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Measurement of Total, Elemental, and Methyl Mercury in Hanford Tank Waste

Technology Transfer from PNNL to Hanford 222-S Laboratory

May 2022

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U.S. DEPARTMENT OF ENERGY

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Executive Summary

This report describes the chemical separations used to measure the amounts and chemical forms of mercury in Hanford tank waste and provides the technical basis and recommendations for transferring and implementing this new ultra-trace mercury analytical technique at Hanford's 222-S Laboratory. In the Hanford tank waste, mercury can exist as a combination of elemental, inorganic, and organic mercury species. Of key interest is understanding the quantification and speciation of total (elemental + inorganic + organic), elemental, and organic (assumed to be only methyl mercury) mercury. The tanks may also have other organic mercury species, but their direct measurement is outside the scope of this report.

The U.S. Department of Energy (DOE) Hanford Site in southeastern Washington State stores 56 million gallons of chemical and radioactive waste 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. When the tank waste is being converted into its final waste forms (such as glass or grout), it will undergo various unit operations such as filtration, cesium ion exchange, evaporation, and vitrification. Secondary waste streams are subjected to many other separation and conversion processes (adsorption, oxidation, reduction). 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 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.[1] Inventory estimates, based primarily on Hanford process knowledge, suggest a total mercury inventory of 2,100 kg[1] in the Hanford tank farms, over time and as more sample based data is collected these inventory estimates improve. A 2018 Best Basis Inventory (BBI) estimate concludes the total mercury inventory of 1,780 kg[2]. Aside from concerns about human exposure to 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 established from toxicity characteristic leaching procedure restrictions for secondary waste disposal, and air emission permits. Under the waste storage conditions at Hanford, volatile elemental mercury is in dynamic equilibrium with inorganic mercury species. The mercury species in the waste solids are still unknown and may be waste-specific. The liquid phase mercury is believed to be in the inorganic (synonymous with ionic) mercury form (Hg^{2+} is presumed; however, Hg_2^{2+} is potential).

Techniques to analyze of the chemical forms of mercury species in Hanford tank wastes were developed at Pacific Northwest National Laboratory (PNNL) and will be transferred to the DOE 222-S Laboratory on the Hanford Site for implementation during waste processing operations.

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[1] 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.

[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.

Having a capability at the Hanford 222-S Laboratory to independently measure total mercury (THg), elemental mercury (Hg^0), and methyl mercury (MeHg), and to quantify by difference in both liquid and slurry samples, offers an important risk mitigation for DFLAW and future high-level waste processing relative to waste disposal, waste acceptance, and facility process operations. Furthermore, such a capability, of both a total mercury and a methyl mercury cold vapor atomic fluorescence spectroscopy (CVAFS), will offer the ability and flexibility to further identify numerous additional mercury species – e.g., monomethyl mercury (MMHg or CH_3Hg^+), dimethyl mercury [DMHg or $(CH_3)_2Hg$], inorganic mercury (Hg^{2+} or Hg_2^{2+}), soluble (or dissolved) mercury, ethyl mercury (EtHg), and particle-bound mercury – as needs arise. Furthermore, these analytical techniques have been demonstrated, at PNNL using Hanford tank waste, in such a way to achieve success using either of two laboratory configurations: single-laboratory and dual-laboratory configuration. A single-laboratory configuration is such that all the handling, preparation, and analysis takes place at a single facility; in a dual-laboratory configuration, the sample handling and preparation takes place in one facility while the analysis is conducted at a separate facility. Washington River Protection Solutions, LLC asked PNNL to facilitate the potential transfer and implementation of these technical advancements into the 222-S Laboratory for future routine mercury measurements in tank wastes throughout the Hanford mission. The work was divided into the following three tasks:

1. Provide recommendations for the appropriate mercury speciation for DFLAW and the future mission.
2. Assess the current capabilities at the 222-S Laboratory for implementing mercury measurements.
3. Provide considerations and technical documentation for implementing mercury speciation and quantification methods at the 222-S Laboratory for total, elemental, and methyl mercury.

This technical report completes Task 1, Task 2, and Task 3 of the proposed work, specifically for the assessments and recommendations for ultra-trace mercury speciation and quantification capabilities, measurements, and methodologies. A similar work scope was completed to address iodine capabilities, measurements, and methodologies and was reported as a letter attachment[3] (Task 1 for iodine only) and PNNL technical report[4] (Task 2 and Task 3 for iodine only).

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[3] Fountain MS, Soderquist CZ. 2021. *FY21 Assessment of 222-S Capabilities for Implementation of a New PNNL Inorganic Iodine Speciation Analytical* Method. Attachment to LTR-OSIF-025. Pacific Northwest National Laboratory, Richland, Washington.

[4] Soderquist CZ, Branch SD, Gartman BN, Fountain MS, Asmussen SE, and Kimmig SR. 2021. *Measurement of Iodine, Iodide, and Iodate in Hanford Tank Waste: Technology Transfer from PNNL to Hanford 222-S Laboratory*. PNNL-32079; RPT-OSIF-015, Rev. 0. Pacific Northwest national Laboratory, Richland, Washington.

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Acronyms and Abbreviations

AFS	atomic fluorescence spectrometer
ALARA	as low as reasonably achievable
APDC	ammonium pyrrolidine dithiocarbamate
BBI	best basis inventory
CA	contamination area
CCV	continuing calibration verification (standard)
CRM	certified reference material
CVAAS	cold vapor atomic absorption spectroscopy
CVAF	cold vapor atomic fluorescence
CVAFS	cold vapor atomic fluorescence spectroscopy
DFLAW	Direct Feed Low-Activity Waste
DI	deionized
DL	detection limit
DMHg	dimethyl mercury
DOE	U.S. Department of Energy
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
EQL	estimated quantitation limit
ESP	Environmental Simulation Program
EtHg	ethyl mercury
FY	fiscal year
GC	gas chromatography
HEPA	high-efficiency particulate air
Hg^0	elemental mercury
HLW	high-level waste
ICP-MS	inductively coupled plasma mass spectrometry
ICV	initial calibration verification (standard)
ID	inner diameter
IPR	initial precision and recovery (samples)
LAW	low-activity waste
MDL	method detection limit
MeHg	methyl mercury
MMHg	monomethyl mercury
NAPL	non-aqueous phase liquid
NIST	National Institute of Standards and Technology
OD	outer diameter

OPR	ongoing precision and recovery (samples)
PNNL	Pacific Northwest National Laboratory
PNNL-Richland	Pacific Northwest National Laboratory Richland Campus
PNNL-Sequim	Pacific Northwest National Laboratory Sequim Campus (formerly Marine Sciences Laboratory, MSL)
QA	quality assurance
QC	quality control
R&D	research and development
RA	radiation area
RF	response factor
RPP	River Protection Project
RSD	relative standard deviation
SRM	standard reference material
SRS	Savannah River Site
THg	total mercury
TSAP	Tank Sampling and Analysis Plan
TSCR	Tank-Side Cesium Removal
UHP	ultra-high purity
WAC	waste acceptance criteria
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

Definitions

analytical sequence	used to describe a set of mercury sample quantifications performed starting with the first calibration standard and ending with the final CCV sample
batch	used to describe a set of samples to be prepared/purged from bubblers at the same time
dimethyl mercury	chemical formula $(CH_3)_2Hg$. Abbreviated as DMHg.
DORM	Canadian reference material fish protein
elemental mercury	chemical formula Hg^0
Hg	chemical formula / abbreviation for mercury
Hg^0	chemical formula / abbreviation for elemental mercury species
Hg^{2+}	typical form of inorganic mercury [inorganic mercury may also occur as Hg_2^{2+} (see definition for Hg_2^{2+})]
Hg_2^{2+}	form of inorganic mercury (also known as Hg^+)
inorganic mercury	chemical formula Hg^{2+} (Hg_2^{2+} (i.e., Hg^+) rare but possible). Synonymous with “ionic Hg”.
methyl mercury	analytically defined as the sum of dimethyl mercury (DMHg) and monomethyl mercury (MMHg). Abbreviated as MeHg. Often used synonymously (erroneously) with MMHg.
monomethyl mercury	chemical formula CH_3Hg^+. Abbreviated as MMHg.
organic mercury	mercury compounds with a Hg-C bond (also referred to as organomercury), organomercury compounds include ethyl mercury, monomethyl mercury, dimethylmercury, and diethyl mercury. These compounds are typically stable toward air and moisture but sensitive to light.
particulate mercury	mercury that is associated with the particle phase (traditionally has not passed through a 0.45-µm filter)
sample	used to describe in general any tank waste or quality control (QC) sample
total mercury	abbreviated as THg; sum of all mercury species
total soluble mercury	total mercury that is not associated with the particle phase (traditionally has passed through a 0.45-µm filter)

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1.0 Introduction

The U.S. Department of Energy (DOE) Hanford Site in southeastern Washington State stores 56 million gallons of chemical and radioactive waste in underground tanks. 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). As a result, the tank waste stored at Hanford is most recently estimated to contain a total mercury inventory of 1,780 kg, based on a 2018 best basis inventory estimate (Fountain et al. 2018).

Over the course of three years, work was conducted at Pacific Northwest National Laboratory (PNNL) that directly supported the tracking of mercury speciation and associated inventories. This new capability and resulting information is intended to ensure future compliance with the Hanford Waste Treatment and Immobilization Plant (WTP) mercury-to-sodium waste acceptance criteria (WAC) (ICD 30, 2021) which was established from secondary waste disposal land disposal restriction requirements, and air permit abatement assumptions during the Direct Feed Low-Activity Waste (DFLAW) mission.

Understanding the movement of mercury, its chemical consequences, its impact on unit operations, and its fate is important in the Hanford flowsheet. Necessary inputs to evaluate the impact of mercury include the magnitude of the mercury feed inventory, how the inventory is distributed throughout the tank farms, how the tank-by-tank mercury speciation inventory is distributed by waste phases (i.e., sludge, saltcake, and supernatant), the expected mercury species during waste processing, the expected final fate of mercury species (e.g., sequestered onto or within treatment systems, captured into secondary waste streams), and finally, the degree of uncertainty in this information.

Closure of the mercury speciation and inventory knowledge gaps will improve confidence in the WAC-affecting feed mercury inventories during waste processing operations and the conclusions drawn in previous testing of the high-level waste (HLW) melter and melter offgas abatement system (Goles et al. 2004) and the WTP mercury pathway and treatment assessment (Cramer 2001). Furthermore, from a Hanford waste processing flowsheet perspective, the fate of mercury is highly dependent on liquid, solid, and gas phase mercury speciation as dictated by the chemical and thermal conditions of the various waste processing unit operations. These assumed flowsheet model stream partitions and associated mercury species remain largely unverified by analyses of samples from representative processes using actual Hanford tank waste.

The focus of the current scope of work was to support the transfer of the ultra-trace mercury speciation and quantification methodology, developed at PNNL during fiscal years (FYs) 2018 through 2020, to the 222-S Laboratory at Hanford. This effort included, but was not limited to, the following three tasks:

1. Assess the current capabilities at 222-S Laboratory for implementing mercury measurements.
2. Provide recommendations for the appropriate mercury speciation for DFLAW and the future mission.
3. Provide considerations and technical documentation for implementing mercury speciation and quantification methods at 222-S Laboratory for total, elemental, and methyl mercury.

A summary and discussion of the recommendations for the appropriate mercury species to support DFLAW and the future mission (Task 1 objective) are provided in Section 3.0. Section 4.0 provides a brief overview of available mercury quantification technologies. An assessment of the current capabilities at 222-S Laboratory for implementing mercury measurements (Task 2 objective) is provided in Section

5.0, and includes a description of the approach and responses provided by 222-S Laboratory technical staff. Section 1.0 documents the methods for mercury speciation and quantification (Task 3 objective) using the ultra-trace mercury speciation methodology developed at PNNL for total, elemental, and methyl mercury (with inorganic mercury determined through calculated difference). The section includes key considerations for equipment and materials, experimental and analytical methods, calculations, and recommendations for modifications for quantification of additional mercury species (i.e., monomethyl, dimethyl, total soluble, inorganic, and particle-bound mercury) and considerations for solid sample quantifications. Lastly, a summary and conclusions of this study are provided in Section 7.0.

2.0 Quality Assurance

This work was conducted under PNNL project 79164, “River Protection Project Integrated Flowsheet Support,” with funding from Washington River Protection Solutions, LLC (WRPS).

All research and development (R&D) work at PNNL is performed in accordance with PNNL’s Laboratory-level Quality Management Program, which provides overall guidance to staff based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. The quality assurance (QA) controls of the WRPS Waste Form Testing Program (WWFTP) QA program, which implements requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008 Quality Assurance Requirements for Nuclear Facility Applications*, graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2, “Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development,” were also applied to this work. The WWFTP QA program includes procedures that provide detailed instructions for performing and documenting research activities and categorizes R&D work into three technology levels based on the amount of QA rigor required: Basic Research, Applied Research, and Development Work (in order of increasing rigor).

The work described in this report was assigned the technology level “Basic Research” and was conducted in accordance with procedure QA-NSLW-1101, *Scientific Investigation for Basic Research*. The analytical work that supports this report is described in Fountain et al. (2018) and Bottenus et al. (2019, 2020), which document the measurement of mercury species in raw waste samples from several Hanford waste tanks. The three reports each state that the work described in the report (also performed under the WWFTP QA program) was assigned the technology level “Applied Research” and was conducted in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. For both the “Basic Research” tasks reported herein and the “Applied Research” tasks reported in Fountain et al. (2018) and Bottenus et al. (2019, 2020), all staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work, and the report was independently reviewed by technical, QA, and project management staff before being issued.

3.0 Key Mercury Species

Pinpointing the best set of mercury species into which the 222-S Laboratory should focus its time, energy, and money is not a trivial endeavor. Numerous variables contributing to this solution are still not well understood, including mercury species concentrations and variability of species fractions both by tank and by waste phase. Opportunistic efforts at PNNL in the last few years have enabled the speciation and quantification of tank waste supernatant and the speciation and quantification of processed (i.e., cesium-ion-exchanged, and particle-filtered) supernatant tank waste samples (Fountain et al. 2018; Bottenus et al. 2019, 2020). Both of these efforts demonstrated the viability and refinement of ultra-trace methods for successful application to Hanford tank waste supernatant and enhanced the knowledge of the parent tank waste supernatant and process impacts on mercury species, but also articulated the unique (e.g., tank-by-tank) mercury speciation characteristic facing DFLAW and the future mission.

Throughout this section and those to follow, the reader may note reference to particular mercury species, e.g., elemental mercury, methyl mercury, dimethyl mercury, monomethyl mercury, inorganic mercury, and total mercury. For clarity and consistency of the lexicon in this report, these mercury species are described in Table 3.1.

The remainder of this section discusses the background and speciation of mercury at Hanford. It also summarizes relevant experience at the Savannah River Site (SRS) as they continue to address their own unique challenges with regard to mercury speciation in tank waste and waste processing operations.

Table 3.1. List of Important Mercury Species

Mercury Species	**Chemical Formula**	**Abbreviation**	**Detection / Notes**
Dimethyl mercury	$(CH_3)_2Hg$	DMHg	Quantified by desorption of Carbotrap®[5]-filled trap, loaded by purging an unacidified sample.
Elemental mercury	Hg^0	Hg^0	Quantified after purging from an unacidified sample onto gold trap and analyzed.
Inorganic (or ionic) mercury	Hg^{2+} *(i.e., mercuric, mercury (II))* and Hg_2^{2+} *(i.e., mercurous, mercury (I))*	None	Quantified independently after purging to remove any elemental mercury, and being reduced (i.e., $SnCl_2$), the sample is purged a second time to quantify the inorganic species. Alternatively, inorganic mercury can be quantified indirectly from difference between: 1. Inorganic mercury = THg - Hg^0 - MeHg or 2. Inorganic mercury = THg - Hg^0 - MMHg - DMHg
Organic (or organo) mercury	None *(Hg-C containing compounds)*	None	Organometallic compounds that contain mercury (compounds containing Hg-C bond). Typical examples include methyl mercury, monomethyl mercury, dimethyl mercury, ethyl mercury, and diethyl mercury. Detected using the methods summarized in this table for specific organic mercury species.
Methyl mercury	None *(mixture of any/all methylated mercury species)*	MeHg	Analytically defined as the sum of DMHg and MMHg. Quantified by desorption of the Carbotrap®-filled trap loaded by purging an acidified sample (for seawater, see Black et al. 2009).
Monomethyl mercury	CH_3Hg^+	MMHg	Quantified by desorption of the Carbotrap®-filled trap loaded by purging of an acidified sample following ethylation with sodium tetraethylborate.
Particulate mercury	None	None	Analytically, this is defined as the mercury collected on a 0.45-µm filter paper. Alternatively defined as the difference between the total mercury in a sample and the dissolved mercury in a sample: Particulate mercury = THg – Soluble mercury
Total mercury	None *(sum of all mercury species)*	THg	Analytically defined as the mercury detected as elemental mercury from desorption of a gold trap loaded by purging of sample after oxidation (e.g., BrCl) and reduction (i.e., $SnCl_2$).
Total soluble (or dissolved) mercury	None *(sum of all mercury species that pass through a 0.45-µm filtration device)*	None	Analytically defined as the mercury detected as elemental mercury from desorption of a gold trap loaded by purging of sample after filtration through a 0.45-µm filtering device, oxidation (e.g., BrCl), and reduction (i.e., $SnCl_2$).

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

3.1 Hanford Mercury Background

As discussed in Section 1.0, 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 on a 2018 best basis inventory estimates, suggest a total mercury inventory of 1,780 kg (Fountain et al. 2018) in the Hanford tank farms. Aside from the obvious concerns about human exposure to tank vapors, mercury species in the tank waste liquid and solid fraction pose a risk to the implementation and execution of the River Protection Project mission due to mercury concentration limits imposed under WTP waste acceptance criteria established by toxicity characteristic leaching procedure restrictions for secondary waste disposal, and air emission permits. While processing of tank waste at Hanford has only recently commenced [with start-up of the Tank-Side Cesium Removal (TSCR) system], continued and accelerated waste processing operations in the WTP are imminent, and as such, representative mercury inventory tracking will be important to anticipating and mitigating WTP stack emissions and secondary liquid waste disposal issues like those experienced at SRS (Bannochie et al. 2017)

Secondary solid waste disposal considerations and approvals for items such as crystalline silicotitanate, grouted Effluent Management Facility overheads, and the WTP low-activity waste (LAW) melters are dependent on total mercury retention. Closing the mass balance around these streams with respect to mercury speciation will provide key information (e.g., species-specific retention characteristics) to resolve or mitigate noncompliant waste issues and can provide insight for optimizing plans for secondary waste treatment and disposal based on the mercury speciation.

3.2 Hanford Mercury Speciation

A more detailed discussion of mercury speciation at Hanford can be found in Fountain et al. (2018). In short, mercury speciation at Hanford has largely been derived from thermodynamic arguments using the Environmental Simulation Program (ESP), a chemical thermodynamic simulator. The prevalent ESP-predicted mercury species in the liquid waste are the inorganic mercury species mercury hydroxide ($Hg[OH]_2$) and mercury chloride ($HgCl_2$), and the only ESP-predicted mercury species in the solid waste inventory is mercury oxide (HgO) based on high waste pH (Anderson 2016; Meacham 2015). As such, the predominant liquid phase mercury in the waste tanks is believed to be in the mercury (II) or mercuric ion form (Hg_2^{2+}) and is tracked by flowsheet modeling in this form. In addition to the inorganic mercury content, organic liquid phase mercury species in the tank farms are primarily believed to be dimethyl mercury, elemental mercury, and methyl mercury. However, considerable uncertainty exists as only limited mercury speciation has currently been measured and only a total mercury measurement is conducted at Hanford, as described and discussed in more detail in Section 5.0.

The mercury species in the waste solids are largely unknown, likely waste-type-specific, and currently assumed to exist predominantly as HgO (based on high waste pH) for flowsheet assessment and modeling purposes.

Analysis for three species of mercury (total, elemental, and methyl) for 11 different Hanford supernatant waste tank samples (where a fourth species, inorganic mercury, could be indirectly calculated from the others) has been successfully completed at PNNL. However, the speciation fraction of total mercury measured, and the overall concentration of mercury species, has ranged broadly depending on tank and waste treatment, with the elemental mercury fraction of the total mercury concentration ranging from a low of 2% to a high of 43% (Bottenus et al. 2019, 2020) and methyl mercury fraction ranging from a measured low of 0.3% to a high of 25% (Bottenus et al. 2020). This variability is presumed to be a direct reflection of the variability of mercury concentrations and speciation present in the Hanford waste tanks. Increasing the quantity and quality of mercury speciation data surrounding Hanford tank waste processing operations (e.g., DFLAW) will help to elucidate the variability and potentially help to guide predictions of the impact.

Furthermore, the evaporation rate of mercury species, which is governed by the vapor pressure, depends on the volatility of the compound and the associated temperature. Mercury compounds can vary significantly in their vapor pressures and volatilities such that physiochemical changes can affect the phase concentrations (Robles et al. 2014). As such, without more detailed understanding of the mercury speciation at distinct points throughout the Hanford flowsheet, it becomes challenging to accurately predict the mercury speciation, especially when such broad variability in ranges of mercury speciation has already been demonstrated.

3.3 Savannah River Site Mercury Speciation

Significant investigative quantification efforts have taken place at SRS in response to the detection of unexpectedly high levels of mercury in the leachate derived from a Saltstone sample (Miller 2015) and discovery of monomethyl mercury in the feed to the Saltstone process (Jain et al. 2015). In response, thorough evaluations throughout the SRS flowsheet were performed and included mercury speciation conducted at commercial laboratories such as Brooks Applied Laboratories and Eurofins Frontier Global Sciences, LLC. The recent evaluations have included seven mercury species [dimethyl mercury, methyl mercury, ethyl mercury, total mercury, elemental mercury, inorganic mercury, and dissolved (total soluble) mercury], with the eighth species (particulate mercury) determined by difference.

Several surprises were identified from this characterization effort. Bannochie et al. (2017) found that a processing tank (Tank 39) that was expected to contain nearly 100% of the mercury in the form of inorganic mercuric ion had only about one-fourth of the total mercury in the form of inorganic mercury. The next surprise was the measurable concentration of methyl mercury (Bannochie et al. 2017), which led to the postulation that inorganic mercury reacted in the presence of organic s-containing tank waste to form monomethyl mercury. Comparison of the dimethyl mercury concentrations in Bannochie et al. (2017) to results from Wilmarth et al. (2004) showed lower dimethyl mercury concentrations in Bannochie et al. (2017), perhaps due to a change in the antifoam agent being used at the evaporator, but the change in antifoam agent also could have contributed to the increase in methyl mercury (if the new antifoam agent were only singly methylating the mercury).

Overall, the assessments of mercury at SRS have provided improved guidance for identifying mercury separation technologies, but they have also demonstrated that the predictability of the behavior of mercury across the liquid waste system requires knowledge about the mercury species contained in the liquid, solid, and vapor phases.

Most recently, Stone (2020) investigated the potential application of the SRS mercury speciation assessments for informing the mercury speciation at Hanford and during waste processing at Hanford. Despite these careful assessments and comparisons based on notable differences between SRS and Hanford Site waste and processing, the speciation efforts at PNNL have already suggested differently. As an example, Stone (2020) notes the expectation for “very little elemental mercury”; however, the elemental mercury fraction of the total mercury concentration was shown to be as high as 43% (Bottenus et al. 2019, 2020). Until further assessments can be made on Hanford tank waste and during Hanford waste processing, it is likely that “surprises” (like those referenced by Bannochie et al. 2017) will continue to enlighten the knowledge of mercury speciation in the Hanford flowsheet.

3.4 Key Mercury Species Conclusions

Typically, mercury can exist in three primary forms: organic, inorganic, and elemental. Mercury can also be bound to a solid phase (i.e., particle-bound). It is also known that the speciation of mercury strongly affects the distribution of mercury in the various phases, (i.e., aqueous, liquid, vapor, or particle-bound), and furthermore affects the transfer of mercury between these phases. Additionally, chemical properties important to these understandings such as the boiling point, density, vapor pressure, and solubility are also species-dependent. Therefore, the fate of mercury that enters each unit operation will depend strongly on speciation and partitioning between the aqueous, liquid, vapor, and particulate-bound phases.

Efforts to speciate and quantify mercury in complex tank waste (e.g., at SRS and Hanford) and understand the drivers for these speciation trends have revealed challenges associated with attempting to apply conclusions from the mercury speciation at SRS to Hanford tank waste. Generally, the Hanford tank waste has much higher concentrations of organic compounds (e.g., carbon-containing compounds like benzene or butanol) and chloride-containing compounds than at SRS. However, the overall quantity of mercury in the waste is significantly lower in the Hanford tank waste compared to SRS. Fountain et al. (2018) estimated, using best basis inventory (BBI), a total mercury inventory in Hanford tank waste of 1,780 kg, while it is estimated that more than 30 times that amount, 60 metric tons, of mercury have been used and discharged to the SRS tank farms (Jain et al. 2015). Unit operations between the two sites are also planned to operate differently. For example, while antifoam agents are used at both sites, the chemical compositions are different and could result in a completely different impact during Hanford operations, depending on the species of mercury entering the evaporator; the evaporators across the two sites will inherently impact the mercury speciation differently. The Hanford evaporators operate under vacuum rather than atmospheric pressure (as at SRS), leading to potentially more readily volatilized species such as elemental and dimethyl mercury into the condensate (i.e., overhead) streams, which are ultimately routed as a secondary liquid effluent to the Liquid Effluent Retention Facility and Effluent Treatment Facility at Hanford. However, these operations can potentially concentrate lower-volatility species into the concentrate (i.e., bottoms) stream, which enter the recycle stream and could result in a potential accumulation scenario within the WTP LAW Facility.

Ideally, a sample train approach that quantifies the eight species – total mercury, elemental mercury, methyl mercury, monomethyl mercury, dimethyl mercury, inorganic mercury, total soluble mercury, and particulate mercury (by difference) – would offer the most insight into the fate and impact of mercury in the DFLAW flowsheet. This type of speciation effort would be most valuable early on and around key unit operations or facility transfers, once the behavior is known, the speciation needs could be focused to the most critical based on location within the flowsheet. Then capabilities could be re-energized if ever an upset was suspected, or a major flowsheet change was anticipated. Section 6.4 further describes the opportunities and options for these additional mercury species quantifications. However, the most critical baseline mercury species are total mercury, elemental mercury, methyl mercury (analyzed as a combination of monomethyl and dimethyl), and inorganic mercury (by difference). Investing in the instrumentation and developing the capability for quantification of these four mercury species will allow the greatest flexibility in the future if analyses of additional mercury species (monomethyl mercury, dimethyl mercury, total soluble mercury, particulate mercury, ethyl mercury, etc.) are desired later.

4.0 Summary of Available Mercury Quantification Technologies

Various analytical techniques are available for mercury quantification. The most common approaches are briefly described below.

Cold Vapor Atomic Absorption Spectroscopy (CVAAS). Quantification by atomic absorption is a commonly used technique and is the reference method for mercury in drinking water under the Safe Drinking Water Act following EPA Method 245.1 (EPA 1994a). Mercury detection limits using CVAAS are typically around 1 ng/L. This technique can be applied to many different sample matrices such as water, soil, and fish tissue. In brief, a digested, acidified, liquid sample is introduced into a mixing chamber where all the present mercury is reduced (typically with $SnCl_2$) to elemental mercury. The gaseous elemental mercury is then carried into the atomic absorption detector for quantification. Total and elemental mercury forms can be quantified with CVAAS by varying the pre-quantification steps.

Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). Similar to CVAAS is mercury quantification by fluorescence. The major benefit of CVAFS is the lower detection limit and larger dynamic range than CVAAS. Detection limits can be further improved by incorporation of a preconcentration step through gold amalgamation (single or double gold-coated sand-filled trap or gold-coated bead-filled trap), allowing for mercury to be quantified to the ultra-trace, approximately 0.01 ng/L, level. EPA Method 1631 (EPA 2002) and EPA Method 245.7 (EPA 2005) provide method details for the determination of THg by CVAFS with and without gold amalgamation, respectively. EPA Method 1630 (EPA 1998) provides method details for the determination of MeHg by CVAFS.

Direct Analysis by Thermal Decomposition. Alternatively, mercury can be measured directly by drying and then combusting a sample directly to liberate mercury into the gas phase, which is then quantified with atomic absorption. Direct mercury analyzers do not require a chemical digestion of the sample prior to analysis, unlike with CVAAS or CVAFS. In this process, mercury is thermally desorbed from the sample matrix prior to analysis of total mercury, thus allowing quantification of solids, liquids, or gases. The detection limits associated with direct mercury analysis by thermal decomposition are typically around 0.001 ng of mercury. Since various matrix types can be analyzed, detection limits are reported in terms of total mercury mass. However, most systems have limitations on sample size/volumes that can be introduced into the system, and for liquid samples this often translates to a detection limit much higher than can be achieved with CVAAS or CVAFS. For example, the Milestone DMA-80 direct mercury analyzer has a maximum sample mass limit of 1.5 g. For solid sample testing, a direct analyzer can be the preferred system because the analysis does not require time-consuming pre-digestion of samples. Direct mercury analyzers can only measure total mercury and are unable to distinguish between mercury species, including methylated forms.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Coupling gas phase separation (e.g., CVAFS) with ICP-MS allows for the simultaneous quantification of enriched stable mercury isotopes (i.e., an internal standard) that can be added to the sample and used to normalize results for isotope recovery. Such a technique removes the need to account for volume changes (i.e., via dilutions or reagent additions) over the course of preservation, storage, and sample preparation (including distillation). However, such systems are typically costly and require experienced ICP-MS technical staff. ICP-MS can provide ultra-trace level detection limits and can be paired with the required pre-quantification steps in EPA Method 1630 (EPA 1998) to measure methyl mercury and EPA Method 1631 (EPA 2002) to measure total and elemental mercury.

While several mercury quantification methods are available, each with benefits and limitations, the bulk of this report will focus on recommendations surrounding mercury quantification using CVAFS. Ultra-trace levels of total, elemental, and methyl mercury in Hanford tank waste samples using CVAFS were successfully measured at PNNL (Fountain et al. 2018; Bottenus et al. 2019, 2020).

5.0 222-S Laboratory Mercury Capabilities

The first task addressed in this work scope was to assess the current capabilities, measurements, and methodologies at the 222-S Laboratory for implementing mercury measurements. Sections 5.1, 5.2, and 5.3 describe the approach taken by the PNNL teams along with the results and conclusions of the investigative effort. While inquiries for both the mercury and iodine speciation capabilities were performed simultaneously and discussions in the results section (Section 5.2) address both iodine and mercury topics, the conclusions (Section 5.3) are specific to only the discussion of mercury speciation capabilities. Results and conclusions addressing iodine capabilities at the 222-S Laboratory have been previously documented in a letter attachment to LTR-OSIF-026 (Fountain and Soderquist 2021).

5.1 Approach

PNNL staff conducted preliminary phone conversations and email exchanges with Stacey Bolling, (Research and Technology Development Manager), to inform her of the intended work scope and to solicit recommended expert technical contacts at the 222-S Laboratory. Support for these activities was approved and key expert contacts Michael J. Lindberg, [title], and Mikaela L. Alexander, [title], were identified to cover both iodine and mercury method development discussions. Subsequent preliminary contact was made with Mr. Lindberg to briefly discuss the mercury and inorganic iodine speciation methods scope. A follow-on group meeting was established to 1) gather 222-S Laboratory capabilities details; 2) convey an overview of PNNL's mercury and iodine analytical methods; and 3) allow for all expert contributors to share experiences, clarify details, and generate any additional lines of inquiry as preliminary information was shared. A separate set of key questions was documented by PNNL staff and posed to 222-S Laboratory experts (Mr. Lindberg and Ms. Alexander) during two separate email threads (in July 2021 and January 2022) and those results are documented in Section below for completeness. Again, both PNNL technical teams (mercury and iodine experts) met with the 222-S Laboratory experts at the same time and posed the line of questioning below addressing both analytical techniques.

5.2 Results

The line of questioning below was applicable for understanding the capabilities at 222-S Laboratory for both mercury measurements and iodine measurements; therefore, responses are provided below in their entirety. However, as stated previously, discussions of iodine measurements are outside the scope of this report and are documented elsewhere. Minor changes have been made to the questions and answers supplied below, these changes have not altered the intent or meaning of the information but have been made to resolve typographical errors or to make sentences more complete.

Resulting key lines of questioning from PNNL and subsequent replies (italicized text) from 222-S Laboratory staff (Michael J. Lindberg and Mikaela L. Alexander):

- What current methods of iodine/mercury measurements do you have in place?
    - *HLMI-PRO-LA-51150, Total Mercury Analysis by Cold Vapor Atomic Absorption*
    - *HLMI-PRO-LA-51158, Iodine-129 in Tank Farm Solids*
    - *HLMI-PRO-LA-51157, Determination of I-129 in Waste Tank Sample.*
- Can you please provide electronic copies of the procedures?
    - *Provided as e-mail attachments.*

- Can you provide a list of equipment (model/type) used in these methods?
  - *Currently, our customers have only requested iodine as ^{129}I (extracted by methylene chloride and counted by gamma energy analysis). A new method can be spun off from the current method incorporating Chuck's [PNNL scientist Chuck Soderquist] process steps for speciation followed by ICP-MS analysis for ^{127}I and ^{129}I.*
  - *Mercury analysis is performed using a PerkinElmer FIMS 400 Flow Injection Mercury System. The amalgam unit, presently not connected, is a PerkinElmer amalgamation unit.*
- Do you have a radiological inductively coupled plasma mass spectrometry (ICP-MS) with a collision cell to address xenon (Xe) interference?
  - *Yes, we have an Agilent 8900 QQQ with reaction cell. O_2 will be used as a reaction gas to eliminate the Xe interference.*
- Do you have a cold vapor atomic fluorescent spectrometer (CVAFS) for elemental mercury detection?
  - *Yes*
  - If so, what model and brand?
    - *See above PerkinElmer system.*
  - Does it include two stages in the desorption columns?
    - *No. Single-stage desorption columns are currently used.*
  - Is it routinely used, calibrated, etc.?
    - *The instrument is routinely used for total mercury analysis in support of tank waste characterization.*
- If specific standards, reagents, ultra-pure water, special purge gases, etc., are used in these method measurements, can you provide a list?
  - *There are no specialty standards, reagents, or gases. All are available from your typical vendors. All water is deionized and finished by a benchtop polishing unit.*
- Are there any "pre-qualification" measures or verifications taken/done prior to any iodine/mercury measurements?
  - *Not for Hanford waste tank samples.*
- Can (or do) any of these measures "disqualify" samples from further analysis?
  - *N/A (no pre-qualification measures or verifications).*
- Are these qualifications inherent to all analysis done at 222-S Laboratory (maybe overarching safety qualifications) or are they specific to iodine or mercury samples only?
  - *N/A (no pre-qualification measures or verifications).*
- Historically, have there been alternative methods for iodine/mercury speciation and measurement that are no longer used?
  - *No.*
- If so, what are the key differences to existing methods, and why were they changed?
  - *N/A (previous answer was "No").*

- What are the typical volumes used in current methods of iodine/mercury measurements?
  - *For iodine it is typically 1 mL.*
  - *For mercury it is typically 1 mL or less.*
- Are these volumes dictated by procedure or method limits, radiological limitations, experience, etc.?
  - *Volumes are typically dictated by procedure, but volume can be adjusted based on radiological and/or experience.*
- What is the approximate volume of supernatant liquid that would be allowed to move from the hot cell to a contamination area (CA) fume hood posted as a radiation area (RA)?
  - *Typically 15 mL or less.*
- What are the current detection limits (DLs) for iodine/mercury measurement methods? What is the biggest factor contributing to the current DLs?
  - *The estimated quantitation limit (EQL) for ^{129}I is 9.88 E-06 µCi/mL. Actual detection limits will vary with sample size.*
  - *The established EQL for mercury is 2.84 E-03 µg/L. Actual detection limits will vary with sample size.*
- Do you have a prescriptive process used to develop and implement a new analytical technique at 222-S Laboratory?
  - *Yes, there are two options: 1) test plans for non-routine analysis and 2) analytical procedures for routine analysis. During this process, a test plan will be used for method development followed by analytical procedure when the process is dialed in.*
- If yes, what is the procedure or plan and can we get a copy?
  - *Provided as an e-mail attachment:*
    - *HLMI-PLN-ASYS-51131, Procedure Program Description*
    - *HLMI-PRO-ASYS-50030, Test Planning, Method Verification, and Instrument Qualification*
    - *HLMI-PRO-LO-51015, Laboratory Test Planning*
- We assume you operate under the Hanford Analytical Services Quality Requirements Document (HASQARD; DOE/RL-96-68) like PNNL's Analytical Services Operations (ASO). Please confirm.
  - *Yes.*
- How are analytical methods executed at 222-S Laboratory, all by technicians or chemists too?
  - *Non-routine analyses are typically performed by a chemist. Once the process becomes routine, it will be performed by a chem. tech.*
- When supernatant samples come into 222-S Laboratory, is there a specification on the minimum volume required?
  - *Typically, the sample volume is 250 mL at the specified tank elevation for liquid grab samples. If requested, multiple samples can be taken at each sampling location. The Tank Farms Contractor directs sampling by a Tank Sampling and Analysis Plan (TSAP).*

- And are there prioritized analysis sequences when samples arrive with volume below the minimum necessary to conduct "all" analysis?
  - *Yes, this is directed by the TSAP. If this occurs, it is usually related to solid grab and core sampling. This is usually not an issue for liquid grab samples unless a re-run is requested.*
- What are the typical dilution factors required?
  - *For mercury it is typically 20-fold with a digestion factor.*
- Are there any methods historically, active, or planned that would be focused toward solid or slurry phase sample measurements?
  - *There are active procedures for both slurry and solid samples.*
- Do you have methods for solid phase analysis and speciation? Or other matrixes?
  - *Currently there are no active procedures for speciation for any matrices.*
- How much time does it take from sampling at the tank to entry of sample into hot cell?
  - *Every effort is made to load the samples immediately as they arrive from the tank farms. With no issues, this happens within a couple of hours from sampling to hot cell load in and no longer than 1 working day.*
- In an effort to help identify the most feasible system configuration(s) for a total, elemental, and methyl mercury quantification, please elaborate on the following topics:
  - What is the current and/or expected sample throughput (per week, per month, etc.)?
    - *Currently we analyze 12 to 15 samples per analytical batch. With current staffing, this equates to 1 to 2 batches per week.*
  - If exact future throughput is still unknown, can an estimated range be specified (e.g., between 5 and 20 samples for each mercury species, etc.)?
    - *Same as current throughput.*
  - What is the approximate footprint currently used for mercury speciation in 1) a CA fume hood, 2) benchtop (if applicable), 3) other space if applicable?
    - *Currently we are using three CA fume hoods.*
  - What is the available footprint in a CA fume hood to handle mercury speciation work?
    - *This is based on priority and will need to be determined by laboratory management.*
  - What is the available footprint on a benchtop to perform rad work? What are the radiological limits associated with any of the available benchtop space?
    - *Currently the analytical support area of 222-S Laboratory is a CA. All available benchtops and fume hoods are in the CA. Typically, radiological work is performed in a fume hood.*
  - Would there be a preference and concern(s) with the use of either a manual system or an autosample-based system for mercury speciation and quantification?
    - *No preference, but autosampler would be more efficient.*

  - Previously (first round of inquires circa August 2021), it was noted that samples are typically analyzed within 1 workday of arrival into the hot cell. Is this generally a whole day/half day/etc., activity for the chemist or chem. tech? Is it usually a 1-person activity or are 2+ workers typically involved?
    - *Sample are loaded out of the hot cell ASAP, typically 1 day. Samples for mercury are analyzed within 28 days. Mercury analysis is typically one person for 2 days.*
  - Are there limits to the number of people allowed in the available laboratory space (used and/or available for mercury speciation work)? If there are occupation limits implemented due to COVID-19 requirements, can you please specify both the pre-COVID limitations and the current limitations?
    - *No. Just physical space of the individual laboratories.*

- Which, if not all, steps of the mercury quantification and sample handling/preparation/etc., are conducted inside a CA fume hood? If applicable, which steps or equipment are conducted outside of the CA fume hood?
  - *All work is performed in a fume hood.*
- Has there been quantification of solely the elementary mercury species in samples? If so, can you please provide more information on the methods, procedures, or modifications necessary to perform the elementary mercury quantification? Or has the elementary mercury quantification been based on the digestion of all mercury species to elementary mercury, resulting in the previously described total mercury quantification?
  - *We have only measured total mercury.*
- Are there existing reference methods or procedures for the use of the PerkinElmer amalgamation unit?
  - *No.*
- Has the amalgamation unit ever been used with tank waste samples previously?
  - *No.*
- Is there interest in using the amalgamation unit for its ultra-trace capabilities or other? Or are there known challenges that have prevented its installation/use?
  - *There is an interest. Installation is dependent on facility modifications.*
- Which chemicals and reagents being used are specifically denoted as being mercury-free or similar (e.g., 0.0000005% max) from their vendors? Recognizing that the procedure HLMI-PRO-LA-51150 specifies minimum 99.0% minimum mercury free for $KMnO_4$.
  - *This has not been verified. Acids are trace metal.*
- Which chemicals and reagents being used are specified as low-mercury or similar? Which, if any, have a different designation with regards to mercury content?
  - *Could you please clarify?*
- What sample storage containers are currently used (type and material, sizes if possible)? If possible, please specify from the grab sample through the end of analysis. Please include any known details on lids.
  - *All storage containers are borosilicate. Analysis containers are polypropylene.*

- Are there any other containers, flasks, etc., used in the sample preparation that are used? Or are all chemical additions handled in either in a primary sample container (information provided above) or in the instrument?
  - *No.*
- How are currently used sample containers cleaned or prepared prior to use? Are any re-used? If so, how are they cleaned and stored?
  - *All containers are one time use.*

5.3 222-S Laboratory Mercury Capabilities Conclusions

Historically, the 222-S Laboratory has provided total mercury quantification to customers, but with no further speciation (elemental, inorganic, monomethyl, dimethyl, etc.). Total mercury techniques for both liquid and solid samples exist at 222-S Laboratory: HLMI-PRO-LA-51150, *Total Mercury Analysis by Cold Vapor Atomic Absorption* (HLMI 2020a). This procedure is based on SW-846, Methods 7470A, *Mercury in Liquid Waste (Manual Cold-Vapor Technique)* (EPA 1994b), and 7471B, *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)* (EPA 2007a). A new capability to speciate and quantify, at a minimum, total mercury, elemental mercury, methyl mercury, and inorganic mercury (by calculated difference) is to inform mission planning and anticipate compliance with secondary waste disposal and air permitting. The necessary analytical equipment to quantify total mercury, elemental mercury, methyl mercury, and inorganic mercury (by difference) using the ultra-trace mercury speciation and quantification methods developed at PNNL does not currently exist at the 222-S Laboratory. The new 222-S Laboratory analytical procedures will need to be developed using the documented analytical guidance provided in the following sections of this report. However, it is likely that expert PNNL consultation, reviews, and troubleshooting support will be necessary to ensure that the liquid separations techniques are implemented efficiently. An experienced 222-S Laboratory chemist will be required to ensure adequate execution and documentation of the separations during initial implementation of this new analytical method. The 222-S Laboratory has knowledgeable chemists (e.g., Michael J. Lindberg and Mikaela L. Alexander) who can conduct this work reliably and reproducibly.

An existing capability to quantify total mercury using a PerkinElmer FIMS 400 flow injection mercury system does exist at the 222-S Laboratory. A PerkinElmer amalgam unit, presently not installed but previously purchased, is also available; if connected, it offers the ability to quantify total mercury to lower "ultra-trace" levels (based on PerkinElmer product information) but does not allow for mercury speciation. As such, investment in new equipment is identified as necessary to successfully implement this new ultra-trace mercury analytical method. Additional reagents will need to be purchased, but these are readily available and routine.

Typical sample volumes used previously at 222-S Laboratory for total mercury quantification have been about 1 mL but could be as large as 15 mL based on typical tank waste dose rates, radiological limits, and ALARA considerations for bringing this material into a fume hood from the hot cell. Hanford tank waste sample volumes used previously at PNNL have ranged from 0.2 to 4.5 mL depending on the mercury species of interest, number of replicates desired, and tank waste dose rate. The necessary sample volume will be dictated by procedure and adjusted as needed to achieve detection targets while minimizing radiological exposure and risk. The current 222-S Laboratory EQL and method detection limit (MDL) for total mercury are 2.84×10^{-3}µg/L and 2.58×10^{-4} µg/L, respectively, based on a typical sample size of 1 mL. The PNNL estimated MDL for ultra-trace mercury speciation for total and methyl mercury are 4.7×10^{-5} µg/L and 2.5×10^{-5}µg/L, respectively (roughly one order of magnitude more sensitive).

Sample handling at the 222-S Laboratory and PNNL is very similar – specifically, the immediate entry of samples into hot cells and subsampling occurring as soon as possible for time-sensitive samples. Analytical separations can then begin that day or the next working day, as needed.

Procedurally, 222-S Laboratory will need to execute either HLMI-PRO-LO-51015, *Laboratory Test Planning* (HLMI 2021b)*,* or more likely HLMI-PRO-ASYS-50030, *Test Planning, Method Verification and Instrument Qualification* (HLMI 2020b)*,* to safely plan and perform the new analytical method development work. As mentioned previously, details of the key technical steps to separate mercury species, key equipment, reagents, and important cautions are provided in Section 1.0 to serve as the technical reference for the 222-S Laboratory mercury speciation method qualification and test procedure development.

6.0 Measurement of Mercury Species

The protocols, considerations, and suggestions discussed in the following sections are primarily derived from direct experience at PNNL in conducting ultra-trace mercury speciation and quantification activities with Hanford tank waste samples. The PNNL ultra-trace mercury speciation and quantification analytical methodology is based on EPA Method 1630 (Draft), *Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* (EPA 1998), for the methyl mercury speciation, and EPA Method 1631 Rev E, *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* (EPA 2002), for the elemental and total mercury speciation and quantification. While these methods are specific to liquid phase samples, identical methods can be adopted for solid and slurry samples with the addition of an initial sample treatment step, as discussed in Section 6.5.6.

Ultra-trace analysis requires careful avoidance of sample contamination. Successful contamination control requires that ambient samples, standards, and blanks do not come into contact with materials or an atmosphere that contains mercury. Rigorous cleaning of sample storage bottles and sample preparation containers is required. Precleaned glassware suitable for trace mercury analysis is also commercially available. Samples are especially susceptible to contamination when open to laboratory air. A class 100/ISO 5 level cleanroom is recommended for sample processing. Alternatively, non-metal hoods equipped with laminar flow through high-efficiency particulate air (HEPA) filters or mercury-free air can be used when cleanrooms are not available. Hood surfaces should be wiped clean prior to sample processing with lint-free wipes to remove particles. Cross-contamination can also introduce mercury into samples. Non-powdered gloves must be worn when handling samples or any surface that will contact sample solutions. Gloves must be removed and replaced after any contact with a material of high or unknown mercury content. Handling of high-mercury-concentration standard stocks should be spatially and temporally separated from handling of ambient samples. If sample storage bottles or sample preparation containers are cleaned in-house, any container known to have contained high mercury content should be pre-cleaned and tested prior to mixing with general labware for samples, blanks, and calibration standards.

In addition to minimizing contamination risks, the successful implementation and execution of the recommended ultra-trace mercury speciation and quantification methodology techniques requires attention to several considerations and evaluations (e.g., preparatory work) prior to receiving samples or implementing the recommended methodology. The following subsections address these topics along with the primary methodology discussion, as follows:

Methods (Sections 6.1 through 6.4)

1. Stabilization and Preservation Procedures (Section 6.1)
2. Preconcentration and Separation Procedures (Section 6.2)
3. Sample Quantification by CVAF Spectroscopy (Section 6.3)
4. Mercury Speciation Flowchart (Section 6.4)

Requirements and Considerations (Sections 6.5 through 6.18)

5. Considerations for Speciation and Quantification of Additional Mercury Species (Section 6.5)
6. Waste Disposal Considerations (Section 6.6)
7. General Hazards (Section 6.7)
8. Equipment and System Options (Section 6.8)
9. Laboratory and Sample Configuration Considerations (Section 6.9)
10. Chemicals, Mercury Standards, and Reagents (Section 6.10)
11. Quality Control Samples and Data Quality Objectives (Section 6.11)
12. Blanking and Trap Quality Checks (Section 6.12)
13. Analysis Testing Order Considerations (Section 6.13)
14. Notes on Material Selection (Section 6.14)
15. Stability of Mercury Species Collected on Solid Adsorbents or in Distilled Solutions (Section6.15)
16. Sample Size and Trap Saturation Evaluation (Section 6.16)
17. Methyl Mercury Distillation and Efficiency (Section 6.17)
18. Considerations for Dual-Laboratory Configuration Laboratory Handoff (Section 6.18)

6.1 Stabilization and Preservation Procedures

Ultra-trace mercury quantification is very sensitive and dependent on the ability to appropriately collect and sufficiently stabilize and maintain the integrity of the mercury speciation within a sample in a timely manner. This is because mercury species can, under certain conditions, react and transform between species or be lost from the primary phase (e.g., volatilization from the liquid phase), thus potentially confounding analytical results of samples with less-than-adequate treatment and handling. To prevent such processes from occurring, stabilization and preservation steps need to be taken. Stabilization steps limit mercury loss or conversation and includes either minimizing the headspace as to prevent volatilization or decreasing the pH below 2 for stabilization of methyl mercury in solution. Preservation efforts on the other hand convert all species to a more stable form. Total mercury preservation is done by adding an oxidizing agent which converts all mercury species to stable Hg^{2+} to prevent loss.

Since mercury quantifications involve one or more readily volatilized mercury species (e.g., elemental mercury and dimethyl mercury), if extended sample holding times are expected (on the order of days or longer) prior to stabilization and/or preservation, then samples should be stored in such a way to minimize headspace in the container. However, care needs to be taken when selecting the container size as to not unintentionally dilute samples below detection limits when minimizing headspace. Overall, it is a best practice to store all samples that are still in the liquid phase in tightly sealed, light-limiting conditions at temperatures as close to 4 °C as possible. Once samples have been purged onto solid phase traps, they should again be appropriately sealed and maintained cool and in conditions that prevent the accumulation of water vapor. This discussion is also strongly tied to the discussions found in Section 6.14, which specifically address considerations of material selection and the impact of materials on mercury sample integrity.

6.1.1 Total Mercury

To quantify all the mercury in a sample (i.e., total mercury), all mercury species must be first oxidized to Hg^{2+}. Hg^{2+} is stable, and thus this preservation step should be completed as soon as possible to ensure sample quality. If the sample cannot be immediately preserved, then minimization of headspace is an acceptable method of stabilization until oxidation can be complete. Bromine monochloride [BrCl, 2.5% (w/v), Brooks Rand Instruments, Seattle, Washington, USA] is the recommended oxidant to ensure sample preservation as well as to liberate mercury from organic complexes and particulates prior to preconcentration, separation, and analysis (EPA 2002; MSL-I-013).[6] When using BrCl for total mercury analysis, 2.5% (w/v) BrCl solution should be added to the tank waste samples in 0.5-mL increments until a yellow color persists for a minimum of 12 hours. The yellow color indicates excess BrCl is present, and the sample is properly preserved. For reference, the tank waste samples analyzed by PNNL required between 1 and 2 mL BrCl per milliliter of raw tank waste sample and between 0.5 and 0.83 mL BrCl per milliliter of treated (i.e., filtered and cesium-decontaminated) tank waste sample (Bottenus et al. 2020). Recommendations for storage container material are further detailed in Section 6.14, but in brief, glass containers are recommended over plastic or Teflon bottles.

6.1.2 Elemental Mercury

Elemental mercury samples need to be preserved in a manner that prevents off-gassing of elemental mercury into the vapor phase. This requires sample storage bottles to be completely filled to minimize headspace (and does not require preservation reagents). Headspace minimization is best completed by adding a known volume of high-purity deionized (DI) water (> 18 MΩ and of known low-mercury content). Without proper storage, elemental mercury can volatilize into the headspace during extended sample storage, reaching an equilibrium between the dissolved and gaseous content. Recommendations for storage container material are further detailed in Section 6.14, but in brief, glass containers are recommended over plastic or Teflon bottles, and metal containers should be avoided. Plastic and Teflon containers are less suitable for elemental mercury storage as they permit gas exchange, albeit only very slowly.

6.1.3 Methyl Mercury

Preservation of samples for methyl mercury analysis requires the addition of 10% HCl (trace metal grade) to decrease pH to ~2, stabilizing the methyl mercury species in solution (EPA 1998). Sample acidification is also necessary for the analytical separation via distillation. For reference, the tank waste samples analyzed by PNNL in FY 2020 required between 0.75 and 1 mL of concentrated HCl per milliliter of raw tank waste sample and between 0.38 and 0.47 mL of concentrated HCl per milliliter of treated (i.e., filtered and cesium-decontaminated) tank waste sample (Bottenus et al. 2020). Recommendations for storage container material are further detailed in Section 6.14.

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[6] MSL-I-013. *Total Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-013, Rev. 14. 2019. Document is not publicly available.

6.2 Preconcentration and Separation Procedures

6.2.1 Total and Elemental Mercury Separation from Hanford Tank Waste

In preparation for total mercury separation, the preserved (as discussed in Section 6.1.1) sample is brought to a known volume with high-purity DI water (> 18 MΩ and of known low-mercury content) and receives 0.25 mL of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, 30% w/v) per 25 mL of diluted, preserved sample to destroy any unreacted BrCl. Next, a 0.25-mL aliquot of stannous chloride ($SnCl_2$; 20% w/v) solution is added to the sample to reduce inorganic Hg^{2+} to gaseous elemental Hg^0, which can be purged and collected on a gold-coated sand-filled trap or gold-coated bead-filled trap (hereafter referred to as a gold trap). The elemental mercury is purged from solution with an inert gas (ultra-high purity N_2 for previous PNNL work) at a rate of 350 mL/min, passed through an acid gas moisture trap (i.e., soda lime), and preconcentrated onto a gold trap as depicted in Figure 6.1.

Elemental mercury is separated in a similar manner, albeit without the addition of BrCl, $NH_2OH \cdot HCl$, or $SnCl_2$ in the bubbler system since the elemental mercury samples are inherently in the reduced elemental Hg^0 form. In fact, the addition of BrCl to the sample would oxidize elemental mercury to ionic mercury. The elemental mercury samples, after dilution to a known volume to minimize sample vial headspace, were directly added to the bubbler system and then purged from solution with an inert gas (N_2 for the PNNL work) at a rate of 350 mL/min, passed through an acid gas moisture trap (soda lime), and preconcentrated onto gold traps as depicted in Figure 6.1.

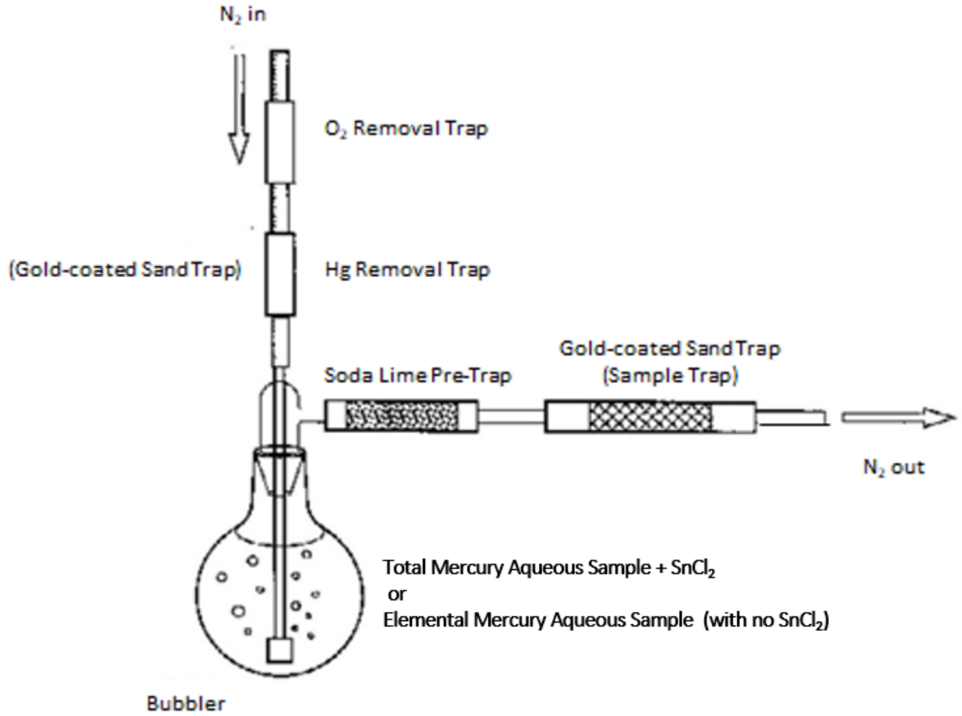

Figure 6.1. System schematic for total mercury or elemental mercury purging.

6.2.2 Methyl Mercury Separation from Hanford Tank Waste

A stabilized and preserved methyl mercury sample (discussed in Section 6.1.3) is distilled to decrease the presence of other constituents, including other inorganic mercury species, in the aqueous sample. Distillate samples are then ethylated and captured on Carbotrap®-filled traps prior to separation and quantification (EPA 1998; MSL-I-014)[7].

The isolation of methyl mercury species is conducted as a two-step process, with the determination (e.g., analysis and quantification) being a third step (discussed in Section 6.3.2). First the preserved sample is distilled to produce a less-complex matrix by heating and purging the "sender" vial and capturing the condensed liquid in a chilled "receiver" vial (Figure 6.2). The distillation receiver vial (containing the distillate) is then surveyed out of the CA fume hood. Based on prior total and gamma activity measurements, the distillate liquid was demonstrated to have minimal radiological content (Fountain et al. 2018). After distillation, the distillate samples are then ethylated to react and convert all methylated mercury species to a volatilized species, methylethyl mercury. The methylethyl mercury species is then purged from solution and captured on Carbotrap®-filled trap adsorbent (Figure 6.4) prior to being separated and thermally desorbed from the trap and quantified using cold vapor atomic fluorescence (CVAF) spectrometry (EPA 1998; MSL-I-014)[8]. Again, this separation of methylethyl mercury from other organo-mercury 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 is discussed in more detail in Section 6.3.2.

The tank waste samples analyzed by PNNL did not require any additional chemicals (beyond HCl for sample preservation) to be added prior to distillation. Although the precise role that the tank waste background matrix plays during the distillation process is largely unknown, the tank waste constituents likely supply sufficient compounds for inorganic mercury to bind to, allowing for inorganic mercury species to remain behind during the distillation process and only organic mercury to volatilize. It is exceedingly important to recognize the significance of the QC matrix spikes in recognizing potential unique tank waste matrix interferences prior to the final separation and analysis of any tank waste samples. These QC samples along with others are discussed further in Section 6.11. A key take away is if methyl mercury distillations prove to be ineffective or inorganic mercury interferences are indicated by poor recovery of matrix spikes or the presence of additional peaks in the chromatogram, additional chemicals can be added to the distillation sender vials to reduce effects. For instance, additions of 200-µL 20% KCl and 50-µL 8 M N_2SO_4 to the sender vials or 100- to 200-µL 1% ammonium pyrrolidine dithiocarbamate (APDC) solution are recommended to enhance distillation recovery of unacidified freshwater samples (EPA 1998; MSL-I-014)[8]. On the other hand, it should be noted that excess chloride (e.g., saline sample with chloride ion concentration > 500 ppm) can also cause a distillation interference (EPA 1998). If excess chloride is expected in the sample, then the sample preservation step should be completed with 9 M H_2SO_4 instead of HCl.

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[7] *MSL-I-014. Methylmercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-014, Rev 10. 2019. Document is not publicly available.

[8] *MSL-I-014. Methylmercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-014, Rev 10. 2019. Document is not publicly available.

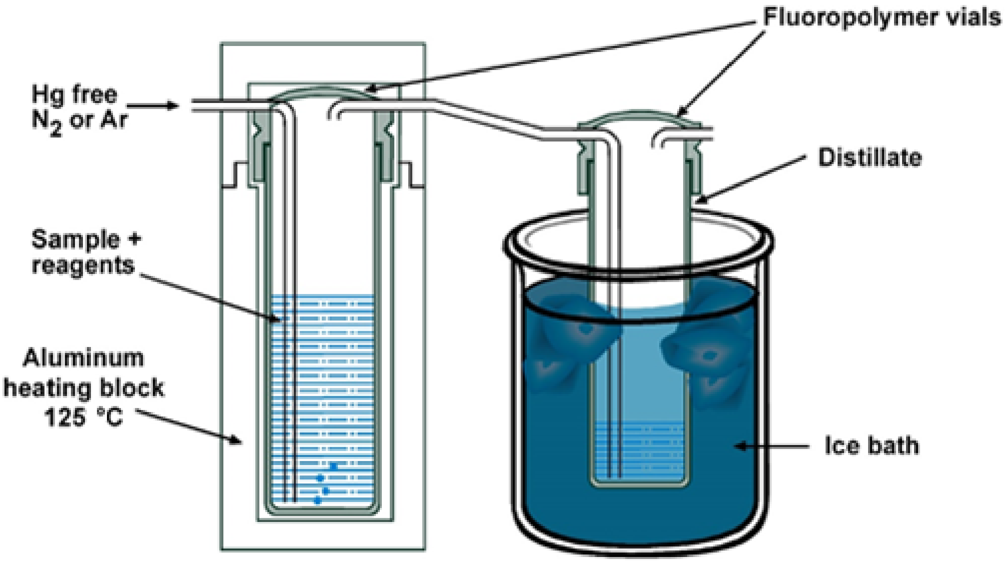

Figure 6.2. System schematic for methyl mercury distillation.

Distillation heating blocks can either be custom-designed and manufactured or purchased from suppliers such as Brooks Rand Instruments or Tekran Instruments Corporation. Experience with a custom-built heating block, like the one shown in Figure 6.3, includes sufficient attention to minimizing ambient heat loss to the heating block, which can result in uneven and fluctuating temperatures of the sender vial samples during the distillation process. The target temperature of the heating block is 125 °C. A custom distillation lid and an insulation package can be used to help retain heat during the distillation, shortening distillation times and improving methyl mercury recoveries. The distillation process should occur until the receiver vial volume has reached approximately 45 mL (accounting for the initial 5 mL water added to the receiver), which can take 3 to 5 hours. This final receiver volume is also based on the assumption that the sender vial initially contained 50 mL.

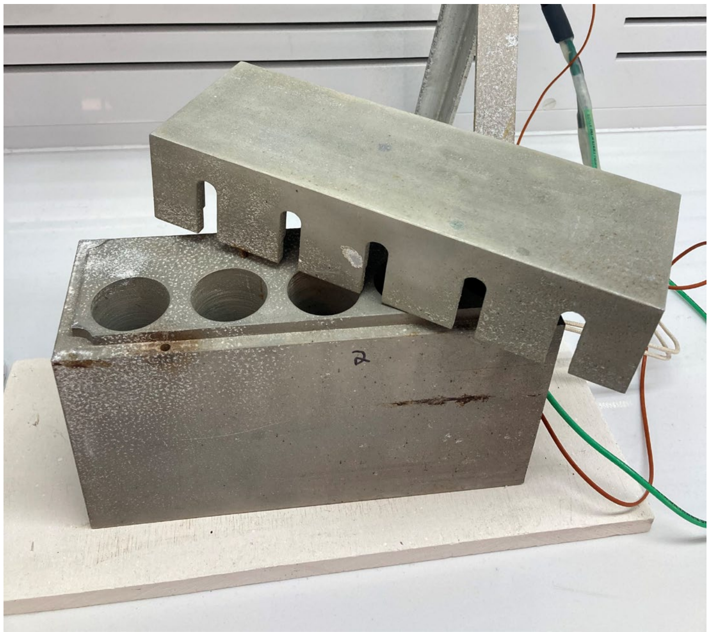

Figure 6.3. Custom-built distillation heating block with lid for a batch of five methyl mercury samples.

After the distillation is completed, the distillate is transferred into a bubbler system containing a dilute acetate buffer (Figure 6.4). A 125-µL volume of ethylating reagent tetraethyl borate (1% w/v in 2% KOH) solution is then added to the bubbler and allowed to react with the sample to convert all methylated mercury species to a volatilized species, methylethyl mercury. The methylethyl mercury species is then purged from solution using an inert gas (N_2 for the PNNL work) at a rate of 200 mL/min and trapped onto a Carbotrap®-filled trap adsorbent. Methylethyl mercury is then thermally desorbed from the Carbotrap®-filled trap adsorbent, separated by GC, pyrolyzed to elemental mercury, pre-concentrated and introduced to a CVAF spectrometer for detection (see Section 6.3.2).

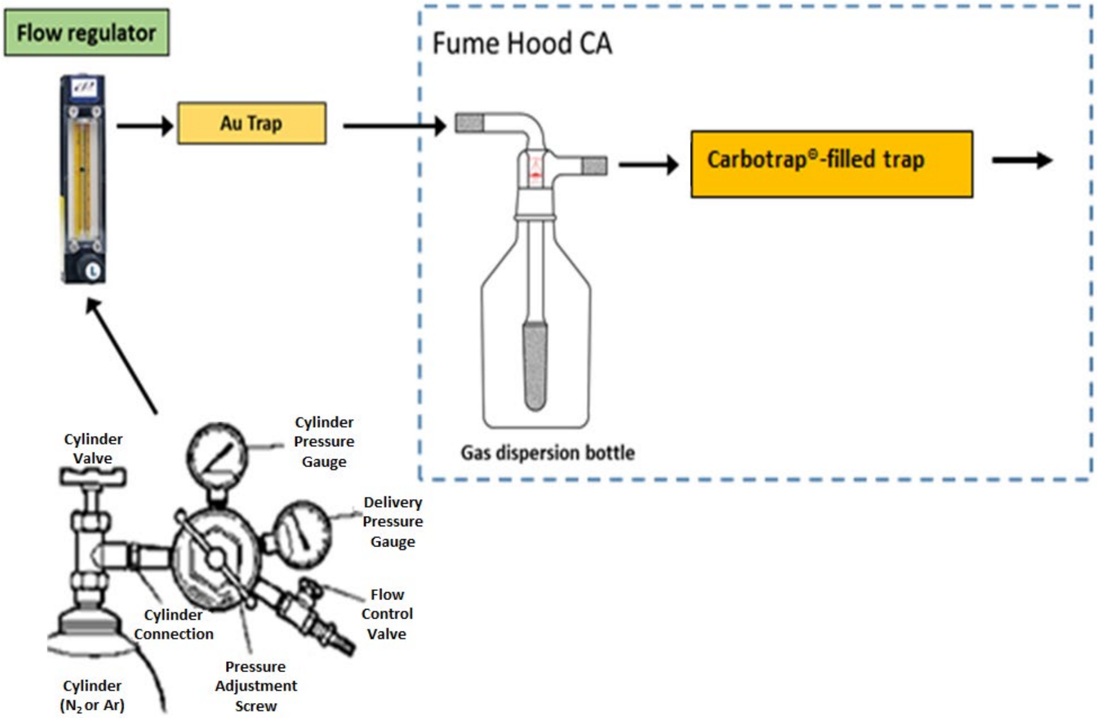

Figure 6.4. Schematic of the purging system used to strip volatile methylethyl mercury from an aqueous sample onto a solid adsorbent such as a Carbotrap®-filled trap.

6.3 Sample Quantification by CVAF Spectroscopy

6.3.1 Determination of Total and Elemental Mercury by CVAF Spectrometry

Quantification of total and elemental mercury is conducted using CVAFS detection. The CVAF spectrometry system consists of a two-stage gold amalgamation gas train to preconcentrate elemental mercury vapor and transfer it into the cuvette of an atomic fluorescence spectrometer (AFS) detector. A schematic of the layout of this system at PNNL's Sequim, Washington campus (PNNL-Sequim, formerly Marine Sciences Laboratory [MSL]) is given in Figure 6.5.

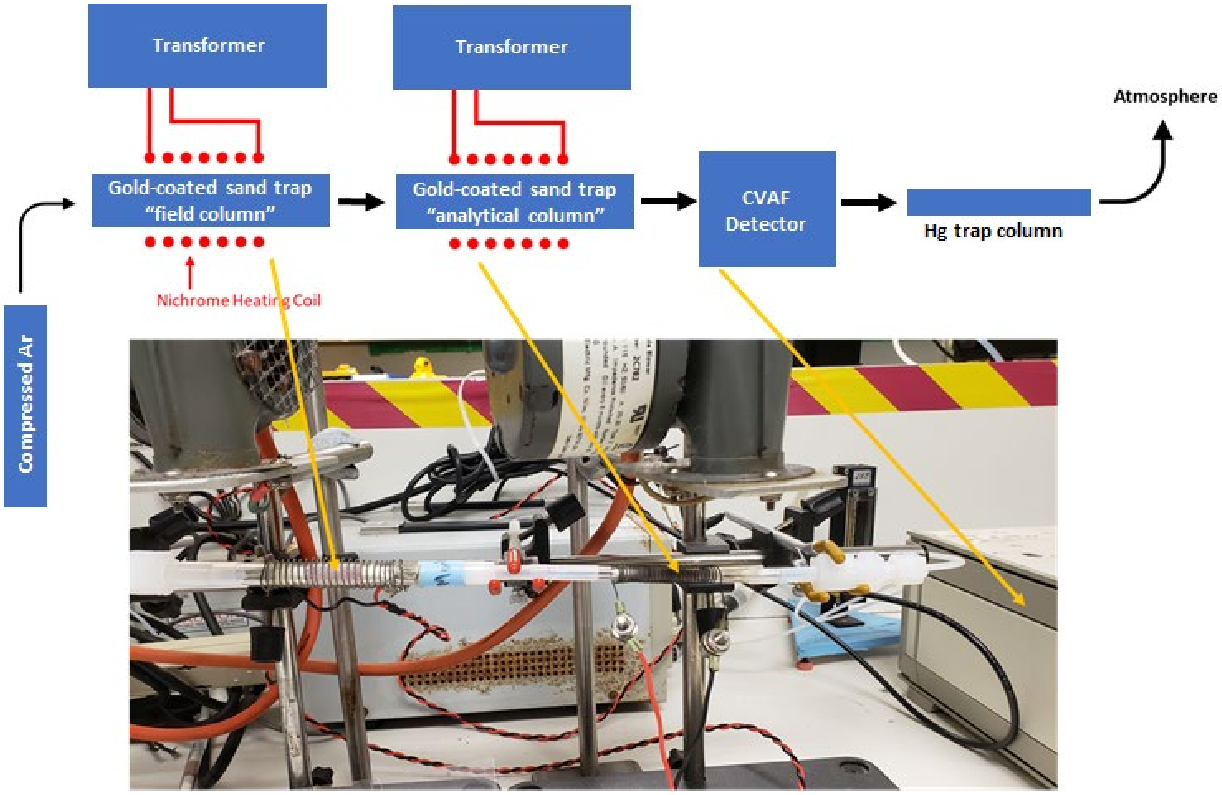

Figure 6.5. Two-stage gold amalgamation gas train for introducing elemental mercury into an atomic fluorescence detector for quantification of mercury collected on a gold trap.

For quantification, mercury is first preconcentrated by collection onto a gold trap in the gas train at the "field column" position (the upstream gold column in Figure 6.5). The mercury collected is transferred from the "field column" to the "analytical column" (the downstream gold trap in Figure 6.5) by controlled heating (temperature > 450 °C) of the nichrome wire heating coil around the "field column," releasing mercury from the "field column" into an argon gas stream and re-amalgamating onto the unheated "analytical column." The mercury on the "analytical column" is then released by controlled heating and swept into the gas cell of the AFS, where a signal is generated proportional to its fluorescence. The resulting signal from the detector is captured in a chromatogram that is integrated using Chromperfect SL software (Version 1.2).

6.3.2 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-mercury 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, based on EPA Method 1630 (EPA 1998; MSL-I-014)[9].

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[9] *MSL-I-014. Methylmercury in Aqueous Samples by Cold Vapor Atomic Fluorescence (CVAF).* Marine Sciences Laboratory Standard Operating Procedure MSL-I-014, Rev 10. 2019. Document is not publicly available.

Stripping of the methyl mercury from the distillate samples onto Carbotrap®-filled traps is to be conducted within a radiologically controlled CA. The isolation of the methyl mercury from solution is conducted using a bubbler with a Carbotrap®-filled trap attached to the outlet (Figure 6.4). First, the distillate samples are added to the bubbler and acetate buffer is added to maintain the pH at approximately 4.9. Then the ethylating agent tetraethyl borate is added to convert the methyl mercury to methylethyl mercury, which is volatile and can be purged from solution using an inert gas (e.g., Ar), and collected onto the Carbotrap®-filled trap. For the prior work conducted at PNNL N_2 was used as the purging gas. 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 6.6, 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% OV3 on 60/80 Chromosorb WAW/DMCS (Supelco) held at 120 °C in a small benchtop GC oven. The pyrolysis column consists of a hollow quartz tube that is packed with quartz glass wool at both end and is heated to approximately 700 °C. The pyrolysis column converts the incoming methylethyl mercury to elemental mercury, which is then swept into the cuvette of the CVAFS detector by the Ar gas stream. The detector generates a signal proportional to the fluorescence of the sample. The resulting signal from the detector is captured in a chromatogram that is integrated using Chromperfect SL software (Version 1.2). The detector is a Tekran model 2500 CVAFS detector.

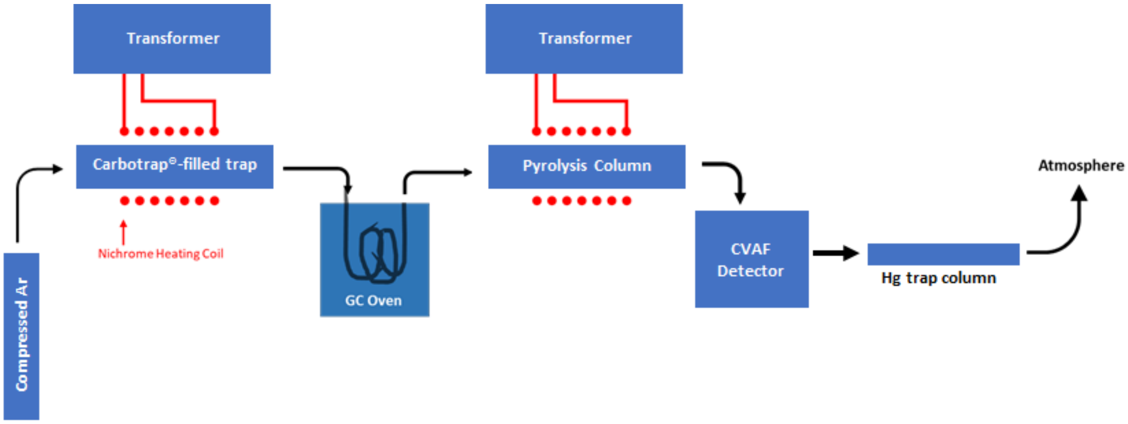

Figure 6.6. Schematic of the gas train system used to quantify methyl mercury collected on a Carbotrap®-filled trap by ballistic heating, GC separation, pyrolysis of methylethyl mercury to elemental mercury, and detection of elemental mercury by CVAF.

6.4 Mercury Speciation Flowchart

In the previous sections (Sections 1.0 through 6.3) the methods for speciation of total mercury, elemental mercury, and methyl mercury have been described and discussed using the ultra-trace methods developed and demonstrated by PNNL. Figure 6.7 illustrates these methods visually as they would occur in parallel. In the following section, Section 6.5, additional mercury speciation analyses are briefly addressed, as are the considerations documented for how these added analysis steps can be combined alongside and within the baseline total, elemental, and methyl mercury methods described previously and depicted in Figure 6.7. Later discussions in Section 6.9 will elaborate on how this methodology can be further specialized to accommodate the potential need for sample handling and analysis to take place at two separate facilities (referred hereafter as a dual-laboratory configuration) versus the more typical single-laboratory configuration where all sample handling and analysis occur within a singular facility or laboratory.

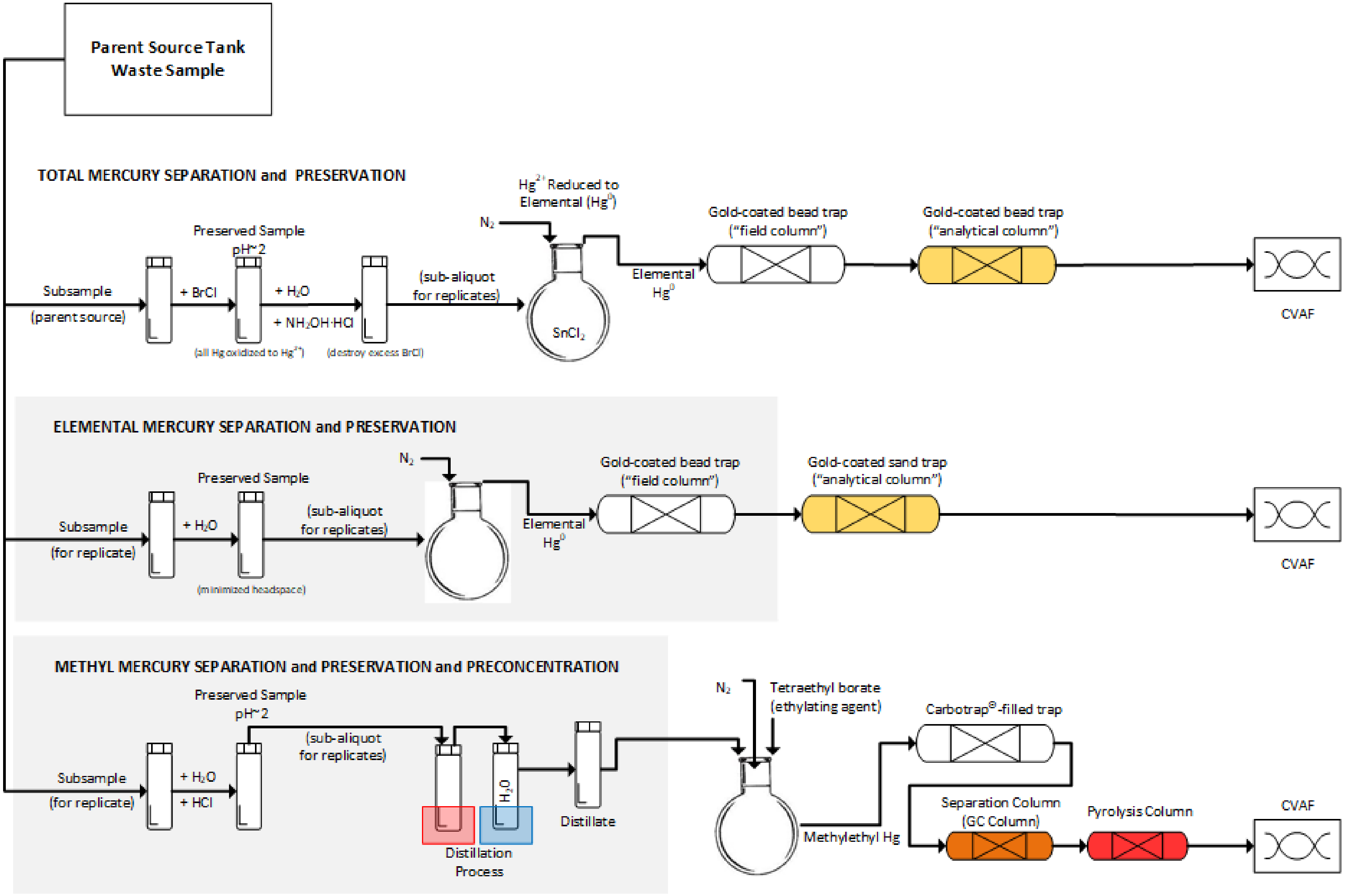

Figure 6.7. Total, elemental, and methyl mercury sample flowchart using a single-laboratory configuration.

6.5 Considerations for Speciation and Quantification of Additional Mercury Species

The following sections discuss considerations for adaptations to the tank waste supernatant ultra-trace mercury speciation methods provided in Sections 1.0 through 6.3. These include opportunities and options for additional speciation and quantification of dimethyl mercury, monomethyl mercury, inorganic mercury, total soluble mercury, and particulate mercury (in supernatant samples), and considerations for solid phase samples. The combined capability of both a total mercury CVAFS and a methyl mercury CVAFS (whether manual or automated) allows for the flexible adaptation for a customizable suite of mercury speciation based on end user needs.

Figure 6.8, Figure 6.9, and Figure 6.10 represent the sample analysis paths for realizing these additional mercury speciation efforts to integrate with an existing procedure developed for the direct speciation and quantification of total mercury, elemental mercury, and methyl mercury by CVAFS.

6.5.1 Dimethyl Mercury Speciation and Quantification

The method used to determine methyl mercury for Hanford waste, based on EPA Method 1630 (EPA 1998), analytically defines methyl mercury as the methyl mercury that is ethylated from acidified samples. Chemically, both monomethyl mercury and dimethyl mercury are quantified as methyl mercury using this method because dimethyl mercury is unstable in acidified water and will demethylate to form monomethyl mercury.

Dimethyl mercury can be quantified directly from fresh, unpreserved samples that are kept cool, in the dark, with the headspace volume minimized prior to analysis. As noted for other mercury species, plastic sample bottles should be avoided to prevent or minimize loss of gaseous dimethyl mercury. Dimethyl mercury content has not been exclusively determined for Hanford tank waste (although any dimethyl mercury would have been included in the methyl mercury quantification, since the methyl mercury method quantifies all methylated mercury species together), and therefore the required volume for quantification and the associated MDL have not been determined. As mentioned in Section 3.3, dimethyl mercury has been quantified in tank waste samples from SRS by Eurofins Frontier Global Sciences (Bannochie et al. 2017). However, a direct link between sample volumes used at SRS and those needed for Hanford tank waste cannot be readily extrapolated.

Dimethyl mercury can be purged from samples and trapped directly onto the Carbotrap®-filled trap using nitrogen gas and analyzed using the methyl mercury instrument after reducing the GC column temperature to 80 °C.

Direct determination of dimethyl mercury is not routine in most laboratories. No certified reference materials (CRMs) or standard reference materials (SRMs) exist to independently verify dimethyl mercury. As a result, full quality control (QC) objectives cannot be achieved according to EPA Method 1630 criteria. However, it is still possible using one or more dimethyl mercury standards (e.g., liquid DMHg standards in methanal) to conduct the 5-point calibration curve, initial calibration verification, continuing calibration verification, and matrix spikes (similar to those described in Section 6.11 for methyl mercury).

Important note: It is important to note that dimethyl mercury is a highly toxic neurotoxin compound that readily absorbs through the skin, severe toxic dose requires the absorption of less than 0.1 mL (Blayney et al. 1997). Standard latex, neoprene and butyl gloves do not provide suitable protection for direct contact.

Concentrated stocks of dimethyl mercury are extremely hazardous to human health and require special considerations for safe handling. If using dimethyl mercury stocks, laboratories should stock the most dilute standards that will allow for sample quantification.

An alternative approach to analyze for elemental mercury, is to sample after the quantification step described for dimethyl mercury. However, based on observations by Bannochie (2016) this has been noted to lead to significant loss of elemental mercury being quantified in the elemental mercury sample due to loss of the volatile elemental mercury species, from the liquid phase and into the vapor phase headspace that is created in the sample bottle during the dimethyl mercury quantification process. Therefore, this approach for elemental mercury speciation is not recommend and rather the method outlined earlier in Sections 6.1.2, 6.2.1, and 6.3.1 should be followed.

6.5.2 Monomethyl Mercury Speciation and Quantification

Monomethyl mercury can be quantified in the same sample that is used for the dimethyl mercury quantification. After purging of the unacidified dimethyl mercury sample onto a Carbotrap®-filled trap, the sample is then acidified as described for methyl mercury samples in Sections 6.1.3, 6.2.2, and 6.3.2. The sample analysis train for the combined dimethyl mercury and monomethyl mercury speciation is represented in Figure 6.8.

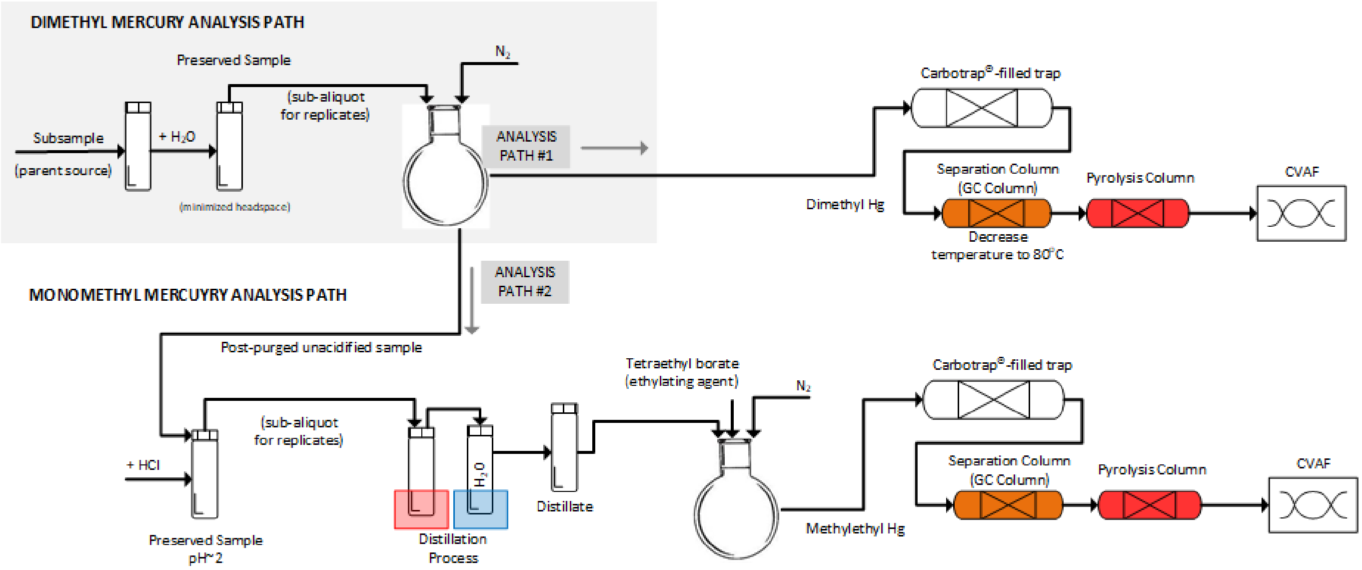

Figure 6.8. Combined dimethyl mercury and monomethyl mercury sample speciation and analysis train.

6.5.3 Inorganic Mercury Speciation and Quantification

Quantifications of inorganic mercury can be approached in two ways. The first is indirectly from a calculated difference determined from the total mercury sample quantification minus the sum of all the other quantified species. For example, in the case of total mercury, elemental mercury, and methyl mercury measurements, inorganic mercury can be calculated from Eq. (6.1):

$$[Inorganic\ Hg] = [THg] - [Hg^0] - [MeHg] \qquad (6.1)$$

If total, elemental, monomethyl, and dimethyl mercury are all quantified, Eq. (6.2) could be used to calculate the inorganic mercury concentration:

$$[Inorganic\ Hg] = [THg] - [Hg^0] - [MMHg] - [DMHg] \tag{6.2}$$

With any differencing method, the resulting calculated value is only as good as the individual values. The analytical error associated with each measurement is incorporated into the summed error of the calculated value.

Alternatively, a direct measure of inorganic mercury can also be made if desired. Inorganic mercury can be directly quantified using the post-purged elemental mercury tank waste sample following the operations described in Sections 6.1.2, 6.2.1, and 6.3.1. Following the elemental mercury operations, samples can be further analyzed (purged onto a new gold trap, then thermally desorbed into a CVAFS). The sample analysis train for the combined elemental mercury and inorganic mercury speciation is represented in Figure 6.9.

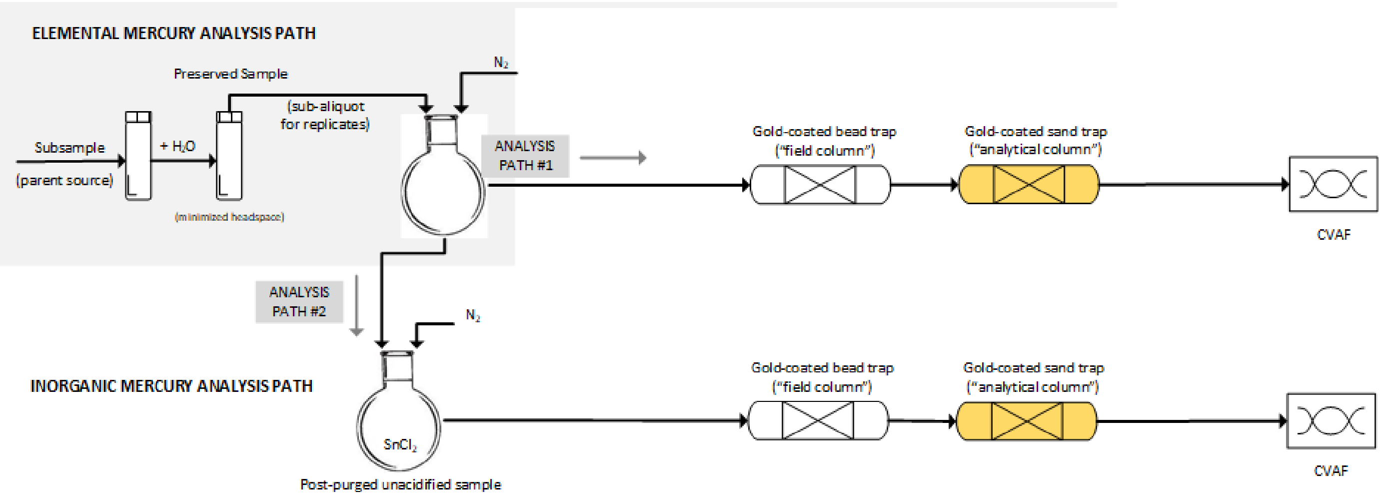

Figure 6.9. Combined elemental mercury and inorganic mercury sample speciation and analysis train.

6.5.4 Total Soluble Mercury Speciation and Quantification

The total soluble mercury (alternatively referred to as total dissolved mercury) can be quantified by first filtering the sample through a 0.45-µm disposable filtration device and then using the same operations for a total mercury tank waste sample as described in Sections 6.1.1, 6.2.1, and 6.3.1. The sample analysis train for total soluble mercury speciation is represented in Figure 6.10.

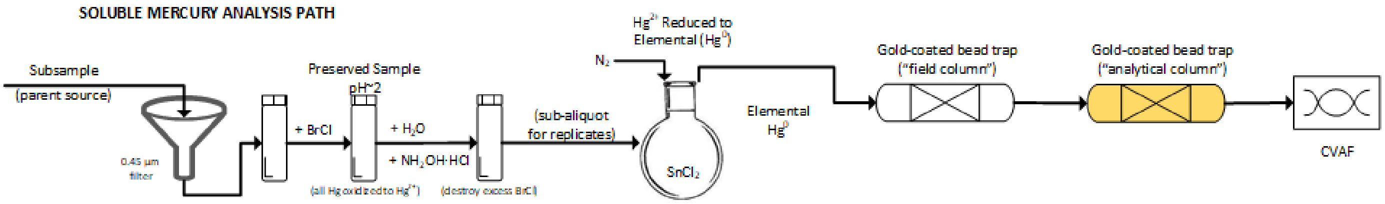

Figure 6.10. Total soluble mercury sample speciation and analysis train.

6.5.5 Particulate Mercury Speciation and Quantification

Quantifications of particulate mercury can be approached in two ways. The first is indirectly from a calculated difference determined from the total mercury sample quantification minus the total soluble mercury sample. Particulate mercury can be calculated from Eq. (6.3):

$$[Particulate\ Hg] = [THg] - [Soluble\ Hg] \tag{6.3}$$

If the total soluble mercury concentration is not being quantified or a direct quantification of particulate mercury is desired, this can be done by filtering the tank waste sample through a 0.45-µm disposable filtration device and then using a solid phase extraction method (see Section 6.5.6.2) to liberate Hg bound to solids before analysis for total mercury.

6.5.6 Solid Phase Quantification

6.5.6.1 Direct Measure

Total mercury in the solid phase can be directly quantified following EPA Method 7473 (EPA 2007b). EPA Method 7473 is designed to quantify total mercury in “soils, sediments, bottom deposits, and sludge-type materials.” Commercially available direct mercury analyzers by thermal decomposition (e.g., Milestone DMA-80) automatically measure mercury in a solid phase sample following EPA Method 7473. Many direct mercury analyzers can also analyze liquid or gas phase samples on the same instrument, albeit with a slightly different configuration setup. The direct quantification method does not require any sample preparation setups and instead relies on heating the sample to liberate mercury from the sample matrix. However, this direct analysis method is not applicable when mercury is bound in complex matrices where thermal decomposition is not able to fully liberate all the mercury. Mercury bound in silicates is a known instance where thermal decomposition is not sufficient. In such circumstances, a microwave-assisted acid digestion [EPA Method 3052 (EPA 1996)] is recommended to fully digest the matrix prior to mercury analysis.

6.5.6.2 Solid Phase Extraction Methods

Total mercury can also be extracted from a solid sample using a chemical digestion method prior to quantification. 222-S Laboratory has indicated the ability to quantify total mercury in solid samples based on EPA Method 7471B (EPA 2007a). The aqua regia digest used in EPA Method 7471B is likely sufficient to digest tank waste solid matrices; however, a microwave-assisted acid digestion [EPA Method 3052 (EPA 1996)] could provide an alternative digest if aqua regia proves inadequate for the tank waste sample matrices.

Methyl mercury can also be extracted from solid phases, albeit with more complex processes than total mercury. One method is to use a nonaqueous phase extraction (after Bloom et al. 1997) that is commonly employed on environmental matrixes. While this method is for environmental samples, it may be applicable to more-complex media such as tank waste. In brief, two extraction solutions, 1) potassium bromide (KBr) and sulfuric acid (H_2SO_4) and 2) copper sulfate ($CuSO_4$), are added to the vial containing the solid material to produce a final concentration of 1.26 M KBr, 0.75 M H_2SO_4, and 0.17 M $CuSO_4$. Vials are shaken vigorously overnight on a shaker tray. This process drives methyl mercury from the solid phase into the aqueous phase. Next, 10 mL of methylene chloride (CH_2Cl_2) is added to the vials before the vials are shaken again for 1 hour. This step moves the methyl mercury from the aqueous phase into the non-aqueous phase liquid (NAPL) (i.e., methylene chloride). Vials must be compatible with the non-aqueous phase of methylene chloride. 50-mL polypropylene centrifuge tubes are commonly used (as in Muller and Brooks 2018). However, glass centrifuge tubes are also available and used (e.g., PNNL-

Sequim mercury laboratories) and would remain the recommended material for storage or analysis containers for any mercury containing sample. Next, 20 mL of DI water is first added to the 50-mL polypropylene centrifuge tubes, then a subsample of the CH_2Cl_2 extract is added. To back-extract the methyl mercury from the CH_2Cl_2 into the aqueous phase, the vials are placed in a hot water bath, sealed with caps that have two small holes (one for the N_2 gas line in, one for NAPL to evaporate-off through and be collected for waste disposal). N_2 is bubbled through the line to encourage the removal of the NAPL. The overall extraction process removes most of the inorganic mercury and other impurities. Note that either an internal standard or quantification of method extraction efficiency is needed to correct results for this method. For example, Muller and Brooks (2018) added an internal standard of $Me^{200}Hg$ or $Me^{202}Hg$ prior to the extraction process; however, in that case, mercury quantification required the coupling of CVAFS to ICP-MS (i.e., using a Brooks Rand MERX-M mercury speciation GC and pyrolysis coupled with an ELAN DRC-e ICP-MS). Such mercury-isotope-based internal standards are not applicable to methods that do not employ MS for mercury quantification.

6.6 Waste Disposal Considerations

Mercury analysis techniques must account for any planned discharge of the liquid waste from the 222-S Laboratory to the Hanford tank farm. The analysis process will generate anywhere from 30-40 QC sample volumes for each analytical batch of total and elemental mercury tank waste samples (associated with typically 25 tank replicate speciation waste samples), and 15-20 QC sample volumes for each analytical batch of methyl mercury tank waste samples (associated with typically 20 tank replicate speciation waste samples). Each quality control sample will generate between 50 and 100 mL of waste volume. Additionally, each replicate tank waste sample may include an additional combined water and reagent volume of approximately 35 mL. There should be limited-to-no added total mercury inventory returning to the Hanford tank farm, as all the mercury (introduced in the form of mercury standards to the QC samples) contained in the QC samples will be volatilized and then purged onto the solid substrate traps (i.e., gold traps or Carbotrap-filled traps). As for the tank waste samples, the total mass of mercury of each tank waste sample, will inherently be reduced (non-total mercury samples will retain non-quantified species in sample) if not fully removed from the tank waste matrix. However, the expected added volume of water and reagent chemicals must be addressed. One possible option to address the added volume is to volume reduce the post-purged samples by evaporation. Considerations should be made to address volume reduction of QC post-purged sample volumes separate from efforts to volume reduce post-purged tank waste samples due to the nature of concentrating tank waste containing liquid volumes.

6.7 General Hazards

Chronic exposure to mercury or methyl mercury can harm the central nervous system and cause neurological or cardiovascular illness. High-concentration standard stocks or salts of mercury and methyl mercury are not recommended for ultra-trace analysis due to the need for extensive dilutions for typical calibrations. Dilute standard stocks are commercially available and should be handled only by appropriately trained personnel. Carbon traps are generally installed on the outlet of mercury detectors to trap the gaseous mercury analytical waste. Traps should be disposed of as hazardous waste and replaced annually. One possible alternative consideration, to collecting radiological hazardous waste on to these carbon traps, is to determine if it provides appropriate safety to route the detector exhausts directly to the fume hoods and by-pass this carbon trap.

Safety glasses should be worn at all times in the lab; face shields, when appropriate, should be used to protect the eyes and face. Those working with acids and/or caustics should follow the safety practices associated with each acid/caustic that they are using. Work should be performed in chemical fume hoods when there is potential for spills or the release of toxic vapors. Temperature sources as high as 700 °C will be used during analysis.

Small amounts of radiological and non-radiological liquid and solid wastes will be generated from the testing conducted under this methodology. All regulated wastes must be managed and properly disposed of per requirements and procedures dictated by 222-S Laboratory.

6.8 Equipment and System Options

The multi-year speciation analysis of Hanford tank waste at PNNL used custom-built manual systems (Fountain et al. 2018; Bottenus et al. 2019, 2020). Commercially available automated systems for total mercury and methyl mercury can also be purchased from vendors and have been used on a regular basis at PNNL-Sequim; note, however, use of these automated systems has not been demonstrated specifically with Hanford tank waste samples.

6.8.1 Analytical Instrumentation

There are three different configurations for analytical instrumentation that can be generally considered, which implement the ultra-trace mercury methods using a CVAFS discussed in this report:

- **Fully Manual** – This configuration consists of two analytical instruments: a manual elemental/total CVAFS system used to quantify both total and elemental mercury, and a manual methyl mercury CVAFS system used to quantify the methyl mercury.
- **Maximum Automation** – In this configuration, elemental mercury will be quantified on a manual elemental/total CVAFS system (identical to the fully manual elemental/total CVAFS system), an automated total mercury CVAFS system is used to quantify the total mercury, and an automated methyl mercury CVAFS system used to quantify the methyl mercury.
- **Hybrid** – In this configuration, a manual total elemental CVAFS system is used for quantifying both the elemental and total mercury while an automated methyl mercury CVAFS system is used to quantify the methyl mercury.

The succeeding three tables, Table 6.1, Table 6.2, and Table 6.3, convey the key equipment requirements for methyl mercury analysis using CVAFS, the key equipment for the total mercury analysis using CVAFS, and the key equipment for elemental mercury analysis, respectively. These include the equipment specification for the manual system (found under “Specifications”) and alternatively for automated systems (“Automation Notes”).

Table 6.1. Methyl Mercury Equipment

Equipment	Specifications	Recommended Quantity	Intended Use	Automation Note
Air rotameter	0-150 cc/min	10	Used in CA hood for distillation of samples for methyl mercury analysis.	Commercially available distillation systems are available from vendors, including Brooks Rand Instruments and Tekran Instruments. These systems incorporate the distillation heating block, purge gas flow, and chiller system needed for sample distillation. Depending on commercial system, separate ice bath may be required
Distillation heating block	Solid aluminum with 10-20 wells to fit 50-mL Teflon vials. Temperature controlled to maintain 125 °C	1-2	Used in CA hood for distillation of samples for methyl mercury analysis. Placement should accommodate ice bath for receiving vials.	
Distillation vials	60-mL Teflon vials with caps having 1/8 in. in-flow and out-flow ports threaded with 1/8-in. tubing such that one port is open and the other contains tubing that extends from the floor of the vial to 5 in. outside the vial	20	Used in CA for distillation of samples for methyl mercury analysis. Half of total vial count is used as distillation sending vials. Half is used as receiving vials.	
Ice bath	Capable of holding 10 distillation receiving vials at 2 °C	1	Used in CA hood to keep methyl mercury distillation receiving vials cold during distillation.	
Sample bottles	Fluoropolymer or amber borosilicate, cleaned in HCl	1 per sample	Preservation and storage of samples	Needed
Packed Carbotrap®-filled traps	Supelco, Carbopack B, Fritted glass, 1/4 × 3 ½. Borosilicate, silanized quartz tubes filled with low mercury Carbotrap® adsorbent material and plugged with quartz wool.	≥ 20	A set of 7-10 should be retained for "non-rad" QC samples, while another set of 10-15 should be retained for "rad" tank waste samples.	Commercial methyl mercury analytical instruments are available from vendors: MERX-M (Brooks Rand Instruments) 2700 (Tekran Instruments) These systems incorporate sample purging, trapping, heating, and detection. *Automated systems require 40-60 mL borosilicate glass vials with Teflon-coated septa.
Trap caps	Teflon end plugs	50	Used to cap ends of Carbotrap®-filled traps.	
Bubblers (methyl mercury)	125- or 250-mL flask, standard taper 20/40 neck. Equipped with purging stopper with coarse glass frit extending to within 0.5 cm of flask bottom	≥ 4	Purging of methyl mercury onto gold trap. A separate set of bubblers can be maintained outside the CA for non-rad blanks and standard preparation.	
Air rotameter	0-250 cc/min	≥ 1	Minimum of one per "non-rad" methyl mercury bubbler set. *Optional* set of non-rad rotameters for "non-rad" QC MeHg samples.	
Keck clips		10	Used to clip the joint of each bubbler.	
GC-CVAFS	• Mercury fluorescence detector • Air rotameter (0-250 cc/min) Pyrolysis column nichrome coil/heater: This column consists of a 20-cm length of	1	Separation and detection of desorbed mercury species following sample ethylation.	

Equipment	Specifications	Recommended Quantity	Intended Use	Automation Note
	7-mm O.D. by 4.5-mm I.D. quartz tubing with the central 10 cm packed with quartz wool. The column is wrapped with 1.5 m of 22-gage Nichrome wire that is electrically heated from an autotransformer. • Trap nichrome coil/heater/timer GC separation column/heater. 1.3-m packed GC column is made to the following specification (Supelco Inc. custom product): made of 0.25-in. O.D. borosilicate glass column tubing with 4-mm I.D. bore. The tube is formed into an 8-cm diameter coil of 1.0-m length with two 15-cm arms extending in parallel up from the coil. The column is silanized, and packed with 1 m (in the coil section only) of preconditioned 60/80 mesh 15% OV-3 on Chromasorb WAW-DMSC, held in place with silanized glass wool plugs. • Data recorder (e.g., computer linked to analog to digital converter from detector)			

Table 6.2. Total Mercury Equipment

Equipment	Specifications	Recommended Quantity	Intended Use	Automation Note
Sample bottles	Fluoropolymer or borosilicate, cleaned in HCl	1 per sample	Preservation and storage of samples	Needed
Gold traps	6.5-mm OD, 4.0-mm ID quartz tubing, cut into 10-cm lengths, crimped 2.0 cm from end, filled with gold trap plugged with quartz wool	≥ 30	A set of 7-10 should be retained for "non-rad" QC samples, while another set of 15-20 should be retained for "rad" tank waste samples. Those used for elemental versus used for total mercury analysis are interchangeable. Additional gold traps can be used in line to purify purge or carrier gases.	Commercially available total mercury analytical instruments are available from vendors: MERX-T (Brooks Rand Instruments) 2600 (Tekran Instruments) These systems incorporate sample purging, trapping, heating, and detection. *Automated systems require 40-mL borosilicate glass vials with Teflon coated septa.
Glass storage tube for the gold traps	Culture tubes with rubber stoppers	≥ 30	One for each gold trap	
Trap caps	Teflon end plugs	100	Used to cap ends of gold trap.	
Soda lime trap	0.9-cm ID Teflon tubing filled with 2-3 g of 8-14 mesh soda lime plugged with salinized glass wool	≥ 4	Minimum of one per bubbler system. Soda lime is typically replaced after each batch of samples.	
Bubblers (total mercury)	250-mL Florence flask, standard taper 20/40 neck, equipped with purging stopper with course glass frit extending to within 0.2 cm of flask bottom	≥ 4	Purging of total mercury onto gold trap. A separate set of bubblers can be maintained outside the CA for non-rad blanks and standard preparation. Only those bubblers used for total mercury sample purging should have tin chloride added to them.	
Air rotameter	0-150 cc/min	≥ 1	Minimum of one per "non-rad" total mercury bubbler set. *Optional* set of non-rad rotameters for "non-rad" QC THg samples.	
Keck clip	N/A	25	Used to clip to the joint of each bubbler.	
Dual amalgam CVAFS	• Mercury fluorescence detector • Air rotometer (0-150 cc/min) • Pyrolysis column nichrome coil/heater • Trap coil/heater (2) • Goal-coated sand analytical trap • Data recorder (e.g., computer linked to analog to digital signal converter)	1	Detection of total mercury following sample digestion and purging as well as elemental mercury following sample purging.	

Table 6.3. Elemental Mercury Equipment (in addition to the equipment listed in Table 6.2)

Equipment	Specification	Quantity	Intended Use	Notes
Sample bottles	Fluoropolymer, cleaned in HCl	1 per sample	Preservation and storage of samples	n/a
Bubblers (elemental mercury)	250-mL Florence flask, standard taper 20/40 neck, equipped with purging stopper with course glass frit extending to within 0.2 cm of flask bottom	≥ 4	Purging of elemental mercury onto gold trap. A separate set of bubblers can be maintained outside the CA for non-rad blanks and standard preparation.	Bubblers for elemental mercury should not be exposed to $SnCl_2$ reducing agent.
Keck clip	N/A	10	Used to clip to the joint of each bubbler.	n/a

6.8.2 Additional Equipment and Labware

Table 6.4 provides suggestions for additional measurement equipment necessary for the execution of the ultra-trace mercury speciation methods outlined previously. All efforts were made to make this list as complete as possible, but it may not be all-inclusive.

Table 6.4. General Laboratory Equipment

Equipment	Specification	Quantity	Intended Use
Balance	Analytical balance capable of weighing to the nearest 0.01 g	≥ 1	Weighing samples. At a minimum, one balance must be maintained as rad. Optional non-rad balance can be maintained for non-rad QC samples.
Dwyer gas rotameter	30-200 cc/min air (For Information Only)	1	Used to regulate N_2 carrier gas flow to bubbler lines.
Aalborg purge gas mass flow controller	0-500 sccm N_2	≥ 4	Minimum one per bubbler system / nitrogen carrier gas line. These can be interchanged between total mercury, elemental mercury, and methyl mercury bubbler systems assuming they (total, elemental, or methyl bubblers) are not planned to be run concurrently. Set specified as “rad” for tank waste and rad QC samples.
Gold traps	6.5-mm OD, 4.0-mm ID quartz tubing, cut into 10-cm lengths, crimped 2.0 cm from end, filled with gold-coated beads (or gold-coated sand) plugged with quartz wool	1-2 per gas line	Used in line to purify purge or carrier gases.
Various pipettes	5-50 µL 20-200 µL 100-1000 µL 500-5000 µL	≥ 1	Sample preparation additions
Reference weight set	Weight masses bracket balance working range; should meet American Society for Testing and Materials criteria for Class 1 (analytical balances)	1	Daily performance check of balances

6.9 Laboratory and Sample Configuration Considerations

6.9.1 Laboratory Configuration Schemes

At the PNNL-Sequim campus, a single-laboratory configuration for ultra-trace speciation and quantification of mercury allows for samples to be brought directly into the laboratory and preserved or diluted appropriately (based on the mercury species of interest). The samples, analytical QC samples, and instrument QC samples are all prepared, purged, and analyzed in the same facility. This configuration minimizes shipping and handling requirements, reduces scheduling conflicts, and better streamlines the process from sample collection through sample analysis. It is envisioned that this configuration carries the greatest advantage when speciating and quantifying Hanford tank waste samples for mercury. However, it is recognized that there can be capital, scheduling, and other limitations that make an alternative configuration more desirable.

In the case of the multi-year Hanford tank waste mercury speciation effort at PNNL, a dual-laboratory configuration capitalized on the existing expertise across two geographically separate facilities. In this case, superior radiological handling capabilities and controls existed at PNNL's Richland, Washington campus (PNNL-Richland) for raw sample handling, sub-sampling, and preconcentration, while access to the needed capital equipment existed at the PNNL-Sequim facility, which could handle any final preconcentration and analysis steps. In this dual-laboratory configuration, unique process modifications were developed to ensure the successful implementation of the ultra-trace mercury speciation methods. In this configuration, as depicted in Figure 6.11, samples were received and treated at the PNNL-Richland campus (referred to as Laboratory Site 1) and then transported to the PNNL-Sequim campus (referred to as Laboratory Site 2) for final preconcentration and analysis. It is important to note that the content and management of samples depicted in Figure 6.11 are identical in all but one way to those depicted previously in Figure 6.7. The one difference in the two flowcharts is that for a dual-laboratory configuration the total and elemental mercury samples are transported to the second facility as soon as they have been purged onto their respective gold traps, and the methyl mercury receiver vial distillate is transported to the second facility and purged onto the Carbotrap®-filled traps at the second facility.

These modifications were developed to ensure radiological safety, minimize sample loss or degradation, and ensure that appropriate QA controls were implemented. This dual-laboratory configuration might also be an appropriate consideration in the case where an external or outside laboratory is contracted to analyze all, or part, of the tank waste samples. However, radiological licensing limits at commercial facilities are much lower than Hanford site limits and this must be considered in the strategy for external sample analyses. Note that a dual-laboratory configuration was successfully demonstrated, across two PNNL-Laboratory facilities, over the course of three years while PNNL conducted ultra-trace mercury speciation and quantification on 14 Hanford tank waste types originating from four different Hanford tank supernatant samples. Section 6.18 is devoted to specifically discussing the majority of the unique considerations for the successful implementation of a dual-laboratory configuration based on the experience at PNNL.

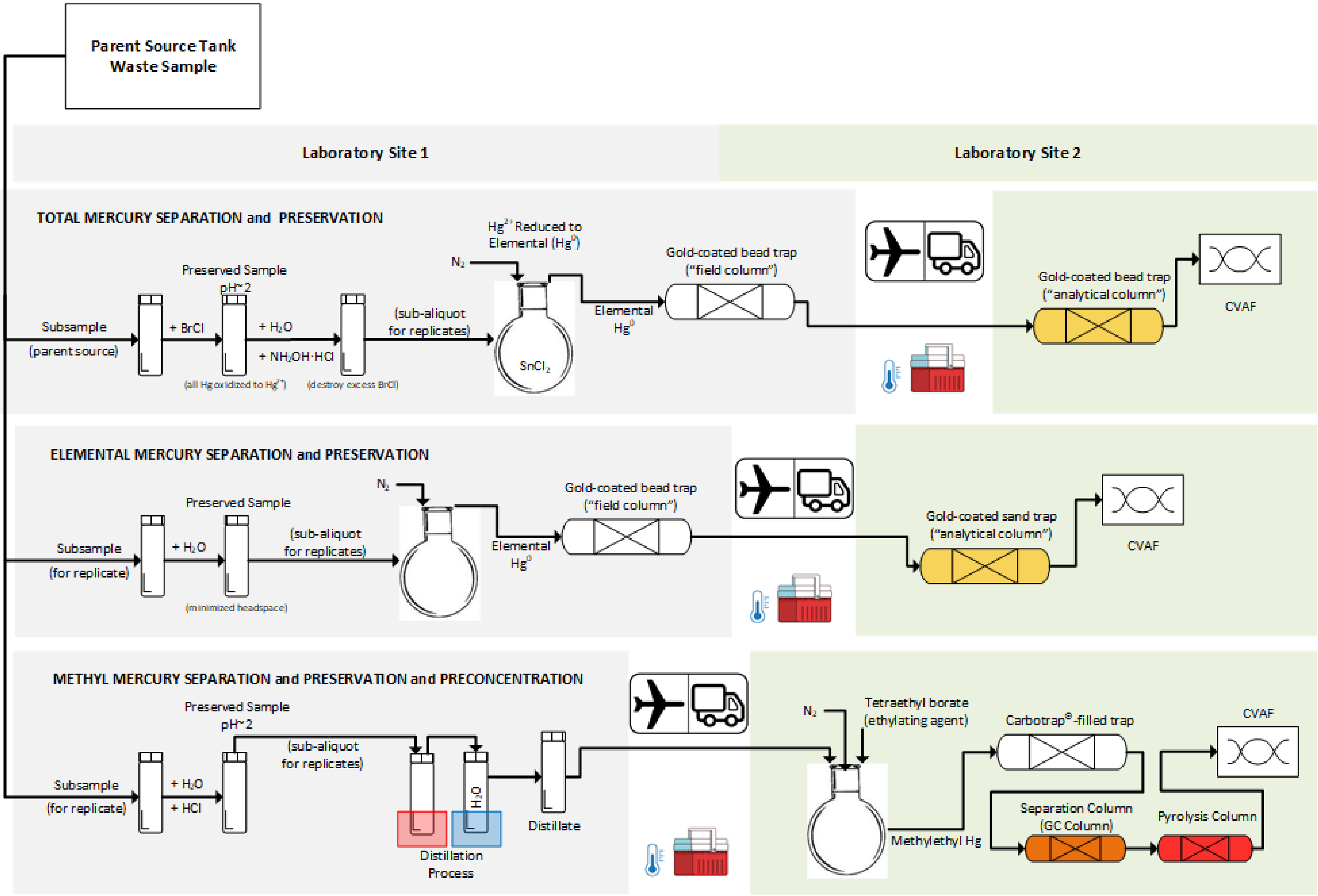

Figure 6.11. Total, elemental, and methyl mercury sample flowchart using a dual-laboratory configuration.

6.9.2 Analytical Sample Batching and Configuration Schemes

Analytical runs typically contain approximately 15 to 20 samples in order to incorporate the necessary QC samples required for an analytical run (Table 6.7 and Table 6.8). In addition to the necessary QC samples, tank waste samples should also be prepared in a minimum of three replicates. Due to the nature of the data quality samples to be analyzed concurrently with any single tank waste set of samples, it is ideal to pre-plan a system configuration optimized for the available laboratory and fume hood space, the cost of duplicate systems (glassware, mass flow controllers, etc.), and an expected number of samples (QC and tank waste) in the test sequence for an ideal batch design.

For total mercury analysis, sample digestions can be completed in individual bottles. Purging of either undigested elemental mercury or digested total mercury samples onto traps is then completed in batches.

For methyl mercury analysis, both sample distillation and purging of samples onto traps are completed in batches. Distillation of methyl mercury samples can take hours to complete and therefore is most easily accomplished the day prior to analysis or requires calibration by a second analyst during sample distillation.

Laboratory-produced and commercially available distillation blocks and rotameters typically allow for three to six samples to be prepared concurrently. As an example, batches of four samples were processed concurrently in the CA fume hood at PNNL-Richland, while batches of either three or five were used for non-tank-waste-containing calibration and QC samples at PNNL-Sequim. Ideally, CVAFS analysis of loaded traps takes place simultaneously to the preparation of the subsequent batch of sample trap loading.

Therefore, when there are two scientists available to implement testing in tandem, the use of batched bubblers is a distinct advantage. Batching is also possible with a single staff member; however, expertise and familiarity with the procedure will strongly dictate the appropriate level of multi-tasking that ensures safe operation and maintains quality data.

The second consideration for configuration and batching is the use of a second system outside of a CA fume hood that is maintained for only non-tank-waste-containing calibration and QC samples. This can be done for both methyl mercury and elemental/total mercury systems.

For example, the methyl mercury bubbler system that is used for tank waste samples must be maintained in a CA fume hood. However, a second methyl mercury bubbler system may be maintained outside of the CA fume hood for purging of non-tank-waste-containing QC samples if both the bubblers and the Carbotrap®-filled traps are maintained as non-tank-waste-containing. Likewise, a tank-waste version of total and elemental bubblers may be maintained along with a non-tank-waste-containing total mercury bubbler system (for the dedicated calibration and QC samples).

The advantage of these dual systems is flexibility in preparing tank-waste-containing samples and non-tank-waste-containing calibration and QC samples in separate benchtop/fume hood spaces and the minimization of liquid radioactive waste. The main disadvantages are tracking radiologically contaminated equipment versus non-radiological equipment, the additional space considerations, and the added cost of dedicated bubblers, rotameters/mass flow controllers, gold traps/ Carbotrap®-filled traps, and bubblers.

6.10 Chemicals, Mercury Standards, and Reagents

This section in general lists the key chemicals, mercury (total and methyl mercury) standards, and reagents needed for conducting the ultra-trace mercury speciation methods previously discussed in Sections 6.1 through 6.3. Details also include desired purity or grade when applicable.

- Ultra-high-purity nitrogen gas (UHP, 99.999% or higher), used as carrier gas for bubbler.
- Ultra-high-purity argon gas (UHP, 99.999% or higher), used as carrier gas for analysis.
- Both nitrogen and argon gases can be further purified by installing a gold trap downstream of the gas regulator. This is recommended if there is a concern to the purity of either compressed gas supply. These compressed gas supplies are specifically managed at the PNNL-Sequim laboratories to ensure no mercury content.
- Reagent water, 18MΩ minimum, used in tank waste sample dilutions and data quality samples. Analysis of DI water should be routinely completed to verify low mercury content. This analysis of the DI water can be accomplished by preparing and purging a sample volume of DI water onto a gold trap as though it were an unknown mercury sample.
- Reagent grade 8-14 mesh soda lime, for replacing soda lime traps.
- Hydrochloric acid, concentrated, containing less than 5 pg/mL of mercury, trace metal grade or equivalent (Fisher and JT Baker have been used at PNNL-Sequim).
- Sulfuric acid, concentrated, containing less than 5 pg/mL of mercury, trace metal grade or equivalent (Fisher and JT Baker have been used at PNNL-Sequim).
- Stannous chloride. Dissolve 200 g of $SnCl_2 \cdot 2H_2O$ and 100 mL of concentrated HCl in reagent water and bring to 1.0 L. Purge with nitrogen gas at 500 mL/min to remove trace mercury. Solution can be re-purged if reagent blanks indicate contamination.
- Bromine monochloride. Dissolve 27 g reagent grade KBr in 2.5 L of concentrated HCl on stir plate. Stir for 1 hour. While still stirring, slowly add 38 g reagent grade $KBrO_3$.
- Hydroxylamine hydrochloride. Dissolve 300 g of $NH_2OH \cdot HCl$ in reagent water and bring to 1.0 L. Prior to use, add 0.1% stannous chloride reagent and purge with nitrogen gas at 500 mL/min to remove trace mercury.
- APDC. Dissolve 1.0 g of reagent grade APDC in reagent water and shake to dissolve.
- Acetate buffer. Dissolve 272 g reagent grade sodium acetate and 118 mL reagent grade glacial acetic acid in reagent water and bring to a final volume of 1.0 L.
- Sodium tetraethylborate. Dissolve 2 g KOH in reagent water and chill to 0 °C. Dissolve 1.0 g sodium tetraethyl borate in pre-chilled KOH solution and aliquot among 15-mL fluoropolymer vials. Store frozen and keep on ice between uses.
- Primary inorganic mercuric chloride standard stock can be purchased as certified stock from commercial vendors at 1-µg/mL concentrations (High-Purity Standards and Brooks Rand have been used at PNNL-Sequim).
- Secondary inorganic mercury standard stock: an independent standard is needed to confirm calibration. Can be purchased from second vendor or as second lot number from same vendor as primary stock.
- Primary methyl mercury standard stock can be purchased as certified stock from commercial vendors at 1-µg/mL concentrations (Brooks Rand has been used at PNNL-Sequim).

- Secondary methyl mercury standard stock: an independent standard is needed to confirm calibration. Can be purchased from second vendor or as second lot number from sample vendor as primary stock.
- Standard reference material: National Institute of Standards and Technology (NIST) Standard Reference Material 1641e, Mercury in Water.
- Standard reference material: NRC DORM-4, trace metals and methyl mercury in fish protein (now replaced with DORM-5). Note that no standard reference materials exist for methyl mercury in water. Alternatively, digestion of solid standard reference material (DORM mercury is nearly 100% methylated) can be analyzed.

6.10.1 Prepared Solutions and Standards

The various necessary undigested/undistilled and digested/distilled solutions are listed below along with a brief description of each. Undigested/undistilled solution samples are prepared in DI water and undergo purging onto traps with subsequent analysis using the same analytical method (same temperature, same gas flow, same detector sensitivity) as samples. The digested/distilled solution samples are prepared as a matrix equivalent to that of the batch samples and are then carried through the same preparation and digestion/distillation steps as are undergone by tank waste samples.

Undigested/Undistilled Solutions:

- Bubbler blanks/calibration blanks are prepared by addition of reagents to DI water and subsequently analyzed.
- Reagent blanks (total mercury analysis) are prepared by addition of BrCl and $NH_2OH{\cdot}HCl$ to reagent water at volumes used for sample digestion. If samples within a batch require additional BrCl to sustain the yellow color during digestion and additional $NH_2OH{\cdot}HCl$ to reduce excess BrCl, the reagent blank should contain the maximum volumes of each reagent used in the batch.
- Calibration standards are prepared by addition of known volumes of working standard stocks and reagents to DI water and analyzed.
- Initial/continuing calibration verification (ICV/CCV) standards are prepared by addition of known volumes of working standard stocks at half the calibration mid-point and reagents to DI water and analyzed.
- Initial/ongoing precision and recovery (IPR/OPR) samples are prepared by addition of known volumes of working standard stocks to DI water at 5 ng/mL (for total mercury) or 0.5 ng/mL (methyl mercury) and analyzed.

Digested/Distilled:

- Method blanks are prepared from a low-mercury matrix (DI water, acid-washed quartz), similar to that of the sample matrix.
- Certified or standard reference material (CRM or SRM) samples are prepared from a known volume or mass of a CRM of a matrix similar to that of the sample matrix.
- Laboratory control samples are prepared from the addition of working standard stocks or similar to low-mercury matrices at concentrations equivalent to the midpoint of the calibration range.

6.11 Quality Control Samples and Data Quality Objectives

Note that the types and quantities of QC samples are typically dictated on a per-day basis. This requirement becomes more challenging if samples are to be shipped to an outside laboratory. Therefore, pre-planning for the need to run new sets of all QC samples each day to verify that tank waste samples are purged and analyzed is imperative in the sample planning and staging process. If all sample preparation and analysis will be conducted in a single facility, it is strongly recommended that test sequences be planned in such a way that all tank waste samples that are purged or distilled are also analyzed on the same day. As was the case in the experimental work conducted at PNNL (FYs 2018 through 2020), it became necessary to evaluate the impact of storage time on the quantification of samples and to account for this trend during the final quantification steps.

In the case that tank waste samples [i.e., purged gold traps and distillates (see discussion in Section 6.15)] are to be transported to an outside facility for analysis (i.e., a dual-laboratory configuration), efforts should be made to coordinate the use of identical batches of reagents, mercury standards, and water sources between the two facilities [as was done in the PNNL analysis (Fountain et al. 2018; Bottenus et al. 2019, 2020)]. This will ensure that analysis laboratory QC samples (such as calibrations) will seamlessly correlate with tank waste samples and laboratory QC samples. Note that this should include the use of identical water sources for tank waste sample dilutions. If coordinated use of reagents, mercury standards, and/or water cannot be accomplished between the two facilities, redundant QC samples (e.g., bubbler blanks, method blanks, OPR blanks, OPRs, and CRMs/SRMs) must be conducted at both facilities. However, this is strongly discouraged due to the compounding uncertainties in the quantification steps.

PNNL has successfully demonstrated both single-laboratory sample handling and analysis protocols (conducted weekly at PNNL-Sequim campus) and dual-laboratory/facility configuration (conducted over the course of a three-year project at PNNL where sample handling was conducted at the Richland campus and the sample analysis handled at the Sequim campus). Therefore, implementing a dual-laboratory configuration is just as achievable as a single-laboratory/facility configuration; however, it does require additional planning, coordination, and communication, as well as additional QC laboratory samples to ensure efficient procedure execution and quality data generation and quantification.

The following two tables designate the recommended data quality objectives (DQOs) for both the total and elemental mercury system (Table 6.5) and the methyl mercury system (Table 6.6). These objectives align with the DQOs followed in the ultra-trace mercury analysis laboratories at the PNNL-Sequim campus.

Table 6.5. Total and Elemental Mercury Data Quality Objectives

QC Sample Type	Acceptance Limit	Reference
Calibration	Relative standard deviation (RSD) ≤15% and lowest std is 75%-125%	MSL-I-013, Section 7.1
Lab reagent blank, method blank, or OPR blank[a]	≤ 50 pg	EPA Method 1631, Section 9.4.4.2
Certified/standard reference material (CRM/SRM)	77%-123% of certified value	MSL-I-013, Table 1
Ongoing precision and recovery (OPR)	77%-123% of computed value	MSL-I-013, Table 1
Matrix spike	71%-125% recovery	MSL-I-013, Table 1
Matrix spike duplicate	< 24% relative percent difference	MSL-I-013, Table 1
Initial and continuing calibration verification (ICV, CCV)	< 15% of initial calibration	MSL-I-013, Table 1
Bubbler blanks	<50 pg and average < 25 pg and RSD <10 pg	EPA Method 1631, Sections 9.4.1.2 – 9.4.1.3

(a) MSL-I-013 Table 1 specifies <5x the method detection limit.

Table 6.6. Methyl Mercury Data Quality Objectives

QC Sample Type	Acceptance Limit	Reference
Calibration	RSD ≤ 15% of mean calibration factor and lowest std is 65%-135% of expected value	MSL-I-014, 1.4.1, and EPA Method 1630, Sections 10.1.1.4 – 10.1.1.5
Ethylation blank or laboratory reagent blank	≤ 2pg MeHg (EPA)[a]	EPA Method 1630, Section 9.4.1.2
Method blank (also called a distillation blank)	Max < 0.1 ng/L and avg < 0.05 ng/L	EPA Method 1630, Table 2 in body of document, Section 17.0 (not Table 2 in Appendix A)
Certified / standard reference material (CRM/SRM)	67%-133% of certified value	MSL-I-014, Table 1
Ongoing precision and recovery (OPR)	67%-133% of computed value	MSL-I-014, Table 1, and EPA Method 1630, Table 2 in body of document, Section 17.0 (not Table 2 in Appendix A)
Initial and continuing calibration verification (ICV, CCV)[b]	< 20% of initial calibration	MSL-I-014, Table 1
Matrix spike	65%-135% recovery	MSL-I-014, Table 1
Matrix spike duplicate	< 35% relative percent difference	MSL-I-014, Table 1

(a) EPA Method 1630 refers to a 50-mL ethylation blank sample volume, mass is scaled on this basis.
(b) EPA Method 1630 refers to an ICV as a quality control sample. EPA Method 1630 does not define a CCV as part of its recommended quality control samples.

The following two tables offer the suggested set of QC samples for the single-laboratory/facility configuration for total and elemental mercury, (Table 6.7) and methyl mercury (Table 6.8), respectively. . Additionally, these tables provide details on the frequency and quantity of such samples in alignment with the procedures developed and followed in the ultra-trace mercury analysis laboratories at the PNNL-Sequim campus.

Note: In cases where limited sample volumes prohibit preparation and analysis of matrix spike and matrix spike duplicate pairs, two matrix spikes are recommended for every 10 samples analyzed. In such cases, analytical precision can be determined from analysis of method duplicates.

Tables developed for the dual-laboratory/facility configuration implemented at PNNL (Richland and Sequim locations) are found in Section 6.18 and provide additional considerations for this configuration.

Table 6.7. Total and Elemental Mercury Required Quality Control Samples for a Single-Laboratory Configuration

Total and Elemental QC Samples	**Notes**
Calibration standard (total)	**Minimum of five** non-zero points required each day. Standards from standard working stocks are prepared in reagent water in the range of expected mercury concentrations in tank waste samples. Low-level or high-level standards can be run if initial calibrations do not bracket tank waste sample ranges.
Bubbler blank (total)	**Three** required for every batch or every 20 samples. If more than three bubblers are being used for tank waste samples, prepare a minimum of one bubbler blank in each bubbler. Required for calibration. **One** done on each bubbler (minimum of three). These include the addition of $SnCl_2$.
Bubbler blank (elemental)	**Three** required for every batch or every 20 samples. If more than three bubblers are being used for tank waste samples, prepare a minimum of one bubbler blank in each bubbler. Required for calibration. **One** done on each bubbler (minimum of three).
Method blank or laboratory reagent blank (total)	**Three** required for every batch or every 20 samples, digested with sample reagents as samples. If more than three bubblers are used for samples, run a method blank on each bubbler.
OPR blank	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Used to determine blank from long-term storage.
OPR (total)	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Used to determine instrument reliability.
Reference material sample (total)	**One** required for every batch or every 20 samples. Used to verify total mercury from a similar matrix (SRM) or (NIST Std) QC sample.
ICV standard #1 (total)	**One** required following calibration. Prepared from a separate standard stock at a concentration near the mid-range of calibration.
CCV standard (total)	**One** required for every 10 samples and at end of analytical sequence.
Matrix spike/matrix spike duplicate (total)	**One** pair required every 10 samples.

Table 6.8. Methyl Mercury Required Quality Control Samples for a Single-Laboratory Configuration

Methyl Mercury QC Samples	Notes
Calibration standard	**Minimum of five** non-zero points required each day. Standards from standard working stocks are prepared in reagent water in the range of expected mercury concentrations in tank waste samples. Low-level or high-level standards can be analyzed if initial calibrations do not bracket tank waste sample ranges.
Ethylation blank (calibration)	**One** required after calibration standards are run.
Ethylation blank (OPR)	**One** required after each OPR. This sample is not distilled like other methyl mercury samples.
OPR	**Two** required for every batch or every 20 samples at beginning and end of analytical run. Must be preceded each time by an ethylation blank. Sample is distilled.
OPR blank	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Sample is distilled.
Reference material sample	**One** required per batch of 20. Sample is distilled.
ICV standard	**One** required following calibration. Prepared from a separate standard stock at a concentration near the mid-range of calibration.
CCV standard	**One** required for every 10 samples and at end of analytical sequence.
Method blank (distillation blank)	**One** required on each methyl bubbler. Sample is distilled.
Matrix spike/matrix spike duplicate	**One** pair required every 10 samples.

6.11.1 Calculations and Quantification

6.11.1.1 Total and Elemental Mercury Calculations

The total and elemental DQOs for calibration, blanks, matrix spikes, and continuing calibration verifications are provided in Table 6.5. For the initial calibration to be valid, the following DQOs need to be met: a minimum 5-point calibration, bubbler blanks for each bubbler, ICV, and CCV. The initial calibration needs to be completed before any samples can be run. A flowchart detailing the process of the initial calibration with all the DQO checkpoints and remedies if a DQO fails is presented in Figure 6.12. Calculations corresponding to individual DQOs are described below.

Total Mercury Calibration Standards. The response factor (blank-corrected) *(RF)* for each calibration standard is calculated as follows:

$$RF = \frac{(PA_{cal} - PA_{BB})}{M_{cal}} \tag{6.4}$$

where *RF* is the blank-corrected response factor [PA/ng]; PA_{cal}, PA_{BB} are the peak area for the calibration standard and bubbler blank, respectively; and M_{cal} is the known mercury mass in the calibration standard [ng].

Using all the calibration standards, compute the average, standard deviation, and relative standard deviation (RSD) *RF*. Compare calibration RSD to the DQO.

Calculate the deviation of the individual calibration *RF*s from the average *RF (Avg RF)*. Compare to the DQO requirements. If five or more calibration points pass the calibration DQOs (Table 6.5), then the overall calibration has passed. If fewer than five calibration points pass the DQO, then additional calibration standards need to be run until a valid five-point calibration curve has been achieved.

Total Mercury Blanks. The amount of mercury mass in all blanks (M_{blank}) (i.e., bubbler blank, lab reagent blank, method blank, and OPR blank) is calculated using the $Avg\ RF$ calculated from the accepted five-point calibration standards using Eq. (6.5):

$$M_{blank} = \frac{PA_{blank}}{Avg\ RF} \tag{6.5}$$

where M_{blank} is the mercury mass in the blank [ng]; $Avg\ RF$ is the average blank-corrected response factor; and PA_{blank} is the peak area for the blank in question (i.e., bubbler, lab regent blank, method blank, or OPR blank).

The total mercury mass in the blank can then be compared to DQOs. If a bubbler blank fails, attempt to eliminate the source of mercury contamination from the specific bubbler. The bubbler blank then needs to be repeated until the specific bubbler meets the DQO.

External Total Mercury Standards. The recovery of external total mercury standards (i.e., ICV, CCV, SRM) is computed as:

$$R = \frac{\frac{PA_{std}}{Avg\ RF}}{C_{std}V_{std}} \tag{6.6}$$

where R is the recovery of mercury mass, computed as the measured amount in the standard compared to the known amount of mercury present in the sample; PA_{std} is the peak area measured from the mercury standard; C_{std} is the known mercury concentration in the standard; and V_{std} is the volume of mercury standard added.

Eq. (6.6) is used to determine mercury recovery for any known external standard, including ICV, CCV, and reference material sample initial and continuing calibrations.

If ICV or CCV recoveries do not meet initial DQOs, then prepare a new ICV and re-run the sample. If the ICV or CCV fails a second time, a new five-point calibration curve must be prepared and validated by the associated calibration DQO testing.

Matrix Spike Recovery. The recovery of a matrix spike can be calculated with the following steps. First, the total mercury measured in the matrix spike sample (M_{total}) is quantified using the peak area (PA) and the average blank-corrected response factor (RF) [similar to Eq. (6.2)]. Using independent measurements of parent samples, the mercury mass in the sample from the parent sample (M_{parent}) is determined. Ideally, at least triplicate measurements of the parent sample are measured, and the average is used for the matrix spike recovery calculation. Subsequently, the known Hg mass of the spike (M_{spike}) is determined (i.e., $M_{spike} = C_{spike}V_{spike}$). This information is then used to determine the matrix spike recovery (R_{MS}):

$$R_{MS} = \frac{M_{total} - Avg\ M_{parent}}{M_{Spike}} \tag{6.7}$$

6.11.1.2 Methyl Mercury Calculations

The methyl mercury data quality DQOs for calibration, blanks, matrix spikes, and continuing calibration verifications are provided in Table 6.6. The calculations detailed in Eqs. (6.4) through (6.7) are also applicable for methyl mercury. A flowchart detailing the process of the initial calibration with all the DQO checkpoints and remedies if a DQO fails is presented in Figure 6.12.

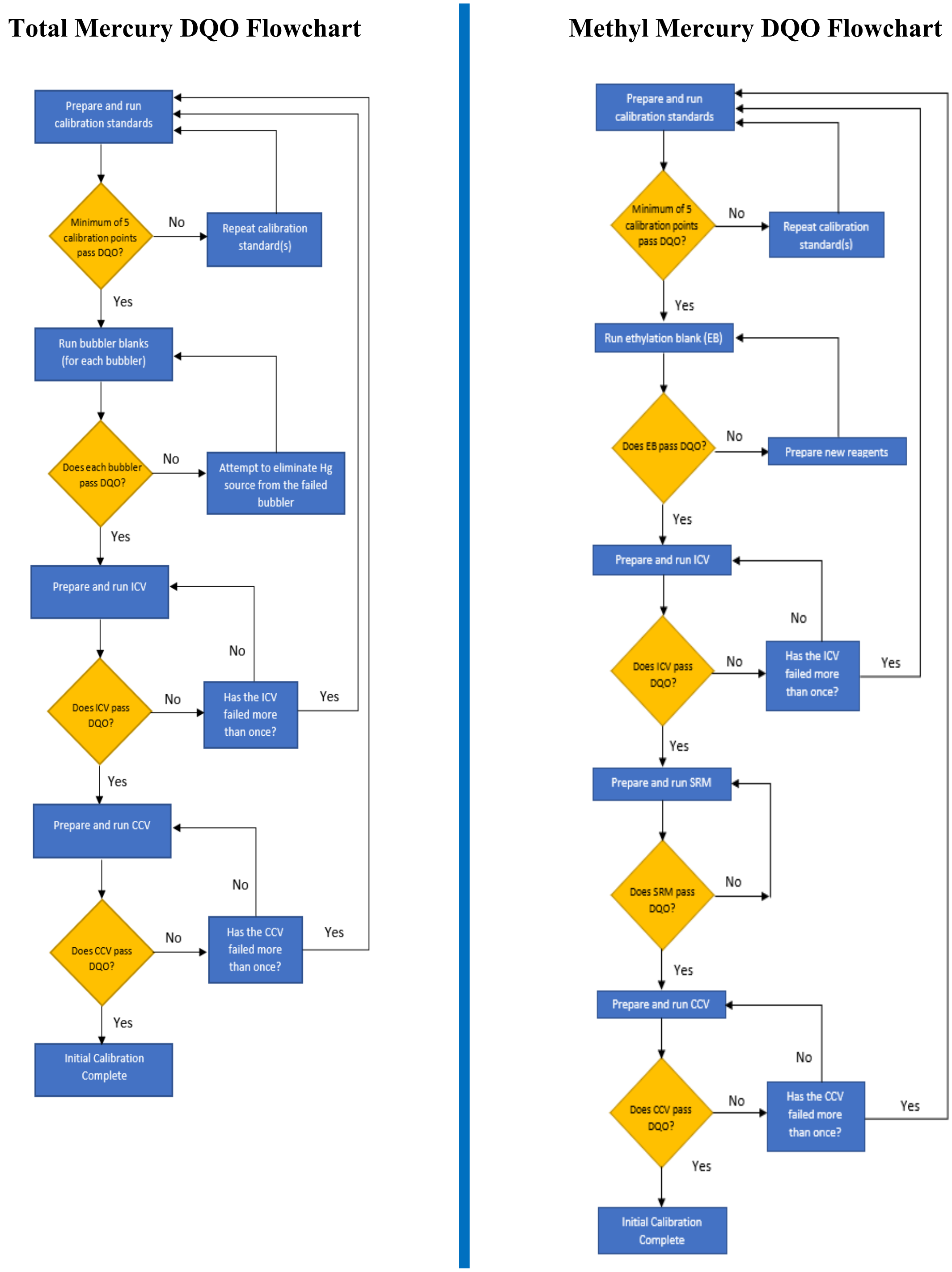

Figure 6.12. Total mercury calibration and methyl mercury calibration – data quality objective flowchart.

6.12 Blanking and Trap Quality Checks

There are separate considerations needed depending on whether a manual or automated CVAFS analytical system is being used. These two cases are discussed below.

6.12.1 Manual CVAFS

In all CVAFS analytical methods for mercury, a solid phase trap is used to concentrate the mercury species (elemental mercury or methylethyl mercury). Because manual analytical systems use sets of traps, it is critical to ensure that traps are blanked and checked for consistency and reproducibility. One key tip is to have a unique identifier for each trap; that way, the performance and reproducibility can be tracked over the course of time and traps demonstrating any undesirable trends can be removed from the test circulation. However, it is important not to mark the gold traps but rather label the storage tubes they are held in. Any labels or marker inks can introduce elemental mercury signal into the trap. Commercially filled Carbotrap®-filled traps (used for the methyl mercury) are typically uniquely laser etched from the supplier.

Gold traps are prone to accumulate elemental mercury from the ambient environment. To minimize accumulation, traps are often stored and sealed appropriately in individual glass culture tubes. However, quality checks are needed to ensure that these traps are blank prior to sample loading. Traps are heated on the CVAFS system to confirm no mercury accumulation. The process should result in a fully blanked trap. However, if a large elemental mercury signal is seen, it may be justifiable to re-run the same trap to ensure it is fully blanked.

A second quality check, in which identical spikes of known mercury standard are added to each trap in the set, is conducted on all traps to confirm signal reproducibility. A relative percent difference of < 5% is the criterion for use of traps in analysis.

6.12.2 Automated CVAFS

Commercially available automated systems are programmed with methods that blank system components prior to sample loading and consist of between one and three “field traps” paired with an “analytical trap” (for total mercury) or GC column (for methyl mercury). As a result, separate quality checks of the traps are not necessary, and trap performance can be determined from evaluating peak shape and the calibration. In systems with single “field traps,” variability between traps is eliminated completely, while variability for those with two or three “field traps” can be determined from evaluating bias in the calibration standards and QC samples.

6.13 Analysis Testing Order Considerations

While an absolute defined analysis order does not have to be followed, some requirements do apply to determining the analysis order. For example, calibration standards must precede ICVs, which must precede CCVs. It is also advisable to test the QC blanks and reference material QC samples before ever running a tank waste sample. Table 6.9 shows an example case of the analysis order both for the set of elemental/total mercury samples and for the methyl mercury samples. Note that the unique samples necessary in a dual-laboratory configuration (as addressed more completely in Section 6.18) have been marked in Table 6.9 with an asterisk (*). These samples are not necessary in a single-laboratory configuration. It is important to recognize that each of the tank waste samples (for a specific mercury species) and “parent sample” should be run in replicates (preferably ≥ 3 replicates each). Furthermore, these tank waste sample replicates do not need to be run in a back-to-back order, although replicates should all be handled in the same day.

Table 6.9. Total / Elemental Mercury and Methyl Mercury Recommended Analysis Testing Order

Analysis Order	Total and Elemental Samples	Methyl Mercury Samples
1	Calibration standards	Calibration standards
2	Bubbler blanks (total)	Ethylation blank (calibration)
3	ICV std	ICV std
4	CCV std	OPR blank
5	SRM	OPR
6	Laboratory reagent blank	Laboratory control standard
7	OPR blank	Method blank (distillation blank)
8	OPR	CCV std
9	Bubbler blank (elemental mercury) *	Matrix spike tank
10	Bubbler blank (total mercury) *	Waste samples 1-10
11	Bubbler blank (total mercury)	CCV std
12	Laboratory control sample	Tank waste samples 11-20
13	Laboratory reagent blank	OPR blank
14	Laboratory reagent blank	OPR
15	Matrix spike	Matrix spike duplicate
16	Tank waste samples 1-10	CCV std
17	CCV std	
18	Tank waste samples 11-20	
19	OPR blank	
20	OPR	
21	CCV std	
22	Tank waste samples 21-25	
23	Matrix spike duplicate	
24	OPR blank	
25	OPR	

(*) Denotes samples specific to the dual-laboratory configuration.

6.14 Notes on Material Selection

Quantification of ultra-trace mercury species requires avoiding contamination from materials in order to obtain acceptable detection limits. Teflon and borosilicate glass are used for components that contact aqueous samples or the gaseous sample flow during analysis due to their ease of cleaning or low-mercury background.

All sample storage and preparation bottles should be pre-cleaned in-house or purchased certified as mercury-free prior to initial use and re-cleaned between uses. Bottles are cleaned in heated acid baths. Hydrochloric acid baths are sufficient for mercury laboratories. In trace metal laboratories such as PNNL-Sequim, bottles can be cleaned by heating in concentrated nitric acid. Following cleaning, bottles should be rinsed copiously with reagent water and filled with dilute hydrochloric acid until emptied and rinsed for use. Teflon and borosilicate glass bottles with Teflon-lined caps can be used for sample storage. Polyethylene and polypropylene bottles should be avoided for sample storage because they are permeable to gaseous elemental mercury. That being said, many automated CVAFS and CVAAS system incorporate the use of polypropylene centrifuge tubes for analysis. This can be acceptable if no alternative is available, but it should be noted that the material does allow gaseous elemental mercury to permeate thus potential underrepresenting the true total mercury quantification. All samples should be stored in a light-limited environment. Methyl mercury samples should be stored away of sunlight to avoid demethylation. For distillation of methyl mercury, distillation vials with Teflon tubing are used. Vials can be cleaned between sample sets by distilling acidified reagent water and analyzing distillate as blanks to confirm that no carryover is detected.

Borosilicate glass bubblers are used to load samples onto analytical traps. After initial cleaning when purchased, bubblers can typically be used repeatedly during batch processing or analytical runs without the need for extensive cleaning between samples. During the preparation of calibration standards, additional standard stock can be added to previously purged reagent water in the bubbler flask. In between tank waste samples, bubbler flasks can be rinsed three times using a small amount of reagent water gently swirled on the inside of the bubbler while avoiding drips and splashing. Bubblers used for the digestion of total mercury samples with $SnCl_2$ should not be used for the digestion of elemental or methyl mercury samples.

6.15 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 (i.e., single-laboratory configuration) and completed within a limited time frame (typically < 1 day). However, it is possible to quantify the loss rate over a finite period of time if these activities are not co-located (i.e., dual-laboratory configuration) or there will be a known waiting time prior to sample analysis.

6.15.1 Total and Elemental Mercury Stability

Total (via conversion of all species to elemental) and elemental mercury species are isolated from the aqueous matrix by purging onto a gold trap following EPA Method 1631 (EPA 2002). In the case of a dual-laboratory configuration, the gold traps are then shipped for analysis. The EPA method does not provide storage time limits for samples collected on gold-coated sand or gold-coated bead. Past environmental mercury research indicates that mercury collected on gold 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 or gold-coated bead, future work could potentially necessitate stability testing of elemental mercury collected onto gold traps. However, it is possible for elemental mercury to accumulate (though traps were capped and transported in glass culture tubes to minimize elemental accumulation) onto the gold traps over time from environmental exposure.

6.15.2 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 a 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 could become a critical requirement, and understanding the stability associated with short-term storage of samples isolated from the parent sample could be deemed fundamental.

There are two options for transferring methyl mercury samples isolated from the raw sample to a second laboratory facility for analysis or for an unexpected pause in analysis: as a distillate sample or as methylethyl mercury retained on a Carbotrap®-filled trap. Investigations were conducted (Bottenus et al. 2019) to determine the stability of methyl mercury in these two matrices and sample transfer processes. The results of the stability experiments identified which matrix/process was most stable and generated 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 has been demonstrated in previous work to exhibit almost no radiological dose (Fountain et al. 2018). The stability of both means of isolating methyl mercury from the parent sample for shipment was experimentally demonstrated.

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 at room temperature and in the dark 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 (Bottenus et al. 2019).

6.16 Sample Size and Trap Saturation Evaluation

There are separate considerations needed depending on whether a manual or automated CVAFS analytical system is being used. These two cases are discussed below.

6.16.1 Manual CVAF

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 for tank waste, caution must be taken to ensure that 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 CVAFS detector. Therefore, it would be advisable to conduct similar evaluations, especially when analysis of a new or not-well-characterized tank waste sample is planned, prior to preparing the final samples.

An evaluation to ensure appropriate sample size was conducted at PNNL using an available volume of filtered waste from Hanford tank 241-AP-107 (Bottenus et al. 2019). In the worked conducted, three filtered AP-107 sample volumes were analyzed. Filtered AP-107 sample was selected simply because of available source volume. However, the total mercury analysis was selected based on total mercury always representing the maximum mercury mass (and peak intensity). The three AP-107 sample volumes (0.084 mL, 0.835 mL, and 8.335 mL) were loaded onto gold traps and analyzed. 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 or gold-coated bead 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.

6.16.2 Automated CVAF

As with manual systems, commercially available CVAFS system detectors have ranges that can be exceeded by high-concentration samples. Manufacturers generally provide recommendations for detector sensitivity to optimize the lifespan of detector components and signal consistency. The range for each individual instrument can vary but can be determined empirically by extending the calibration range during instrument installation until the detector is saturated. Ranges of daily calibrations should not exceed saturation.

Should the detector range be exceeded, reagent water blanks should be analyzed to ensure that the autosampler probe, tubing, and traps do not display carryover. For these blanks, reagent water is added to sample containers without additional reagents and the blanks are analyzed with the same instrument method as the previous sample. For systems with a single “field trap,” a single reagent water blank may be sufficient to indicate no carryover. For systems with two or three “field traps,” multiple reagent water blanks are required until the trap used for the high-concentration sample is confirmed to be free of carryover.

For new analytical batches with the potential to have high mercury species concentrations, reagent water blanks can be spaced in between initial samples to estimate appropriate dilution factors for sample batches.

6.17 Methyl Mercury Distillation and Efficiency

The normal distillation process transfers 40 mL of the 50-mL acidified sample volume into a distillation receiver vial pre-filled with 5 mL of reagent water. To avoid transfer of HCl from the distillation-sending vial, samples should not be completely distilled. Complete distillation of the entire volume (e.g., 50 mL) would result in a low pH and a carryover of sample matrix components associated with 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 distillation recovery factor that accounts for this intentional incomplete distillation.

The distillation recovery factor differs by laboratory and should be regularly determined and documented. Typically, a running mean of the last 30 recoveries is used to determine the laboratory distillation recovery factor 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 and the resulting factor is used to correct measured distillation.

6.18 Considerations for Dual-Laboratory Configuration Laboratory Handoff

Throughout this document, there have been mentions of the unique challenges and additional consideration necessary when an outside laboratory is used to evaluate and quantify tank waste samples. This unique dual-laboratory configuration scheme was successfully developed, implemented, and modified over the course of three years conducting ultra-trace mercury speciation and quantification of Hanford tank waste at PNNL. The two laboratory/facilities are the Radiochemical Processing Laboratory at the PNNL-Richland campus and the Mercury Analytical Laboratory at the PNNL-Sequim campus. For these efforts specifically, the dual-laboratory configuration was used since each laboratory maintained existing and unique expertise and capabilities. The PNNL-Richland laboratory could best handle the raw tank waste samples and could support the stabilization, preservation, and preconcentration of samples. The PNNL-Sequim laboratory maintained the ultra-trace mercury speciation and quantification analytical

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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.

systems and expertise. While a dual-laboratory configuration is not ideal, it is appropriate to identify the primary considerations if such a configuration needs to be used in any capacity.

6.18.1 Shipping Protocols

Although PNNL-Sequim 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 traps and distillation receiver vials from the PNNL-Richland laboratory was necessary to leverage the existing mercury analytical capabilities at the PNNL-Sequim laboratory while also mitigating the high radiological dose observed with tank waste samples by conducting the preliminary mercury separations at the PNNL-Richland laboratory. Previous work scope activities reported by Fountain et al. (2018) presented 10^6 and 10^4 total activity reductions obtained by the separation processes at the PNNL-Richland laboratory measuring the gold-coated sand or gold-coated bead (outside the glass columns) and the distillate liquid samples, respectively. Dose reductions on the order of 10^8 were measured for the gold trap and Carbotrap®-filled trap.

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

Reduced Shipping Duration: Storage time can be reduced by coordinating the completion of separations such that samples can be removed and staged for shipping the same day. For example, sample pickup by the representatives from PNNL's hazardous material transportation organization is once a day; thus, coordination with these timeframes helped to ensure minimum storage times. Additionally, avoiding separations and shipments on Fridays ensures next-business-day receipt of samples and an opportunity to start analysis activities sooner at PNNL-Sequim. Thus, understanding the shipment and delivery times for the receipt facility becomes critical to ensuring that samples do not need to wait over weekends.

Control Sample Shipping Temperature: Overnight shipping can still expose samples 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, ambient temperatures can range from room temperature (~68 °F; ~20 °C) to freezing, and depending on the time of year and location, may exceed 100 °F (38 °C). If sample shipping occurs via overnight air, shipments of samples should include ice packs (or equivalent) to control temperature. Alternative shipping by ground courier will mitigate larger potential variations in temperature and pressure, but temperature control would still be beneficial in minimizing environmental variabilities during shipping.

Mitigate Sample Volume Loss: Ensure when liquid samples are transported or stored for any duration that they are placed in appropriate containers which can be sealed and remain sealed for conditions that they may potentially encounter. For example, the vented cap on the distillation receiver vial (used during distillation process) should be replaced with a flat cap. The vented caps have the risk of leaking during transportation and/or may be prone to leak if they are ever over-pressurized during transportation (e.g., airplane shipment). It is always most advisable to minimize unnecessary volume transfers, due to potential risk of sample losses; however, options that can be considered (for the example of the distillation vial) are: 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 but 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.

6.18.2 Sample Stability

The methyl mercury distillates were determined to be more stable than the methyl mercury samples purged on the Carbotrap®-filled traps (Fountain et al. 2018). Therefore, it is advised to ship methyl mercury distillate samples rather than ship methyl mercury samples that are already purged onto the Carbotrap®-filled traps. As such it should be ensured that the receiving facility has the appropriate equipment and materials, reagents, compressed gases, etc. for purging methyl mercury distillate samples onto Carbotrap®-filled traps.

6.18.3 Quality Control Samples

The challenge of mitigating and preventing quality issues associated with sample handling, storage, and processing increases as the number of facilities conducting sample preparation increases. The dual-laboratory configuration requires additional steps to ensure that both facilities avoid sample contamination, can sufficiently recovery mercury species from the sample matrix, and can adequately store samples until transfer or analysis. For example, this involves incorporating redundancy in QC samples of both known mercury species concentrations and blanks to account for sample processing steps that are split between the two separate facilities. If there are options for “sharing” reagents between the two facilities, this is recommended. Table 6.10 and Table 6.11 summarize the quality control sample requirements implemented during the dual-laboratory configuration conducted at PNNL for total and elemental mercury sample analysis (Sections 6.1.1, 6.1.2, 6.2.1, and 6.3.1), and for methyl mercury sample analysis (Sections 6.1.3, 6.2.2, and 6.3.2).

Table 6.10. Total and Elemental Mercury Required Quality Control Samples for a Dual-Laboratory Configuration

Total and Elemental QC Samples	Sample Preparation Site (dual-configuration)[(a)]	Sample Purge Site (dual-configuration)[(a)]	Notes
Calibration standard (total)	Site 2b	Site 2b	**Minimum of five** non-zero points required each day. Standards from standard working stocks are prepared in reagent water in the range of expected mercury concentrations in tank waste samples. Low-level or high-level standards can be run if initial calibrations do not bracket tank waste sample ranges.
Bubbler blank (total site 2b)	Site 2b	Site 2b	**Three** required for every batch or every 20 samples. If more than three bubblers are being used for tank waste samples, prepare a minimum of one bubbler blank in each bubbler. Required for calibration. **One** done on each bubbler (minimum of three). These include the addition of $SnCl_2$.
Bubbler blank (total site 2a)	Site 2a	Site 2a	**Three** required for every batch or every 20 samples. If more than three bubblers are being used for tank waste samples, prepare a minimum of one bubbler blank in each bubbler. Required for calibration. Required for calibration. **One** done on each bubbler (minimum of three) These include the addition of $SnCl_2$.
Bubbler blank (elemental)	Site 2a	Site 2a	**Three** required for every batch or every 20 samples. If more than three bubblers are being used for tank waste samples, prepare a minimum of one bubbler blank in each bubbler. Required for calibration. Required for calibration. **One** done on each bubbler (minimum of three).
Method blank or laboratory reagent blank (total)	Site 2a	Site 2a	**Three** required for every batch or every 20 samples, digested with sample reagents as samples. If more than three bubblers being used for samples, run a method blank on each bubbler.
OPR blank	Site 2a[(b)]	Site 2a	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Used to determine blank from long-term storage.
OPR (total)	Site 2a[(b)]	Site 2a	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Used to determine instrument reliability.
Reference material sample (total)	Site 2b[(b)]	Site 2b	**One** required for every batch or every 20 samples. Used to verify total mercury from a similar matrix (SRM) or (NIST Std) QC sample.
ICV standard (total)	Site 2b	Site 2b	**One** required following calibration. Prepared from a separate standard stock at a concentration near the mid-range of calibration.
CCV standard (total)	Site 2b	Site 2b	**One** required for first 10 samples and at the end of the analytical sequence.
Matrix spike/matrix spike duplicate (total)	Site 2a[(b)]	Site 2a	**One** pair required every 10 samples.

(a) Site 2a refers to the tank waste sample handling site in a dual-laboratory/facility configuration; Site 2b refers to the sample analysis site in a dual-laboratory/facility configuration.

(b) Assumes that the same sets/batches of reagents, mercury standards, and water are being used at the two facilities.

Table 6.11. Methyl Mercury Required Quality Control Samples for a Dual-Laboratory Configuration

Methyl Mercury QC Samples	Sample Preparation and Distillation[(a)] Site (dual-configuration)[(b)]	Sample Purge Site (dual-configuration)[(b)]	Notes[(c)]
Calibration standard	Site 2b	Site 2b	**Minimum of five** non-zero points required each day. Standards from standard working stocks are prepared in reagent water in the range of expected mercury concentrations in tank waste samples. Low-level or high-level standards can be run if initial calibrations do not bracket tank waste sample ranges.
Ethylation blank (calibration)	Site 2b	Site 2b	**One** required after calibration standards are run.
Ethylation blank (OPR)	Site 2b	Site 2b	**One** required after each OPR. This sample is not distilled like other methyl mercury samples.
OPR	Site 2a	Site 2b	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Must be preceded each time by an ethylation blank. Sample is distilled.
OPR blank	Site 2a	Site 2b	**Two** required for every batch or every 20 samples at beginning and end of analytical sequence. Sample is distilled.
Reference material sample	Site 2b	Site 2b	**One** required per batch of 20 samples. Sample is distilled.
ICV standard	Site 2b	Site 2b	**One** required following calibration. Prepared from a separate standard stock at a concentration near the mid-range of calibration.
CCV standard	Site 2b	Site 2b	**One** required for every 10 samples and at the end of the analytical sequence.
Method blank (distillation blank)	Site 2a	Site 2b	**One** required on each methyl bubbler. Sample is distilled.
Matrix spike/matrix spike duplicate	Site 2a	Site 2b	**One** pair required every 10 samples.

(a) Some samples do not have a distillation process step, check notes for details.
(b) Site 2a refers to the tank waste sample handling site in a dual-laboratory/facility configuration, Site 2b refers to the sample analysis site in a dual-laboratory/facility configuration.
(c) Assumes that the same sets/batches of reagents, mercury standards, and water is being used at the two facilities.

7.0 Conclusions

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). Aside from concerns about human exposure to tank vapors, mercury species in the tank waste liquid and solid fraction pose significant risk to the implementation and execution of the RPP mission to treat tank waste due to mercury limits imposed under waste acceptance criteria established from toxicity characteristic leaching procedure restrictions for secondary waste disposal, and facility air emission permits. Therefore, understanding the movement of mercury, its chemical consequences, its impact on unit operations, and its fate is important in the Hanford flowsheet.

Over the course of three years, development work was conducted at PNNL that directly supported the tracking of mercury speciation and associated inventories (Fountain et al. 2018, Bottenus et al. 2019, 2020). This new analytical capability and resulting information initiated long-term development of the necessary inputs to evaluate the impact of mercury include the magnitude of the mercury feed inventory, how the inventory is distributed throughout the tank farms, how the tank-by-tank mercury speciation inventory is distributed by waste phases (i.e., sludge, saltcake, and supernatant), the expected mercury species during waste processing, the expected final fate of mercury species (e.g., sequestered onto or within treatment systems, captured into secondary waste streams), and finally, the degree of uncertainty in this information.

To enable future flowsheet risk mitigation efforts relative to mercury, this report provides the technical bases for, describes the chemical separations used to measure, identifies key considerations, and makes recommendations for transferring and implementing a new ultra-trace mercury analytical technique at Hanford’s 222-S Laboratory.

Implementation of the ultra-trace mercury speciation and quantification methods developed and documented for Hanford tank waste at PNNL (Fountain et al. 2018; Bottenus et al. 2019, 2020) for total, elemental, and methyl mercury using a CVAFS are recommended. Additionally, it is recommended that inorganic mercury be determined, if not directly, at least by difference. Investing in the instrumentation and developing the capability to quantify these four mercury species will allow the greatest flexibility in the future when additional mercury speciation (monomethyl mercury, dimethyl mercury, total soluble mercury, particulate mercury, ethyl mercury, etc.) is desired.

It is also PNNL’s experience that this type of mercury speciation work is most efficiently conducted at a single laboratory facility (i.e., single-laboratory configuration). In such a configuration all the sample handling, preparation, and analysis takes place at a single facility. However, it is important to reiterate that this method has also been successfully demonstrated, using Hanford tank waste, using a dual-laboratory configuration. In a dual-laboratory configuration where the sample handling and preparation take place in one facility followed by the separation and analysis conducted at a separate facility. Thus, while conducting this type of work in a dual-laboratory configuration does require an extra level of coordination of equipment, materials, and scheduling to ensure consistency, optimal sample handling and storage planning, and timely analysis, it does offer an opportunity to reduce capital equipment investment.

The overall conclusion is that the transfer of the ultra-trace mercury analytical method carries moderate risk for implementation and would necessitate a more substantial capital expenditure. The majority of costs incurred would be the capital cost investment of the CVAFS systems. This investment can be somewhat tailored depending on the desired analytical instrumentation configuration (i.e., fully manual, hybrid, or maximum automation). Additionally, moderate investment will be required for procedure development and training of chemists (and chemical technicians) at 222-S Laboratory to perform the mercury separation process reproducibly with minimal analytical error. Lastly, some resources for PNNL experts to review, consult, and provide troubleshooting assistance should be allocated to speed up and reduce overall costs to implement this new method at the 222-S Laboratory.

8.0 References

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