Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

MERCURY SPECIATION USING MICROCOLUMNS WITH A DIRECT MERCURY ANALYZER (DMA)

DEVELOPMENT OF ANALYTICAL METHOD FOR THE SAVANNAH RIVER SITE LIQUID SYSTEM

B. B. Looney
T. L. White
T. B. Peters
A. J. Boggess
H. H. Vermeulen
E. D. Fabricatore
A. T. Brown

December 2020
SRNL-STI-2020-00148, Revision 0

Cover Photograph: Microcolumns used for direct analysis of mercury on the Milestone DMA 80. Columns contain various example media used in this work. From left to right: gold-coated sand, silver beads, Carbotrap B (graphitic carbon) granules, and Adsoquick (high surface area activated carbon) beads.

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2020-00148
Revision 0

Keywords: *mercury, methylmercury, dimethylmercury, organomercury, Liquid Waste System, Microcolumn, Tank Farm, Sludge*

Retention: *Permanent*

MERCURY SPECIATION USING MICROCOLUMNS WITH A DIRECT MERCURY ANALYZER (DMA)

DEVELOPMENT OF ANALYTICAL METHOD FOR THE SAVANNAH RIVER SITE LIQUID SYSTEM

B. B. Looney
T. L. White
T. B. Peters
A. J. Boggess
H. H. Vermeulen
E. D. Fabricatore
A. T Brown

December 2020

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

Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

{“blank” page}

REVIEWS AND APPROVALS

AUTHOR:

B. B. Looney, Environmental Material and Energy Sciences, SRNL Date

T. L. White, Analytical Development, SRNL Date

T. B. Peters, Chemical Processing and Technology, SRNL Date

A. J. Boggess, Analytical Development, SRNL Date

H. H. Vermeulen, Environmental Sciences and Dosimetry, SRNL Date

E. D. Fabricatore, Environmental Sciences and Dosimetry, SRNL Date

A. T. Brown, Tank Farm Area Safety and Health, Savannah River Remediation (SRR) Date

Note: Digital and physical signatures are considered Personally Identifiable Information (PII); Approval signatures for this document are securely and permanently maintained in the SRNL Electronic Laboratory Notebook System (T6751-00178-11)

TECHNICAL REVIEW:

J. A. Dyer, Environmental Sciences and Dosimetry, SRNL Date

APPROVAL:

B. D. Lee, Program Manager, Environmental Material and Energy Sciences, SRNL Date

S. D. Fink, Director, Chemical Processing Sciences, SRNL Date

R. T. McNew, Nuclear Safety and Engineering Integration, SRR Date

{“blank” page}

EXECUTIVE SUMMARY

Mercury in the Savannah River Site (SRS) Liquid Waste System (LWS) exists in various forms, including: a) ionic inorganic mercury, organomercury (e.g., methyl Hg), and other less abundant species dissolved in LWS fluids, b) mercury solids such as oxides, hydroxides, amalgams, sulfides, and sorbed mercury, c) accumulations of dense liquid elemental mercury, and d) vapor phase elemental and organomercury mercury in tank headspace gas and in evaporators. Strategic and proactive management of the estimated 60,000 Kg mercury in the LWS requires deployment of efficient and effective paradigms for sampling and analysis of the total quantity of mercury in the various physical-chemical forms. Scoping tests of selective gas-phase sorbents for mercury speciation were performed to support LWS objectives.

This research specifically focused on developing and testing streamlined methods to obtain high-quality analytical results for gaseous mercury species. The proposed methods are straightforward, using small columns (microcolumns) filled with materials that selectively sorb one or more target forms of mercury. Simple differentiation of mercury species and quantification is then achieved using an efficient thermal-desorption-based total mercury analyzer as the final step. Benefits associated with transitioning from multistep procedures such as EPA Methods 245.1, 1630 and 1631to streamlined microcolumn approaches include reduced analysis time, labor, and waste generation. Such transitioning would maximize the value of the current deployment of direct mercury analysis (EPA Method 7473) at SRS.

This work has two target end uses: 1) simplifying the analysis steps and reducing costs for liquid samples (e.g., developing a total organic mercury (TOM) method), and 2) providing options for high-quality onsite analysis and rapid turnaround for gas samples in support of SRS LWS industrial hygiene (IH) objectives.

The tests of sorbents confirmed and extended the information in the scientific literature on the affinity of various materials toward organomercury and/or elemental mercury. Additionally, the data validated the quality, reproducibility, and predictability of the performance of a compact in-vial sparge system. This validated performance, combined with the simplicity and other potential benefits of using in-vial sparging with microcolumns, support future development and deployment of this platform for mercury analysis of SRS LWS samples when possible.

The work identified several materials that performed well in differentiating mercury species. Key findings include

- Materials that effectively capture both elemental mercury and organomercury: a) gold-coated sand (amalgamation), b) Adsoquick activated carbon (sorption), c) iodinated activated carbon Flue Gas Sorbent for Total Mercury (sorption and reaction), and d) Honeywell 75852P100L Packing from mercury and chlorine respirator cartridge (sorption and reaction),

- Materials that effectively capture elemental mercury but do not effectively capture organomercury: a) silver (amalgamation), and b) Anasorb C300 (reaction and amalgamation), and

- Materials that effectively capture organomercury mercury but do not effectively capture elemental mercury: Carbotrap B (sorption).

The results support continued transitioning of Savannah River National Laboratory (SRNL) liquid waste analysis protocols toward microcolumn-based configurations that are compatible with the direct mercury analyzer -- providing a uniform platform for mercury quantification. Based on our data, more work is needed to overcome the requirement for heating Carbotrap B to temperatures exceeding manufacturers recommendations when used on the direct mercury analyzer for organomercury release. Thus, this material is currently validated for single use only. Additional study of Carbotrap B and similar sorbents such as

Tenax TA/GR and Bond Elute ENV is recommended to support developing an efficient TOM protocol, along with additional study of derivatization and sparging. A total mercury sorbent, such as Adsoquick, may be an alternative TOM strategy if the appropriate mercury species are selectively formed and sparged.

For support of the air sampling (IH) application in the LWS, initial field testing documented that direct mercury analysis (EPA Method 7473) is a simple, rapid, and robust method to detect and quantify mercury collected using standard mercury passive dosimeters and total mercury tubes/traps. Interlaboratory comparison showed a close correspondence between the paired data (correlation, $r^2 = 0.95$). Scoping field testing of Carbotrap B indicated that this organomercury-selective material may provide a reasonable basis for developing a simple, effective, and robust sampling protocol for operational speciation of mercury in LWS air samples. This microcolumn protocol pairs efficiently with direct mercury analysis and would provide the capability for rapid onsite analysis. Further, the research resulted in a recommended best-practice IH sampling strategy to identify low levels of dimethylmercury in the presence of relatively higher levels of elemental mercury. Additional development and field testing are recommended, however, to assure that the speciation performance is adequate to meet IH needs.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic absorbance spectrometer
ACTL	Aiken County Technical Laboratory
AFS	Atomic fluorescence spectrometer
Ag	silver
Au	gold
Cu	copper
CV	cold vapor
CVAAS	cold vapor atomic absorbance spectroscopy
CVAFS	cold vapor atomic fluorescence spectroscopy
DI	deionized
DF	dilution factor(s)
DMA	direct mercury analysis
DMA-80	direct mercury analyzer
dMeHg	dimethyl mercury
DOE	Department of Energy
DPPO	2,6-diphenyl-p-phenylene oxide
EM	Environmental Management
EPA	Environmental Protection Agency
FTSM	flue gas sorbent for total mercury
GC	gas chromatography
GCMS	gas chromatography mass spectrometry
HDPE	high density polyethylene
Hg	mercury
Hg^o	elemental mercury
IH	Industrial Hygiene
LWS	Liquid Waste System
MeHg	methyl mercury
n	number of replicates
NA	not applicable
O/E	Observed-to-Expected (ratio)
RSD	relative standard deviation
SDVB	styrene-divinyl benzene
SPE	solid phase extraction

SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TOM	total organic method
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
UV	ultraviolet
VOA	volatile organic analysis
v/v	Notation to indicate associated percent is based on volume/volume

1. Introduction

The Savannah River Site (SRS) Liquid Waste System (LWS) contains liquids, salts, and sludges that are currently being processed into final wasteforms for disposal. These wasteforms include waste glass that incorporates sludges, solids, and liquids with high levels of radioactivity, as well as saltstone grout that incorporates lower activity decontaminated liquid solutions. The LWS also contains approximately 60,000 kg of mercury (Hg) which is present in several physical and chemical forms, including: a) ionic inorganic Hg, organomercury (e.g., methyl Hg (MeHg)) and other minor components in LWS fluids, b) Hg solids such as oxides, hydroxides, amalgams, sulfides, and sorbed Hg, c) accumulations of dense liquid elemental mercury (Hg^o), and d) vapor phase Hg^o and organomercury Hg in tank headspace gas and evaporators. Strategic and proactive management of Hg in the LWS requires deployment of efficient and effective paradigms for sampling. Analysis of the total quantity of Hg in the various physical phases, as well as data on the chemical composition or speciation of mercury in those phases, is also necessary.

2. Background

2.1. Liquid Samples

In response to programmatic needs, Savannah River Remediation (SRR) and the Department of Energy (DOE) Office of Environmental Management (EM) have worked with both the Savannah River National Laboratory (SRNL) and international experts in the field of Hg analysis and speciation (e.g., scientists at Frontier Geosciences/Eurofins USA and at Brooks Applied Labs) to develop and implement supporting analytical capabilities. As shown below (Figure 2-1), the baseline methods used for LWS were relatively complex and require numerous, complex sample handling steps. Moreover, the baseline methods for LWS were initially developed to support analysis of environmental samples with lower Hg concentrations (e.g., < 10 ng/L nominal) compared to the higher concentrations of Hg in the LWS (e.g., 100,000,000 ng/L nominal). Figure 2-1 specifically identifies the “environmental level” Environmental Protection Agency (EPA) reference methods represented in the baseline (EPA Method 1631, EPA Method 1630, and EPA Method 245.1). These standard methods all rely on chemically converting the Hg to a volatile form at room temperature, so they are designated as cold vapor (CV) methods. The volatile Hg is purged into either an atomic fluorescence spectrometer (AFS) or an atomic absorbance spectrometer (AAS) for detection and quantification.

As a consequence of applying environmental analysis protocols to analyze high-concentration LWS samples, as well as the need to safely send samples to Seattle for processing by commercial laboratories, dilution factors (DF) of 100,000x or greater have been typically employed. The required levels of dilution introduce a variety of associated risk factors, such as the potential for trace levels of Hg in blanks or dilution water influencing sample results. Despite these challenges, the application of these standard methods over the past decade has generated high-quality information and demonstrated commendable care and quality assurance in both the SRNL and offsite laboratories.

For measuring total Hg, the baseline methods are cold vapor atomic fluorescence spectroscopy (CVAFS) or cold vapor atomic absorbance spectroscopy (CVAAS). These approaches utilize addition of a strong oxidant like bromine monochloride or sodium persulfate to the sample followed by a 12- to 24-hour reaction period for the conversion of organomercury to inorganic ionic Hg. The excess oxidant is neutralized using hydroxylamine hydrochloride and the sample is then analyzed by converting all Hg into purgeable Hg^o using a strong reductant (stannous chloride). This method generates a significant quantity of waste liquid and uses multiple hazardous acidic/oxidizing/reducing reagents. Some of the reagents contain relatively high levels of chloride that are not compatible with the High-Activity Drain system in SRNL.

For measuring organomercury, EPA Method 1630 is the baseline approach. This full protocol includes distillation, derivatization, purging, gas chromatography (GC), pyrolysis, and detection. Note that the distillation step is intended to eliminate the effects of humic and fulvic acids in environmental samples. Since these natural organic compounds are not present in significant concentrations in the LWS, distillation in an optional step for SRS LWS samples. The remainder of the method includes a number of manual steps, including: 1) derivatization of samples in acetate-buffered sodium tetraethyl borate solution (MeHg is derivatized to methyl ethyl Hg, ethyl Hg derivatized to diethyl Hg, etc.), 2) purging into a gas chromatograph for separation, 3) passing samples through a pyrolysis zone to convert Hg into the elemental form, and 4) final detection and quantification by AFS. Some of the species are determined using modified variants of the baseline methods. For instance, purgeable (Hg^o and dimethylmercury (dMeHg)) Hg is determined by direct purging of the sample with no reagents. Determination of inorganic ionic Hg by selective reduction is a second example. This process uses application of stannous chloride to the sample without the oxidant step followed by purging. The baseline method for particulate Hg in liquid samples relies on calculation: subtracting the sum of all dissolved mercury species from the total.

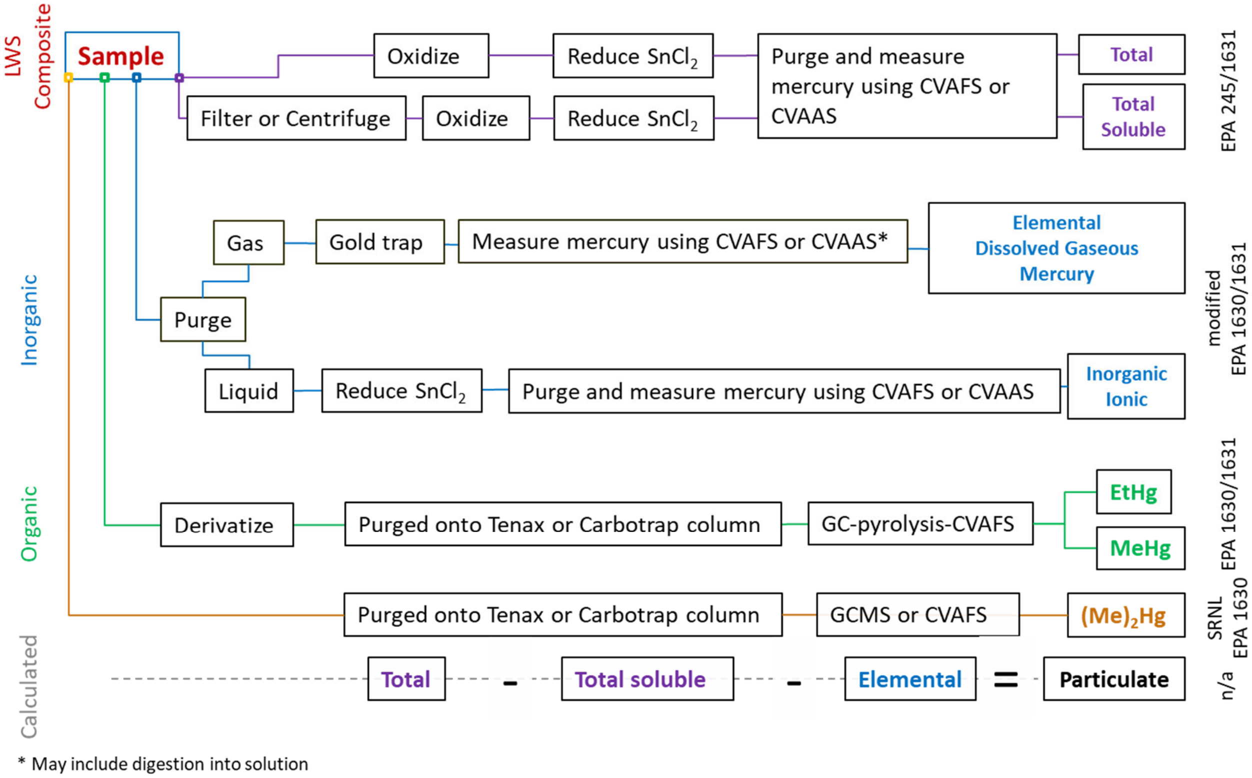

Figure 2-1. Outline of Past-Baseline Mercury Analysis Methods used for the Initial Period of Mercury Analysis of SRS LWS Samples and Corresponding EPA Method References

SRNL recently implemented EPA Method 7473 for measuring total Hg in samples. This direct Hg analysis method detects and quantifies total Hg in a sample using sequential pyrolysis, catalysis, amalgamation, thermal release, and AAS. EPA Method 7473 can be conceptualized as a “hot vapor” AA method since it replaces the labor-intensive chemical reaction and purging steps with automated pyrolysis and catalysis as carrier gas moves the sample through a series of sequential steps. The pyrolysis step heats samples at 500 to 800˚C depending on the matrix for 3 to 5 minutes to volatilize all forms of Hg into the flowing carrier gas. The catalysis step then uses mixed metal oxide granules at 585˚C to convert the released Hg to elemental Hg^{o}. The amalgamator containing gold-coated (Au-coated) sand captures the Hg^{o}. After pyrolysis is complete, the amalgamator is heated to 900˚C to release the Hg^{o} as a sharp pulse into the AAS for detection. The method is matrix independent, so it can provide data for liquids, solids, and gases. Liquids, both aqueous and organic, and solids are placed in sample boats and gases are sorbed on appropriate microcolumns. All steps are automated using a Milestone Direct Mercury analyzer (DMA-80) which is fitted with a carousel that can hold up to 40 samples. Two DMA 80 analyzers have been deployed in SRNL, one for nonradioactive service and one for radioactive service. A simplified schematic of the DMA-80 is shown in Figure 2-2. EPA Method 7473 allows measurement of samples without the need for digestion or extraction, reducing sample preparation time, worker exposure, and secondary wastes. Another benefit of direct mercury analysis (DMA) is the ability to measure Hg in the particulates captured during filtration, providing an independent direct measurement of this minor fraction.

Based on these advantages, DMA has been formally adopted in the current protocols for measuring total Hg in the LWS (Figure 2-3). As shown in Figure 2-3, the processing of legacy nuclear waste for long-term disposition is currently supported by deployment of several nuclearized analytical instruments, non-nuclear development instruments, and corresponding methods; all of which are dedicated to the analysis of nuclear waste and simulants for Hg and Hg species. From a typical LWS aqueous sample, the following species are typically determined: total Hg, inorganic Hg, purgeable mercury (primarily Hg^{o} plus trace dimethylmercury), organo-Hg (primarily methylmercury plus trace ethylmercury), particulate Hg, soluble Hg, and dMeHg. These analyses support environmental compliance, industrial hygiene (IH), process support, and science/engineering projects. In the existing Hg speciation analysis schema, the methods for organomercury species and purgeable Hg are unchanged from the initial baseline methods described above.

Building on the success of developing and deploying direct Hg analysis for total Hg, current applied research efforts focus on developing simplified methods for the organomercury and purgeable Hg species. Specifically, methods emphasize: a) in-vial (disposable vessel) purging where applicable to reduce sample size and eliminate the need to disassemble and clean complex glassware in a radioactive laboratory, b) use of selective sorption media to differentiate Hg species and isolate the target fractions for analysis, and c) use of the DMA-80 for detection and quantification of the various isolated fractions. The use of a single instrument platform for multiple species-fraction has the potential to improve consistency and quality assurance, streamline operations, and utilize instruments with detection limits that are well matched to LWS solutions and conditions in addition to reducing labor, exposure, and waste.

The SRNL team is determining the characteristics of various sorbents to differentially sorb Hg^{o} versus organomercury to support a schema where the organomercury species can be separated and quantified as total organic mercury (TOM). The proposed TOM method eliminates the GC step indicated in Figure 2-1 and Figure 2-3 for organic mercury; therefore, it will not separately quantify ionic MeHg and ionic ethylmercury. However, in the LWS, almost all the organomercury in the system is MeHg and there is no actionable difference for SRR among the various organomercury forms. Therefore, use of a TOM method for routine work with the capability to perform the standard EPA Method 1630 for unique studies will support LWS operation and simultaneously result in potential cost savings, faster turnaround, increased throughput, waste reduction, and dose reduction.

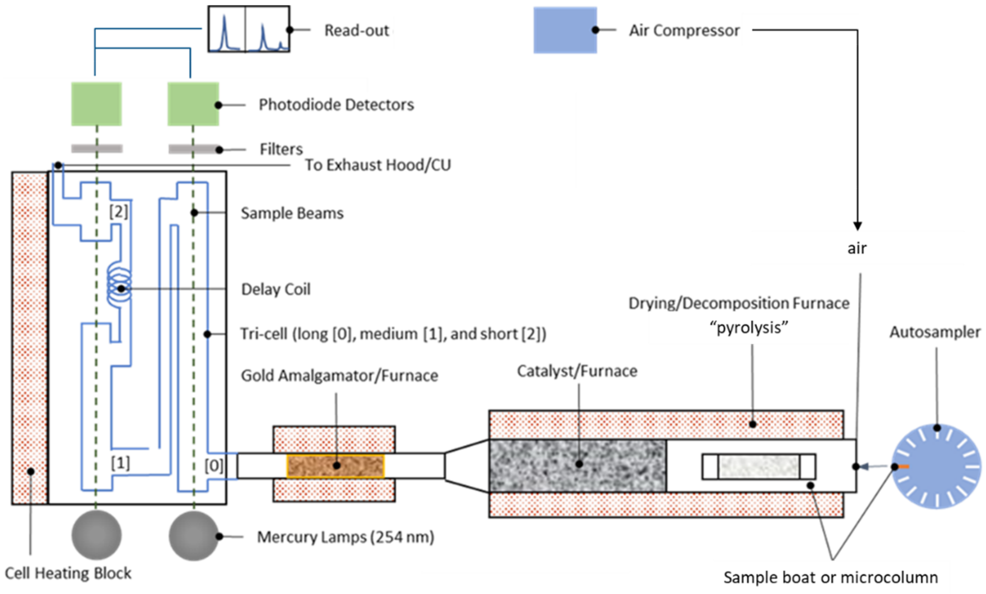

Figure 2-2. Simplified Schematic of the DMA-80

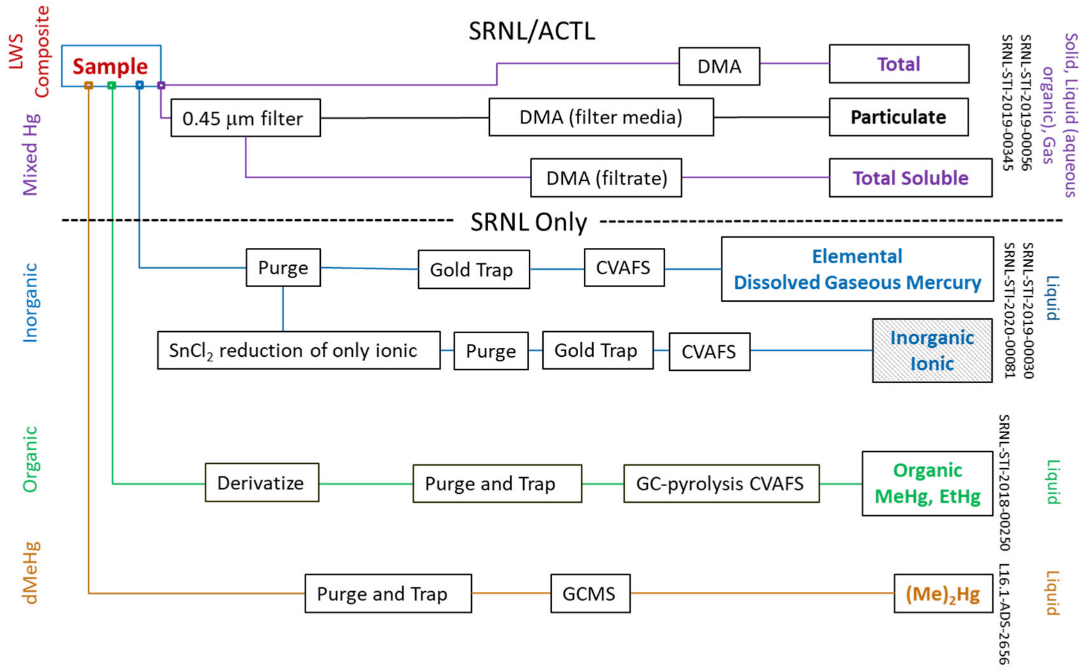

Figure 2-3. Outline of Existing-Updated SRNL Mercury Analysis Methods for SRS LWS Samples[†]

[†] The deployed DMA-80 instruments are located in 773-A SRNL for radioactive samples and 999-1W Aiken County Technology Laboratory (ACTL) for nonradioactive samples. The corresponding SRNL reference reports documenting deployment are identified.

2.2. Air Samples (IH Support)

The presence of tons of Hg in the SRS LWS has the potential to generate vapor-phase Hg contamination (DOE, 2016; Chew et al., 2019). Hg^o is a significant component of the total Hg in the LWS and this chemical form is relatively volatile. Therefore, Hg^o is the primary form of Hg vapors in the LWS. However, process studies and monitoring indicate that the complex chemistry in LWS tanks and evaporators results in measurable conversion of Hg into organomercury species such as ionic MeHg or volatile, highly toxic dMeHg. For example, Bloom et al. (2004) documented measurable formation of dMeHg in the conditions of the SRS LWS "over time scales of days to months." The dMeHg has also been directly detected in LWS vapors.

SRS has implemented robust IH protocols to protect workers from vapor exposures of all types, including Hg vapors. These protocols include sampling of Hg in breathing space air, tank headspace gases, and evaporator systems using active (pumped air) tubes/traps (EPA Method 30B) and passive sampling capsules (OSHA Method ID-140). LWS workers who enter Hg-contaminated environments or who work on/near Hg treatment systems or tank exhaust systems have expressed interest in IH collection of high-quality information on total Hg and on key vapor-phase forms of Hg, such as Hg^o and dMeHg.

The passive breathing space air samples are typically collected using a dosimeter sampler consisting of a capsule containing a mixed metal oxide (e.g., Hydrar or Anasorb C300) placed behind a polyethylene mesh diffusive barrier/spacer. The sampling strategy is based on Fick's Law. Because the sorbent material strongly partitions Hg into the solid, the air on the internal surface of the diffusive barrier is assumed to have a concentration near zero. Therefore, the rate of diffusion of Hg into the sampler is directly related to the concentration of Hg in the air on the outside surface of the diffusive barrier. In practice, the total quantity of Hg collected over a known time period is used to estimate the average air concentration during that exposure period. This system was developed for gaseous Hg^o with a sorbent material optimized for this chemical species. The potential for uptake of organomercury by the mixed metal oxide has not been examined in the literature. Notably, the traditional analysis of the sorbent is based on a labor-intensive extraction with 5% or 10% nitric acid plus 5% or 10% hydrochloric acid, followed by dilution, addition of stannous chloride, and analysis by CVAAS or CVAFS. In Europe, Anasorb C300 sorbent protocols include DMA as an accepted method (Hebisch et al. 2018). To support our key objectives related to IH air sampling for the SRS LWS, Anasorb C300 related tasks include: a) testing Hg^o and organomercury sorption characteristics, and b) confirming that the acid extraction and CVAAS analysis schema can be reliably replaced by direct Hg analysis (EPA Method 7473).

The active (pumped air) samples are typically collected using a tube or trap filled with an appropriate sorbent. Active samples are collected for both total Hg and dMeHg. A standard material used for total Hg is iodinated activated carbon. This material was developed by Frontier Geosciences/Eurofins and is known as Flue Gas Sorbent for Total Mercury (FSTM). The effectiveness of FSTM in capturing both elemental, oxidized, and organo- Hg species is well documented in the literature (Živkovi´c et al., 2020). Alternatively, tube packings made from graphitic carbon, such as Carbotrap B, or synthetic polymers, such as Tenax TA or BondElute, have been used to selectively sample vapor-phase organomercury species such as dMeHg (e.g., Bloom et al., 2005; Trujillo and Campbell, 1975; Baya et al., 2013). The literature and documentation related to organomercury selectivity and performance of alternative analysis protocols is limited, however. The analytical protocol EPA Method 30B specifies that samples may be processed using either a wet extraction or a thermal extraction.

Currently, Hg sampling capsules and traps collected by IH to support LWS operations are transported to Eurofins in Seattle for certified analysis. Eurofins performs a liquid extraction on all samples and then detects and quantifies Hg in the solutions using a modified Method 1631 (CV-AFS) or 1630 (CV-GC-AFS). An advantage of this approach is the ability to repeat analysis of samples from the extracts if there are instrument problems or at a different dilution if a sample result is out of range. In addition, it is possible to confirm that the Hg trapped on the selective Carbotrap B is in fact MeHg if the GC step is included. The primary disadvantages are potential delays associated with clearing and shipping samples and the time, labor, and cost required for the complicated multistep protocol. An alternative protocol would use DMA of the trap materials for detection and quantification. This would allow rapid onsite analysis and eliminate the complicated extraction and preparation protocols. Often, IH requires an early confirmation of the presence of organomercury to rapidly and correctly address personnel exposure issues. A disadvantage of DMA, however, is that the measured sample is consumed during the analysis and the protocols would require close communication between the laboratory and IH staff to collect samples that contain an appropriate target mass of Hg to avoid overloading the instrument. Note that the trap material may be weighed and subsampled to support dilutions with practical DF values ranging from 1 to 3. Further, because the bulk of the Hg in the LWS vapors is Hg^o (the ratio of Hg^o to dMeHg is often in the range of 100:1 to 1000:1), developing a selective trap for Hg^o that can be used in front of an organomercury trap would provide additional confidence that the organomercury (dMeHg) measurement is not influenced by any trace fraction of Hg^o that might be captured by the organomercury trap.

2.3. Candidate Materials for Mercury Speciation by Selective Capture

A number of investigators have studied sorbent selectivity for a variety of gaseous Hg species (e.g., Ballantine and Zoller 1984; Baya et al., 2013; Bloom et al., 1988; Bloom et al., 2005; Hebisch et al., 2018; Kvietkus, et al. 1995; Liang et al. 1994; Shewchuk et al. 2016; Sommar, 1999; Trüe et al. 2011; Trujillo and Campbell, 1975; Wilhelm et al., 2006; Živkovi´c et al., 2020). Several of these projects also combined sorbents into sorbent trains for operationally separating and quantifying Hg species (e.g., Baya et al., 2013; Bloom et al., 2005; Sommar, 1999; Trujillo and Campbell, 1975; Wilhelm et al., 2006). These various sampling schemas were tested and validated using laboratory and field studies. Table 2-1 summarizes information for available-candidate sorbents for use in developing Hg speciation strategies that are matched to SRS LWS needs. In general, the listed materials capture Hg by sorption, amalgamation, reaction, or a combination of mechanisms.

Following a literature review, it was determined that several column packing materials have the potential to capture both Hg^o and organomercury species. These packings materials include two types of high surface area activated carbon, activated carbon beads (Adsoquick) and iodinated activated carbon (FSTM), as well as Au coated sand. The carbon materials both use sorption as a primary capture mechanism, while the Au uses amalgamation. Sorption reactions rely on the interaction of the target vapor phase constituent with active sites on the surface of the packing. Amalgamation is the reaction of Hg to alloy with another type of metal to form a solid solution, or amalgam. Amalgams are formed through metallic bonding into a stable crystal lattice structure. While many metals can form amalgams with Hg, Au and silver (Ag) are notable examples that have been widely studied. Au-Hg amalgams are particularly strong and are used for extraction of Au from the ore. Ag-Hg amalgams have been important in dentistry.

Adsoquick is a spherical bead form of activated carbon with rapid kinetics, high capacity and high surface area. FSTM has been modified by incorporating 4 to 5% iodine, providing supplemental capture by Hg reactions to improve performance, particularly at higher temperature such as when sampling flue gases.

Au has been used in several formats to for capturing vapor phase Hg. These formats include a gold coated glass tube (denuder) that captures Hg as gases flow through the tube, as well as more standard packed column formats using Au coated substrates (sand or glass beads). Early conceptualizations of Au traps suggested potential for selective capture of Hg^o as the chemical form that directly participates in the amalgamation reaction. However, testing of Au traps and films confirmed that Au quantitatively capture both Hg^o and organomercury (Hawkins 2016; Prestbo et al. 2006; Sommar et al., 1999; Trujillo et al. 1975). For example, in research to support the SRS LWS, Prestbo et al. (2006) documented that a Jerome (now Arizona Instruments) Au film Hg detector responded quantitatively to both Hg^o and to dMeHg. Since the detector is responding to Hg that amalgamates into a gold film (changing the electrical resistance of the film), the data indicate that the organomercury is subject to the amalgamation reaction. The data suggest that amalgamation with Au is highly favored and that the Hg portion of the organomercury molecule is embedding into the Au film, likely leaving the attached methyl groups deformed above the amalgam interface. The quantitative capture of both Hg^o and organomercury has been further demonstrated by laboratory and field studies by multiple research organizations.

Two column packing materials have the potential to selectively capture Hg^o but not capture organomercury species, per literature review. These packings materials include elemental Ag and a mixed metal oxide (manganese dioxide/copper oxide) catalyst. Elemental Ag uses amalgamation as the capture mechanism. Ag is a weaker amalgamator compared to Au. The key to the differential capture and speciation performance is effective amalgamation of Hg^o and minimal amalgamation of organomercury. This weaker amalgamation has been attributed to the presence of organic groups in the molecule. The mixed metal oxide catalyst captures Hg^o by both reaction and amalgamation.

Based on the literature, there are several materials that selectively capture organomercury but do not capture Hg^o. These materials all work by sorption, relying on the organic portion of the molecule to interact with an organic substrate. The selective organomercury capture materials have a relatively low surface area compared to activated carbon to minimize the collateral capture of Hg^o. Organic substrates that have been tested for selective capture of organomercury include graphitized (not activated) carbon, various organic polymers, and composite carbon/polymer materials.

Table 2-1. Candidate Sorbents for use in Developing Mercury Speciation Strategies that are Matched to SRS LWS Needs

Sorbent	Description	Capture Mechanism(s)	presumptive Target Mercury Form(s) based on listed references		Comments	Example References:
			elemental	organo-		
Gold	Gold coated sand (other forms such as denuders tested in the literature)	amalgamation	☑	☑	Standard material for capturing mercury in standard analytical methods. Some lab and field testing for speciation in combination with other traps.	Bloom et al. 2005 (LSC, LSP); Hawkins 2016; Prestbo et al. 2006 (LSC); Sommar et al., 1999 (LSP, FSP); Trujillo et al. 1975 (LSC, LSP) ; Wilhelm et al. 2006 (LSP, FSP); Kvietkus et al. 1995 (LSC, LSP)
iodinated activated carbon - "FSTM"	Activated carbon that has been modified to include 4 to 5% iodine to improve mercury capture, alternate names include flue gas sorbent total mercury (FSTM)	sorption and reaction	☑	☑	Standard material for sampling flue gases for total mercury.	Živkovi´c et al. 2020 (LSC, LSP, FSP; Trüe et al. 2011 (FSP)
Adsoquick	Activated carbon (beads) with a high surface area (approximately 1200 m^2/g)	sorption	☑	☑	Used in europe for total mercury sampling (industrial hygene) and distributed as a gas sampling tube for use with the Milestone DMA-80	White et al. 2019 (LSC); Shewchuk et al. 2016 (LSC, LSP, FSP)
Silver	silver beads (other forms such as denuders and impregnated porous solids tested in the literature)	amalgamation	☑	☒	Weaker amalgamater than gold. Silver denuders and silver impregnated solids used in lab and field studies of proposed speciation schema.	Sommar et al., 1999 (LSP, FSP); Trujillo et al. 1975 (LSC, LSP); Kvietkus et al. 1995 (LSC, LSP)
Anasorb C300	mixed metal oxide (manganese dioxide/copper oxide) catalyst, alternate names include Hydrar and Carulite	reaction and amalgamation	☑	☒	used in SKC passive sampling dosimeters for elemental mercury	Hebisch et al. 2018 (LSC, LSP, FSP)
carbotrap B / carbopack B	Graphitized carbon with low to moderate surface area (approximately 100 m^2/g)	sorption	☒	☑	Lower surface area and less active surface for sorption compared to activated carbon. Reference material used in standard analytical protocols. Some lab and field testing in proposed speciation schema.	Baya et al. 2013 (LSC, LSP); Bloom et al. 2005 (LSC, LSP); Bloom et al. 1988 (LSC, LSP); Liang et al. 1994 (LSC, LSP); Sommar et al., 1999 (LSP, FSP); Wilhelm et al. 2006 (LSP, FSP)
Tenax TA	2,6-diphenylene-oxide polymer resin with a low surface area (approximately 35 m^2/g)	sorption	☒	☑	Reference material used in standard analytical protocols (Alternative for carbotrap B).	Baya et al. 2013 (LSC, LSP); Bloom et al. 2005 (LSC, LSP); Kvietkus et al. 1995 (LSC, LSP)
Tenax GR	2,6-diphenylene-oxide polymer resin plus 30% graphite composite with low surface area (approximately 24 m^2/g)	sorption	☒	☑	Composite material similare to Tenax TA and Carbopack B. Performance should be intermediate between these predecessors.	Baya et al. 2013 (LSC, LSP)
BondElute ENV	Crosslinked polystyrene-divinylbenzene polymer (beads) with a high surface area	sorption	☒	☑	Composite material similare to Tenax TA. Lab studies indicate good stability and performance.	Baya et al. 2013 (LSC, LSP)

Notes:
LSC = Lab study related to vapor phase capture of mercury species
LSP = Lab study related to vapor phase selective sampling protocol
FSP = Field study of vapor phase selective sampling protocol

3. Objectives

This study had two main objectives: (1) to streamline the analysis of liquid samples from the LWS; thus simplifying the analysis steps and reducing costs and (2) to support air sampling (IH) in the tank farm and DWPF by providing options for high-quality analysis of key Hg species with a rapid-turnaround and reducing need for offsite analysis.

The work in this study specifically focuses on developing and testing streamlined methods to collect, detect, and quantify key gaseous Hg species. The basis of the work is use of small columns, or traps, that selectively sorb a particular form of Hg to allow for simple differentiation of species using an efficient total Hg analyzer as the final step. This would allow SRS to realize maximum value from the deployment of the DMA-80 (EPA Method 7473) and maximize the value of any certification process for this method/platform.

4. Experimental Procedures

Development of a protocol for gas samples to support monitoring and measuring Hg speciation was investigated using microcolumns and a DMA-80. The microcolumns were prepared in sets with various packing materials. The capture efficiency of the candidate materials was tested by generating known quantities of either Hg^o or organomercury and purging the compounds from an aqueous solution into a gas flowing through the microcolumns. Methylethylmercury is a safer alternative to dMeHg and was used as a representative (surrogate) organomercury for testing because it can be easily generated from methylmercury in aqueous solution by derivatization.

4.1. Reagent Preparation

For speciation studies, spiked solutions with concentrations of 100 ng/mL (as Hg) were prepared by dilution with deionized water from certified standards of known speciation: (1) inorganic ionic mercury in 2% (v/v) nitric acid (High Purity Standards, 10^6 ng/mL, Item 100033-1) and (2) methylmercury in 0.5% (v/v) acetic acid and 0.2 % (v/v) hydrochloric acid (Brooks Rand Instruments, 10^3 ng/mL, Item 06601).

Stannous chloride reagent (per EPA Method 1631) was prepared using ACS-grade stannous chloride dihydrate (Fisher Scientific, Item T142) and trace-metal-grade hydrochloric acid (Fisher Scientific, Item T003080500)

Ethylation reagent kit (Brook Rand Instruments, Item 51578-1-1) that contains premixed 2M acetate buffer and component materials to prepare 1% (v/v) sodium tetraethylborate was used. Ethylation reagent components were mixed upon receipt, separated into 1 mL daily use vials/aliquots, and then frozen.

4.2. Microcolumn Testing Apparatus

A microcolumn testing station was deployed to implement a manually operated in-vial purge strategy (Figure 4-4). This station comprises a flow meter (TSI Inc., model 4146), standard 40 mL Volatile Organic Analysis (VOA) septum vial, a specialized in-vial purge needle assembly (Tekran Instruments Corporation, 80-2621MPS manual probe stand, 38-26205-03 septum piercing probe assembly, and a quartz wool microcolumn to remove water droplets), a test station for a microcolumn, a backup column, and an adjustable vacuum pump to control the purge flow. The flowmeter is equipped with a filter and a Hg trap to assure clean Hg-free air is supplied to the experiment. The inlet to the vacuum pump employs a Hg scrubber to limit emission of any Hg that is not captured by the microcolumns. After loading, each capture microcolumn was analyzed on the DMA-80 to assess the Hg retention for the test conditions. Conditions include column packing material, Hg species, and purge volume. DMA of all backup microcolumns was also completed to evaluate Hg breakthrough for the test conditions. Adsoquick or Au were used for backup microcolumns to effectively capture all forms of Hg.

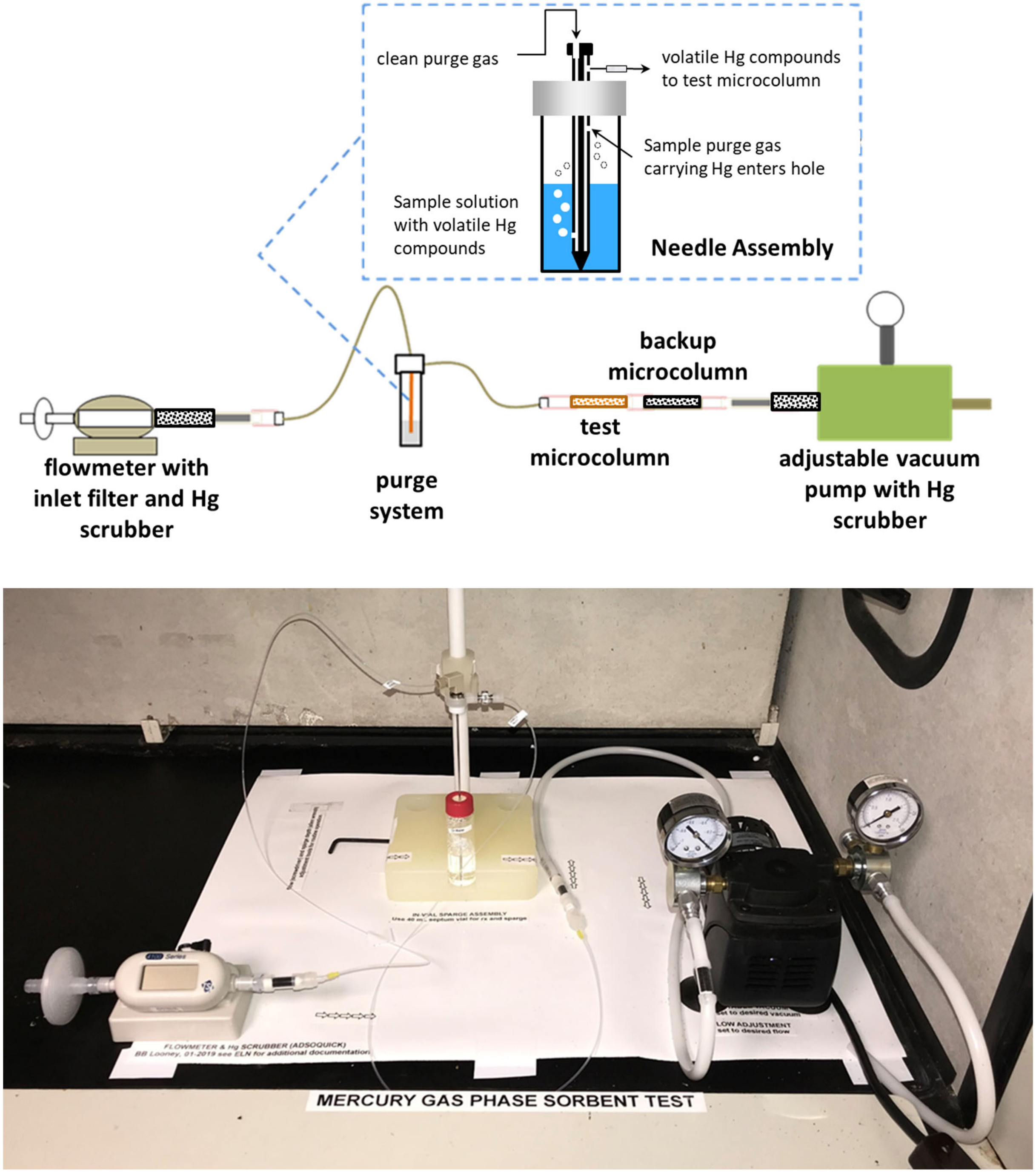

Figure 4-1. Schematic and Photograph of the Microcolumn Testing Equipment in a Chemical Hood

Testing relied on generating the target gas phase Hg species, Hg^o and organomercury, in the purge vials as a first step. For each column being tested, a known quantity of aqueous phase Hg (either inorganic ionic Hg or (mono)methylmercury) was spiked into 15 mL of deionized water in a VOA vial. Most of the tests used a nominal spike quantity of 10 ng as Hg.

For testing Hg^o capture, an inorganic-ionic Hg-spiked sample was chemically reduced using 0.5 mL of stannous chloride reagent in each vial to convert the Hg to the elemental form. Each vial was immediately capped and staged for use.

Organomercury capture was tested using derivatization of a methylmercury-spiked sample with 0.5 mL of 2M acetate buffer and 0.05 mL of 1% sodium (v/v) tetraethyborate ethylation reagent (per EPA method 1630). Directly prior to use, a vial of ethylation reagent was thawed to allow for pipetting. Vials were capped and staged immediately as in the Hg^o capture tests.

Several initial tests were performed to assess the performance of the microcolumn testing station and to finalize the experimental protocols. The focus was on validating the in-vial sparge system to support potential transitioning to this streamlined method for all species fractions in future SRS LWS samples. Currently, several of the species fraction methods use standard full-scale sparge systems (e.g., 200 mL sparge vessel volume). The full-size systems have the advantage that they are optimized for effective sparging of volatile Hg as described in Figure 4-2a. However, the full-size systems (Figure 4-2a) use large quantities of sample, require significant sample handling, and are difficult and labor intensive to operate and clean. Large volumes of acidic waste are also generated during the cleaning process.

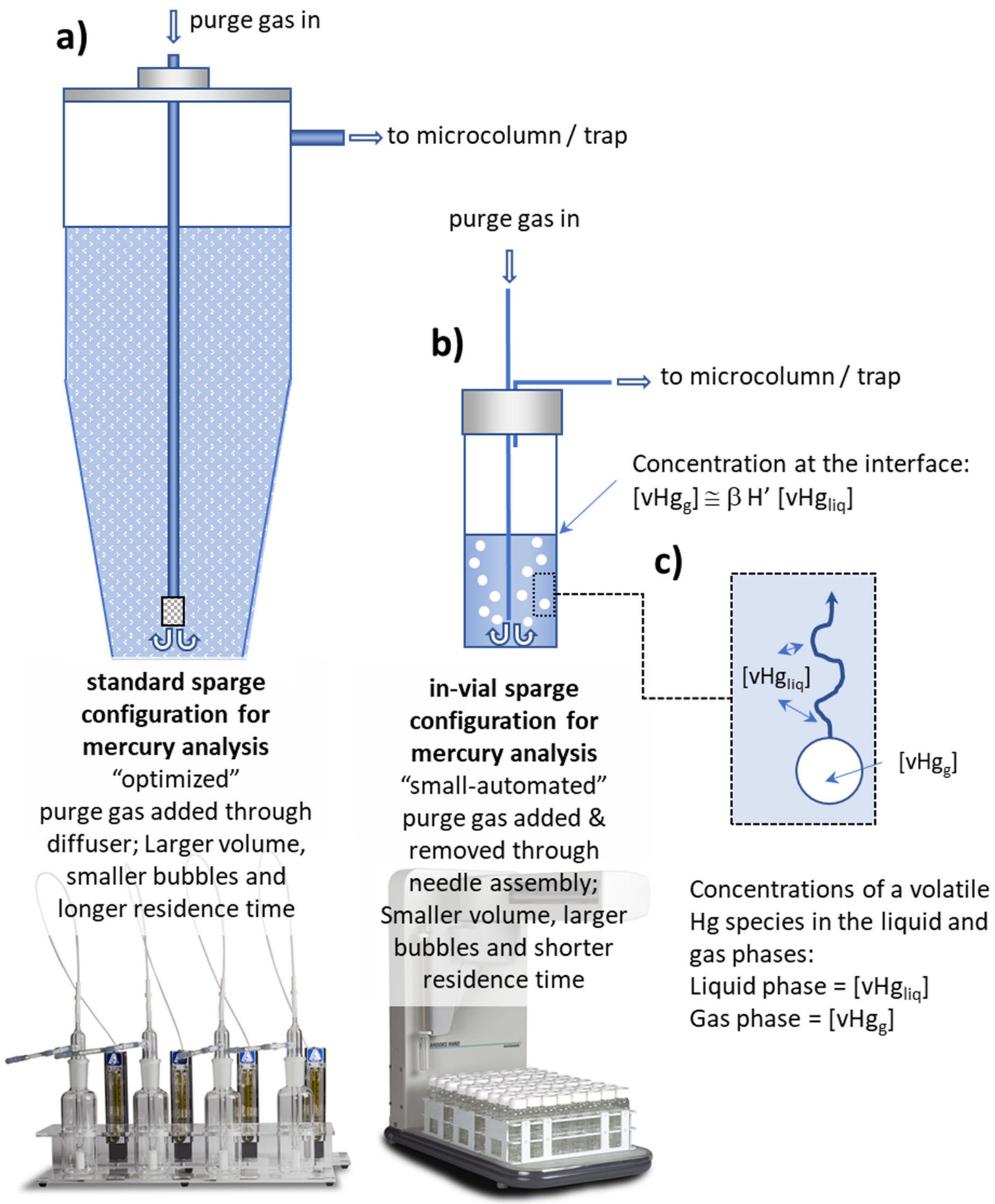

Figure 4-2. Schematic Diagram and Commercial Exemplars for a (a) Standard Full-Scale Sparge System, (b) an In-Vial Sparge System, and (c) a Depiction of the Mathematical Relationships used to Model Sparge Performance

The simpler in-vial sparge system is emerging as a practical alternative to the full-scale design. In the in-vial protocol, all steps in the analysis occur in a disposable 40 mL septum-capped vial using a specialized needle assembly to introduce and collect the sparging gas (Figure 4-1 and Figure 4-2b). Following sparging, the small volume of residual sample and the vials can be disposed, minimizing labor, waste, and cost. Another advantage of the in-vial sparge system is that it can be automated as depicted in Figure 4-2b. A disadvantage of the in-vial sparge system, however, is that the small sample vials are not optimally configured for sparging Hg. Bubbles produced by the needle are larger than those generated by a diffuser and bubble residence time in solution is limited due to the small sample volume/height.

There are no literature publications comparing the performance of the full-size standard sparge system and the in-vial sparge system. Many commercial laboratories are actively transitioning to the in-vial sparge systems, typically setting a short-constant sparge time (e.g., 3 minutes) for samples and standards. Use of a standardized sparge time supports sparging a consistent fraction of the Hg. While this is an effective method for generating a reproducible standard curve, high-quality data, and rapid throughput, such a short sparge time is inadequate to completely sparge Hg from aqueous samples (Looney et al. 2003; Boggess et al, 2019).

In this work, the initial system testing was focused on defining the sparging effectiveness of the in-vial sparge system, comparing it to the standard full-scale sparge system, developing a model to support optimizing sparge time, and determining the flow rate and sparge time to be used throughout the remaining stages of the experiment. The sparge model is an extension of the simple analytical solution initially developed by Looney et al. (2003) in which volatile Hg partitions into the sparge gas according to a dimensionless Henry's Law coefficient (H'):

$$H' = \frac{\text{(concentration of Hg in the gas phase in units of ng/mL)}}{\text{(concentration of Hg in the liquid phase in units of ng/mL)}}$$

The dimensionless Henry's Law coefficient for Hg^0 at 20 ˚C is approximately 0.34 (Looney et al., 2003). In an optimized system, the sparge gas is assumed to reach equilibrium with the contacted liquid. Mercury is removed from the liquid, resulting in an exponential equation describing sparge progress. Based on mass balance and integration over time, the normalized purge performance of an optimized sparger can be fully approximated as a simple function of H' and the air:water ratio, η':

η' = the ratio of the purge air volume to the fixed water volume in the vessel
= (gas flow rate in std mL per second x purge time in seconds) / (liquid volume in purge vial)

We extended the analytical solution to assess the relative performance of an in-vial sparge system by assuming that the incoming sparge gas may not achieve complete equilibrium and including a term (β, ranging from 0 to 1) representing how much progress is made toward equilibrium in the gas bubbles before they exit the liquid surface. The modified analytical solution is:

normalized fraction of mass removed as a function of air:water ratio = $M_{(\eta')} / M_{(0)} = 1 - e^{-\beta H'\eta'}$

In an optimized sparge system, $\beta = 1$ and the resulting equation simplifies to a form that is analogous to that reported by Looney et al. (2003). This simple approximation has been validated for standard full-scale systems by matching sparging data from multiple investigators (Looney et al. 2003; Bogess et al. 2019).

We anticipate that the measured performance of in-vial sparge system will support generating a reproducible β value (e.g., below 1) that will support technically based deployment of this the in-vial sparge configuration.

4.3. Microcolumn Preparation and Packing Materials

For those packing materials that were tested, DMA-80 compatible quartz tubes (10 mm od x 30 mm length) were prepared. Each quartz tube has one end tapered and is initially fitted by using a packing tool with quartz fiber or ceramic felt as shown in Figure 4-3. Packing material types were varied and prepared in triplicate. Micro columns were capped on both ends, using either quartz fiber (Au, Ag and Carbotrap B) or ceramic felt (Adsoquick, Anasorb C 300, and Sorbent from Honeywell 75852P100L Hg and chlorine respirator cartridge). Each column contained between 0.6 and 1 mL of packing that was consolidated by tapping prior to placing the top plug. The packing materials that were subject to detailed testing are depicted in Figure 4-4. The remaining packing materials were harvested from IH sampler tubes or respirator cartridges and were tested in collaboration with technical experts from LWS IH. For these materials, the IH tubes or respirator cartridges were disassembled and the contents repacked into SRNL tubes for DMA evaluation.

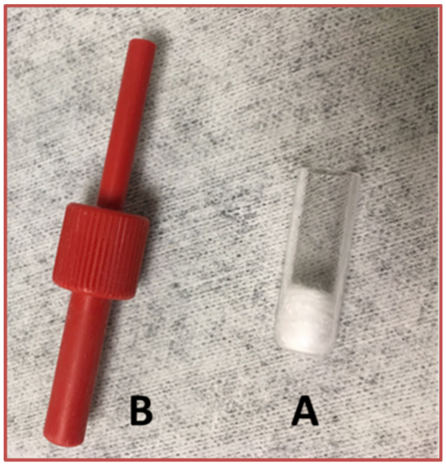

Figure 4-3. Quartz Microcolumn with Quartz Fiber (A), Packing Tool (B)

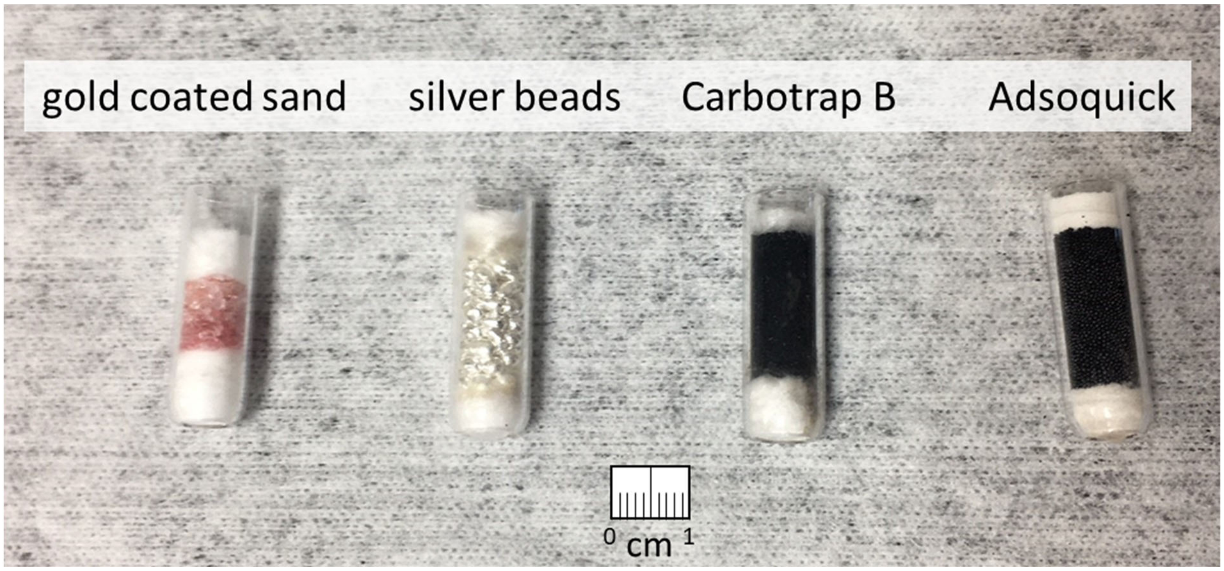

Figure 4-4. DMA Compatible Columns Containing Media for Total or Selective Capture of Mercury

4.4. Microcolumn analysis on the Direct Mercury Analyzer

For samples where the solids are analyzed as microcolumns, no additional sample preparation is needed prior to detection and quantification using the DMA-80. Microcolumns charged with Hg compounds are removed from the microcolumn testing unit and placed directly on the autosampler carousal of the instrument for analysis (Figure 4-5). Analysis conditions are set based on the packing material used. Desorption pyrolysis temperatures were set at 800 ˚C for Au, 550 ˚C for Adsoquick, 650 ˚C for Ag, and either 225 ˚C or 650 ˚C for Carbotrap B. The desorption time was set in the range of 4 to 6 minutes and the total analysis time, including the heating ramp and cool down, was approximately 10 minutes.

Figure 4-5. Various Microcolumns Staged for Analysis on the Carousel of the Milestone DMA-80

4.5. Field Testing, Interlaboratory Comparison, and SRS LWS IH Support Activities

Several collaborative field tests and supplemental lab studies were performed in partnership with SRR IH experts. The three studies include:

1) Demonstrating the applicability of DMA (EPA Method 7473) to detect and quantify Hg collected by standard passive Hg samplers containing Anasorb C300 (dosimeters for Hg^o) and active (pumped) total Hg collection tubes containing FSTM iodinated carbon. These sample results were compared to an independent certified laboratory (Eurofins USA) and/or historical information.
2) Performing laboratory experiments to assess the Hg species captured by Anasorb C300 in support of IH interpretation and decision making (i.e., Does this material only capture Hg^o or does it also capture dMeHg?). As a supplement to this laboratory task, SRR IH requested that SRNL test the packing of the respirator cartridge used to protect workers who enter Hg-contaminated environments or work near systems that contain high concentrations of Hg vapors to document removal of both Hg^o and organomercury. These laboratory studies were performed using the equipment and the general method described above.
3) Demonstrating the applicability of DMA (EPA Method 7473) to detect and quantify dMeHg and total Hg collected by active (pumped) tubes containing Carbotrap B and FSTM, respectively. These sample results were compared to historical information.

5. Results and Discussion

5.1. Method Development

Adsoquick was used as the primary microcolumn packing material for method development because it is the manufacturer's reference material for Hg vapor capture on the DMA-80. As shown in Figure 5-1, initial capture tests using vapor-phase Hg^o generally validated the protocols; specifically: a) steadily increasing sparge progress was observed with complete and quantitative recovery of the spiked Hg for samples with a long sparge time (high air-water ratio), b) accuracy and precision were within the documented performance of the instrument ($2\sigma \cong 15\%$), and c) no Hg was observed on the backup trap. Note that Hg^o was used for the initial method development since the H' for Hg^o is lower (it is less volatile) compared to the surrogate organomercury (methylethylmercury). The initial analyses were performed at flow rates ranging from 50 to 75 standard mL/min for periods from 0 to 13 minutes (0 to 780 seconds). These air flowrates are similar to those used for existing sparge-based analytical protocols and to flowrates and total air volumes used for IH sampling in the SRS LWS. Over the limited flowrate range in the tests, there was no observable influence of flowrate in the data. The initial results confirmed accurate spiking, complete conversion of the inorganic ionic Hg in solution to volatile Hg^o, effective sparging, and complete capture of the sparged Hg^o by Adsoquick.

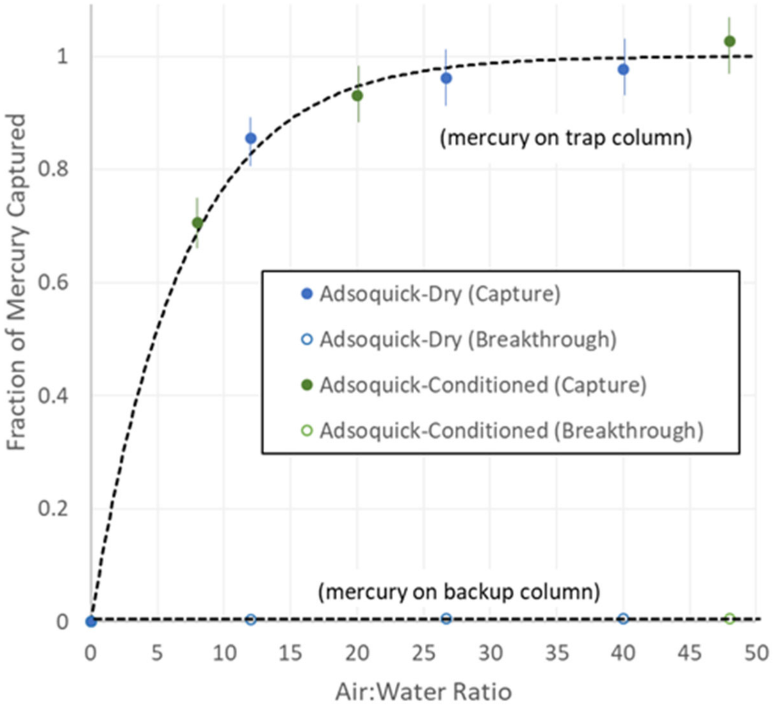

Figure 5-1. Initial Runs for Elemental Mercury Trapping on Adsoquick (Activated Carbon)

To assess the potential influence of moisture/humidity, experiments were performed with dry Adsoquick starting material and with starting material that was preconditioned for 10 minutes using humid air that had been purged through deionized water. There was no observable difference in the data for the dry and preconditioned material. The initial analyses generally validated the in-vial sparge protocols and equipment. Based on the results, the remaining experiments were conducted using approximately 15 mL liquid volume and a target gas flowrate of 75 standard mL/min for 10 minutes (resulting in an air water ratio ≅ 50). This strategy allowed for complete transfer of the generated Hg to the microcolumns and supported a mass balance on the experiment as an additional validation and quality assurance step.

The data from the in-vial sparge system method development study was used to determine the applicability of the proposed analytical model and asses the quality of the model predictions (Figure 5-2). The general shape of the model fit, and each individual model prediction closely matches the measured data for a β value of 0.43. This suggests that the purge gas in the in-vial system reached approximately 43% of its theoretical equilibrium value before exiting the liquid surface for the conditions of the testing. For commercial laboratories using a short sparge time to increase throughput, a 3-minute sparge time (equivalent to an air:water ratio of 10) would reproducibly purge a constant amount (approximately 80%), of the Hg^o from each sample/standard. To put these results for the in-vial sparge system in perspective, the model predictions for an optimized system with a β of 1.0 is plotted for comparison (Figure 5-2) along with measured data generated using standard full-size sparge equipment. The comparison data was previously documented in the literature (Looney et al. 2003; Bogess et al. 2019) and assumes the sparge gas reaches 100% of its theoretical equilibrium value. The standard-full-size sparge system purges “all” Hg^o at air:water ratios greater than approximately 15, while the small in-vial sparge system purges “all” Hg^o at air:water ratios greater than approximately 40. This difference may be less significant in practice, however, because the full-size system uses larger volume samples that have been diluted.

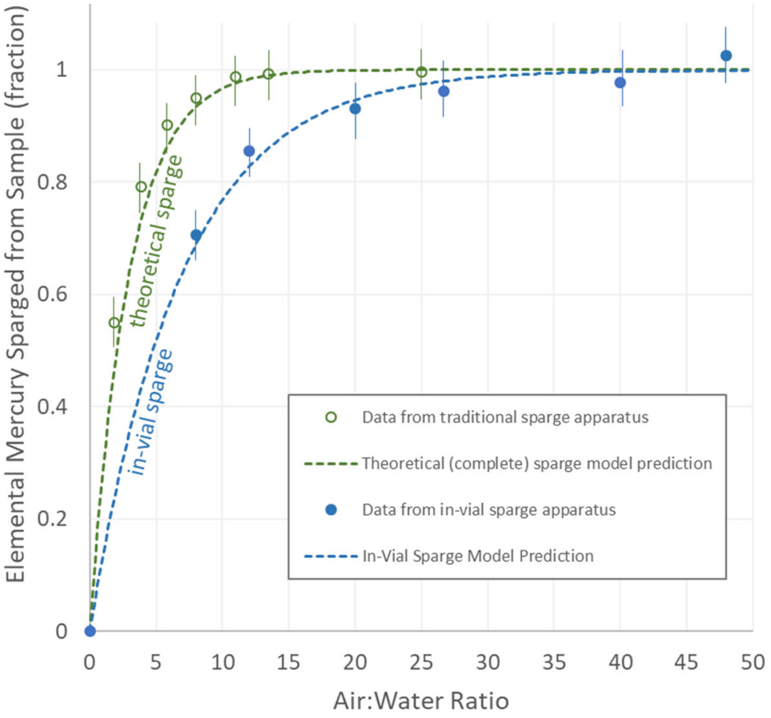

Figure 5-2. Theoretical vs Experimental Elemental Mercury Relative Sparging Efficiencies

The calculated mass balance for the various test condition trials in the method development study are shown in Figure 5-3. In this figure, the observed-to-expected (O/E) Hg ratio is plotted. A perfect match would result in a ratio equal to 1. The plotted values range from 0.98 to 1.03 and are bound by the nominal instrument uncertainty (2σ = 15%). These results provide additional validation of the quality, reproducibility, and predictability of the performance of the in-vial sparge system.

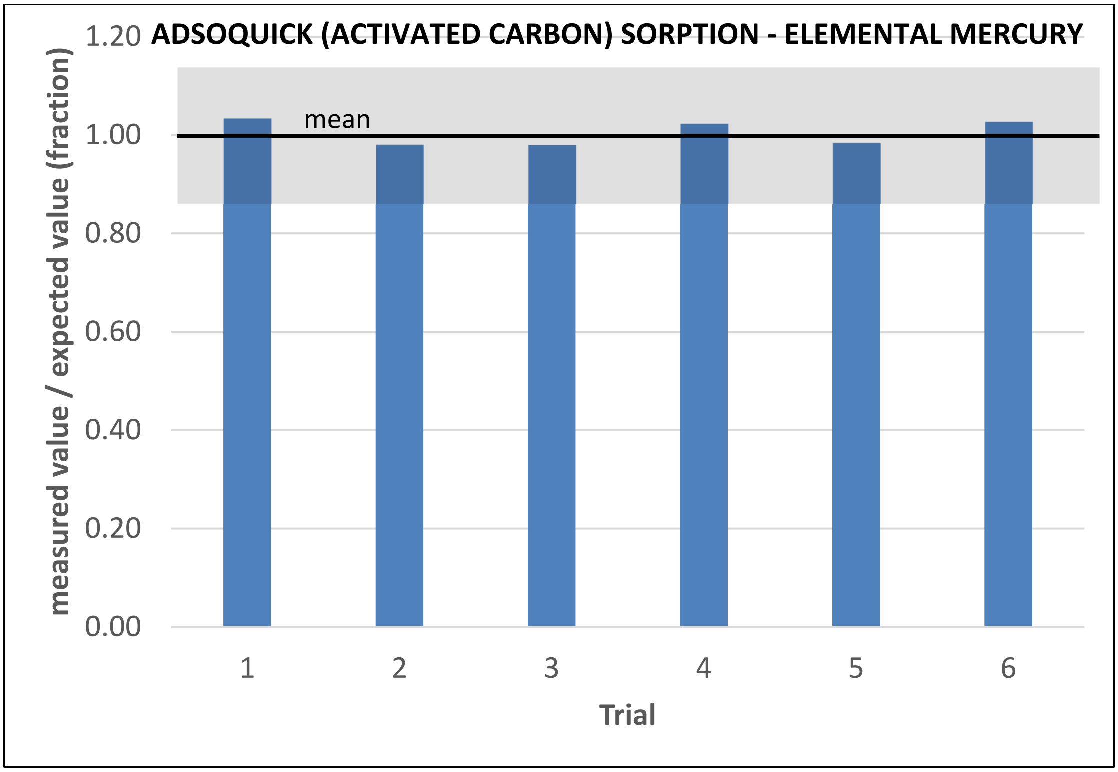

Figure 5-3. Observed-to-Expected (O/E) Ratio of Elemental Mercury Sorption with Adsoquick Activated Carbon

One final method development experiment was conducted to support the use of Adsoquick. The initial measurements indicated that desorption at high temperature (650 ˚C) resulted in slow degradation of the packing and the need for frequent repacking. To extend the useful life of the columns, an experiment was conducted to assess if a lower desorption temperature could be used. The fraction of Hg^o desorption from Adsoquick was determined as a function of temperature (Figure 5-4). The data showed minimal desorption at lower temperatures (below 150 ˚C) and relatively high desorption at higher temperatures (above 450 ˚C). The resulting s-shaped curve was fit with a logistic function. Based on the results, a nominal desorption program was developed with a desorption temperature of 550 ˚C.

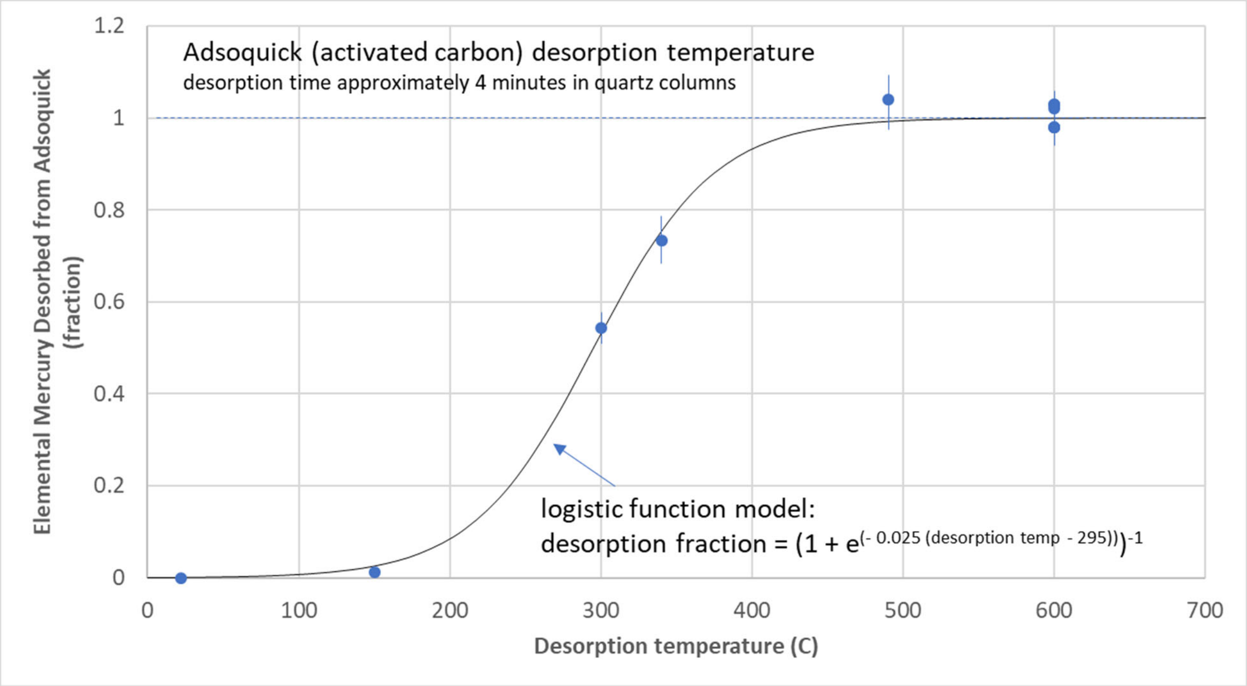

Figure 5-4. Elemental Mercury Desorbed from Adsoquick as a Function of Desorption Temperature

5.2. Microcolumn Speciation Testing

5.2.1. Data Workup and Presentation

For the laboratory studies, multiple trials were performed for each column packing material using Hg^o and a representative surrogate organomercury (methyethylmercury). Total Hg was measured on both the capture column and backup column for each trial. As a first data workup step, a recovery for the trial was calculated by mass balance. Recovery is defined as the sum of the masses on the capture and backup columns divided by the total quantity of Hg spiked into the trial. For example, if 10 ng was spiked into a trial and the capture column contained 9.63 ng of Hg, while the backup column contained 0.17 ng of Hg, then the calculated recovery would be 0.98 [i.e., (9.63+0.17) / 10 or 9.8/10]. The recovery mass balances for all trials ranged from 0.8 to 1.16, with most recovery mass balance values between 0.9 and 1.1.

The relative amounts of Hg on the capture and backup of the columns were calculated based on the amount of Hg captured in the individual trial. For the example above, the fraction of the Hg in the trial on the capture column was 0.983 and the fraction of the Hg on the backup column was 0.017. This example was one of the trials for Au coated sand.

The next step in the data workup was to examine the consistency of the results across all trials for a material. Figure 5-5 shows the results for all trials to test Au microcolumns. For consistency, the graphs in this report will use a standardized formatting: solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough. The data for the individual trials were then consolidated into a summary table showing the averages and recovery mass balances for each material, as well as a summary bar graph displaying the averages and error bars representing the range of the measured data.

The consolidated summary data table and summary graphs for each material are presented in the next section and the results from each individual trial are organized by material and included in Appendix A.

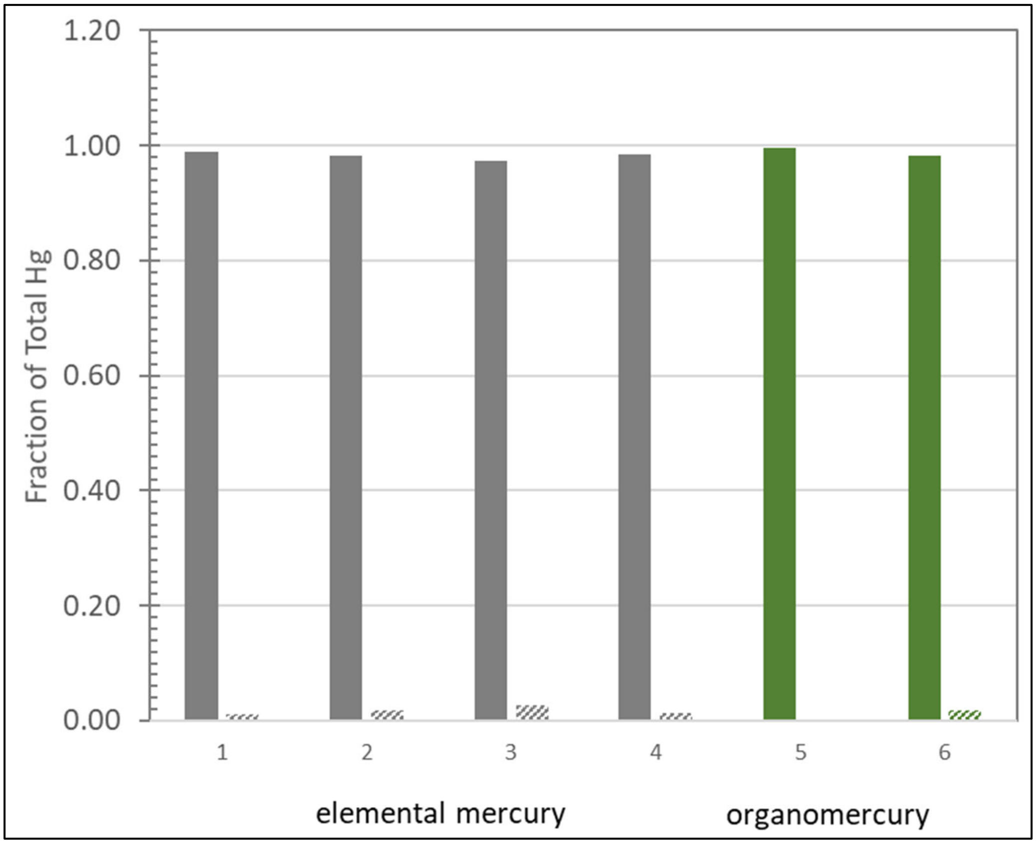

Figure 5-5. Example Data from Individual Trials for Gold Microcolumns Capture and Backup Columns for Both Elemental Mercury and Organomercury[*]

5.2.2. Summary Speciation Data for Each Tested Microcolumn Material

5.2.2.1. Gold Microcolumns

Figure 5-6 and Table 5-1 document the summary results for Au (Au-coated sand) microcolumns. The capture columns (solid bar) for both Hg^o and organomercury are near one (0.98 and 0.99, respectively). Values near one indicate that Au is a relatively effective microcolumn media for sampling all forms of gaseous Hg. These data are consistent with the literature. The data from all trials were tightly clustered and the tests showed reasonable recovery mass balances for both Hg^o and organomercury.

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

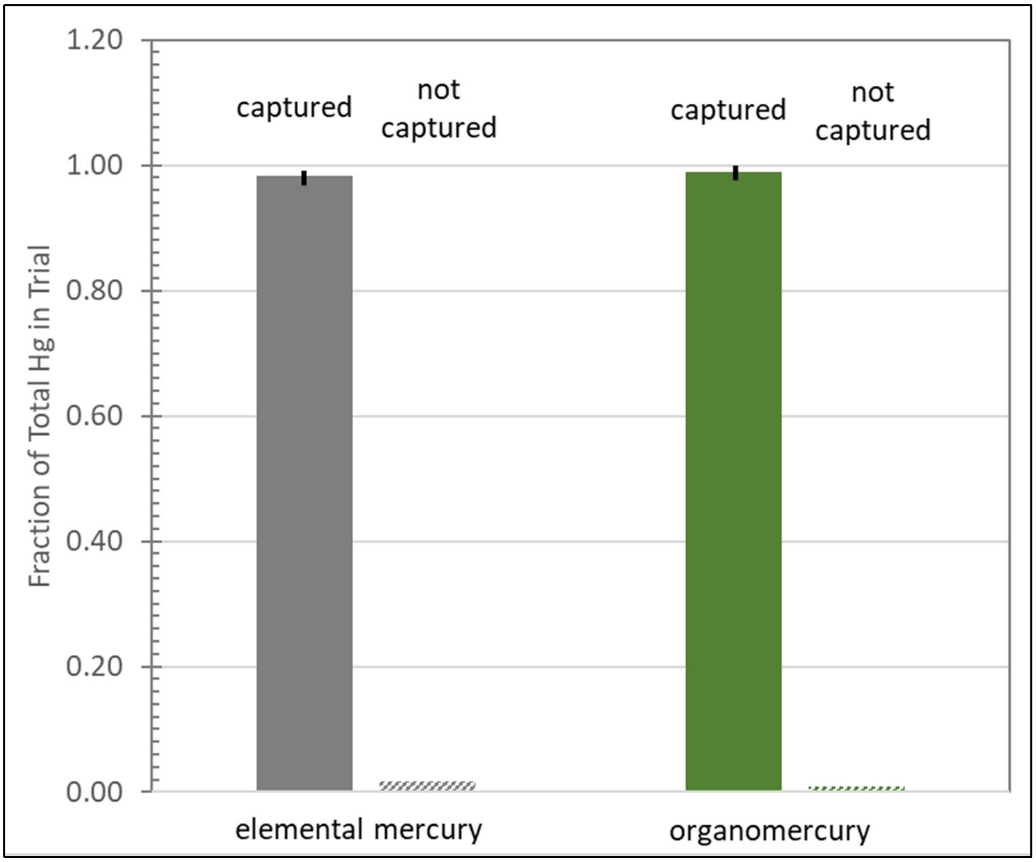

Figure 5-6. Consolidated Summary Results for Gold Microcolumns[*]

Table 5-1. Consolidated Summary Table of Gold Microcolumn Results

	Capture column	Backup column	Mass balance
Elemental mercury	0.98	0.02	0.96 to 1.14
Organomercury	0.99	0.01	0.95 to 1.07

5.2.2.2. Adsoquick Microcolumns

Figure 5-7 and Table 5-2 document the summary results for Adsoquick (activated carbon bead) microcolumns. The capture columns (solid bar) for both Hg^o and organomercury are near one (0.99 and 0.99, respectively), indicating that Adsoquick is a relatively effective microcolumn for sampling all forms of gaseous Hg. These data are consistent with the manufacturer recommendations and the use of Adsoquick in Europe as a standard material in IH applications. The data from all trials were tightly clustered and the tests showed reasonable recovery mass balances for both Hg^o and organomercury. A follow-up study to evaluate loading was performed and the results are included in Appendix A. The data in that study indicated reasonable capture of both Hg^o and organomercury to levels of 100 to 200 ng or higher.

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

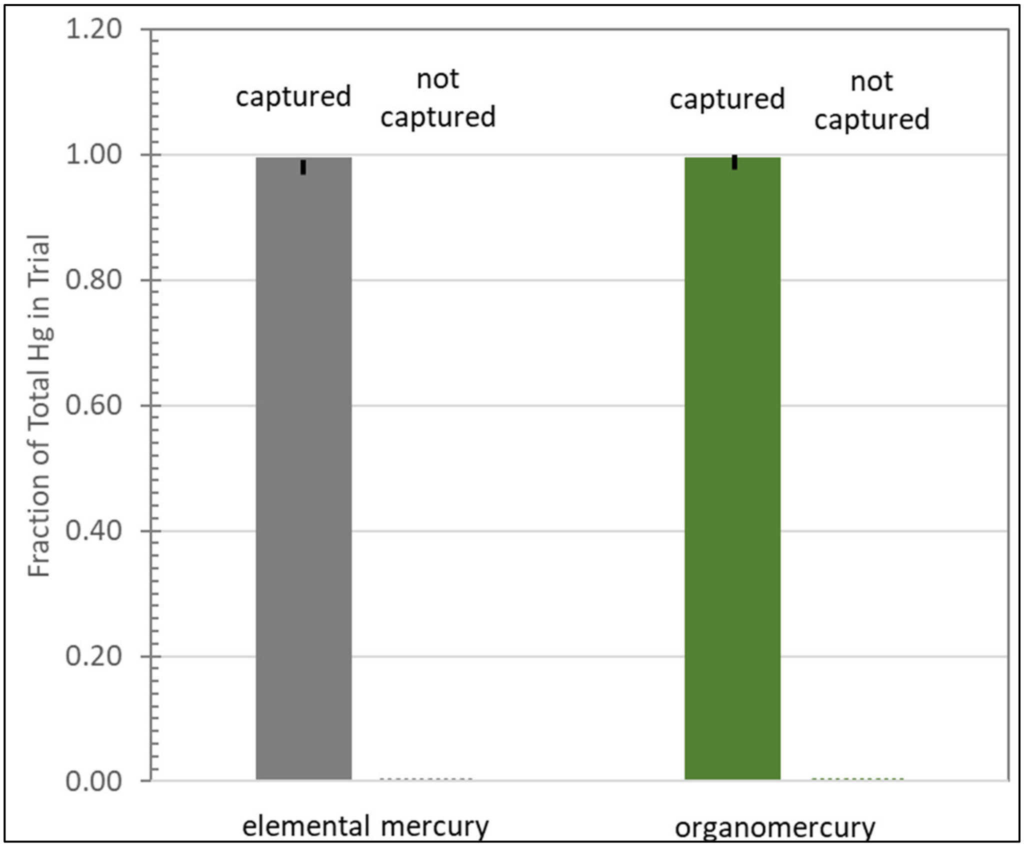

Figure 5-7. Consolidated Summary Results for Adsoquick Microcolumns[*]

Table 5-2. Consolidated Summary Table of Adsoquick Microcolumn Results

	Capture column	**Backup column**	**Mass balance**
Elemental mercury	0.99	0.01	0.99 to 1.04
Organomercury	0.99	0.01	0.80 to 0.90

5.2.2.3. Silver Microcolumns

Results for Ag microcolumns are summarized in Figure 5-8 and Table 5-3. The recovery on the capture column for Hg^o is 0.88, indicating that Ag is a moderately effective microcolumn for sampling Hg^o. The recovery on the backup column for organomercury is relatively high (0.92), indicating that Ag does not effectively capture organomercury. While not fully quantitative, Ag appears to be a good candidate material for supporting microcolumn-based operational Hg speciation protocols. Such protocols may be particularly useful for cases where a pre-column to remove the bulk of the Hg^o would be helpful, such as in the SRS LWS where Hg^o is typically present at 10 to 1000x higher levels compared to dMeHg. The data from all trials were tightly clustered and the tests showed reasonable recovery mass balances for both Hg^o and organomercury.

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

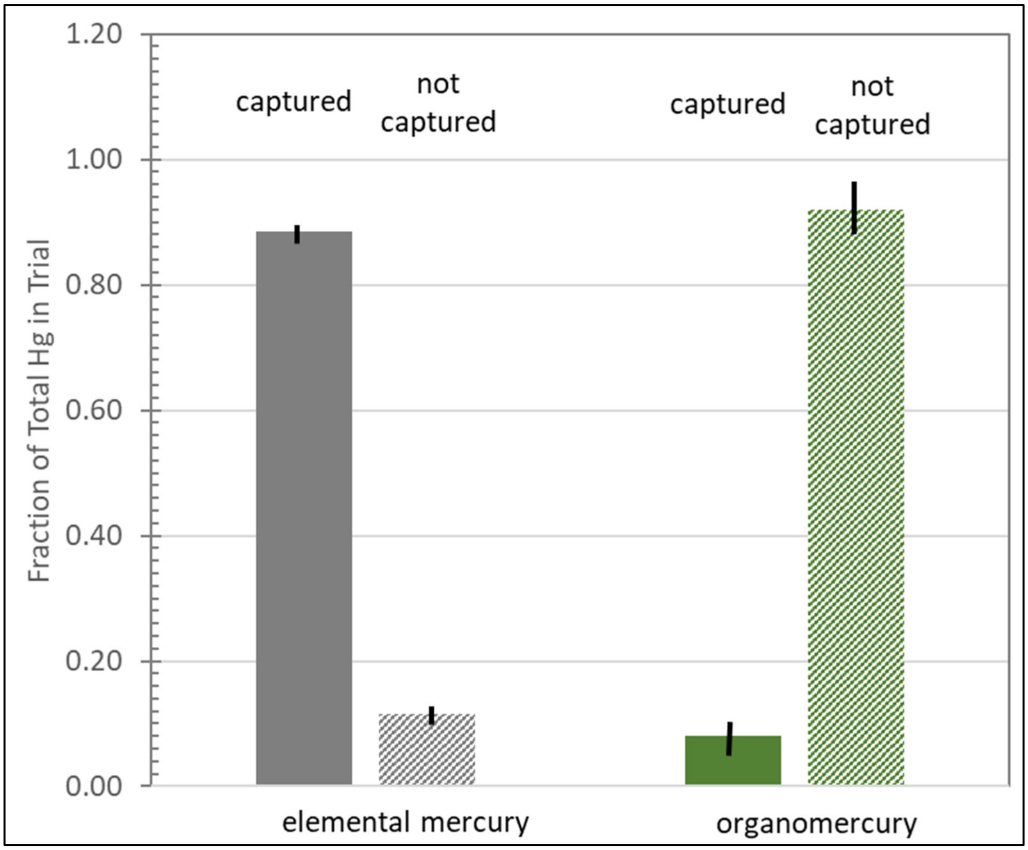

Figure 5-8. Consolidated Summary Results for Silver Microcolumns*

Table 5-3. Consolidated Summary Table of Silver Microcolumn Results

	Capture column	**Backup column**	**Mass balance**
Elemental mercury	0.88	0.12	0.99 to 1.04
Organomercury	0.08	0.92	0.80 to 0.90

5.2.2.4. Carbotrap B Microcolumns

Summary results for Carbotrap B microcolumns are presented in Figure 5-9 and Table 5-4. Carbotrap B does not effectively sample Hg^o, as demonstrated by the high Hg^o backup column value (0.99). The capture column value of 0.95 for organomercury is high, indicating that Carbotrap B is a reasonably effective material for sampling organomercury. Carbotrap B appears to be a good candidate material for supporting microcolumn-based Hg speciation protocols with the following caveats related to desorption temperature requirements on the DMA-80.

Initial tests showed poor but reproducible recovery mass balance for organomercury. Further testing indicated that the planned desorption temperature of 225 ˚C was insufficient to release organomercury from the Carbotrap B microcolumn in the DMA-80. Reheating the columns to 650 ˚C resulted in complete and reproducible recovery mass balance. On the summary graph, the amount of organomercury that desorbed

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

is shown as a stacked bar. The solid section of the bar represents desorption at 225 ˚C, while the stippled section represents desorption at 650 ˚C. The range of data for each sub-fraction is shown using error bars.

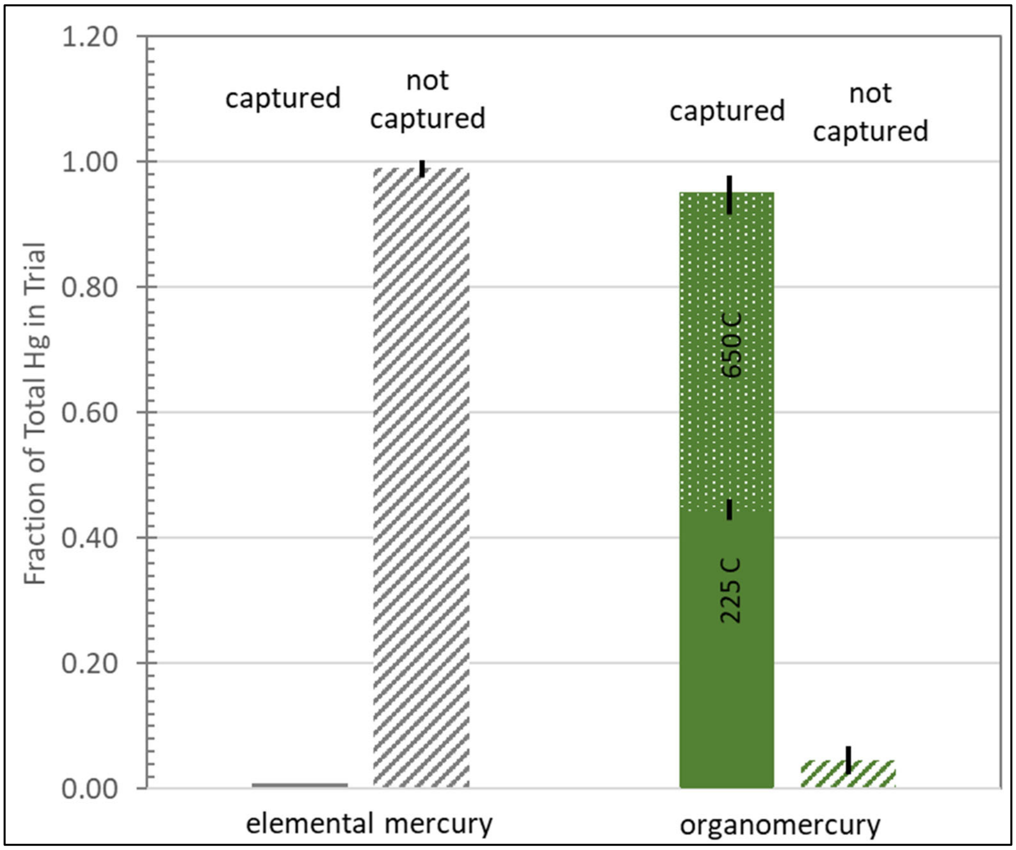

Figure 5-9. Consolidated Summary Results for Carbotrap B Microcolumns*

Table 5-4. Consolidated Summary Table of Carbotrap B Microcolumn Results

	Capture column (total)	Backup column	Mass balance
Elemental mercury	0.01	0.99	0.99 to 1.02
Organomercury	0.95	0.05	1.00 to 1.16

When using a higher desorption temperature, the data from all trials were tightly clustered and the tests showed reasonable recovery mass balances for both Hg^o and organomercury. Unfortunately, the higher desorption temperature is above the manufacturers recommended maximum for Carbotrap B, so it is unlikely that the microcolumns could be reused in this scenario. Columns would have to be sacrificed during sampling/analysis. This strategy is generally consistent with IH application, where sampling columns are typically deployed as single-use items and sacrificed for analysis. However, the need to use sacrificial columns would reduce efficiency and increase costs for any applications as a part of liquid analysis protocols since new columns would need to be prepared for each set of measurements.

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

5.3. Field Testing, Interlaboratory Comparison, and SRS LWS IH Support Activities

Technical collaborators from SRS LWS IH collected a split samples for analysis by SRNL and an independent certified laboratory. Two types of samples were collected as part of the study: 1) Hg collected by standard passive Hg samplers (dosimeters for Hg^o) containing Anasorb C300, and 2) active (pumped) total Hg collection tubes containing FSTM iodinated carbon. The primary objective of this collaboration was to provide an initial assessment of the performance and potential viability of using DMA (EPA Method 7473) to support rapid and technically defensible analysis of standard IH Hg samples. The raw data are provided in Appendix A and summarized in Figure 5-10 and Table 5-5. For clarity, this figure is a simple direct comparison of the Hg collected (ng) in equivalent samples sent to the two laboratories. In practice, these data would be converted to air concentrations through a standard calculation (passive dosimeter) or by dividing the Hg mass by gas volume sampled (active tubes/traps). Both types of sampling media are included in Figure 5-10 and Table 5-5. The two media are identified using different symbols and colors.

There was a close correspondence in the data from the two laboratories, suggesting that use of direct Hg analysis is a viable alternative for standard IH samples. The regression line for the split data from the two laboratories and the associated confidence intervals are clustered around the perfect match line. The correlation of the paired data is $r^2 = 0.95$.

The use of DMA streamlines the sample handling and analytical logistics. This method simplifies transportation, eliminates the need for complex multi-step sample extraction, and reduces labor and waste. DMA is generally matrix independent, so both media were analyzed by SRNL by transferring the materials from the capsule or tube into a sample boat and placing the filled boat on the autosampler carousel. Approximately six samples per hour are processed by the Milestone DMA-80 and diagnostic information was stored for each sample. The capability for analysis at SRS provides the ability for rapid response if needed. The test samples were collected and cleared for transfer (11/11/2019) one day prior to SRNL data being provided to SRR (11/12/2019). In contrast, the nominal timeframe to receive data from an offsite lab like Eurofins is two to four weeks. This duration includes shipping, sample processing, analysis, and report generation.[**]

Eurofins analysis of all gas sampling tubes/traps involves wet extraction with acid, followed by dilution and analysis using modified EPA Methods (1631 or 1630). Some advantages of Eurofins' approach include: a) the ability to repeat analysis of samples from the extracts if there are instrument problems or at a different dilution if a sample result is out of range and b) assuring that the Hg trapped on the selective Carbotrap B is in fact methylmercury if the GC step is included. The primary disadvantages of Eurofins approach, however, include potential delays associated with clearing and shipping samples and the time, labor, and cost required for the complicated multistep extraction and analysis protocol.

DMA supports rapid onsite analysis because it relies on thermal release of Hg from the traps with no chemical extraction. A disadvantage of DMA is that the measured sample is consumed during the analysis. The protocols would require close communication between the laboratory and IH staff to collect samples that contain an appropriate target mass of Hg to avoid overloading the instrument, as well as to collect contingency samples in case a sample is spoiled. Note that the trap material may be weighed and subsampled to support repeated analysis of samples and/or to allow for dilutions with practical DFs ranging from 1 to 3.

[**] The offsite data for these samples was delayed due to a laboratory relocation and the data were returned to SRR in February 2020.

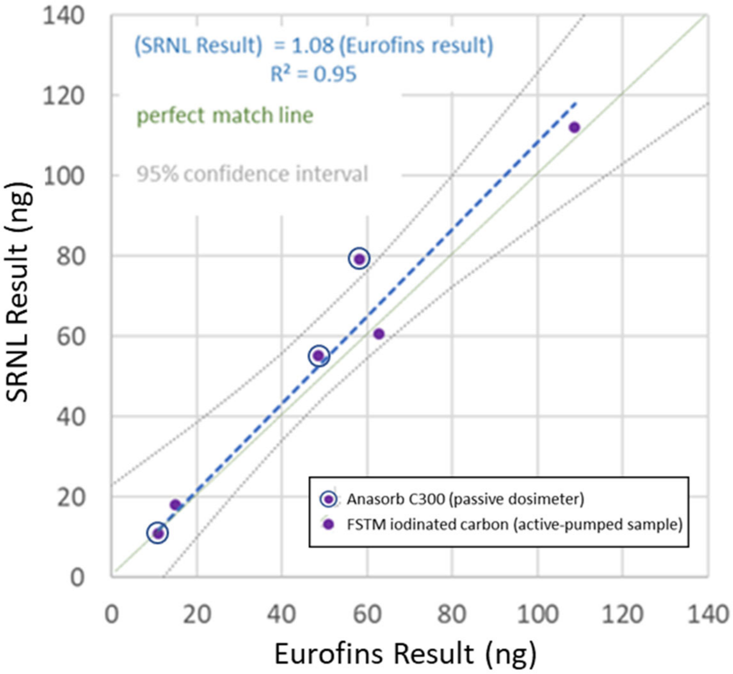

Figure 5-10. Interlaboratory Comparison of Total Mercury Collected by Air Samplers Deployed at the SRS LWS

Table 5-5. Data from Initial Field Testing of Direct Mercury Analyses of Standard IH Air Sampling Dosimeters and Tubes/Traps

Sample Date	Survey ID	Sample ID	Assessment	Lab Result	Unit	Air Volume	Avg Flow	Lab	
11/5/2019	SID10415	SID1041503	Air Sample	10.8	NG	n/a	n/a	SRNL	replicate passive dosimeters (Anasorb C300) deployed in a flow through box
11/5/2019	SID10415	SID1041504	Aie Sample	11.0	NG	n/a	n/a	Eurofins	
11/5/2019	SID10415	SID1041505	AREA AIR	55.2	NG	n/a	n/a	SRNL	replicate passive dosimeters (Anasorb C300) deployed in a flow through box
11/5/2019	SID10415	SID1041506	AREA AIR	48.5	NG	n/a	n/a	Eurofins	
11/5/2019	SID10415	SID1041507	AREA AIR	79.3	NG	n/a	n/a	SRNL	replicate passive dosimeters (Anasorb C300) deployed in a flow through box
11/5/2019	SID10415	SID1041508	AREA AIR	58.3	NG	n/a	n/a	Eurofins	
11/5/2019	SID10415	SID1041511	AREA AIR	18.2	NG	0.2	0.1	SRNL	replicate total mercury tubes/traps (Iodinated Activated Carbon FSTM) loaded using a Dräger hand pump (0.1 L/stroke)
11/5/2019	SID10415	SID1041512	AREA AIR	15.1	NG	0.2	0.1	Eurofins	
11/5/2019	SID10415	SID1041513	AREA AIR	60.6	NG	0.4	0.1	SRNL	replicate total mercury tubes/traps (Iodinated Activated Carbon FSTM) loaded using a Dräger hand pump (0.1 L/stroke)
11/5/2019	SID10415	SID1041514	AREA AIR	62.8	NG	0.4	0.1	Eurofins	
11/5/2019	SID10415	SID1041515	AREA AIR	112	NG	0.6	0.1	SRNL	replicate total mercury tubes/traps (Iodinated Activated Carbon FSTM) loaded using a Dräger hand pump (0.1 L/stroke)
11/5/2019	SID10415	SID1041516	AREA AIR	109	NG	0.6	0.1	Eurofins	
11/6/2019	SID10415	SID1041519	AREA AIR	102	NG	0.6	0.1	SRNL	additional sample after reconfiguration
11/6/2019	SID10415	SID1041520	AREA AIR	63.3	NG	0.6	0.1	SRNL	additional sample after reconfiguration

A second collaborative study performed in partnership with LWS IH technical staff focused on the Hg species selectivity of Anasorb C300. This study aimed to definitively address the question of whether the passive dosimeters are sampling only Hg^o, or if they also sample dMeHg. We also evaluated cartridge packing granules from a Honeywell Hg/chlorine respirator cartridge to help assess if these cartridges are protecting workers from both Hg^o and dMeHg. To perform the testing, we deployed a modified version of the speciation protocols that were used for the detailed laboratory test above. The general sequence was: a) opening the capsules/cartridge and then packing the SRR supplied material into microcolumns, b) spiking inorganic or methylmercury into deionized water in a 40 mL VOA vial, c) reducing/derivatizing the solution to generate Hg^o or methylethylmercury, d) performing the in-vial sparging onto the columns, and e) analysis using the DMA-80.

Several modifications were made to support testing the materials supplied by SRR. The granular materials could not be thermally precleaned to avoid potentially impacting the Hg capture performance. For these tests, ceramic felt was used as the endcaps/plugs for the microcolumns and the columns were disassembled for analysis. Because columns were not precleaned, blank measurements were made on all materials (ceramic felt and the tested solids) and the blanks were subtracted from the raw data in each experiment prior to data workup. Previous testing indicated that ceramic felt captures a small amount of Hg; thus, the front plug and the back plugs were separately analyzed and accounted for in the mass balance calculations as shown in Figure 5-11. The resulting summary information and graphs were generated in the same format as in the detained laboratory testing.

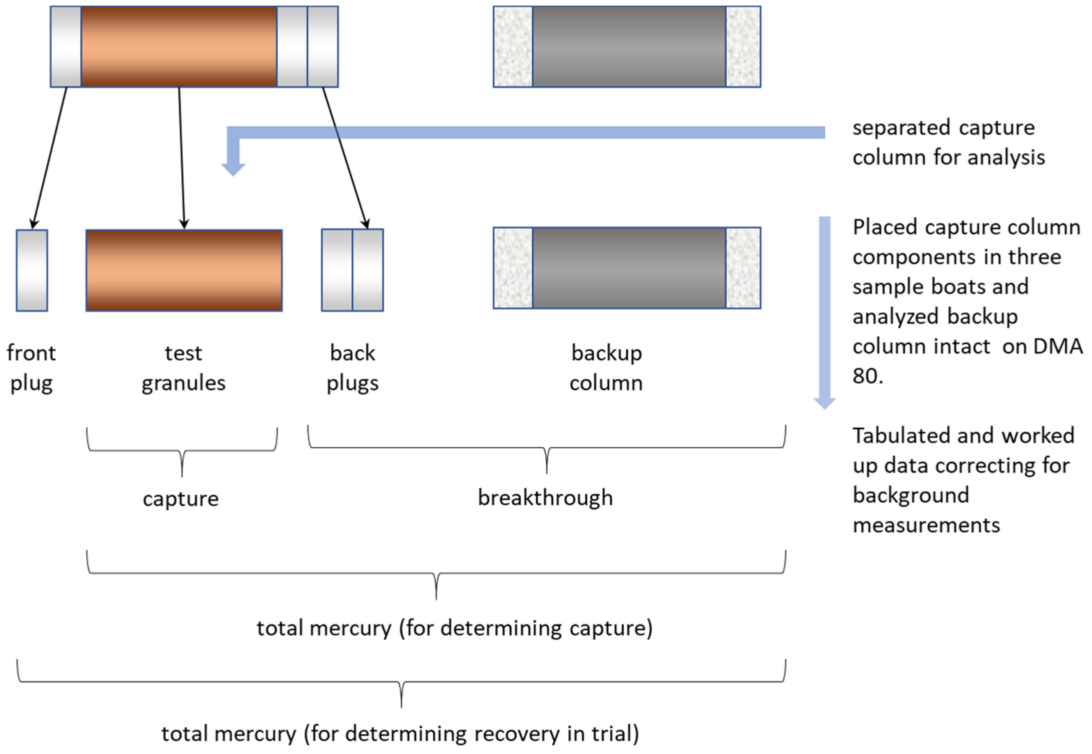

Figure 5-11. Key Modifications Made to Protocols to Evaluate SRR Supplied Materials that could not be Thermally Cleaned Prior to Use

5.3.1. Anasorb C300 Microcolumns

Figure 5-12 and Table 5-6 document the summary results for the Anasorb C300 microcolumn. The capture column value of 0.99 for Hg^o is high, indicating that Anasorb is an effective microcolumn for sampling Hg^o. The backup column for organomercury is relatively high (0.84), supporting that Anasorb C300 does not effectively capture organomercury. These laboratory data suggest that the passive dosimeter does not substantively collect organomercury and confirms the manufacturers description of the passive dosimeter as an Hg^o sampler. While not fully quantitative, Anasorb C300 is a candidate material for supporting microcolumn based Hg speciation protocols. This is particularly true for cases where a pre-column for Hg^o would be helpful, such as in the SRS LWS where Hg^o is typically present at 10 to 1000x higher levels compared to dMeHg. The blank value for the Anasorb C300 was higher (approximately 4.5 ng per cartridge) compared to other tested packing materials. This highlighted the need to carefully measure blanks for IH support applications and to handle and store IH mercury sorbents carefully (i.e., in a low mercury environment and with attention to expiration dates.

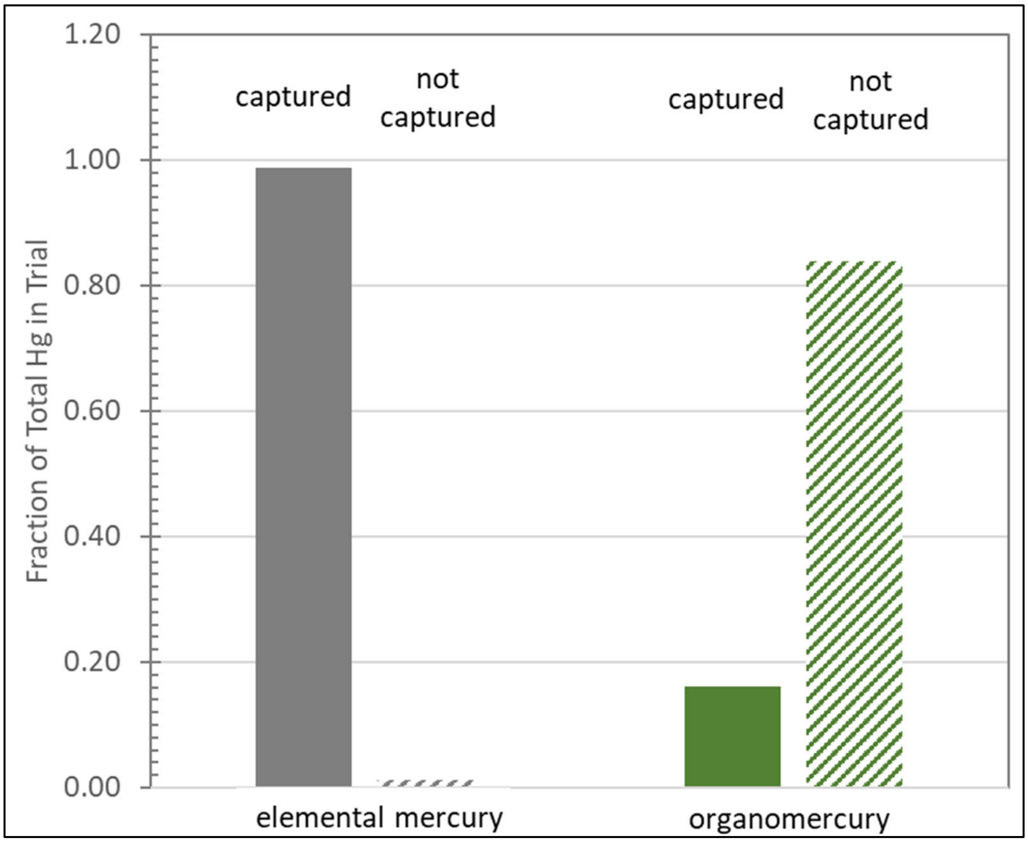

Figure 5-12. Summary Results for Anasorb C300 Microcolumn[*]

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

Table 5-6. Summary Table of Anasorb C300 Microcolumn Results

	Capture	**Breakthrough**	**Mass balance**
Elemental mercury	0.99	0.01	0.86
Organomercury	0.16	0.84	1.05

5.3.2. Honeywell 75852P100L Packing (Mercury and Chlorine Respirator Cartridge) Microcolumn

Summary results for the Honeywell 75852P100L Packing microcolumn are included in Figure 5-13 and Table 5-7. The capture column Hg^o value of 0.92 is high, indicating that the Honeywell 75852P100L Packing is effective for removing Hg^o. Organomercury in the capture column is relatively high (0.93) as well, demonstrating that the Honeywell 75852P100L Packing is effective for removing organomercury. Note that the lab scoping study used a small quantity of the total packing material from the Honeywell respirator cartridge, and the flow rates and humidity conditions were not representative of those recommended by NIOSH for respirator challenge testing, which covers elemental mercury. Therefore, this is not a rigorous evaluation of the material and breakthrough. However, the strong affinity of both Hg^o and organomercury to the material suggests that the packing will provide removal of Hg and, under these conditions, is equally effective for both Hg^o and organomercury.

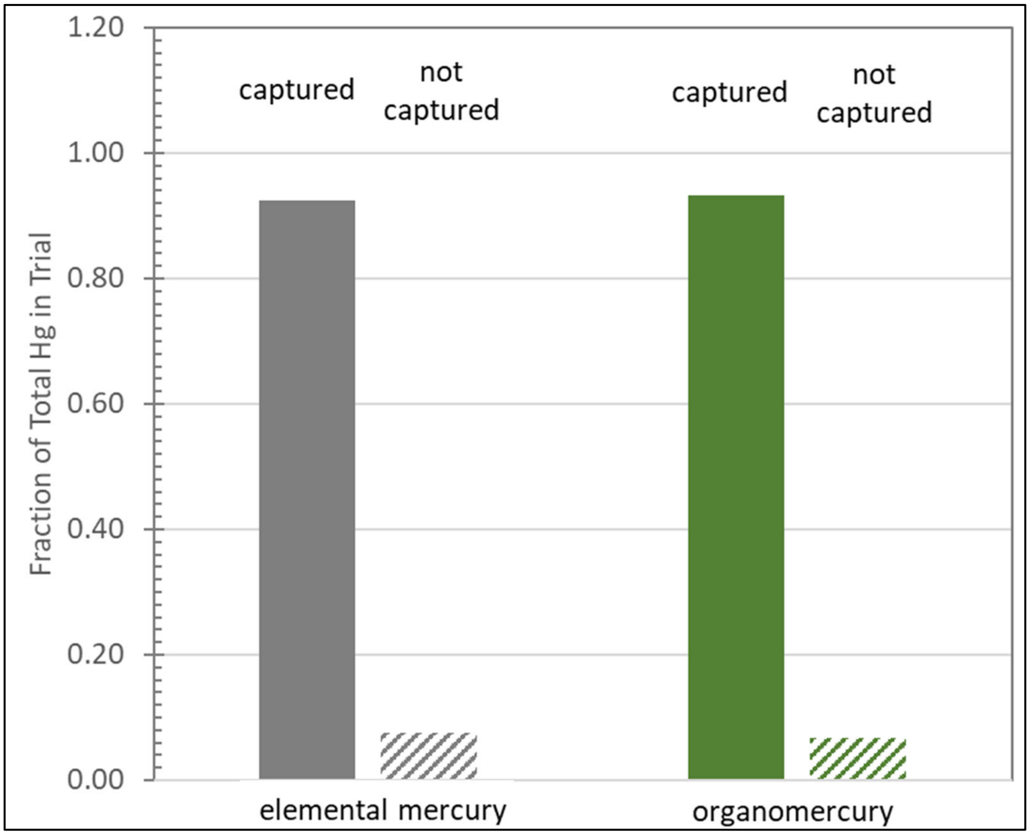

Figure 5-13. Summary Results for Honeywell 75852P100L Packing Microcolumn[*]

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

Table 5-7. Summary Table of Honeywell 75852P100L Packing Microcolumn Results

	Capture	**Breakthrough**	**Mass balance**
Elemental mercury	0.92	0.08	0.89
Organomercury	0.93	0.07	0.94

A third collaborative study performed in partnership with LWS IH technical staff focused on field testing of Carbotrap B for contaminated air samples collected from the LWS. This preliminary study was performed to provide an initial indication of the potential for using microcolumns to separately quantify vapor phase organomercury (i.e., dMeHg sampling) in LWS air samples. These studies used pumped samples and standard-commercial organomercury tubes containing Carbotrap B. In this study, SRR IH personnel collected samples on 10 March 2020 from the headspace of Tank 37 during evaporator operations using a calibrated pump. Samples were pulled through a filter and two Carbotrap B traps in series. The sample (SRR 1213501) included a capture column (A) and backup column (B). The sample volume was selected based on historical data to provide a target dMeHg collection amount of approximately 19 ng (as Hg) on the capture column. Note that dMeHg was anticipated to be a minor component (approximately 0.1%) of the total Hg in the air sample. After the air was pumped through the tubes/traps, they were opened, and the media was poured into quartz boats. No blanks were analyzed of the Carbotrap B sorbent in this first test. The samples were analyzed on the Milestone DMA-80 and the data (Table 5-8) was reported to SRR the next day.

Table 5-8. Field testing of Carbotrap B Data Summary

Sample (column)	**dMeHg captured (ng)**
SRR 1213501A (capture)	20.4
SRR 1213501B (backup)	10.3

In this initial field test of selective media, the total amount of Hg on the traps was relatively low compared to the total quantity of mercury in the samples. This suggests that the Carbotrap B sorbent is not trapping significant amounts of Hg^o. The quantity of putative dMeHg on the capture column (A) was relatively close to the expected value that was calculated based on previous sampling events (analyzed by Eurofins using extraction and modified EPA Method 1630). The measured value for the capture column was similar to the results of a split Eurofins sample (reported on 3/30/2020) in which the capture columns (A) was 15.6 ng; however, the Eurofins backup (B) column contained less mercury, 0.17 ng, compared to the amount measured by SRNL. The backup column (B) was analyzed to help determine if the Hg on the A trap might be influenced by a small amount of sorption of the high levels of Hg^o in the sample. If influenced, then the backup trap would have similar levels of Hg. The backup column captured approximately half of the amount of the lead column. This suggests that, either: 1) there is a small signal from the Hg^o on both traps, but the lead trap selectively captured dMeHg as evidenced by the higher mass, 2) there was some breakthrough of dMeHg that sorbed on the backup column, 3) there was some Hg blank in the material that needs to be accounted for, or 4) some combination of the above. Additional work will be required to finalize a direct sampling dMeHg trap methodology.

The initial data demonstrate significant potential to develop an efficient and robust IH sampling strategy based on selective microcolumns. However, some modifications, field validation, and interlaboratory comparison are needed to validate the protocols. Further study should include reproducing the data with careful measurements of blanks, comparison of results from deployment of Carbotrap B with and without a precolumn to remove Hg^o, and interlaboratory comparison with a laboratory using an independent method.

6. Conclusions and Recommendations

The various tests confirmed and extended the information in the scientific literature.

Initial testing validated the quality, reproducibility, and predictability of the performance of the in-vial sparge system. An analytical model based on Henry's Law partitioning closely matches the data generated by both in-vial and full-scale sparge systems. The calibrated model indicated that the sparge gas in the in-vial system reached approximately 43% of its equilibrium value before exiting the water surface, while a full-scale system reaches approximately 100%. The validated performance of the in-vial sparge system, combined with its simplicity, reduced costs, waste, and labor costs, supports transitioning to this platform for Hg analysis when possible.

Detailed laboratory testing of candidate total Hg and selective speciation capture materials, as well as materials supplied by SRR collaborators, demonstrated:

- Materials that capture both Hg^o and organomercury include a) Au-coated sand (amalgamation); b) Adsoquick activated carbon (sorption); c) iodinated activated carbon FSTM (sorption and reaction); and d) Honeywell 75852P100L Packing from Hg and chlorine respirator cartridge (sorption and reaction),
- Materials that capture Hg^o, but do not effectively capture organomercury include a) Ag beads (amalgamation) and b) Anasorb C300 (reaction and amalgamation), and
- Carbotrap B was the only material tested that captures organomercury, but does not effectively capture Hg^o

The results support continued efforts to transition SRNL liquid waste analysis protocols to microcolumn configurations that are compatible with the DMA-80 as a uniform platform for quantification. More work is needed to overcome the requirement for heating Carbotrap B to temperatures exceeding manufacturers recommendations when using the instrument for measuring organomercury. For a TOM protocol, further investigation of Carbotrap B and similar sorbents is recommended along with additional study of the derivatization and sparging steps. A total Hg sorbent, such as Adsoquick, may be an alternative strategy if the appropriate Hg species are formed and sparged.

For support of air sampling (IH) application in the LWS, initial field testing documented that DMA (EPA Method 7473) is a simple, rapid, and robust method to detect and quantify Hg collected using standard Hg passive dosimeters and total Hg tubes/traps. Interlaboratory comparison showed a close correspondence between the paired data (correlation, $r^2 = 0.95$). Scoping field tests of Carbotrap B indicated that this organomercury-selective material may provide a reasonable basis for developing a simple, effective, and robust sampling protocol for operational speciation of Hg in LWS air samples. This microcolumn protocol pairs efficiently with DMA and would provide capability for rapid onsite analysis. Additional development and field testing are recommended to assure that the speciation performance is adequate to meet IH needs. This testing would address the need for placing a precolumn (e.g., Ag) in front of the Carbotrap B to avoid crossover capture from the high Hg^o present in the system.

7. References

Ballantine D.S., Jr. and W.H. Zoller, 1984. Collection and Determination of Volatile Organic Mercury Compounds in the Atmosphere by Gas Chromatography with Microwave Plasma Detection, Analytical Chemistry, 56:1288-1293.

Baya, P.A., J.L. Hollinsworth and H. Hintelmann, 2013. Evaluation and optimization of solid adsorbents for the sampling of gaseous methylated mercury species, Analytica Chemica Acta, 786:61-69.

Bloom, N.S., A.K. Grout and E.M. Prestbo, 2005. Development and complete validation of a method for the determination of dimethyl mercury in air and other media, Analytica Chemica Acta, 546:92-101.

Bloom, N.S., E. von der Geest, E.M. Prestbo, W. Wilmarth and D. Thaxton. 2004. Formation and Degradation of (CH3)2Hg in Nuclear Waste Tanks, presented at the Seventh International Conference on Mercury as a Global Pollutant, Materials and Geoenvironment, 51:12-15

Bloom, N.S. and W.F. Fitzgerald, 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapour atomic fluorescence detection, Analytica Chimica Acta, 208:151-161.

Boggess, A.J., T.L. White, M.A. Jones, T.B. Edwards and S.P. Harris, 2019. Development and Comparison of Purgeable Mercury Values in SRR Samples Measured by SRNL and Eurofins FGS, SRNL-STI-2019-00300, Savannah River Site Aiken SC, 29808.

Chew, D.P., B.A. Hamm and M.N. Wells, 2019. Liquid Waste System Plan Revision 21, Document No. SRR-LWP-2009-00001 Rev 21, Savannah River Remediation LLC, Savannah River Site, Aiken, SC 29808.

DOE 2016, Technology Plan to Address theEM Mercury Challenge, US DOE Office of Environmental Management, Washington DC.

Hawkins, L., 2016. Tekran 2537X Operator Training Course Rev 1.22, Tekran Instrument Corporation, Seatlle WA.

Hebisch, R. N. Fröhlich, T. Houben, W. Schneider, T.H. Brock, A. Hartwig, and MAK Commission, 2018. Mercury – Method for the determination of mercury vapours in workplace air using atomic absorption spectrometry, The MAK Collection for Occupational Health and Safety, Vol 3, No 1, pp 306-318, doi: 10.1002/3527600418.am743997e2018.

Kvietkus,K., Z. Xiao and O. Lindqvist, 1995. Denuder-based techniques for sampling, separation and analysis of gaseous and participate mercury in air, Water, Air and Soil Pollution, 80:1209-1216.

Liang, L., M. Horvat and N.S. Bloom, 1994. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection, Talanta 41:371-379.

Looney, B.B., M.E. Denham, Jr., K.M. Vangelas and N.S. Bloom, 2003. Removal of Mercury from Low-Concentration AqueousStreams Using Chemical Reduction and Air Stripping, Journal of Environmental Engineering, 819-825.

Prestbo, E. and L. Hawkins, 2006. Research Plan for Development of a Portable Screening Level Air Measurement Capability for Dimethyl Mercury, Elemental Mercury and Total Mercury in Support of Human Health and Operational Monitoring at the Savannah River Site February 13, 2006, Frontier Geosciences Inc., Seattle WA.

Prestbo, E. M.; Hawkins, L.; Cussen, D.; Fowler, C. Determination of Total and Dimethyl Mecury in Raw Landfill Gas with Site Screening for Elemental Mercury at Eight Washington State Landfills for Washington State Department of Ecology; Frontier Geosciences Inc.: 2003;

Shewchuk, S.R., R. Azargohar and A.K. Dalai, 2016. Elemental Mercury Capture Using Activated Carbon: A Review, Journal of Environmental & Analytical Toxicology, doi:10.4172/2161-0525.1000379.

Sommar, J., X. Feng and O. Lindqvist, 1999. Speciation of Volatile Mercury Species Present in Digester and Deposit Gases, Applied and Organometalic Chemistry, 13:441–445.

Trüe, A., P. Forbes, N. Panichev and J. Okonkwo, 2011. The use of sorbent tubes and a semi- continuous emissions monitor for the determination of atmospheric total gaseous mercury in Pretoria, South Africa, URI: http://hdl.handle.net/2263/58346. Anasorb c300

Trujillo, P.E. and E.E. Campbell, 1975. Development of a Multistage Air Sampler for Mercury, Analytical Chemistry, 47:1629-1634.

White, T. L., L. W. Brown B. B. Looney and M. A. Jones, 2019. Total Mercury Analysis Comparison: Deployment of Analytical Method for the Savannah River Site Liquid Waste System, SRNL-STI-2019-00056, Savannah River Site Aiken SC 29808.

Wilhelm, S.M., L. Liang and D. Kirchgessner, 2006. Identification and Properties of Mercury Species in Crude Oil, Energy and Fuels, 20:180-186.

Živkovi´c, I., S. Berisha, J. Kotnik, M. Jagodic and M. Horvat, 2020. Traceable Determination of Atmospheric Mercury Using Iodinated Activated Carbon Traps, Atmosphere, 11:780, doi:10.3390/atmos11080780

Appendix A. Data for Individual Trials in Microcolumn Testing

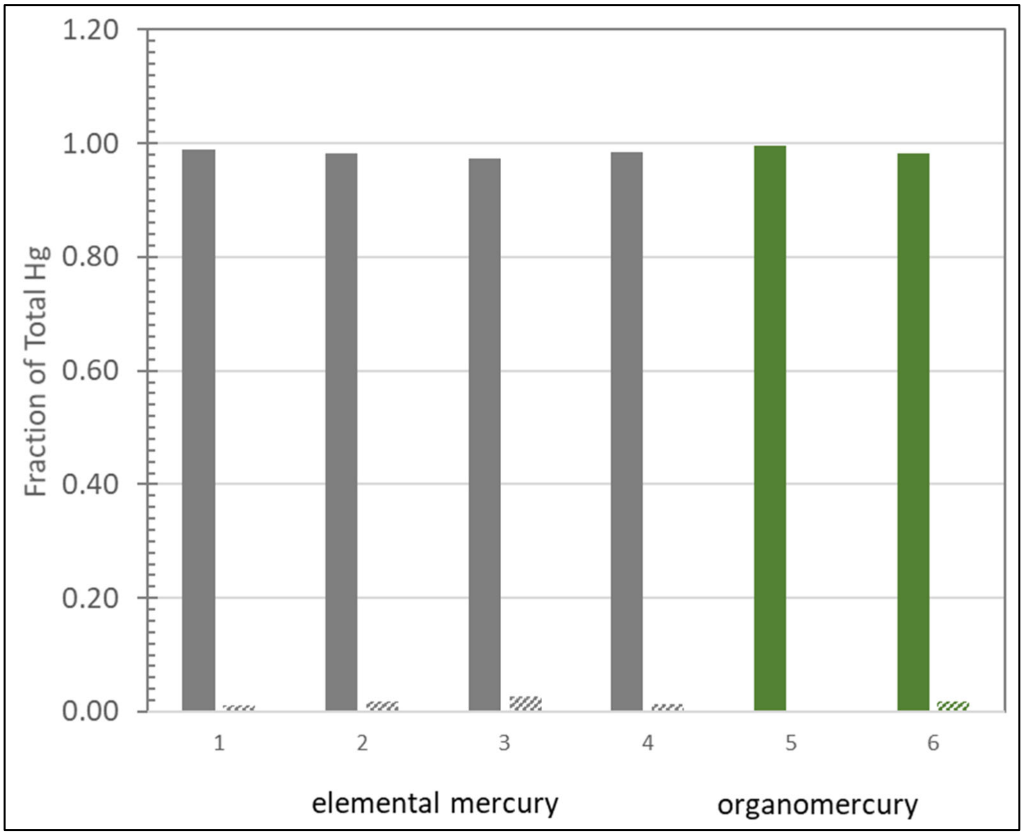

Figure A-1. Summary Results for Gold-Coated Sand Microcolumns[*]

Table A-1. Summary Table of Gold-Coated Sand Microcolumn Results

	Capture column	Backup column	Mass balance
Elemental mercury	0.99	0.01	1.14
Elemental mercury	0.98	0.02	0.98
Elemental mercury	0.97	0.03	0.99
Elemental mercury	0.99	0.01	0.96
Organomercury	1.00	0.00	0.95
Organomercury	0.98	0.02	1.07

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

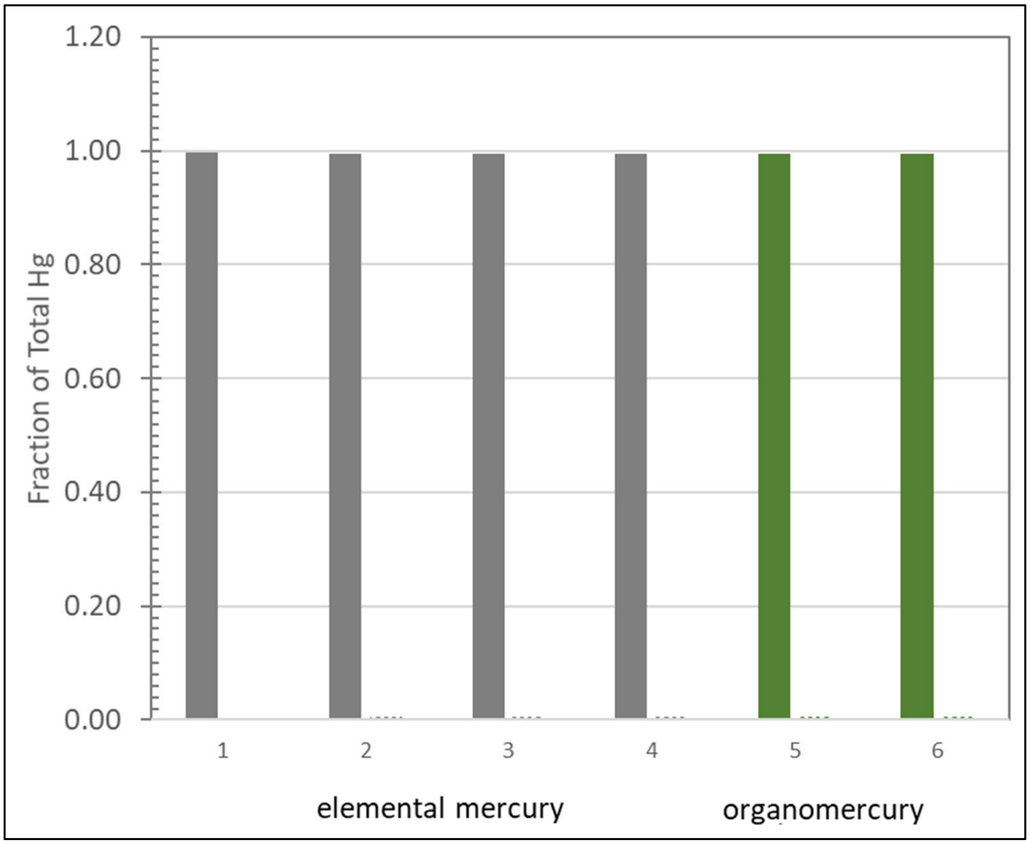

Figure A-2. Summary Results for Adsoquick Microcolumns*

Table A-2. Summary Table of Adsoquick Microcolumn Results

	Capture column	Backup column	Mass balance
Elemental mercury	1.00	0.00	1.04
Elemental mercury	0.99	0.01	0.99
Elemental mercury	0.99	0.01	0.99
Elemental mercury	0.99	0.01	1.03
Organomercury	0.99	0.01	0.80
Organomercury	0.99	0.01	0.90

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

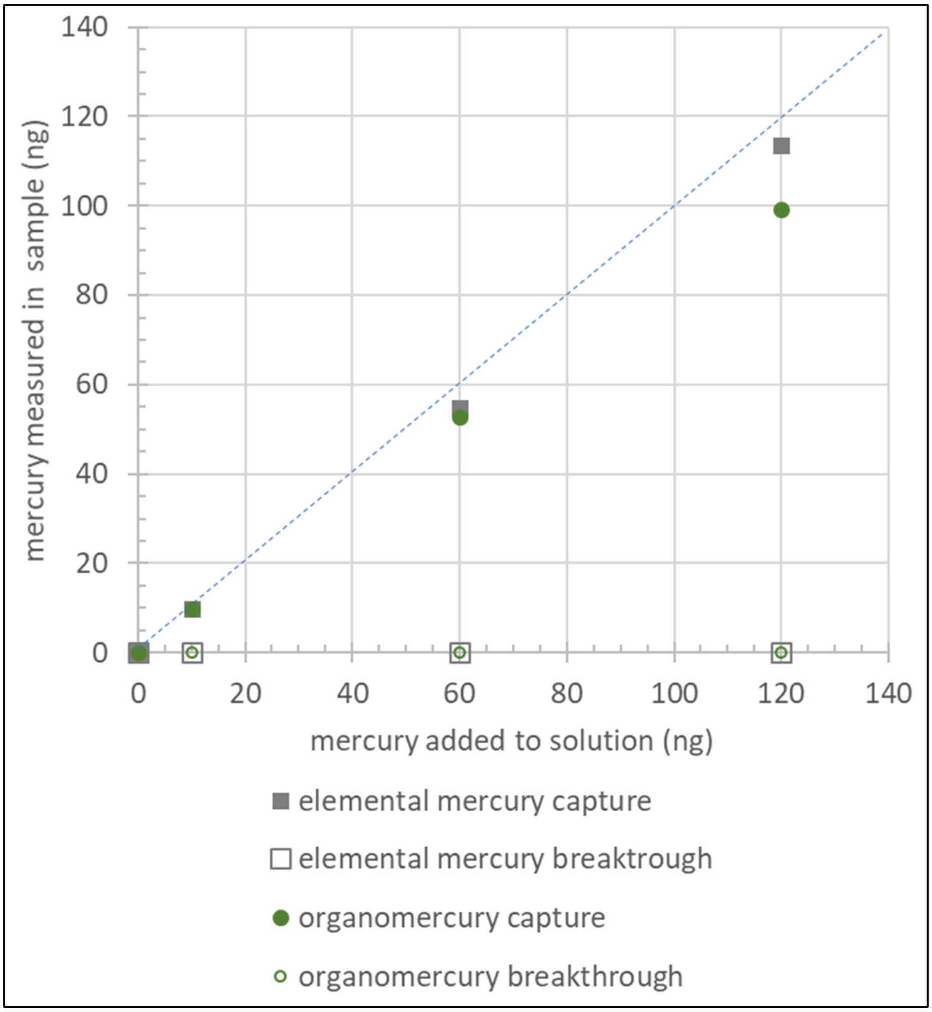

Figure A-3. Adsoquick Loading Test

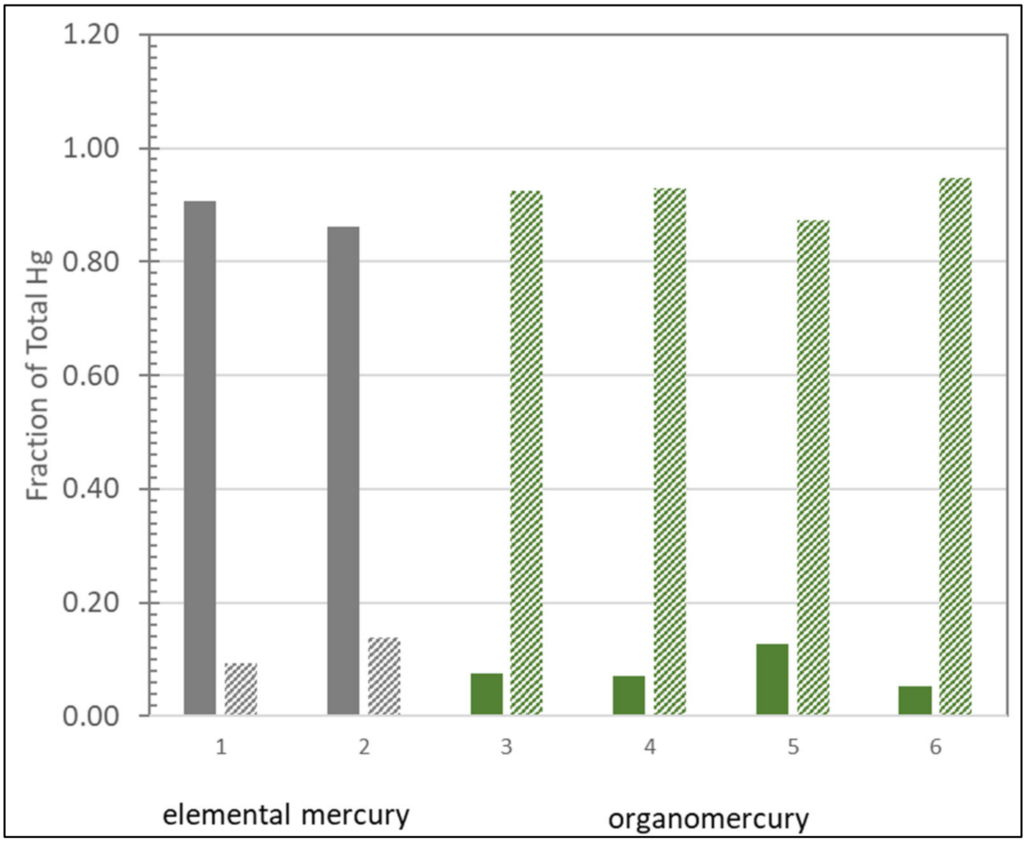

Figure A-4. Summary Results for Silver Microcolumns*

Table A-3. Summary Table of Silver Microcolumn Results

	Capture column	Backup column	Mass balance
Elemental mercury	0.91	0.09	1.04
Elemental mercury	0.86	0.14	0.99
Organomercury	0.07	0.93	0.80
Organomercury	0.07	0.93	0.80
Organomercury	0.13	0.87	0.80
Organomercury	0.05	0.95	0.90

---

* Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg°, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

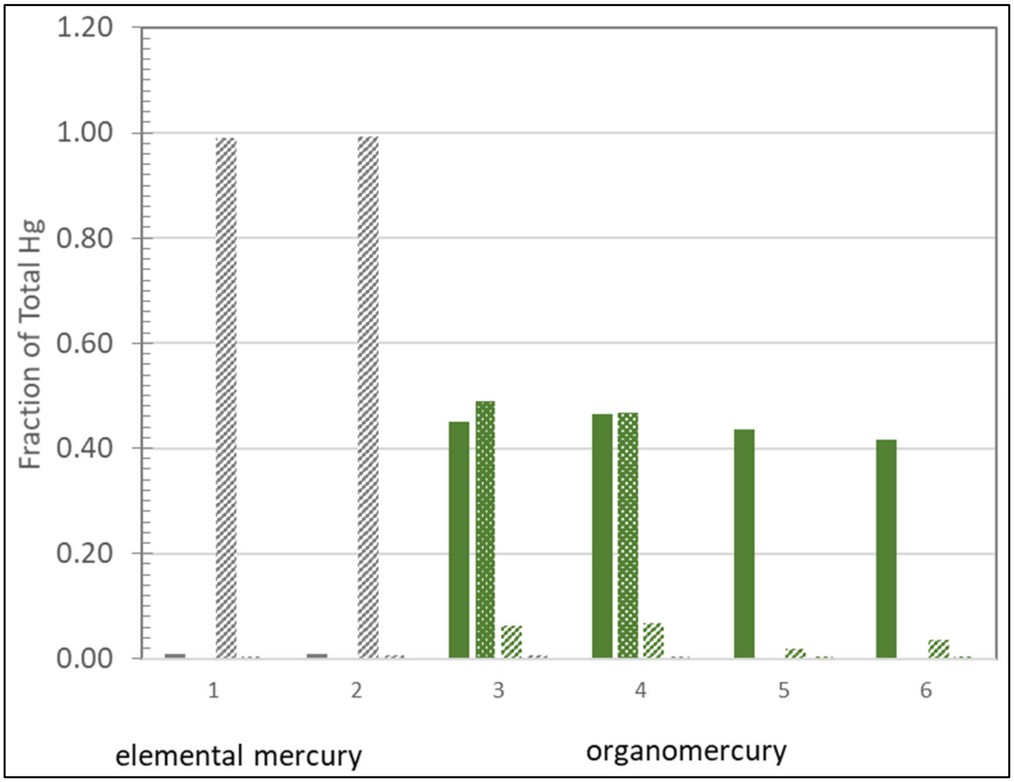

Figure A-5. Summary Results for Carbotrap B Microcolumns*

Table A-4. Summary Table of Carbotrap B Results

	Capture column	Capture column	Backup column	Mass balance	Sum or 225 ˚C and 650 ˚C
	225 ˚C	650 ˚C			
Elemental mercury	0.01	0.00	0.99	0.99	
Elemental mercury	0.01	0.00	0.99	1.02	
Organomercury	0.45	0.49	0.06	1.16	0.94
Organomercury	0.46	0.47	0.07	1.16	0.93
Organomercury	0.44		0.02	0.45	0.98 est
Organomercury	0.42		0.04	0.45	0.96 est

---

[*] Solid bars represent Hg on the capture column and the striped bars represent Hg capture on the backup column. Gray bars represent trials with Hg^o, and green bars represent trials with organomercury. Solid bars near one represent effective capture and striped bars near one represent minimal capture because the mercury was instead captured on the backup column after breakthrough.

Distribution:

Records Administration (EDWS)

cj.bannochie@srnl.doe.gov
alex.cozzi@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
erich.hansen@srnl.doe.gov
connie.herman@srnl.doe.gov
brady.lee@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
Mary.Whitehead@srnl.doe.gov
edward.sadowski@srnl.doe.gov
Joseph.Manna@srnl.doe.gov
john.mayer@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
Amy.Ramsey@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
michael.stone@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
tony.polk@srs.gov
edward.sadowski@srnl.doe.gov
patricia.suggs@srs.gov
Kenneth.Wells@srs.gov

celia.aponte@srs.gov
timothy.baughman@srs.gov
earl.brass@srs.gov
Richard.Edwards@srs.gov
Azikiwe.hooker@srs.gov
Thomas.Huff@srs.gov
Ryan.McNew@srs.gov
phillip.norris@srs.gov
Christine.Ridgeway@srs.gov
Azadeh.Samadi-Dezfouli@srs.gov
Vijay.Jain@srs.gov
arthur.wiggins@srs.gov
terri.fellinger@srs.gov
hasmukh.shah@srs.gov
jeffrey.gillam@srs.gov
chris.martino@srnl.doe.gov