental) and elemental mercury species were isolated from the aqueous matrix by purging onto a gold-coated sand trap following EPA Method 1631 (EPA 2002). The gold-coated sand traps were then shipped to the MSL for analysis. The EPA method does not provide storage time limits for samples collected on gold-coated sand. While this is clearly not evidence of the stability of elemental mercury collected onto gold-coated sand, it does tacitly suggest that this issue has not arisen as a concern. Past experience of environmental mercury research indicates that mercury collected on gold-coated sand traps remains stable (no loss of mercury) for periods of weeks to months. Additionally, while there is no evidence in the mercury literature of a loss of mercury collected onto gold-coated sand; future work will include stability testing of elemental mercury collected onto gold-coated sand traps.

## 4.2 Methyl Mercury Stability

In contrast to elemental mercury stability, EPA Method 1630 indicates that distillates derived from the raw sample may be stored at room temperature and in the dark for up to 48 hours before analysis and methylethyl mercury collected on a Carbotrap®-filled trap is stable for up to 6 hours (EPA 1998). More recent work by Baya et al. (2013) indicates that methylethyl mercury collected onto solid adsorbents can be stable for several months, if the sample is kept in the dark and cold (< 4 °C). They specifically found that methylethyl mercury collected on Carbotrap®-filled trap lost almost 50% of its original amount of methylethyl mercury after storage for 90 days in the dark at -20 °C. The ability to transport/store samples for a few days to a week is a critical requirement for this project, and understanding the stability associated with short-term storage of samples isolated from the parent sample is fundamental to this effort.

There are two options for transferring methyl mercury samples isolated from the raw sample to the MSL for analysis: as a distillate sample or as methylethyl mercury retained on a Carbotrap®-filled trap.

Investigations were conducted to determine the stability of methyl mercury in these two matrices and sample transfer processes. The results of the stability experiments served to identify which matrix/process was most stable and to generate a mercury concentration loss factor as a function of time to correct final methyl mercury measurements. The distillate samples still contained a radiological dose and needed to be handled appropriately while the loaded Carbotrap®-filled trap have been demonstrated in previous work to contain almost no dose (Fountain et al. 2018). The stability of both means of isolating methyl mercury from the parent sample for shipment was experimentally demonstrated.

### 4.2.1 Stability on Carbotrap®-filled traps

The stability of methyl mercury on Carbotrap®-filled trap was evaluated by following the concentration, as a function of time, of a standard of methyl mercury purged (in the form of methylethyl mercury) onto 10 individual Carbotrap®-filled traps. To avoid having to run a new standard calibration curve with every measurement day, the response of each individual trap was compared to a freshly purged standard (conducted in duplicate), thereby providing a consistent relative response. This comparison method avoided any concerns about changes in instrument sensitivity giving different responses with different time periods. Analytical details for the analysis of methyl mercury (e.g., purge flow-rate, purge time) followed the Standard Operation Procedure (SOP) MSL-I-014,[1] developed at the MSL for the analysis of low-level methyl mercury in aqueous environmental samples. Upon loading with methylethyl mercury the Carbotrap®-filled traps were stored in a refrigerator at < 4 °C before analysis.

#### 4.2.1.1 Preparation of Carbotrap®-filled Traps for the Methyl Mercury Storage Stability Test

The Carbotrap®-filled traps used for this investigation were purchased from Brooks Rand Instruments. Prior to conducting the stability test, all of the Carbotrap®-filled traps were evaluated to give an identical analytical response by CVAF to a fixed amount of methyl mercury loaded onto them. Any trap not giving a response within ± 10% of the overall average was discarded. This “pre-test” of the traps helped to assure that any analytical uncertainty observed within the stability test was likely not the result of a poorly performing Carbotrap®-filled trap.

The stability test was conducted by adding 100 pg of methyl mercury to the Carbotrap®-filled traps, following the ethylation and purging procedures outlined in the MSL SOP MSL-I-014. Fifty µL of a 2 ng/mL methyl mercury standard was added into a sparging vessel using a calibrated and verified digital pipette. Immediately after all the traps were loaded, traps 1 and 2 were analyzed to establish the time-zero response. These two traps were then used as reference traps for subsequent comparison to the stored samples. At each time point, traps 1 and 2 were loaded with fresh methyl mercury by sample ethylation and purging immediately before the next time-point sample was to be analyzed. No verification was conducted to demonstrate that any residual methyl mercury resided on a Carbotrap®-filled trap following a temperature-driven desorption and CVAF detection of its content.

An outline of the nominal timeline of the stability test is given in Table 1.

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[1] MSL-I-014. *Methylmercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-014, Rev 09. 2011. Document is not publicly available.

Table 1. Outline of the Carbotrap®-filled trap stability test

| Storage Time (days) | Analytical Activity (traps to be analyzed) |
|---|---|
| 0 | 1 and 2 (initial response) |
| 0.25 | 1, 2 (freshly loaded), and 3 (stored) |
| 1 | 1, 2 (freshly loaded), and 4 (stored) |
| 2 | 1, 2 (freshly loaded), and 5 (stored) |
| 3 | 1, 2 (freshly loaded), and 6 (stored) |
| 4 | 1, 2 (freshly loaded), and 7 (stored) |
| 7 | 1, 2 (freshly loaded), and 8 (stored) |
| 9 | 1, 2 (freshly loaded), and 9 (stored) |
| 13 | 1, 2 (freshly loaded), and 10 (stored) |

#### 4.2.1.2 Results of Methyl Mercury Stability to Storage on Carbotrap®-filled trap

A plot of the percent recovery of the methyl mercury signals (in the form of methylethyl mercury) with time of storage is given in Figure 4. The percent recovery of methyl mercury is based on the ratio of the signal intensity of the stored sample compared to the signal derived from the average signal intensity of the two freshly loaded reference Carbotrap®-filled traps (i.e., traps 1 and 2) at each point in time. Additionally, a linear fit trendline of the data is provided, where the trendline is forced through 100% recovery. Over the course of the 13-day stability test, there was on average 3.3% loss in methyl mercury per day. If the data point at 13 days is excluded as an outlier (and there is no specific reason to do so other than it does not fall very well on a trendline drawn through the other samples), the loss would be even larger (4.6% per day).

As an added check on the investigation, the reference Carbotrap®-filled traps (traps 1 and 2 as represented in Table 1) were re-loaded after they were used for comparison to the stored sample to determine the repeatability of the reference Carbotrap®-filled traps. The reference traps showed strong repeatability over the nine analysis times, having only a 1.7% variation. Additionally, after each sample column was analyzed it was then also re-loaded and then immediately re-analyzed. These eight re-loaded sample traps also demonstrated a strong repeatability in performance, recovering an average of 99.5% ± 2.4% of the spiked amount immediately after use for the storage test. These tests clearly demonstrate that the Carbotrap®-filled traps were performing as expected and the loss observed with time was not due to bias or changes in instrument response over the storage period.

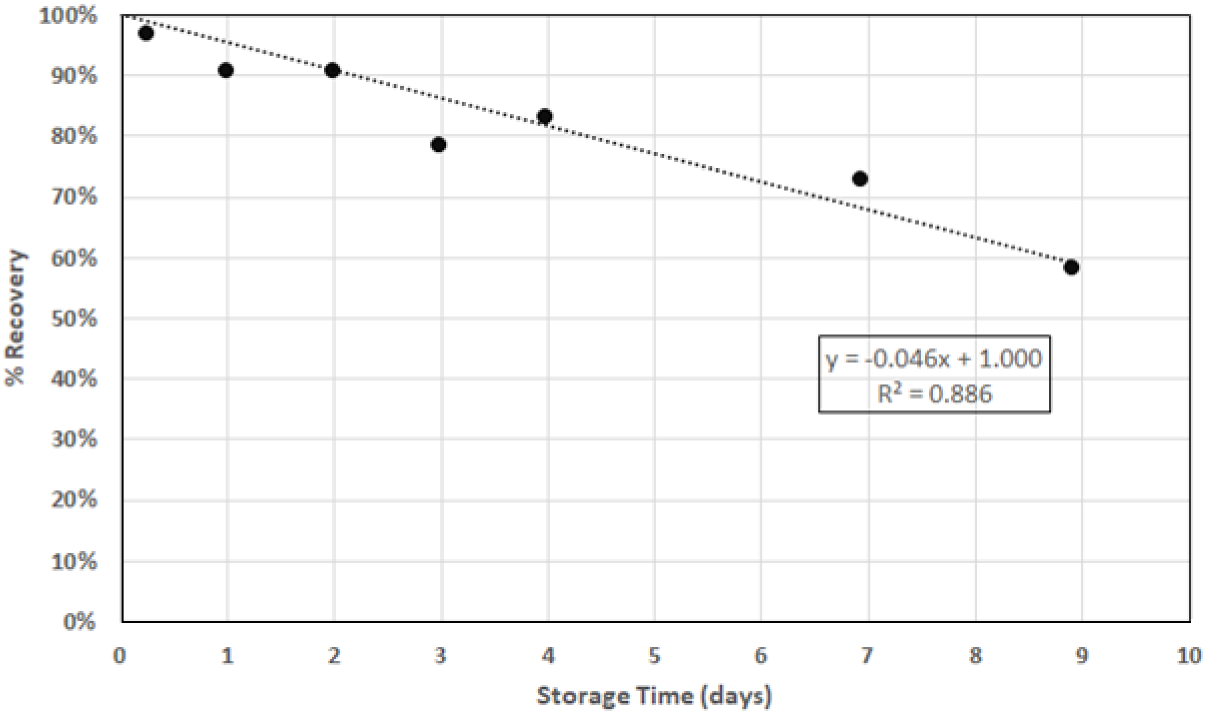

Figure 4. Methyl mercury stability on Carbotrap® adsorbent over time. Percent recovery is based on the ratio of the signal intensity of the stored sample versus the average signal intensity of the freshly loaded reference traps at each time point.

### 4.2.2 Stability in Distillate

The stability of methyl mercury in a distillate sample derived from a raw tank waste sample was evaluated by tracking the concentration of methyl mercury in the distillate of a simulated Hanford tank waste sample. The tank waste simulant was spiked with a known level of methyl mercury, and the samples were distilled and then stored for varying periods before evaluating their methyl mercury content. Daily duplicate samples on day 1, 2, 3, 4, 7, and 11 were used to evaluate the stability of the methyl mercury in the aqueous distillate and the development of a retention curve for correction of methyl mercury loss in a distillate sample with time prior to desorption and analytical quantification.

#### 4.2.2.1 Hanford Tank Waste Simulant

The major ion composition of the Hanford waste tank AP-107 is given in Table 2. A simplified simulant with the final compositions given in Table 3 was prepared using a mixture of sodium salts of nitrate, nitrite, hydroxide, sulfate, phosphate, and chloride. This simulant provided accurate levels of the top six anions, along with an appropriate total sodium content.

Table 2. Major ion composition of supernatant liquid in Hanford waste tank AP-107.[(a)]

| Ion | Target Concentration (g/L) | Target Concentration (M) |
|---|---|---|
| $Na^+$ | 126 | 5.48 |
| $Al^{3+}$ | 9.9 | 0.37 |
| $K^+$ | 3.9 | 0.10 |
| $NO_3^-$ | 106 | 1.70 |
| $NO_2^-$ | 52.6 | 1.14 |
| $OH^-$ | 17.0 | 1.00 |
| $CO_3^{-2}$ | 38.4 | 0.64 |
| $Cl^-$ | 2.52 | 0.07 |
| $SO_4^{-2}$ | 1.5 | 0.016 |
| $PO_4^{-3}$ | 1.6 | 0.017 |

(a) Data are derived from Rovira et al. (2018) and Fiskum et al. (2018).

Table 3. Composition of a simplified simulant to mimic the major anion content of Hanford waste tank AP-107 supernate.

| Salt | Target Concentration (g/L) | Target Concentration (M) |
|---|---|---|
| $NaNO_3$ | 145 | 1.70 |
| $NaNO_2$ | 79.0 | 1.14 |
| $Na_2CO_3$ | 68.0 | 0.64 |
| NaOH | 40.0 | 1.00 |
| $Na_2SO_4$ | 2.3 | 0.016 |
| NaCl | 4.2 | 0.07 |
| $Na_3PO_4$ | 2.7 | 0.017 |
| Total Sodium | 121 | 5.29 |

### 4.2.2.2 Preparation of Distillate Samples for Methyl Mercury Storage Stability Test

One liter of simulated Hanford tank waste aqueous solution was prepared based on Table 3. Two 50-mL aliquots were dispensed from this solution into distillation (sender) vials to serve as duplicate blanks. The remaining 900 mL was then spiked with a methyl mercury standard of known concentration to achieve an overall concentration in the range of 1 – 2 ng/L.[1] The spiked simulant was then dispensed into 14 distillation (sender) vials. The 14 spiked samples along with the two blank samples were distilled into chilled receiver vials to collect the distillate samples following the MSL SOP MSL-I-14, *Methyl mercury*

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[1] Ideally, the spike level used for this test would be very similar to the levels in tank waste. Because the concentration of methyl mercury in Hanford tank waste is not known, a value was chosen that was anticipated to be of the order of possible concentrations. Rasmussen 2019 gives a total mercury concentration of < 2200 ng/L; experience for environmental samples suggests 1% of total mercury being associated with methyl mercury leads to an estimated methyl mercury concentration of (2200 ng/L*0.01) = 22 ng/L. Then with a 10- to 20-fold dilution between parent sample and analyzed sample the analyzed sample concentration was estimated between 1.1 ng/L and 2.2 ng/L (approximately).

*in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF)*, developed at the MSL for the analysis of low-level methyl mercury in aqueous environmental samples. Immediately after distillation, the two blanks and two of the spiked samples were analyzed to establish a time-zero data point. The remaining 12 distillate samples were stored in the dark at ambient lab temperature until analysis. Analytical quantification of the remaining 12 distillate samples took place in pairs over the next 9 days.

#### 4.2.2.3 Results of Distillate Storage Stability for Methyl Mercury

The methyl mercury concentrations of the 12 distillate samples as a function of storage time are shown in Figure 5. A trendline drawn through the data shows that there is a slow loss of 0.552% of methyl mercury per day. Since samples were run in duplicate, there is a qualitative indication of the repeatability of the sample measurements. The determination of methyl mercury has some inherent irreproducibility. To illustrate this, the average relative percent difference (between sample pairs) of the seven sample runs depicted in Figure 5 is 7.6 ± 4.8%.

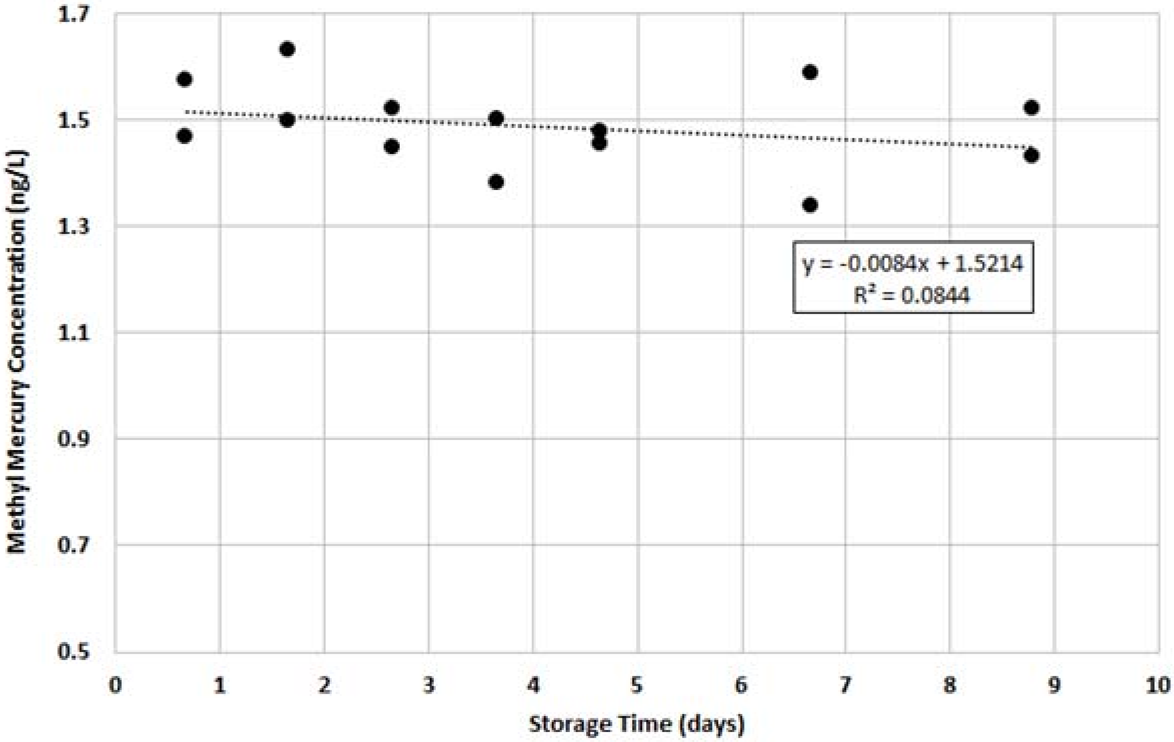

Figure 5. Methyl mercury concentration in distillate over time.

## 4.3 Choice of Methyl Mercury Separation Sample Form for Transport

Separation samples for methyl mercury content were evaluated for stability on Carbotrap® adsorbent and in a distillate liquid form. Both separated sample forms showed losses with storage time. Methyl mercury stored on Carbotrap® adsorbent decreased at 4.6% per day, while the methyl mercury in a distillate form decreased at a slower rate, 0.5% per day. The distillate storage stability tests demonstrated a minimal loss of methyl mercury in the distillate form and were identified as the better means by which the methyl mercury tank waste samples should be transported and stored prior to analytical quantification. For the separated sample transport duration, anticipated to be 2-4 days, methyl mercury sample recovery is expected to be > 98%.

# 5.0 RPL Mercury Species Separation Protocols and System Performance Tests

A goal of this development work was to maximize mercury detection ability through minimal sample dilution while also reducing the radioactive sample dose prior to mercury quantification at the MSL. Significant effort was applied to demonstrate that the mercury separation processes at the RPL were efficient and effective, while at the same time managing and mitigating radiological risk associated with the raw tank waste supernatant sample. Demonstration of the mercury separation processes and radiological dose measurements for various components was documented previously in Fountain et al. (2018). These results were instrumental for anticipating the safe execution of the full process composed of separations at the RPL, sample transport, and quantification at the MSL. However, the mercury separation system constructed in the RPL required several performance checks to quantify new system components and process timing.

The sections below first describe the RPL separation protocol that was followed prior to shipping samples to the MSL for mercury species quantification. The results of the stability experiments served to generate a mercury concentration loss value as a function of time to correct final analytical measurements. Next, the efficiency of the separation processes (distillation and purging) at the RPL were determined using mercury standards. For example, elemental and total mercury measurements rely on purging onto gold-coated sand traps using an inert gas. Determining and confirming the efficiency of this separation and ensuring the tank waste sample size did not saturate the traps were essential to validate measurements of mercury concentration in actual tank waste samples. Similarly, the separation of methyl mercury requires a distillation step where the fraction of available mercury recovered in the distillate (distillation efficiency) can vary between distillation systems. The distillation efficiency factor was determined for the RPL methyl mercury separation system. These performance checks for the RPL separation system are described in detail below.

## 5.1 Total and Elemental Mercury Separation from Parent Tank Waste

The isolation of total mercury was achieved by purging the mercury species from the aqueous waste sample onto a solid adsorbent (i.e., gold-coated sand) using a bubbler, as depicted in Figure 6. The sample was first digested using BrCl along with $NH_2OH \cdot HCl$ added thereafter to digest any remaining and un-reacted BrCl prior[1] to its addition to a bubbler system containing a low concentration of stannous chloride ($SnCl_2$) in water, which serves to reduce the inorganic $Hg^{2+}$ to elemental $Hg^0$. The elemental mercury was then purged from solution with an inert gas ($N_2$ for this work) at a rate of 350 mL/min, passed through an acid-gas moisture trap (i.e., soda lime), and preconcentrated onto a gold-coated sand trap. At this point, the gold-coated sand trap is known to have minimal radiological content based on prior total and gamma activity measurements (Fountain et al. 2018). The entire trap was surveyed out of the CA fume hood, packaged for shipping, and sent to the MSL for mercury quantification.

Since the elemental mercury samples are inherently in the reduced elemental $Hg^0$ form, there is no need for the BrCl digestion and subsequent $NH_2OH \cdot HCl$ addition, nor the need for $SnCl_2$ in the bubbler system. The elemental mercury samples, after dilution to a known volume, were directly added to the bubbler system and then purged from solution with an inert gas ($N_2$ for this work) at a rate of 350 mL/min, passed through an acid-gas moisture trap (i.e., soda lime), and preconcentrated onto a

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[1] For sample UF-01, 0.25 mL $SnCl_2$ was inadvertently added directly to the sample during sample preservation when normally added only to bubbler solution. This resulted in a minor sample dilution.

gold-coated sand trap. At this point, the gold-coated sand trap is known to have minimal radiological content based on prior total and gamma activity measurements (Fountain et al. 2018). The entire trap was surveyed out of the CA fume hood, packaged for shipping, and sent to the MSL for mercury quantification.

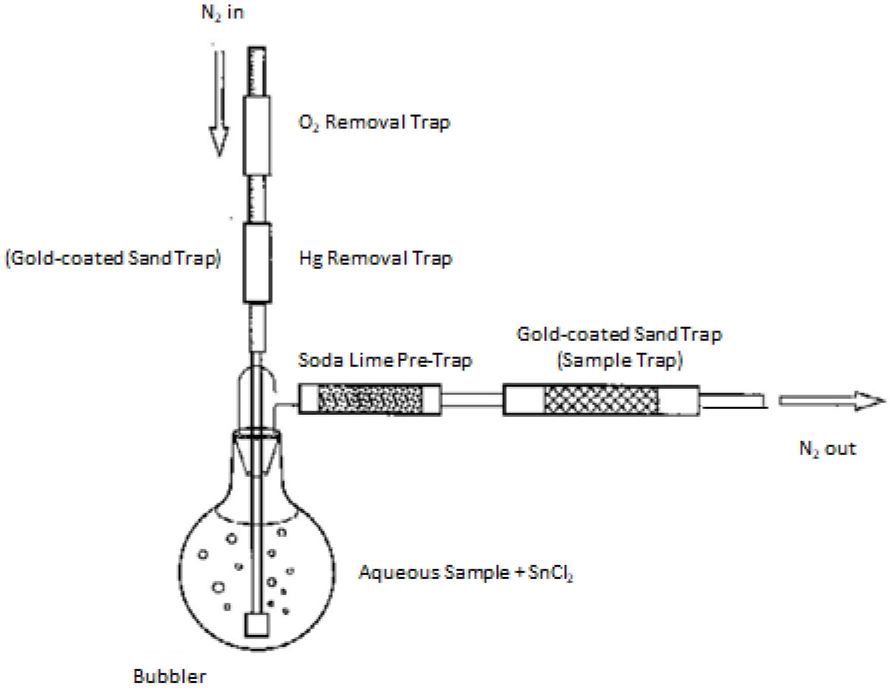

Figure 6. System schematic for total and elemental mercury purging.

## 5.2 Methyl Mercury Separation from Parent Tank Waste

The isolation of methyl mercury species was conducted as a two-fold process: (1) distillation of the sample at the RPL (Figure 7), followed by (2) preconcentration of the methyl mercury species onto a Carbotrap®-filled trap at the MSL (Figure 8). The preserved sample was first distilled at the RPL to produce a less complex matrix by heating and purging the “sender” vial and capturing the condensed liquid in a chilled “receiver” vial. The distillation receiver vial (containing the distillate) was surveyed out of the CA fume hood, packaged for transport, then shipped to the MSL for final separation and quantification of mercury using CVAF spectrometry. Based on prior total and gamma activity measurements, the distillate liquid was demonstrated to have minimal radiological content (Fountain et al. 2018) and could be more safely shipped and handled at the MSL.

For analytical preconcentration at the MSL, the distillate was transferred into a bubbler system containing a dilute acetate buffer (Figure 8). An ethylating reagent (e.g., tetraethyl borate) solution was then added to the bubbler and allowed to react with the sample to convert methyl mercury to a volatilized species, methylethyl mercury. The methylethyl mercury species was then purged from solution using an inert gas ($N_2$ for this work) at a rate of 200 mL/min and trapped onto a Carbotrap®-filled trap adsorbent. At the MSL, methylethyl mercury was then thermally desorbed from the Carbotrap®-filled trap adsorbent and introduced to a CVAF spectrometer for detection.

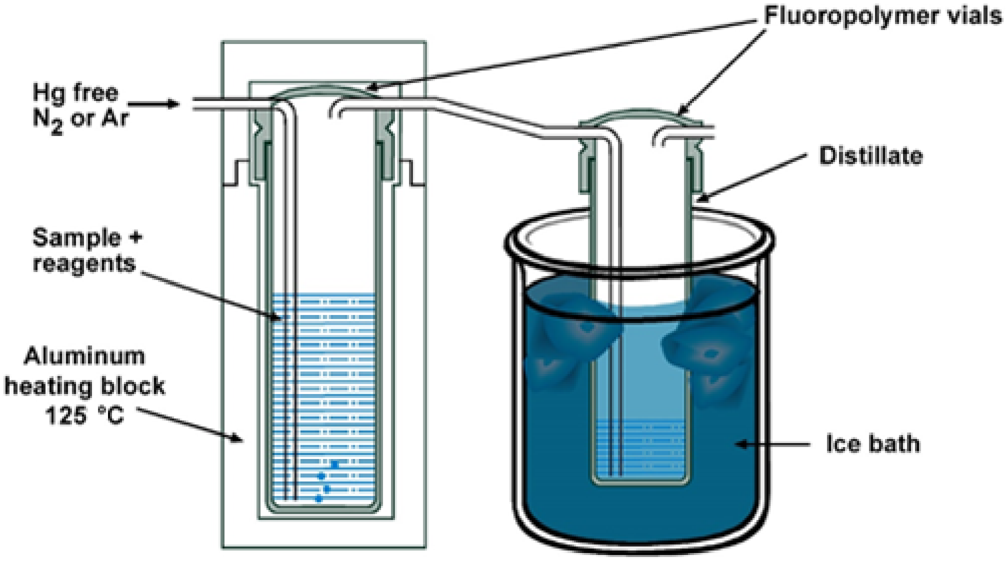

Figure 7. System schematic for methyl mercury distillation.

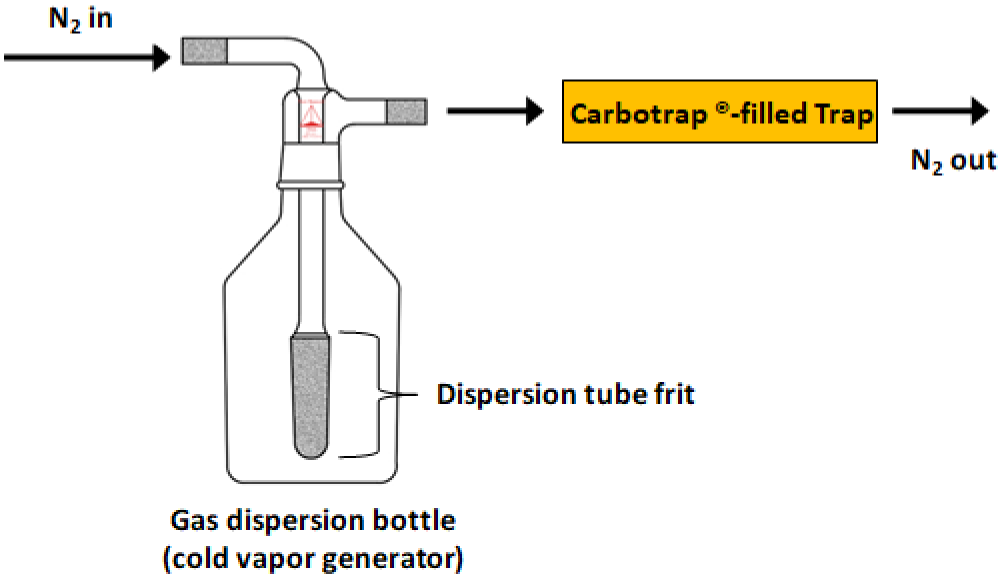

Figure 8. System schematic for methylethyl mercury purging.

## 5.3 Distillation Efficiency

The normal distillation process uses approximately 50 mL of acidified sample with approximately 40 mL of the sample being recovered into the distillation receiver vial pre-charged with 5 mL of high-purity deionized water. Samples should not be completely distilled to avoid taking the sample to dryness and allowing the co-distillation of HCl in the parent sample used as a preservative. Complete distillation would result in a carry-over of the acid content and matrix components of the sample, which could subsequently interfere with the ethylation step. Therefore, all preliminary methyl mercury measurement results should be recovery-corrected with an empirically derived factor (also referred to as the distillation recovery factor) that accounts for this intentional incomplete distillation.

It is standard practice for laboratories conducting methyl mercury measurements to calculate the efficiency of the distillation equipment and protocols used in their laboratory. Typically, this involves a running mean of the last 30 recoveries from measurements of initial and ongoing precision and recovery samples (IPR and OPR, respectively).[1] Individual determinations that are more than two standard deviations from the mean are excluded. Due to the limited scope of this project, it was decided to distill 10 IPR/OPR non-rad samples at the RPL and transfer the distillates to the MSL for analysis, in order to calculate a mean distillation recovery factor for the RPL distillation process. Future IPR/OPR samples would then be used to add to and update the mean distillation recovery factor until the running 30-sample mean can be reached.

### 5.3.1 Preparation of IPR/OPR Samples for Determination of Distillation Efficiency

The IPR/OPR samples for determination of distillation efficiency from the RPL were generated at the MSL using an acidified well water sample that was spiked using a methyl mercury standard (STD 488; [MeHg] = 2.00 ng/mL) with a resulting concentration of 0.5 pg/mL. Ten distilled IPR/OPR samples were prepared at the RPL from the spiked sample according to SOP MSL-I-014 and then returned for analysis at the MSL. Distillates were stored in the dark and at room temperature during storage at the RPL, during transport to the MSL, and while awaiting analysis once at the MSL. Results from the analysis of these 10 samples are summarized in Table 4.

A distillation recovery factor represents the recovery of methyl mercury during distillation. The mean factor was determined from the analysis of 10 samples of an OPR methyl mercury standard. It is important to point out that this calculation is based on the initial volume of raw sample, not the volume of sample that was distilled. Hence, part of the distillation recovery factor determination is based on the initial and final volumes of the sample.

The standard practice for determination of distillation recovery factor is based on distillation to a final distillate volume of 45 mL, including the 5-mL pre-charge of deionized water to the receiver vial. Because this volume was not precisely met in the experimental work, the initial efficiency determinations were normalized to a volume of 45 mL to be compatible with the standard practice used at the MSL (SOP MSL-I-014) and comparable to the distillation recovery factor determined at the MSL. For comparison, the distillation recovery factor at the MSL is determined by the equations

$$DF_r = \frac{[MeHg]_{sample}}{[MeHg]_{OPR}} \times \frac{V_{sample}}{V_{OPR}} \tag{1}$$

$$[MeHg]_{sample} = \frac{PA - BB}{CF_m \times V_{sample}} \tag{2}$$

where $DF_r$ is the distillation recovery factor, $CF_m$ is the mean calibration factor, $V_{sample}$ is the total volume of the receiver vial (distillate volume plus 5 mL deionized water, nominally 45 mL), $V_{OPR}$ is the volume of the sender vial (nominally 50 mL), PA is peak area, BB is bubbler blank in peak area units, $[MeHg]_{OPR}$

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[1] IPR (initial precision and recovery) refers to the first analysis sample (known OPR concentration spike) after the calibration curve has been conducted. OPR (ongoing precision and recovery) refers to all subsequent samples (known OPR concentration spike) after the IPR.

is the concentration of the OPR sample, and $[MeHg]_{sample}$ is the measured concentration of methyl mercury in the distillate.

The mean calibration factor, $CF_m$, was determined from a standard curve using multiple standards spanning the anticipated concentration range for the samples. Quantification of unknowns is based on the mean calibration factor. This method of calibration and unknown concentration determination is based on EPA Method 1630 (EPA 1998) for determination of methyl mercury by CVAF spectrometry. The standard curve used to determine the mean calibration factor was based on five calibrations run from standards ranging between 0.1 and 2.0 pg/µL.

In the case of this work, the samples were distilled at the RPL and then transported to the MSL for analysis several days later; therefore, $DF_r$ [as calculated in Eq. (1)] implies the combined recovery from the distillation process at the RPL in addition to the small loss of methyl mercury that occurs in the distillate with storage (see prior discussion in Section 4.2.2):

$$DF_r = DF_{r(distillation)} \cdot F_{time} \tag{3}$$

$$F_{time} = [1 - t \cdot Loss] \tag{4}$$

where $F_{time}$ is the correction factor associated with the small loss of methyl mercury that occurs with storage time, $t$ is the delay in analysis in days, and *Loss* is the associated degradation of sample in loss per day, which was discussed earlier in Section 4.2.2. $DF_{r(distillation)}$ is the apparent distillation recovery factor had there been no time delay in analysis. Therefore, when samples are analyzed in the same day they are distilled, $DF_{r(distillation)}$ is simply $DF_r$ ($F_{time} = 1$).

Lastly, to remain comparable to the methods used by the MSL to report the ongoing distillation recovery factor, this distillation recovery factor was normalized to 45 mL samples using the following equation:

$$DF_r^* = \left[\frac{DF_r}{1 - t \cdot Loss}\right] \frac{45}{V_{sample}} \tag{5}$$

where $DF_r^*$ is the distillation recovery factor (with loss due to time delay excluded) normalized to 45 mL.

Experimental results demonstrating methyl mercury recoveries from 10 separations on the RPL distillation system are presented in Table 4. The average normalized distillation recovery factor ($DF_r^*$) for the RPL was determined to be 0.831 ± 0.042 with a coefficient of variation of 5.11%. In comparison, the ongoing normalized distillation recovery factor for the MSL was 0.807 ± 0.1651, which was based on the running average of 30 IPR/OPR distillations.

Table 4. Determination of a distillation recovery factor for the RPL from replicate measurements of a well water sample spiked with a low level of methyl mercury.

| Sample Number | Distillate (receiver vial) Sample Volume (mL) | Distillate Storage Time (days) | Methyl Mercury Concentration (ng/L) | Distillation Recovery Factor *not corrected for delayed analysis* ($DF_r$) | Distillation Recovery Factor *corrected for delayed analysis* | Distillation Recovery Factor *normalized to 45 mL* ($DF_r^*$)[(a)] |
|---|---|---|---|---|---|---|
| 1 | 43.730 | 3.64 | 0.427 | 0.740 | 0.785 | 0.807 |
| 2 | 43.571 | 3.64 | 0.443 | 0.773 | 0.819 | 0.846 |
| 3 | 45.281 | 2.77 | 0.434 | 0.787 | 0.822 | 0.817 |
| 4 | 43.953 | 2.77 | 0.476 | 0.836 | 0.874 | 0.895 |
| 5 | 44.543 | 1.88 | 0.427 | 0.771 | 0.794 | 0.802 |
| 6 | 43.052 | 1.88 | 0.475 | 0.826 | 0.851 | 0.889 |
| 7 | 44.650 | 1.88 | 0.472 | 0.837 | 0.862 | 0.868 |
| 8 | 43.216 | 1.69 | 0.443 | 0.775 | 0.796 | 0.829 |
| 9 | 43.217 | 1.69 | 0.429 | 0.746 | 0.766 | 0.798 |
| 10 | 43.491 | 1.69 | 0.414 | 0.719 | 0.738 | 0.764 |
| | | *Average* | *0.444* | *0.781* | *0.811* | ***0.831*** |
| | | *Std. Dev.* | *0.023* | *0.041* | *0.043* | ***0.042*** |
| | | *Coeff. Var.* | *5.10%* | *5.25%* | *5.32%* | ***5.11%*** |

(a) Final methyl mercury distillation recovery factors (DFr*) were corrected for a bubbler blank (not shown here), loss of mercury due to extended storage time before analysis, and lastly normalized to a sample volume of 45 mL.

## 5.4 RPL Sample Recovery Efficiency for Total and Methyl Mercury

Two signal intensity comparison studies were performed, using total and methyl mercury standards on their respective adsorbents (i.e., gold-coated sand and Carbotrap®, respectively), to compare the recovery between traps preconcentrated at the RPL and the same traps preconcentrated and re-analyzed at the MSL. Signal intensity measurements for total mercury and methyl mercury were conducted in triplicate following SOP MSL-I-013[1] and SOP MSL-I-014, respectively. This was done to compare the efficiency of the sample purging and collection system at the RPL to the performance at the MSL. A detailed description of the signal intensity studies and presentation of the results follow in this section.

### 5.4.1 Total Mercury Spiked onto Gold-coated Sand Traps

Three gold-coated sand traps were each loaded with 50 µL of STD 492, ([HgT] = 10 ng/mL) at the RPL as described in Section 5.1. The traps were then transported to the MSL for analysis by thermal desorption and measurement of peak height signal intensity using CVAF detection. The mercury concentrations for the three RPL traps were measured by comparison to a known (average) response factor determined through a six-point calibration curve generated using standards ranging between 0.1 and 10.0 ng/mL. The same gold-coated sand traps were then re-loaded with identical 50-µL STD 492 spikes (this time at the MSL) and re-analyzed for peak height signal intensity and converted to total mercury mass using the response factor.

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[1] MSL-I-013. *Total Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-013, Rev. 13. 2011. Document is not publicly available.

Table 5 outlines the results for these analyses and demonstrates the comparison in signal intensity between the same traps loaded at the two facilities. These results also capture, to a limited extent, the stability of the gold-coated sand trap – the RPL samples were measured 7 days after being preconcentrated with mercury compared to the same traps loaded identically at the MSL and analyzed within 2 hours of being loaded. The study demonstrated an average of 88% recovery from the two RPL-loaded traps (one of the traps loaded at the RPL did not have a peak that could be appropriately quantified) and an average of 91% recovery from the three MSL-loaded traps.

Table 5. Results for gold-coated sand trap signal intensity analysis.

| Sample (Location) | Standard Volume (µL) | Standard Mass (ng) | Signal Intensity (peak height)[a] | Mercury Mass (ng) | % Recovery | Average % Recovery |
|---|---|---|---|---|---|---|
| G-001 (RPL) | 50 | 0.50 | 708848 | 0.448 | 90 | 88 |
| G-002 (RPL) | 50 | 0.50 | poor peak quality | - | - | |
| G-003 (RPL) | 50 | 0.50 | 689308 | 0.435 | 87 | |
| G-001 (MSL) | 50 | 0.50 | 702366 | 0.444 | 89 | 91 |
| G-002 (MSL) | 50 | 0.50 | 795530 | 0.502 | 100 | |
| G-003 (MSL) | 50 | 0.50 | 662742 | 0.419 | 84 | |

(a) Final signal intensities were corrected for bubbler blank (not shown here).

### 5.4.2 Methyl Mercury Spiked onto Carbotrap®-filled traps

Three Carbotrap®-filled traps were each loaded with 50 µL of STD 488 ([MeHg] = 2.0 ng/mL) at the RPL as described in Section 5.2, with the exclusion of the distillation step. The traps were then transported to the MSL for analysis by thermal desorption and measurement of peak height signal intensity using CVAF. The signal intensity was compared to a known (average) response factor (based on a standard curve set by five standards) and used to determine the concentration of methyl mercury. The same Carbotrap®-filled traps were then re-loaded with identical 50-µL STD 488 spikes (this time at the MSL) and re-analyzed for peak height and mercury mass.

Table 6 outlines the results for these analyses and demonstrates the comparison in signal intensity between the same traps loaded at the two facilities. These results also capture, to a limited extent, the stability of the Carbotrap® adsorbent. The RPL samples were measured 1 day after preconcentration occurred, while the MSL samples were measured within 2 hours of loading. The study demonstrates an average of 85% recovery from the three RPL-loaded traps and an average of 98% recovery from the three MSL-loaded traps.

Table 6. Results for Carbotrap®-filled trap signal intensity analysis.

| Sample (Location) | Standard Volume (µL) | Standard Mass (pg) | Signal Intensity (peak height)[a] | Mercury Mass (pg) | % Recovery | Average % Recovery |
|---|---|---|---|---|---|---|
| C-001 (RPL) | 50 | 100 | 19375 | 87.2 | 87 | 85 |
| C-002 (RPL) | 50 | 100 | 18397 | 82.8 | 83 | |
| C-003 (RPL) | 50 | 100 | 18608 | 83.8 | 84 | |
| C-001 (MSL) | 50 | 100 | 22054 | 99.3 | 99 | 98 |
| C-002 (MSL) | 50 | 100 | 21247 | 95.6 | 96 | |
| C-003 (MSL) | 50 | 100 | 21744 | 97.9 | 98 | |

(a) Final signal intensities were corrected for bubbler blank (not shown here).

## 5.5 Sample Size and Gold-Coated Sand Trap Saturation

When measuring ultra-trace mercury concentrations, maximizing sample size offers the best chance for reliable and reportable detection values by minimizing relative errors. However, when approximate mercury concentrations are unknown, as is the case in tank waste, caution must be taken to ensure the adsorbed mercury mass does not exceed the capacity of the collection adsorbent and the peak intensity does not exceed the measurement range of the CVAF detector. To explore and approach the maximum sample volume (or sample size), three filtered AP-107 sample volumes (0.084 mL, 0.835 mL, and 8.335 mL) were analyzed. Filtered AP-107 sample was selected simply because of available source volume. However, total mercury was selected based on expected maximum mercury mass (and peak intensity) and for sample stability (elemental mercury can suffer loss due to volatility and methyl mercury can suffer loss due to distillation efficiency and time degradation on Carbotrap® adsorbent). The three AP-107 sample volumes were loaded onto gold-coated sand traps at the RPL and then shipped to the MSL for analysis.

As illustrated in Table 7, the 0.084-mL sample volume resulted in poor peak magnitude and quality, because the sample size was too small, and the peak area could not be resolved accurately. The 0.835-mL and 8.335-mL sample volumes produced good signal peaks while not saturating the detector and since both measurements were in agreement (i.e., 94.3 and 93.1 ng/L), the gold-coated sand capacity was not exceeded. Therefore, the decision was made to prepare 5-mL samples for the subsequent mercury analyses of all three AP-107 sample types.

Table 7. Results for sample size and saturation.

| Sample | Standard Volume (mL) | Intensity Result (corrected) (peak height) | Mercury Concentration (ng/L) |
|---|---|---|---|
| WG-001 | 8.335 | 1246967 | 94.3 |
| WG-002 | 0.835 | 125046 | 93.1 |
| WG-003 | 0.084 | Poor peak quality | - |

# 6.0 Sample Shipping Protocol

Although the MSL has full separation and quantification capabilities for typical mercury samples in water, air, and soils, the facility has limited radiological capabilities and reduced radiological risk was desired. Therefore, shipping the gold-coated sand traps and distillation receiver vials from the RPL was necessary to leverage the existing mercury analytical capabilities at the MSL while also mitigating the high radiological dose observed with tank waste samples by conducting the preliminary mercury separations at the RPL. Previous work scope activities reported in Fountain et al. (2018) present $10^6$ and $10^4$ total activity reductions obtained by the separation processes at the RPL measuring the gold-coated sand (outside the glass columns) and the distillate liquid samples, respectively. Dose reductions on the order of $10^8$ were measured for the gold-coated sand trap and Carbotrap®-filled trap benefiting from the glass column shielding.

The safe shipment of radiological samples can be ensured with proper planning, packaging, shipping manifests, and environmental controls. However, ensuring the analytical integrity of mercury samples requires consideration of both sample storage and shipping conditions and duration, especially when separation and quantification of mercury-containing samples are performed in two different geographic locations hundreds of miles apart.

A sample shipping protocol was developed and demonstrated to assess and mitigate negative impacts of shipping time-sensitive mercury samples. The executed protocol has room for improvement and future shipping protocols will be modified based on observations made during this mercury separation and quantification of AP-107 tank waste samples. A description of activities and observations made are provided in Section 6.1, followed by discussion of proposed changes to future shipping protocol in Section 6.2.

## 6.1 Implementation and Observations

Separated mercury samples were generated at the RPL within a CA fume hood. Elemental and total mercury samples were in the form of gold-coated sand traps. The gold-coated sand trap samples were generated, capped, and stored at room temperature in the CA fume hood on Tuesday, July 16, 2019. The elemental and total mercury sample traps were removed from the CA fume hood directly into a plastic bag for secondary containment and staged for shipping on Thursday, July 18, 2019. The samples were picked up by representatives from PNNL’s hazardous material transportation organization on Friday, July 19, 2019, shipped overnight via FedEx, and received at the MSL on Monday, July 22, 2019. Upon receipt, the gold-coated sand traps were surveyed for contamination and placed in a CA fume hood at the MSL at room temperature for storage. The elemental and total mercury samples, on gold-coated sand traps, were desorbed with heat and quantified using CVAF on July 29, 2019, 13 days after collection.

A similar sample preparation, staging, and shipping methodology was used for methyl mercury samples; however, these samples were in the form of distillate (liquid) samples. As was discussed in Section 4.0, the stability of the methyl mercury sample in the distillate form was superior to the stability on the Carbotrap® adsorbent. However, an observed loss of methyl mercury over time was noted in the distillate form and accounting for waiting or storage time prior to quantification at the MSL was necessary to correct reported methyl mercury concentrations. Again, this waiting time accounting and correction has been discussed in Section 4.0 and here the sample handling and shipping activities are discussed specifically.

After distillation into the 60-mL fluoropolymer distillate receiver vials, the purging caps were replaced with flat sealing caps, and the vials were stored in the CA fume hood. The six distillate samples were generated between July 15, 2019, and July 18, 2019. Each vial was surveyed for contamination and then removed from the CA fume hood, and each vial cap was wrapped with white vinyl tape before staging for shipment in a large poly bottle with absorbent paper on July 18, 2019. The samples were picked up by the hazardous material transportation organization on Friday, July 19, 2019, shipped overnight via FedEx, and received at the MSL on Monday, July 22, 2019. Upon receipt, the six distillate samples were surveyed for contamination from the secondary poly bottle and placed in room temperature storage within a MSL CA fume hood. On July 23, 2019, the methyl mercury (distillate) samples were each purged onto a separate Carbotrap®-filled trap, desorbed with heat, and quantified using CVAF. Total storage durations varied from 5.0 to 7.8 days from the time distillation stopped to the time the distillate was purged onto Carbotrap® adsorbent.

During the shipment, one of the receiver vials (filled with distillate) leaked, despite using a tight flat cap and wrapping the cap with white vinyl tape, a standard practice for radiological work to mitigate cap leaks. Receipt contamination surveys did not detect contamination on the vial, absorbent paper, or the secondary containment (poly bottle). However, about 5 mL of distillate was lost from one of the raw waste samples for methyl mercury analysis (i.e., OSIF012-S-RMD-002), this volume loss would have been accounted-for in the methyl mercury sample quantification had there been signal for the particular sample.

Shipping of the radiological samples from the RPL in Richland, Washington, to the MSL in Sequim, Washington, was successful, with only a minor impact to one sample. However, lessons learned were developed to improve shipping time and consistency, and to mitigate future leaks.

## 6.2 Future Shipping Recommendations

**Reduced Shipping Duration:** Sample pickup by the representatives from PNNL's hazardous material transportation organization is once a day. Storage time can be reduced by coordinating the completion of separations such that samples can be removed and staged for shipping the same day. Additionally, avoiding separations and shipments on Friday ensures next-day receipt of samples and an opportunity to start analysis activities sooner at the MSL.

**Control Sample Shipping Temperature:** Overnight shipping can still result in samples being exposed to altitudes varying from approximately 300 ft above sea level in Richland, Washington, to airplane cruising altitudes ranging from 30,000 to 40,000 ft. Headspace in samples can pressurize due to altitude change. Furthermore, temperatures can range from room temperature (~68 °F) to freezing, and depending on the time of year and location, temperatures exceeding 100 °F. If sample shipping continues via overnight air, future shipments of samples will include ice packs (or equivalent) to control temperature. Alternative shipping by ground courier will also be considered to mitigate larger potential variations in temperature and pressure, but temperature control would still be considered beneficial in minimizing environmental variabilities during shipping.

**Mitigate Sample Volume Loss:** The vented cap on the distillation receiver vial was replaced with a flat cap. One of the six distillation vials leaked. Several options can be considered and include (1) transferring the distillate sample to a new 60-mL glass sample vial with sealing cap, (2) maintaining the vented distillation cap and vial hardware with a change to the method of transport to prevent spilling or pressurization, or (3) selecting a different sealing cap for the distillation receiver vial. Each of these solutions will be considered in subsequent sample shipments. with flat cap sealing still considered viable and baseline, but any future leaks will need to be prevented.

# 7.0 MSL Preconcentration and Sample Quantification

The subsampling and preservation of the various mercury species from tank waste samples at the RPL was described in Section 3.0, followed by the discussion of sample stability in Section 4.0, which provided a quantifiable impact that the delay between sample separation at the RPL and quantification at the MSL has on mercury concentration results. The separation protocols of the various mercury species at the RPL were then described in Section 5.0. This section describes the procedures followed for the preconcentration and analytical quantification that were conducted at the MSL in Sequim, Washington, for three mercury species: (1) total mercury, (2) elemental mercury, and (3) methyl mercury. While earlier sections spoke in detail regarding the process and procedures followed at the RPL to subsample and preserve the 18 samples, Figure 9 illustrates from a high level the overall flow of sample handling and processing across both locations.

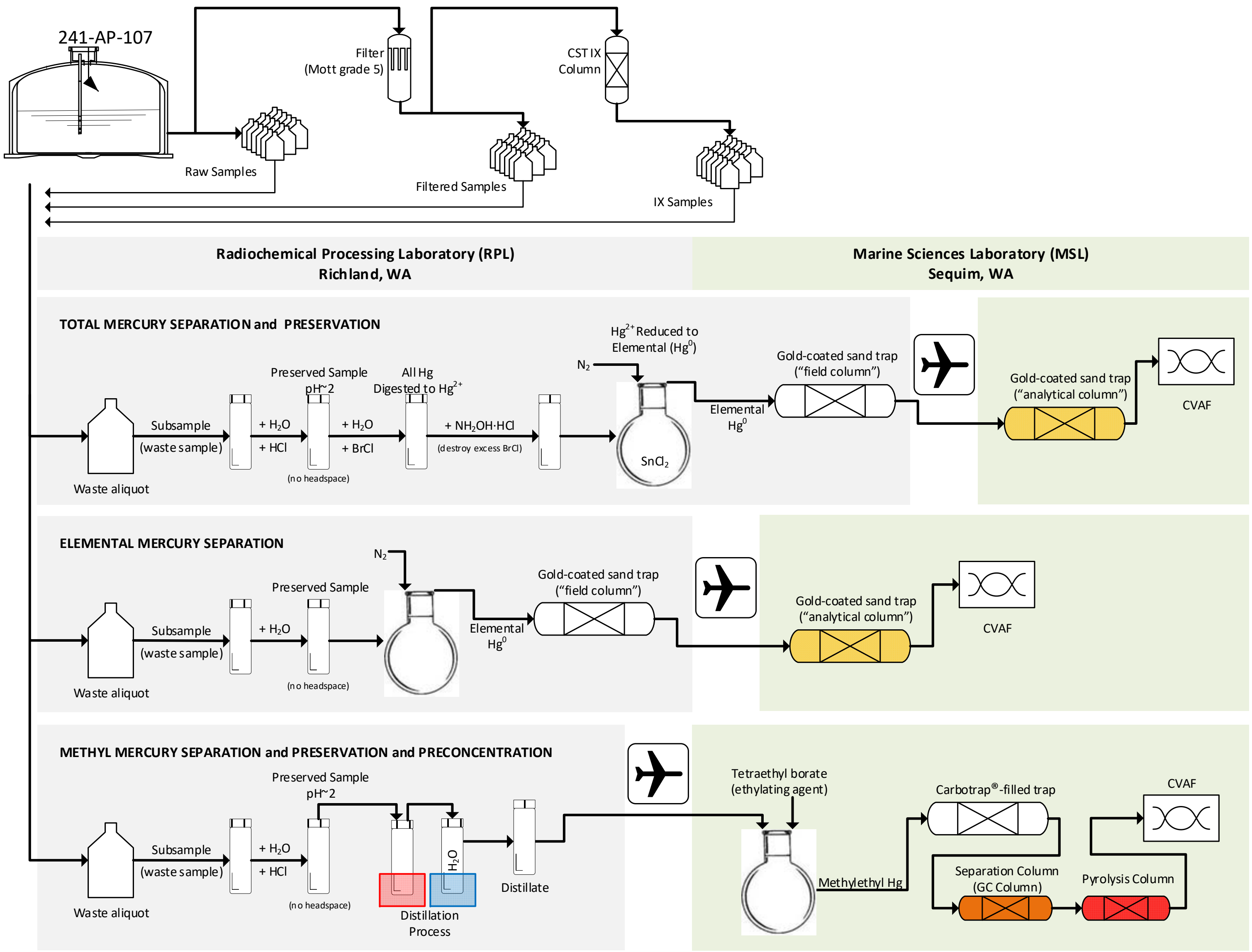

Figure 9. Flowchart of sample handling and processing across the RPL and the MSL.

Two mercury species, total and elemental Hg, were successfully quantified for this work for the three waste streams: (1) the parent/raw tank waste sample, (2) the mixed/filtered sample, and (3) the cesium decontaminated (post ion-exchange) sample. While samples were collected for the determination of methyl mercury, instrument issues with the CVAF system occurred during the analysis, and no quantification of methyl mercury was obtained.

## 7.1 Determination of Total and Elemental Mercury by CVAF Spectrometry

Quantification of total and elemental mercury was conducted using CVAF detection. The CVAF spectrometry system consists of a two-stage gold amalgamation gas train to introduce elemental mercury vapor into the gas cell of an atomic fluorescence spectrometer (AFS). A schematic of the layout of this system at the MSL is given in Figure 10.

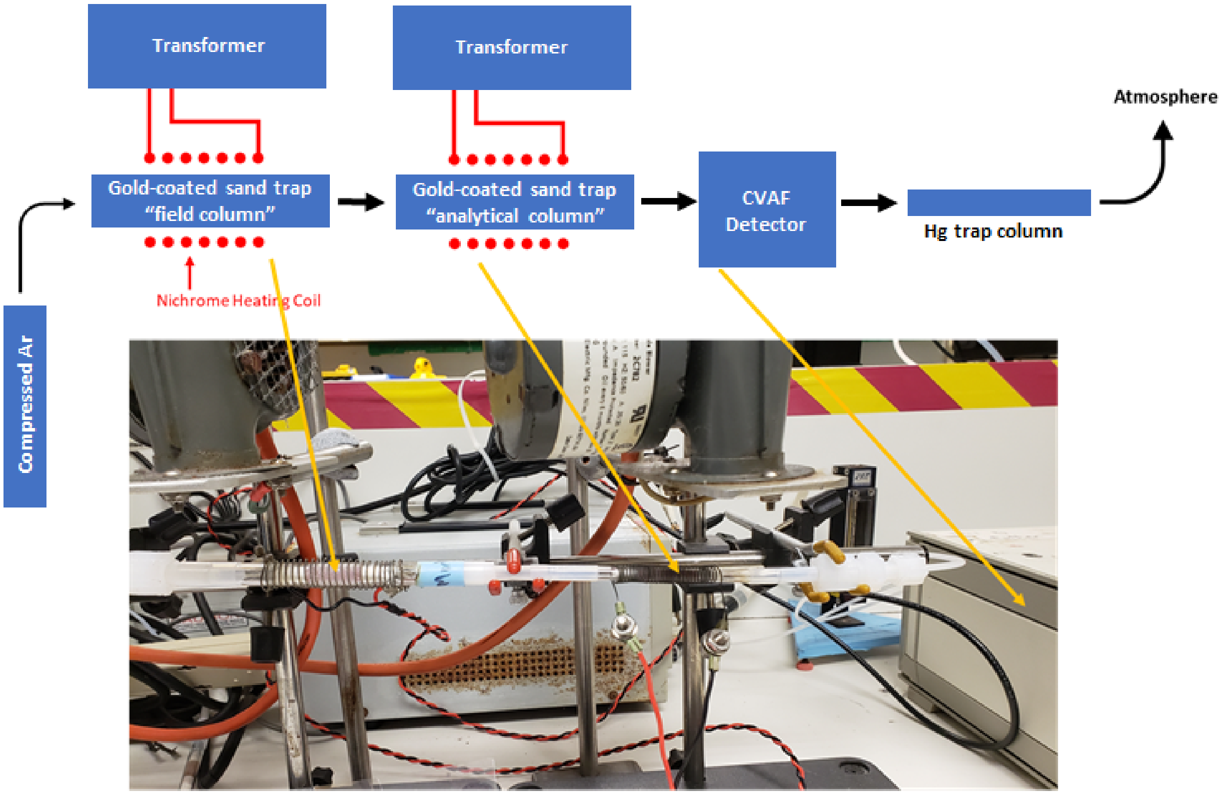

Figure 10. Two-stage gold amalgamation gas train for introducing elemental mercury into an atomic fluorescence detector for quantification of mercury collected on a gold-coated sand trap.

For quantification, mercury separated and collected (at the RPL) onto a gold-coated sand trap is placed in the gas train at the "field column" position (the upstream Au column in Figure 10). The mercury collected is transferred to the "analytical column" (the downstream Au column in Figure 10) by releasing elemental mercury from the "field column" into an argon gas stream using controlled heating (temperatures > 450 °C) where it re-amalgamates onto the "analytical column." The mercury on the "analytical column" is then released by controlled heating and swept into the gas cell of the AFS, where its signal is generated. Elemental mercury signals produced by the detector are captured and the chromatographic signal is integrated using Chromperfect SL software (version 1.2). Quantification of sample signals is generated using the mean calibration factor approach with subtraction of a bubbler blank (EPA 2002). Quality control samples (bubbler blanks, method blanks, initial calibration verification, continuing calibration verification, and ongoing precision and recovery) are included in the sample runs.

## 7.2 Determination of Methyl Mercury by CVAF Spectrometry

The determination of methyl mercury from a raw or preserved sample is a three-step process: (1) distillation of the raw sample to eliminate potential interferences in the subsequent ethylation step; (2) ethylation of methyl mercury to volatile methylethyl mercury, and subsequent purging and preconcentration of the methylethyl mercury onto a Carbotrap® adsorbent; and (3) separation of methylethyl mercury from other organo-Hg species in a simple gas chromatography (GC) system, conversion of the methylethyl mercury evolving out of the GC system to elemental mercury by high temperature pyrolysis, and detection of elemental mercury by CVAF. For this work, the first step of this analytical process was conducted at the RPL in Richland, Washington (see Sections 3.0 and 5.0). Based on the sample stability results in Section 4.0, the distilled samples were then shipped to the MSL for the latter two steps of the analytical process. Specific details about this analytical method can be found in the SOP MSL-I-014, which is based on the EPA Method 1630 (EPA 1998).

Stripping of the methyl mercury from the distillate samples onto Carbotrap®-filled traps was conducted within a radiologically controlled CA (MSL Building 5, room 223R). The isolation of the methyl mercury from solution was conducted using a gas phase dispersion bottle with a Carbotrap®-filled trap attached to the outlet (Figure 11). The distillate samples were added to the purging vessel, buffer was added to maintain the pH at approximately 4.9, and an ethylating agent (tetra ethyl borate) was added to convert the methyl mercury to methylethyl mercury, which is volatile and can be purged from solution using an inert gas (e.g., argon), and collected onto a suitable adsorbent, such as Carbotrap®. The isolation of the methylethyl mercury onto the Carbotrap®-filled trap significantly reduces the radiological background such that further handling and analysis of the Carbotrap®-filled trap can be conducted with less stringent radiological control (Fountain et al. 2018).

As illustrated in Figure 12, methylethyl mercury is desorbed from the Carbotrap® adsorbent and detected through a gas-train using argon carrier gas. The GC column consists of a 1-meter-long coiled glass column (1/4-in. OD, 4-mm ID) packed with 15% OV-3 on 60/80 Chromosorb WAW/DMCS (Supelco) held at 120 °C in a small benchtop GC oven. The pyrolysis column consists of a quartz column that is packed with quartz glass wool and is heated to approximately 700 °C. The pyrolysis column converts the incoming methylethyl mercury to elemental mercury, which is then swept into the CVAF detector in the argon gas stream. The detector is a Tekran model 2500 CVAF detector.

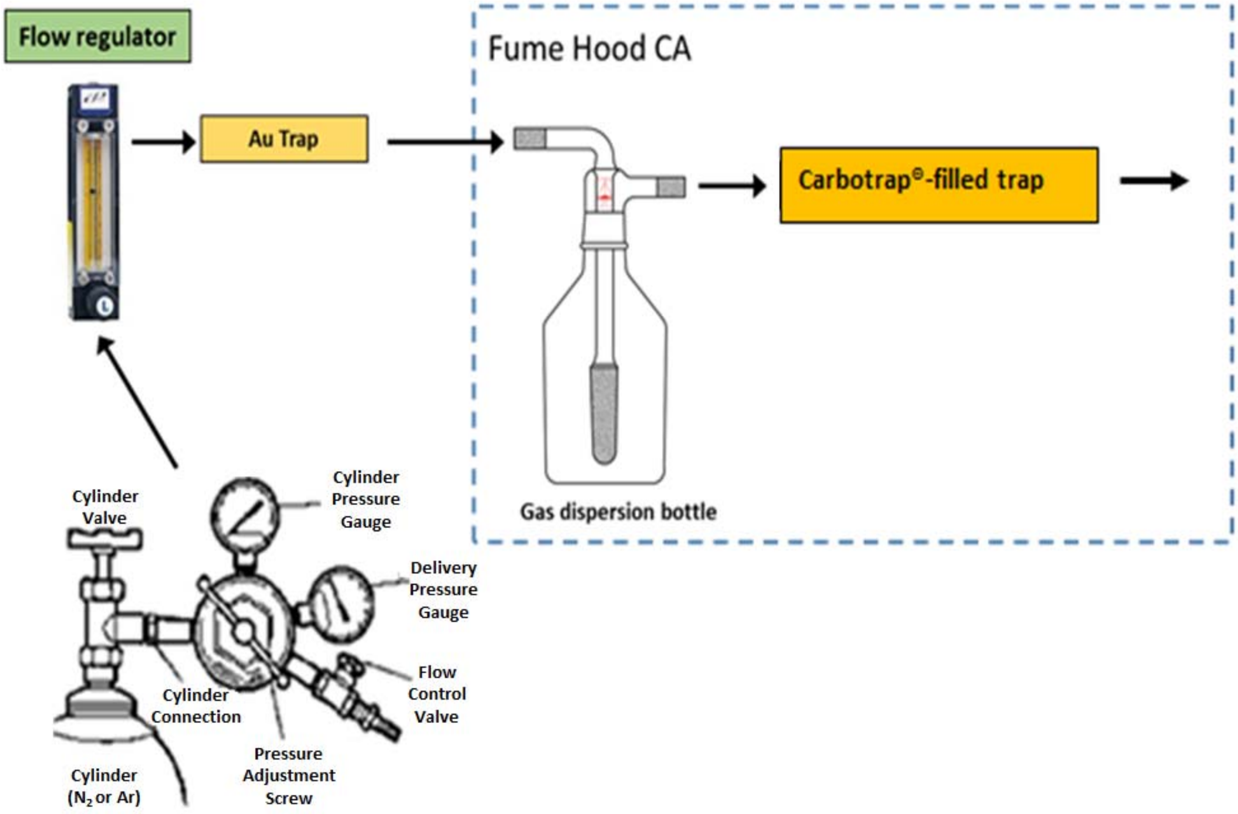

Figure 11. Schematic of the purging system used to strip volatile methylethyl mercury from an aqueous sample onto a solid adsorbent such as a Carbotrap®-filled trap.

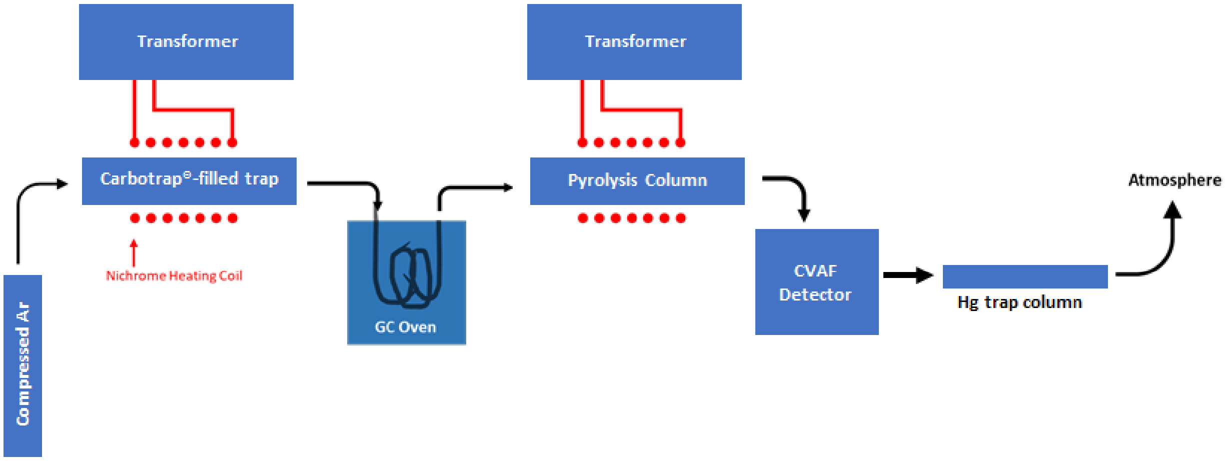

Figure 12. Schematic of the gas train system used to quantify methyl mercury collected on a Carbotrap®-filled trap by ballistic heating, GC separation, pyrolysis of methylethyl mercury to elemental mercury, and detection of elemental mercury by CVAF.

Due to the instability of methylethyl mercury on Carbotrap® adsorbent (see Section 4.2 for more details), liquid distillate samples were shipped to the MSL for subsequent purging onto Carbotrap®-filled traps and CVAF detection, as illustrated in Figure 12. This separation at the RPL to the distillate form, transport, and purging and quantification at the MSL was a variation from the EPA 1630 Method, which specifies the methylethyl mercury collected on the trap is quantitatively stable for up to 6 hours and must be analyzed within that period. A Carbotrap®-filled trap stability study (discussed in Section 4.2.1) was done and showed that the methylethyl mercury was not stable on the Carbotrap® adsorbent for an extended period of time, whereas a study on the stability of the distillate (discussed in Section 4.2.2) showed that the distillate was stable for an extended period of time.

# 8.0 Quantification Results and Discussion

The key objective of this Phase II work was to quantify total, elemental, and methyl mercury species from three distinct waste sample forms derived from the AP-107 tank waste supernatant; raw (unadulterated), filtered (post filtration using Grade 5 sintered stainless-steel filter), and post-IX (cesium-decontaminated using CST media) samples. This objective was accomplished by deliberate and proper sample preservation and storage conditions, determination of separated sample stabilities and adequate sample size, establishment of separation system performance at the RPL, demonstration of sample transport from the RPL to the MSL, and finally analytical quantification of mercury using CVAF detection under low-level radiological conditions.

Results for duplicate determinations of elemental mercury and total mercury in the AP-107 Hanford tank waste supernatant are presented in Table 8. Measurements were conducted on the raw, filtrate, and post-IX sample forms. Success was realized in demonstrating the quantification of both total and elemental mercury for the raw waste feed sample and two treated sample phases. The separation technique for methyl mercury was successfully demonstrated; however, unexpected analytical difficulties prevented quantification of the methyl mercury content of the raw, filtered, and post-IX samples.

During the quantification step for measuring methyl mercury for the raw and treated samples, there was an unexpected and unforeseen issue that resulted in a failure to measure any signal on all six of the methyl mercury samples. While all the calibration and quality control samples ahead of sample measurement for methyl mercury were conducted successfully, no signal was observed for the tank waste sample runs. The reason for this failure continues to be investigated; however, initial indications suggest that the carrier flow used to transport the waste sample from the Carbotrap®-filled trap did not reach the pyrolysis column (identified in Figure 12). It is speculated that there was either a significant leak in the tubing or fittings or a plug in the GC column (identified as the GC oven on Figure 12). To mitigate future data loss, additional instrumentation is planned in subsequent experimental work to actively monitor carrier flow rates as well as administratively require suspension of analyses if any issue is discovered (thus worst case the loss of a single sample measurement). Lastly, triplicate samples will be prepared so that in the event of a failure there will be ample remaining samples to provide, at the minimum, duplicate analysis.

Table 8. Determination of elemental and total mercury in Hanford AP-107 tank waste supernatant liquid.

| AP-107 Source Sample ID | Mercury Analysis | Sample Treatment | Volume of Parent Sample Analyzed (mL) | MDL (ng/L)[(a)] | Mercury Concentration (ng/L)[(b)] |
|---|---|---|---|---|---|
| UF-01 | Total Hg | Raw | 0.26 | 20 | 1534 |
| MF-01 | Total Hg | Filtrate | 0.59 | 8.7 | 1050 |
| IX-01 | Total Hg | Post-IX | 0.59 | 8.7 | 745 |
| UF-02 | Elemental Hg | Raw | 0.27 | 19 | 37[(c)] |
| MF-02 | Elemental Hg | Filtrate | 0.60 | 8.6 | 19 |
| IX-02 | Elemental Hg | Post-IX | 0.60 | 8.6 | 32 |

(a) Sample specific method detection limit (MDL) determinations are based on three times the standard deviation of three method blank measurements.
(b) Concentrations based on the average of duplicate sample results except where noted.
(c) One duplicate measurement was below the MDL of 19 ng/L and therefore is not reported here.

## 8.1 Total Mercury in AP-107 Tank Waste Samples

Total mercury content was determined, through duplicate measurements, using raw, filtrate, and post-IX samples of AP-107 Hanford tank waste supernatant, averaging 1534 ± 115.3, 1050 ± 64.8, and 745 ± 56.5 ng/L, respectively (Table 8). Processing of the waste feed sample (via filtration and cesium IX) results in removal of significant amounts of mercury from the waste stream; of the mercury present in the raw AP-107 supernatant, 32% was removed by 5-µm filtration, and a further 20% by passing the filtrate through cesium IX. These results are dramatic, unexpected, and positive in the context of meeting secondary waste disposal requirements for mercury content. The current flowsheet modeling is conservative and gives no credit to the filtration and IX unit operations for mercury removal. It is not clear at this time if the retained mercury is associated only with filtered solids, some other removal mechanism like plating on surfaces, or a combination of both. Similarly, the reduction in total mercury concentration due to CST (used for IX) could be both from solids filtration and sorption capacity. Filtration was conducted with a sintered stainless-steel disc filter with a pore size of 5 µm (Geeting et al. 2019), allowing a small fraction of small-diameter solids to pass the filter, and the CST IX media has been observed to have a loading capacity for mercury at a concentration of 209 µg/g of CST (Wilmarth et al. 2004).

## 8.2 Elemental Mercury in AP-107 Tank Waste Samples

Elemental mercury content was determined, through duplicate measurements, in raw, filtrate, and post-IX samples of AP-107 Hanford tank waste supernatant, averaging 37,[1] 19, and 32 ng/L, respectively (Table 8). Elemental mercury measurements conducted on sample replicates were all very low and near the MDL compared to the total mercury content of respective sample forms. Replicate filtrate and post-IX measurements relied on 0.6-mL of the parent sample for the elemental analysis (originating from the 3.0 mL parent aliquot) while replicate raw parent measurements used 0.27 mL of the parent sample (originating from the 0.6 mL raw parent aliquot). By analyzing larger parent sample volumes, it would be possible to improve the detection limit of elemental mercury samples. The sample pretreatments (i.e., filtration and cesium decontamination) do not appear to influence elemental mercury concentration. Based on this information, however, the elemental mercury in all waste forms is estimated to comprise an average of 2.8% of the total mercury in the AP-107 tank waste. Future measurements for analysis of elemental mercury should increase the parent sample size that is purged onto the gold-coated sand trap to improve detection capability.

## 8.3 Methyl Mercury in AP-107 Tank Waste Samples

While methyl mercury replicate samples were run for the three tank waste forms (raw, filtered, and post-IX), due to unusual and unexpected analytical difficulties, there was no discernable data obtained from any of these samples. At this point, a complete investigation of the cause has not been finished; however, it is known that carrier flow with the mercury sample could not reach the detector because the flow was hindered from going through the GC column after the initial quality control samples had run through the system successfully. It is unclear if this flow stoppage through the GC column was due to a significant leak in tubing or fittings, or a plug in the GC column. Section 9.7 address the quantification issue along with steps to mitigate it in the future. It is expected, based on all of the preliminary quality control checks and earlier testing for methyl mercury in the system, that the measurement will be successful in future investigations.

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[1] One of the elemental mercury samples in the raw tank waste was 37 ng/L and the other sample had a signal below detection (<19 ng/L).

## 8.4 Parent Sample Volume Analyzed

One of the unknowns in this phase of work was choosing a sample that would achieve a readily quantifiable signal, without isolating so much mercury that it would exceed either the solid phase adsorbent capacity or overrange the CVAF detector. There was very limited information to support estimates of sample sizes.

The analytical results obtained for total and elemental mercury, relative to the sample volume taken for analysis, and its corresponding MDL, are also presented in Table 8. The preliminary sample volume target work, discussed in Section 5.5, allowed for good measurements for total mercury. Signals for total mercury were all above 700 ng/L and the detection limit achieved for sample volumes of < 0.6 mL was < 20 ng/L. The same measurement quality did not occur for elemental mercury measurements. The MDLs that were achieved for elemental Hg (<19 ng/L) were much closer to the range of elemental mercury observed in the samples (19-37 ng/L) (Table 8). As a result, one of the elemental mercury determinations was below detection. Increasing the volume of parent sample used for an individual (replicate) elemental mercury determination by two to five fold (0.5 to 3.0 mL) would lower the detection limit correspondingly and likely lead to a more reproducible and accurate measurement.

## 8.5 Measured AP-107 Mercury Concentration Versus Tank Farm Basis

As of January 1, 2019, the best-basis inventory for AP-107 supernatant is reported to contain a total mercury mass of < 6.04 x $10^{-3}$ kg based on a sample measurement with a reported mercury concentration value of < 2200 ng/L (Rasmussen 2019). As indicated by the less-than value, the reported total mercury concentration is based on a detection limit of the analytical method used at the 222-S Laboratory on the Hanford Site. As reported in Table 8, the PNNL measured total mercury concentration, based on duplicate measurements, is 1534 ng/L, which is comparable in magnitude and strongly supported by a PNNL MDL of 20 ng/L, which is two orders of magnitude better than the 222-S detection limit. These new results indicate that the total mercury inventory basis used by tank farms is conservative and could be reduced.

# 9.0 Future Recommendations

While significant progress has been achieved in Phases I and II, there are still several areas where additional improvements can be made to make the determination of mercury species in tank waste samples more robust and to demonstrate further reliability, as described below.

## 9.1 Sample Preservation

More rapid preservation of parent samples for each of the mercury measurements is desired to maintain speciation information. For this work, to reliably provide accurate mercury speciation information, it is critical that the time between the initial sampling of the waste tank (or post-treatment process) and the preservation of the mercury speciation samples be minimized. If enough of a delay occurs, there could be loss of elemental mercury via degassing and potentially degradation of methyl mercury. The staff involved with the mercury speciation program need to integrate and communicate with the tank waste sampling team and sample receipt team at the RPL to allow the subsampling and proper preservation and storage to occur as rapidly as possible after the initial tank sampling.

## 9.2 Sample Size

When this program began, there was some anecdotal information on the abundance of total mercury in the tank waste, but there was no information on the abundance of elemental mercury or methyl mercury. Sample size was selected based on a quick screening of three sample sizes (see Section 5.5) using total mercury content, but "best guess" for elemental and methyl mercury. Sufficient signal was needed for detection capabilities, but not so much that the mercury species would swamp the sample gold-coated sand trap. Fortunately, the size of the sample for the determination of total mercury was appropriate, but the size of the sample analyzed for elemental mercury needs to be increased by two to five fold (e.g. 0.5 to 1.5 mL replicate volume) would lower the detection limit correspondingly and likely lead to a more reproducible and accurate measurement for improvement in analytical reproducibility and accuracy.

## 9.3 Sample Shipping Protocols

Improvements in shipping protocols are needed. One of the distillate samples leaked slightly during shipping. A more secure means of shipping the samples, while maintaining sample integrity (contamination control), needs to be identified – specifically, use of distillate tube caps that fit and are secure to prevent leaks and contamination. Also, the sample integrity would be improved if the distillate samples can be shipped on ice, to maintain temperatures < 4 ºC. Finally, minimizing the time between sample isolation and analysis at the MSL would reduce the correction for loss of methyl mercury in the distillate with time of storage.

## 9.4 Quality Assurance and Quality Control

Additional QA testing and protocols should be conducted and integrated into the overall program. In Phase II, significant attention was paid to verifying that samples intended for methyl mercury analysis would be sufficiently stable such that a delay of a few days between shipping and analysis would not compromise the measurement. Similar attention was not given to elemental and total mercury samples collected onto gold-coated sand. While it is not possible to lose an element by degradation, in the same manner as observed for methyl mercury, it may be possible for the signal to be biased. For example, mercury being an element is not a guarantee that it will not change into a form that cannot be removed from the gold-sand trap to the analytical system, which from an analytical point of view would qualify as degradation. Additionally, there is a chance that elemental mercury, naturally present in the atmosphere and often elevated in research facilities, could contribute to the blank signal for these measurements. The level of background mercury adsorbed onto the gold-coated sand with time should be checked, and it should be verified that mercury adsorbed on gold-coated sand is stable with time, as assumed by the environmental mercury measurement community.

The current Phase II work was conducted using a single bubbler to purge samples from solution at the RPL, while at the MSL these operations are typically done with four simultaneously operated purging systems. Increasing the number of purging systems at the RPL would allow more samples to be isolated simultaneously and increase the ability to perform replicate analyses, which would permit a better definition of reproducibility. The ability to conduct replicate analyses for element mercury measurements is especially critical. Once the elemental sample container has been opened, any elemental mercury in the sample can escape by degassing. It is important that all replicates for elemental mercury be taken as quickly as possible to minimize this process. Having multiple purging systems available would minimize this potential issue.

## 9.5 Additional Supportive Laboratory Photographic Evidence

Due to the nature of unique samples in this work, there is an advantage to being able to not only capture descriptions of procedures and observations in written form but to also capture photographic evidence of unique appearances (i.e., colorings, precipitates, reactions, etc.) during sample preservation, preconcentration, and other processes.

## 9.6 Analytical Instrumentation

The analytical instrumentation that was used to conduct this current work, while appropriate and successful, was not state-of-the art. Development of a system in Phase II was not warranted until it could be demonstrated that the mercury techniques used for environmental measurements could be applied successfully to radioactive tank waste samples. Improvements could be made to make determinations more robust, which would lead to improvements in accuracy, precision, and sensitivity. For example, advancements in automation are possible. The current system is partially operated by manually turning on and off the heating and cooling systems and manually starting the integration of the chromatographic system. Refinements in the use of the signal capture software would help to improve peak area quantifications and consistency in peak timing. Adding mass-flow controllers to manage flow in the system should also lead to enhanced reproducibility and possibly enhance sensitivity. Better control of temperature might also help with signal sharpness and enhance sensitivity.

## 9.7 Quantification Issue with Methyl Mercury

As noted in Section 8.3, no measurements of methyl mercury in tank waste samples were quantified due to an unexpected and as yet unidentified analytical system problem. Preparation of the calibration curve and the quality control samples immediately after the calibration was successful, indicating that the analytical system was functioning properly. Upon subsequent analysis of the Hanford tank waste samples, no CVAF detector signal was observed. Methyl mercury standards purged onto Carbotrap®-filled traps within a few hours after the analytical detection failure also showed no CVAF signal response. The reason for this failure may never be conclusively identified. However, it is known that at some point after the initial quality control samples and before the last methyl mercury sample, the carrier gas (and methylethyl mercury sample) was not being carried through the GC column. At this time, it can only be speculated that this was due to either a significant leak in the tubing or fittings, or a plug in the GC column preventing mercury from reaching the detector. The path forward to correct for this possibility will be to prepare a completely new gas flow train, purchase a new GC column, prepare a new pyrolysis column, and get new column and tubing connection fittings. Adding carrier gas flow monitoring immediately after the regulator and at the exit from the CVAF detector will also help to monitor for leaks in real time. To mitigate future data loss administratively, analysis will require suspension if any issue is discovered (thus, worst case is the loss of a single sample measurement), and triplicate samples will be prepared so that in the event of any failure there will be ample remaining samples to provide, at the minimum, duplicate analysis.

# 10.0 Conclusions

The direct measurement of two key mercury species, total and elemental mercury, was successfully completed in raw, filtered, and cesium-decontaminated waste supernatant samples from Hanford tank 241-AP-107. This Phase II work demonstrated that low-level environmental mercury speciation techniques can be adapted for the analysis of mercury species in Hanford tank waste samples (raw, filtered, and cesium-decontaminated) using minimal sample sizes, while maintaining an ultra-trace mercury detection capability. The range of parent tank waste sample sizes used for this work was between 0.6 and 3.0 mL, while replicate measurements used between 0.27 and 0.6 mL of the parent sample for analysis. This current work additionally demonstrated that these parent tank waste samples could be separated outside of hot cell containment, have their resulting radiological activity reduced by at least $10^4$ (Fountain et al. 2018), and have subsequent analytical quantification conducted under low-level radiological constraints, enabling future potential use of commercial laboratories without significant sample dilution requirements. The pre-processing to isolate the mercury species from the AP-107 parent waste[1] stream samples resulted in relatively low dilution factors, between 8.3- and 17.5-fold. These dilutions are a significant advancement over previous analytical approaches where high radioactivity background was mitigated by large dilution factors (often 100,000-fold or greater) to reduce radiological background to levels that would permit safe handling and sample analysis at commercial laboratories (Bannochie and Wilmarth 2016).

Measurements of methyl mercury in the tank waste treatments were also attempted, but analytical difficulties associated with the measurement system occurred during the analysis of the sample. While disappointing, there is no reason to believe this was a systemic problem that cannot be resolved, as all the QA testing prior to the analysis showed no issues.

PNNL measured a total mercury concentration of 1534 ng/L, which is well supported by an MDL of 20 ng/L. This is comparable in magnitude to the < 2200 ng/L reported by 222-S based on detection limits (Rasmussen 2019) and indicates that the total mercury inventory basis used by tank farms is conservative and could be reduced. Furthermore, processing of the waste feed sample (via filtration and IX) results in removal of significant amounts of mercury from the waste stream; of the mercury present in the raw AP-107 supernatant, 32% was removed by 5-µm filtration, and a further 20% by passing the filtrate through cesium IX using CST media. The current flowsheet modeling gives no credit to the filtration and IX unit operations for mercury removal and should consider an update with respect to mercury mass behavior during pretreatment.

The ultimate goal of this work is to develop an analytical method to obtain detailed mercury speciation information to verify or update flowsheet modeling assumptions related to mercury speciation and partitioning at Hanford. In the next phase of the work (FY 2020), total mercury, elemental mercury, and methyl mercury concentrations will be quantified in a multiple Hanford tank wastes, with minimal sample dilution, using the protocols developed in FY 2018 and FY 2019. In FY 2020, an opportunity to leverage current tank waste unit operations testing in PNNL's RTP exists, where this mercury speciation and quantification methodology will be applied to representative flowsheet streams (i.e., post filtration, post IX, and post melter submerged bed scrubber) using a supernatant liquid sample from the tank 241-AP-105.

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[1] The determination of mercury species concentration in tank waste is specifically referring to tank waste supernatant.

# 11.0 References

Bannochie CJ and WR Wilmarth. 2016. *Mercury Speciation Comparison: Brooks Applied Laboratories and Eurofins Frontier Global Sciences*. SRNL-STI-2016-00622, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina.

Bannochie CJ, CL Crawford, DG Jackson, HB Shah, V Jain, JE Occhipinti, and WR Wilmarth. 2016. *Mercury Phase II Study – Mercury Behavior across the High-Level Waste Evaporator System.* SRNL-STI-2016-00163, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina.

Bannochie CJ, TL Fellinger, P Garcia-Strickland, HB Shah, V Jain, and WR Wilmarth. 2017. "Mercury in aqueous tank waste at the Savannah River Site: Facts, forms, and impacts." *Separation Science and Technology* 53(12):1935-1947. DOI:10.1080/01496395.2017.1310239.

Baya PA, JL Hollinsworth, and H Hintelmann. 2013. "Evaluation and optimization of solid adsorbents for the sampling of gaseous methylated mercury species." *Analytica Chimica Acta* 786:61– 69.

Boggess AJ, TL White, MA Jones, CJ Bannochie, AA Ekechukwu, and WR Wilmarth. 2018. "Simultaneous sub-picogram speciation of methylmercury and ethylmercury in caustic nuclear tank waste using direct aqueous propylation." *Journal of Radioanalytical and Nuclear Chemistry*, Published online August 14, 2018. https://doi.org/10.1007/s10967-018-6085-9.

Britton MD, JG Reynolds, CLH Bottenus, MS Fountain, ME Stone, and RB Wyrwas. 2018. *One System River Protection Project Integrated Flowsheet Maturation Plan*. RPP-PLAN-58003, Rev. 4 (24590-WTP-PL-MGT-15-0011, Rev. 3), Washington River Protection Solutions, LLC, Richland, Washington.

Britton MD. 2017. *DFLAW Feed Uncertainty*. RPP-RPT-59844, Rev. 0, Washington River Protection Solutions, LLC, Richland, Washington.

Cramer K. 2001. *Mercury Pathway and Treatment Assessment for the WTP.* 24590-WTP-RPT-PR-01-011, Rev. 0, Bechtel National, Inc., Richland, Washington.

EPA. 1998. Method 1630 (Draft), *Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*. U.S. Environmental Protection Agency, Washington, D.C. Document available at: https://www.epa.gov/sites/production/files/2015-08/documents/method_1630_1998.pdf.

EPA. 2002. Method 1631, Revision E, *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*. EPA-821-R-02-019, U.S. Environmental Protection Agency, Washington, D.C. https://www.epa.gov/sites/production/files/2015-08/documents/method_1631e_2002.pdf.

Fiskum SK, AM Rovira, HA Colburn, AM Carney, and RA Peterson. 2019. *Cesium Ion Exchange Testing Using a Three-Column System with Crystalline Silicotitanate and Hanford Tank Waste 241-AP-107*. PNNL-28958, Rev. 0 (RPT-DFTP-013, Rev. 0), Pacific Northwest National Laboratory, Richland, Washington.

Fiskum SK, HA Colburn, RA Peterson, AM Rovira, and MR Smoot. 2018. *Cesium Ion Exchange Using Crystalline Silicotitanate with 5.6 M Sodium Simulant*. PNNL-27587, Rev. 0 (RPT-DFTP-008, Rev. 0), Pacific Northwest National Laboratory, Richland, Washington.

Fountain MS, SD Branch, and GA Gill. 2018. *Separation and Speciation of Mercury from Hanford 241-AP-107 Tank Waste Supernatant*. PNNL-28067, Rev. 0 (RPT-OSIF-004, Rev. 0), Pacific Northwest National Laboratory, Richland, Washington.

Geeting JGH, JR Allred, AM Rovira, and RA Peterson. 2019. *Fiscal Year 2019 Filtration of Hanford Tank AP-107 Supernatant*. PNNL-28780, Rev. 0 (RPT-DFTP-015, Rev. 0), Pacific Northwest National Laboratory, Richland, Washington.

Goles RW, WC Buchmiller, LK Jagoda, BD MacIsaac, and S Rassat. 2004. *Test Summary: WTP Flowsheet Evaluation of Mercury-Containing Hanford Waste Simulant.* PNWD-3437 (WPT-RPT-122, Rev. 0), Battelle—Pacific Northwest Division, Richland, Washington.

Kupfer MJ, AL Boldt, KM Hodgson, LW Shelton, BC Simpson, RA Watrous, MD LeClair, GL Borsheim, RT Winward, BA Higley, RM Orme, NG Colton, SL Lambert, DE Place, and WW Schulz. 1999. *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tank Wastes.* HNF-SD-WM-TI-740, Rev. 0C, Lockheed Martin Hanford Corporation, Richland, Washington.

NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications.* The American Society of Mechanical Engineers, New York, New York.

NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*. The American Society of Mechanical Engineers, New York, New York.

NQA-1a-2009, *Addenda to ASME NQA-1–2008.* The American Society of Mechanical Engineers, New York, New York.

Rasmussen JH. 2019. *Derivation of Best-Basis Inventory for Tank 241-AP-107 as of January 1, 2019.* RPP-RPT-48103, Rev. 11, Washington River Protection Solutions, LLC, Richland, Washington.

Rovira AM, SK Fiskum, HA Colburn, JR Allred, MR Smoot, and RA Peterson. 2018. *Cesium Ion Exchange Testing Using Crystalline Silicotitanate with Hanford Tank Waste 241-AP-107*. PNNL-27706 (RPT-DFTP-011, Rev. 0), Pacific Northwest National Laboratory, Richland, Washington.

Wilmarth JR, VH Dukes, and JT Mills. 2004. *Reactivity of Crystalline Silicotitanate (CST) and Hazardous Metal/Actinide Loading during Low Curie Salt Use.* WSRC-TR-2004-00588, Rev. 0, Washington Savannah River Company, Aiken, South Carolina.

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