

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).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.



SOLUBLE AND PARTICULATE MERCURY

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

T. L. White

B. B. Looney

L. W. Brown

D. M. Missimer

September 2019

SRNL-STI-2019-00345, Revision 0



DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *Total Hg, LWS, MCU*

Retention: *Permanent*

Soluble and Particulate Mercury Deployment of Analytical Method for the Savannah River Site Liquid Waste System

T. L. White
B. B. Looney
L. W. Brown
D. M. Missimer

September 2019

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



REVIEWS AND APPROVALS

AUTHORS:

T. L. White, Analytical Development	Date
-------------------------------------	------

B. B. Looney, Environmental Restoration Technology	Date
--	------

L. W. Brown, Analytical Development	Date
-------------------------------------	------

D. M. Missimer, Analytical Development	Date
--	------

TECHNICAL REVIEW:

J. O. Dixonson, Environmental Restoration Technology, Reviewed per E7 2.60	Date
--	------

T. B. Peters, Chemical Processing Technology, Reviewed per E7 2.60	Date
--	------

APPROVAL:

M. L. Whitehead, Manager Analytical Development	Date
--	------

B. J. Wiedenman, Manager Advanced Characterization and Processing Technology	Date
---	------

S. D. Fink, Director, Chemical Processing Technology	Date
--	------

R. E. Edwards, Manager Nuclear Safety and Engineering Integration, SRR	Date
---	------

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) developed, tested, and deployed in a radiological containment unit (CU) an analytical method for quantifying particulate total mercury and soluble total mercury in radioactive samples such as the those generated by the dilution of Savannah River Site (SRS) High-Level Waste. This method relies on direct mercury analysis and other associated capabilities for matrix independent quantification of total mercury in solids or liquids (i.e., any sample that can be introduced into the instrument oven for pyrolysis to release all mercury for measurement). The matrix independence allows for discreet measurements of the starting sample, the collected particulates and the filtrate liquid, thus enabling a mass balance quality check. For example, an analysis of a diluted sample from the SRS liquid waste system (LWS) resulted in a measured total mercury value of 55.0 mg Hg/L and a nearly matching calculated total mercury value of 55.1 mg Hg/L ($\pm 20\% 2\sigma$) from the summation of measured soluble mercury (47.8 mg Hg/L $\pm 20\% 2\sigma$) and measured particulate mercury (7.26 mg Hg/L $\pm 20\% 2\sigma$).

The advantages of the particulate-soluble mercury analysis method are:

- waste minimization using small radioactive liquid volumes
- minimal radiological sample processing and reduced handling steps protective of workers (ALARA) and improved data quality
- syringe filter technology which eliminates vacuum filtration and the potential loss of volatile species
- small diameter filters (13 mm nominal to 25 mm if needed to avoid clogging) and small disposable poly filter holders (no need to clean) which minimize waste
- flexibility provided for a range of starting concentrations, particulate-soluble ratios, and sample matrix conditions
- soluble and particulate are measured results that, when summed, are in good agreement with the total mercury measurement

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	ix
1.0 Introduction	1
1.1 Scope	1
1.2 Overall Strategic Options	1
1.3 Preliminary Studies	2
2.0 Experimental Procedure	3
2.1 DMA	3
2.2 Quartz Fiber Filter Columns	5
2.3 Particle Size Analyzer	6
3.0 Results and Discussion	6
3.1 Additional Scoping Studies Using Quartz Fiber Column Filters	6
3.1.1 Mercury Capture Performance	6
3.1.2 Filtration Performance of Quartz Fiber Columns	9
3.2 Deployment Testing for LWS System (Radioactive) Samples	10
4.0 Conclusions	14
5.0 References	15
Appendix A: Basis for SRNL Schema Development Strategy: Particulate and Soluble Mercury	16
Appendix B: R & D Directions for Soluble and Particulate Mercury	17
Appendix C: Particle Size Analyzer used to Generate Data for the Quartz Fiber Column Tests	19
Appendix D: Summary of Quartz Fiber Column Filtration Tests	22

LIST OF TABLES

Table 1: Mercury Mass Balance Data from Tests of Quartz Fiber Filters	8
Table 2: SRNL and Offsite Laboratory Analysis of Mercury ($\pm 20\% 2\sigma$)	13
Table 3: Tank 50 %particulate Hg (calculated) and %soluble Hg (measured) by Eurofins	13
Table 4: Microtrac S3500 Instrument Parameters for the Two Microtrac Standards	19

LIST OF FIGURES

Figure 1: Summary of Results from Scoping Filtration Testing Performed by DOE Fellow, Katherine De La Rosa in 2018. ⁴	3
Figure 2: Items used for Mercury Particulate Analysis are Gas Tight Glass Syringe (A), Luer Lock Filter Casing (B) that is Opened to Remove the Filter Paper (E) with Tweezers (F) for Analysis, and the Filter Casing Holder (C).....	4
Figure 3: Packed Quartz Fiber Filter Column (A) and the Packing Tool (B) used to Prepare 10 mm Diameter Columns Configured for Use in the DMA-80 Autosampler Carousel	5
Figure 4: Graphical Summary of Mercury Mass Balance Data for Quartz Fiber Filter Columns	7
Figure 5 Summary of Particulate Removal Performance for “Small” and “Large” Particles by SRNL-Fabricated Quartz Fiber Filters	9
Figure 6: Radiological Containment Unit (CU) Housing a DMA-80 for Analyzing Radioactive Mercury Samples and Work Area for Sample Preparation.	10
Figure 7: Sample Analysis Schema for Particulate and Soluble Mercury Analysis on the Radiologically Contained DMA-80.	11
Figure 8: Triplicate Same Day Analyses ($n = 3$) of Tank 50 for Soluble, Particulate, and Total Hg. Note blank 1 is slightly elevated due to trace mercury carryover from a sample analysis.....	12
Figure 9: Top-Down View Showing the Optical Configuration of the Microtrac S3500.....	19
Figure 10: Photograph of Modified Circulation Line to Incorporate Option to Install Quartz Fiber Filter Column	20

LIST OF ABBREVIATIONS

AD	Analytical Development
ALARA	As Low As Reasonably Achievable
CU	Containment Unit
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
DMA	Direct Mercury Analyzer
DSA	Documented Safety Analysis
HPS	High Purity Standard
LCL	Lower Control Limit
LOD	Limit of Detection
LOQ	Limit of Quantification
LWS	Liquid Waste System
MCE	Mixed Cellulose Ester
MCP	Measurement Control Plan
MCU	Modular Caustic-Side Solvent Extraction Unit
MMHg	Monomethylmercury
PES	Polyethersulfone
RCRA	Resource Conservation and Recovery Act
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SREL	Savannah River Ecology Laboratory
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
TCLP	Toxicity Characteristic Leaching Procedure
TTR	Technical Task Request
TTQAP	Task Technical and Quality Assurance Plan
QC	Quality Control
UCL	Upper Control Limit
WAC	Waste Acceptance Criteria

1.0 Introduction

1.1 Scope

Tank 50 is one part of the Liquid Waste System (LWS) at the Savannah River Site (SRS) that directly feeds low-level radioactive and hazardous liquid waste to the Saltstone Facility where grout is produced. The grout is stored as a solid waste landfill in the Saltstone Disposal Facility (SDF). Total mercury analyses of Tank 50 and the resulting samples generated from the Toxicity Characteristic Leaching Procedure (TCLP) of the low-level grout waste form are performed quarterly to demonstrate compliance with the Saltstone Waste Acceptance Criteria (WAC).¹ Analyses of such samples resulted in higher than expected mercury concentrations in 2014.² With the end goal of developing actionable measures to reduce leachable mercury in grout, researchers began developing analytical methods to speciate mercury from samples taken throughout the LWS. These analytical methods are critical to understanding the behavior of mercury in liquid waste facilities and unit operations and developing measures to adequately control fate of mercury during the processing of radioactive liquid waste streams. As part of this effort, SRNL has been requested to develop analytical methods for both soluble and particulate mercury as described in the Task Technical & QA Plan (TTQAP).³

1.2 Overall Strategic Options

Determination of soluble (dissolved) and particulate mercury in a sample is relatively straightforward in principle, requiring physical separation of solids (particulates) and bulk liquid followed by analysis of total mercury in: a) the resulting separated fractions (liquid and particulate), and b) the original raw sample and other key species (to assess mass balance). In practice, there are a range of strategies for performing the separation and analysis steps. For SRS LWS characterization the following options are employed: 1) separation using a membrane filter, analysis of the initial sample and filtrate (to determine the particulate fraction by difference), and 2) separation using membrane filter or quartz wool followed by direct analysis of the initial sample, the filtrate and the collected particles by direct mercury analysis (DMA).

Strategy 1 - The physical separation is performed using a standard membrane filter (e.g., vacuum filtration via a 0.45-μm mixed cellulose ester or polyethersulfone filter) followed by analyses of total mercury in the initial raw liquid sample and the liquid filtrate, and analysis of purgeable mercury species that would be lost during vacuum filtration. The mercury analyses for these phases would be carried out using EPA methods 1631 or 245 (or equivalent). The particulate mercury value is estimated by difference of measured mercury values as follows:

$$C_{\text{particulate Hg}} = C_{\text{total Hg}} - (C_{\text{filtrate Hg}} + C_{\text{purgeable Hg}}) \quad (1)$$

where C is concentration of Hg

This approach is a reasonable and defensible strategy but is subject to error in cases where the particulate mercury value is relatively small (i.e., the initial bulk sample and the filtrate are similar in magnitude resulting in subtraction of two "large numbers" to obtain a "small

number"). Furthermore, Strategy 1 does not provide the data for an independent mass balance as a quality check (since the particulate phase is not analyzed). In SRS LWS samples analyzed by Eurofins, Strategy 1 is employed in interpreting the data to quantify particulate and soluble fractions.

Strategy 2 - The physical separation is performed using a standard membrane filter (e.g., pressure filtration via a 0.45- μm mixed cellulose ester (MCE) or polyethersulfone (PES) filter or a quartz fiber column) followed by analyses of total mercury in all phases: the initial raw liquid sample, the liquid filtrate, and the separated particulates. The pore size of 0.45- μm filter is defined by EPA 1631 and thus used as the filter standard. The total mercury analyses for these phases would be carried out using EPA method 7473 (or equivalent). Strategy 2 provides discreet measurements of all key phases and allows for an independent mass balance as a quality check. Moreover, Strategy 2 minimizes the potential for loss of purgeable mercury species (by using pressure or syringe filtration to eliminate the vacuum) and improves estimates of the particulate fraction for samples where the initial bulk sample and the filtrate are of similar magnitude. Based on these considerations, SRNL focused on Strategy 2 to develop and deploy a robust method for soluble and particulate mercury in SRS LWS samples (see Appendix A).

1.3 Preliminary Studies

In developing SRS LWS methods for mercury, SRNL employed a two-step process based on preliminary work performed at the Aiken County Technology Laboratory (ACTL, 999-1W) that used simulants and nonradioactive samples. Once the methods were properly scoped, they were ready for preparing the work control and implementation documentation, and for deployment in 773-A for radioactive SRS LWS samples. Both 999-1W and 773-A have the DMA capabilities to analyze samples in a variety of matrices (solids, liquids, and gases) according to EPA Method 7473.

The preliminary work for the particulate and soluble fractions was supported by DOE Office of Environmental Management (EM) through the DOE EM Fellows workforce development program. The research was carried out by Katherine De La Rosa, a DOE EM Fellow, and was documented in her internship report⁴ – “Mercury Speciation via Direct Mercury Analyzer.” In the scoping studies, inorganic mercury and monomethylmercury in aqueous samples were adsorbed on silica thiol (Biotage, SRS SDS No. 51991-1, particle size 50 μm) and the resulting solution was filtered through a standard 0.45 μm MCE filter. The filters were analyzed directly by pyrolysis, catalysis, amalgamation, thermal release and atomic absorption spectrometry using the DMA-80. As shown in Figure 1, the silica thiol was relatively effective in sequestering the mercury in solution - in this case the sorbent collected approximately 90% for inorganic mercury and 100% for monomethylmercury in the solution. The filtered particles were accurately and quantitatively determined by DMA and the blank values were relatively low demonstrating minimal capture of soluble mercury by the filter membrane. Note that De La Rosa tested a variety of conditions and matrices with silica thiol. For inorganic mercury the collection efficiency ranged from approximately 70% to 92% and the collection efficiency for monomethylmercury ranged from approximately 97% to 115 %.⁴

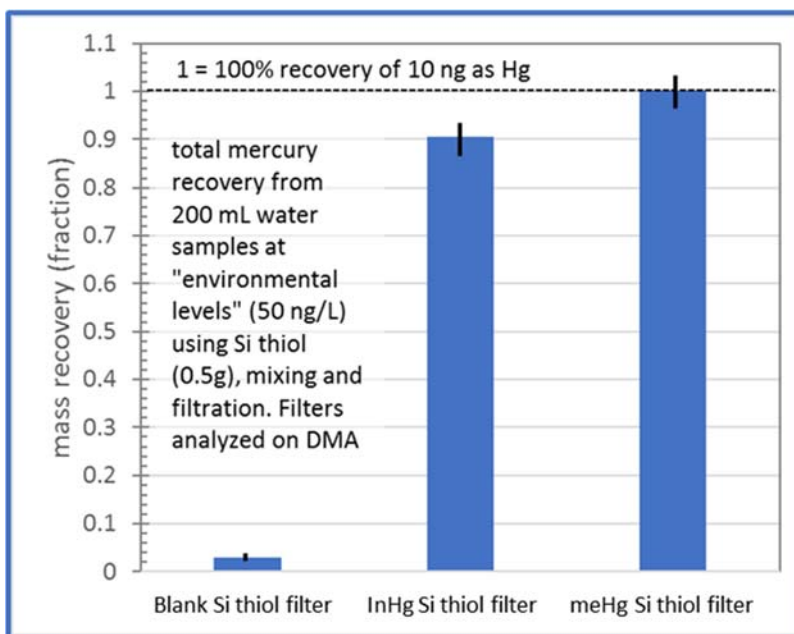


Figure 1: Summary of Results from Scoping Filtration Testing Performed by DOE Fellow, Katherine De La Rosa in 2018.⁴

These preliminary studies supported further development of a strategy based on physical collection of the particulate phase from LWS samples using filters or columns that are suitable for pyrolysis/direct analysis and that are compatible with the DMA-80 sample handling system.

2.0 Experimental Procedure

Data that researchers generated from this project can be found in the Electronic Laboratory Notebook (ELN)⁵ and links found therein. In keeping with outside laboratories, mercury in solution is termed soluble mercury in this report but has also been referred to as dissolved mercury.

2.1 DMA

All total mercury measurements were performed using the Milestone DMA-80. Procedures for the operation of the DMA (based on EPA 7473⁶) are documented in L16.1 ADS-1580⁷ and in SRNL ELN notebook T6751-00351-03⁸. For the DMA, personnel dilute mercury standards purchased from High-Purity Standards (HPS) that are NIST traceable.ⁱ

The SRNL deployment of the DMA-80 instrument for LWS total mercury analysis is covered in a previous report⁹. For liquids, the sample is diluted to the calibration range of the instrument (generally 1 to 50 to 1 to 200) and an aliquot (e.g., 100 μ L) is added to a sampling boat that has been preloaded with a high purity alumina powder. Solid material, such as filter paper, is prepared for analysis in a similar way by placing the material directly into a sample boat without the solid zeolite. The boats are loaded onto the DMA-80 autosampler carousel for direct analysis. Results are reported in units of nanogram (ng) and converted to concentration based on the quantity of sample being measured and any dilution factors with an uncertainty⁹ of $2\sigma \pm 20\%$. A JMP Pro Version 11.2.1 statistical analysis using the DMA with NIST traceable Hg standards, DOE Mixed

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

Analyte Performance Evaluation Program (MAPEP) performance test blind samples, simulated waste samples containing mercury, and Tank 50 samples determined an uncertainty of $\pm 20\% 2\sigma^9$.

The three detector cells (0, 1, and 2) within the DMA instrument have a calibration range (R^2 of at least 0.995) from 0.1 ng of Hg to 300 ng of Hg. Prior to sample analysis two check standards of 1.0 ng (cell 0) and 10 ng (cell 1 and 2) of Hg are analyzed and one 10-ng check standard analyzed at the end of sample analysis. Dilute samples to within the calibration curve using 2 vol % nitric acid (HNO_3) and transfer an aliquot (about 100 μL) to a sample boat containing ~200 mg of Milestone Sample Additive Bⁱⁱ to ensure retention of all mercury compounds. Analyze the boats with blanks to ensure a low background below an absorbance of 0.0015 Au. Dilute samples to near the upper end of the calibration curve of the DMA instrument and filter as described in Appendix A. The filter paper is removed and placed into the sample boat and analyzed. Figure 2 shows all materials used for sample preparation of the LWS test samples. Further details of the sample handling and processing steps for soluble and particulate Hg measurements in LWS samples are provided in the R&D Direction (Appendix B) and discussed in more detail below.

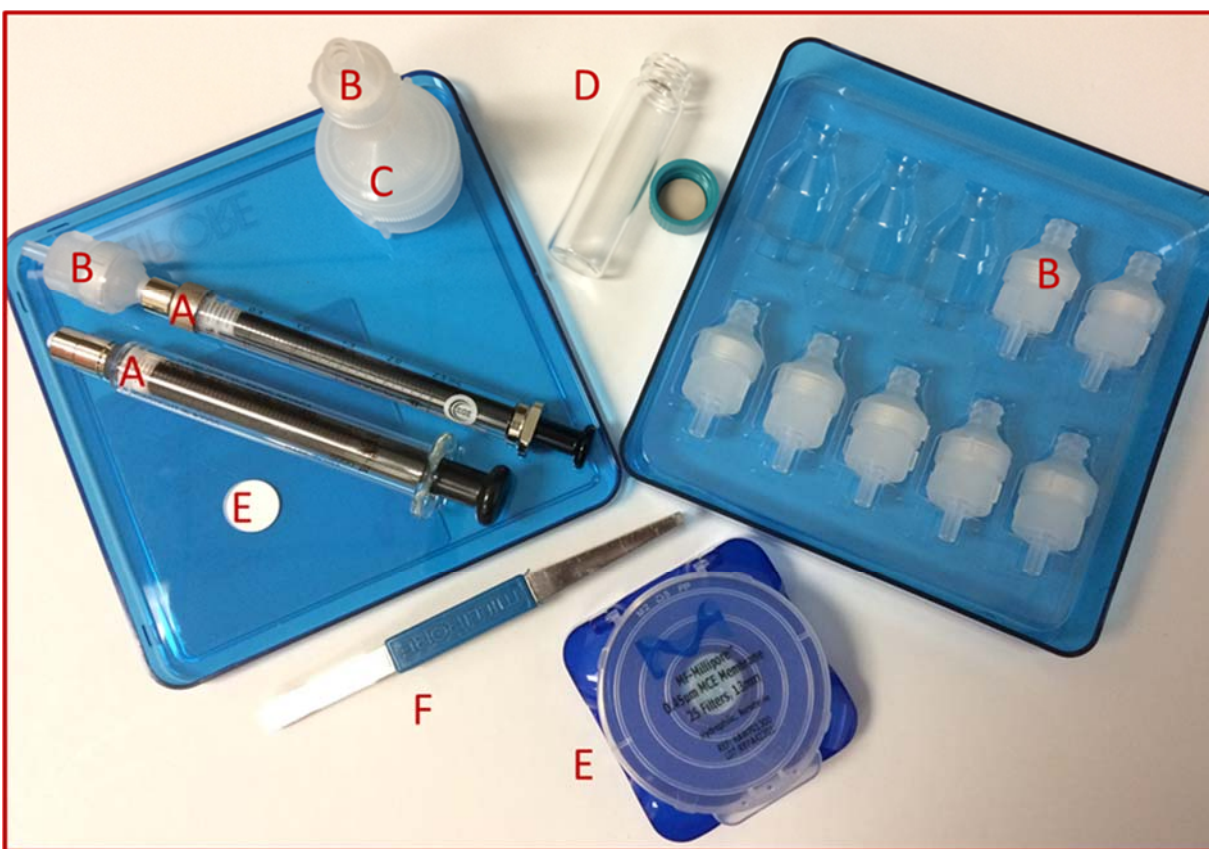


Figure 2: Items used for Mercury Particulate Analysis are Gas Tight Glass Syringe (A), Luer Lock Filter Casing (B) that is Opened to Remove the Filter Paper (E) with Tweezers (F) for Analysis, and the Filter Casing Holder (C).

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

2.2 Quartz Fiber Filter Columns

A quartz filter column was assembled to provide expanded options for the physical separation of particulates from liquid samples. The column (Figure 3A) was configured to fit on the autosampler of the DMA-80. The empty column (Swiss Innotech AG, DMA00724, 10 mm diameter x 30 mm length quartz tube with one end flared inward) was packed with approximately 0.14g (0.12 to 0.17g) Fine Quartz Wool (Chemglass Life Sciences). Quartz wool was selected as the filter media because previous data from De La Rosa demonstrated that ceramic fiber felt absorbed significant quantities of both inorganic and organomercury species from solution. The handling operations (cutting, weighing and packing) for the quartz wool were performed in the hood to avoid creation of dust. The quartz wool was compressed with a column filling and packing tool (Figure 3; Swiss Innotech DMA00724 DMA quartz column filling and ejection tool set). After packing, each column was rinsed 4 times using deionized water and repacked tightly with the filling tool after each rinse to consolidate the quartz wool. The packed columns were placed on the DMA and cleaned at 700°C to eliminate any mercury background prior to use. The quartz fiber filter columns were then ready for testing the retention of mercury containing particulates using the same approach previously employed for the membrane filters (i.e., sorption of various mercury species onto silica thiol, filtration, and direct pyrolysis/analysis of the filter on the DMA-80).

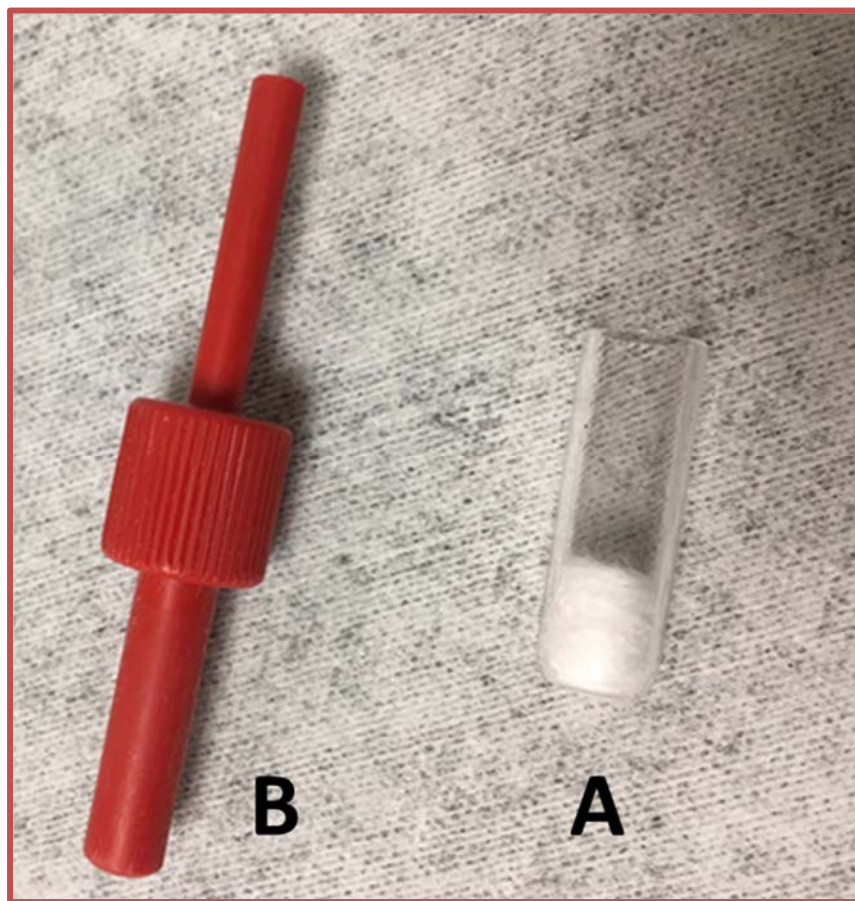


Figure 3: Packed Quartz Fiber Filter Column (A) and the Packing Tool (B) used to Prepare 10 mm Diameter Columns Configured for Use in the DMA-80 Autosampler Carousel

2.3 Particle Size Analyzer

To assess the filtration performance of the quartz fiber filter columns, the particulate removal efficiency was evaluated for standard solutions containing glass particles of 1.5 μm and 50 μm nominal diameters. These tests were performed using a Microtrac S3500 particle size analyzer. Procedures for the operation of the Microtrac S3500 Particle Size Analyzer (L16.1 ADS-1126 Revision 4¹⁰) comply with Manual 1Q, Procedure 2-7, QA Program Requirements for Analytical Measurement System. The operation and setup of the Microtrac S3500 particle size analyzer for this study is described in more detail in Appendix C.

3.0 Results and Discussion

3.1 Additional Scoping Studies Using Quartz Fiber Column Filters

3.1.1 *Mercury Capture Performance*

The mercury mass balance data for the quartz fiber filter column tests are presented in pairs for each analysis/condition (Figure 4). The inorganic standard (1000 mg/L Hg in 2 wt% nitric acid) was purchased from HPS and the monomethylmercury standard (1 ppm in 0.5 vol% acetic acid and 0.2 vol% HCl) was purchased from Brooks Rand. Independent solutions of monomethylmercury and inorganic mercury were tested on the potential filtering media ceramic felt and quartz fiber. Within each pair, the captured (particulate) mercury is shown in darker color and filtrate in lighter color. Inorganic mercury analyses are depicted in brown / yellow. Monomethylmercury is depicted in dark green / light green. The data are organized with soluble mercury (no particulates) on the left and particulate mercury on the right. The left most data pair used a sintered ceramic felt as the filtering material (instead of the quartz fiber) – the ceramic felt sorbed a significant fraction of the soluble mercury, confirming the earlier scoping tests by De La Rosa.⁴ The remaining tests for soluble mercury with the quartz fiber confirmed that there is minimal uptake or sorption of mercury on the quartz fiber filter material.

For the particulate samples where Si Thiol is added, most of the mercury should be collected by the filter. The target ranges shown are based on the earlier work of De La Rosa⁴ with membrane filters. All the measurements for the quartz column filters were within the target ranges, indicating that the quartz fiber filters are effective in filtering the tested 50 μm Si Thiol sorbent particles. The data indicate that, coupled with DMA, the quartz fiber filter columns are an effective and viable mercury analysis protocol for those particles that are captured by the filter. The raw data for all the test analyses and calculated mass balances for each data pair in the quartz fiber mercury capture tests are provided in Table 1.

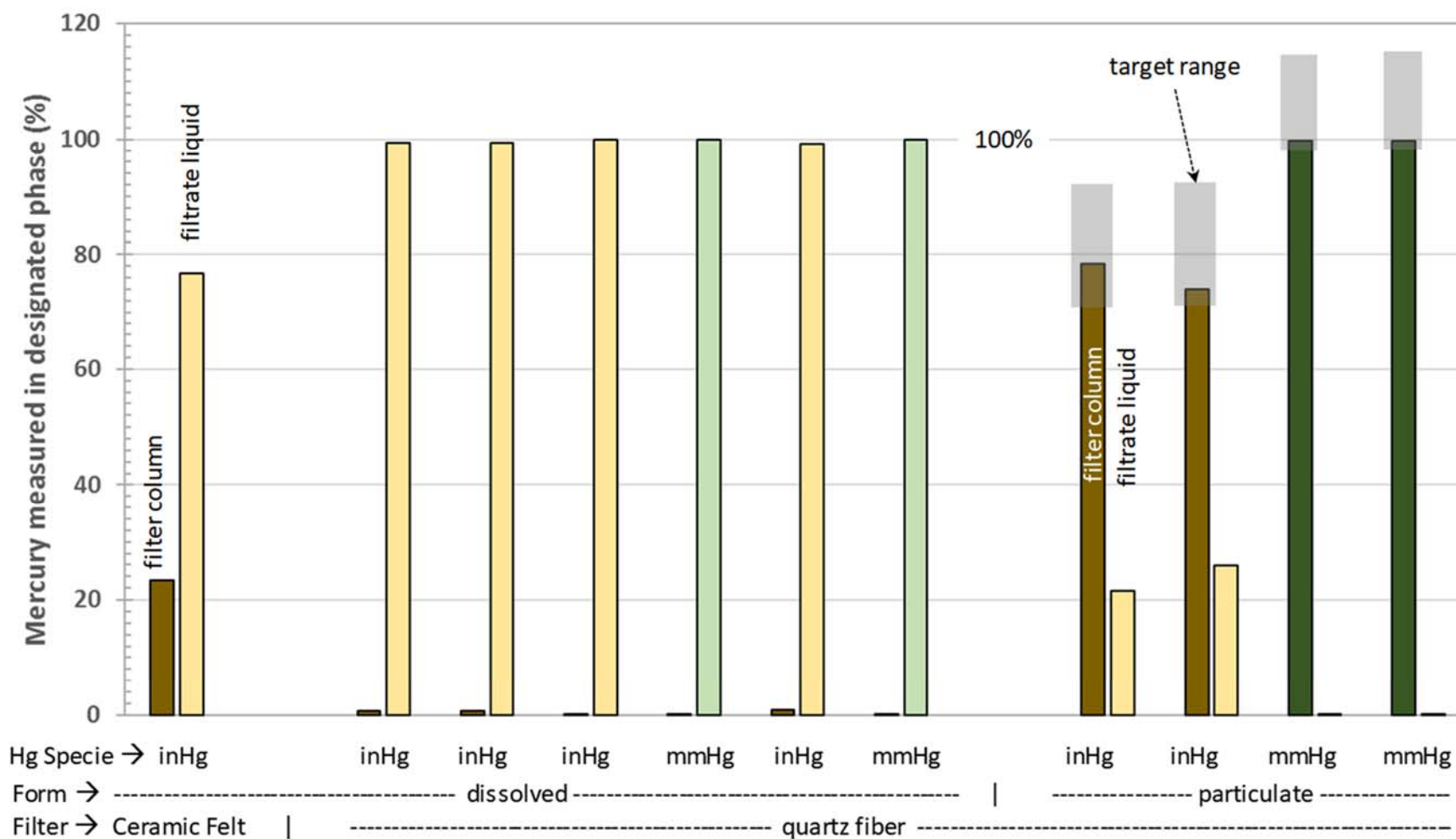


Figure 4: Graphical Summary of Mercury Mass Balance Data for Quartz Fiber Filter Columns

(species codes: inHg = inorganic ionic mercury, mmHg = monomethylmercury)

Table 1: Mercury Mass Balance Data from Tests of Quartz Fiber Filters

Analyte		Filter Material and Loading		Filter Rinse		Measured Hg		Hg Distribution		Recovery
Analyte	physical form	Filter Material	total ng as Hg	Solution	Volume (mL)	Column (ng)	Solution (ng)	% on filter	% in solution	% of total
inorganic Hg	dissolved	ceramic felt	1000	2% nitric acid	19	199	654	23.33	76.67	85
inorganic Hg	dissolved	quartz fiber	1000	2% nitric acid	19	6.6	972	0.67	99.33	98
inorganic Hg	dissolved	quartz fiber	1000	2% nitric acid	19	6.6	926	0.70	99.30	93
inorganic Hg	dissolved	quartz fiber	1000	deionized water	19	0.6	876	0.06	99.94	88
monomethyl Hg	dissolved	quartz fiber	1000	deionized water	19	0.2	952	0.02	99.98	95
inorganic Hg	dissolved	quartz fiber	1000	2% nitric acid	9	8.6	988	0.86	99.14	100
monomethyl Hg	dissolved	quartz fiber	1000	deionized water	9	0.4	1050	0.03	99.97	105
inorganic Hg	mixed (SiThiol)	quartz fiber	100	2% nitric acid	19	80.1	22	78.45	21.55	102
inorganic Hg	mixed (SiThiol)	quartz fiber	100	2% nitric acid	19	79.9	28	74.05	25.95	108
monomethyl Hg	particulate (SiThiol)	quartz fiber	50	2% nitric acid	19	46.7	< 0.1	99.79	< 0.2	94
monomethyl Hg	particulate (SiThiol)	quartz fiber	50	2% nitric acid	19	50.9	< 0.1	99.80	< 0.2	102

3.1.2 Filtration Performance of Quartz Fiber Columns

To quantitatively assess the performance of the quartz fiber filter columns, a series of tests were performed by passing through the filters standard solutions containing two different particle sizes (1.54 μm nominal diameter [“small”] and 58 μm nominal diameter [“large”] glass particles). The objective of these tests was to determine if the filtration performance of this filter is comparable to a standard-reference membrane filter such as a 0.45 μm MCE or PES filter.

The solutions were filtered using the quartz fiber filter columns. The particles in the standard solution and the remaining particles in the filtered samples were counted using a Microtrac 3500 particle size analyzer. The removal efficiencies for each particle size were calculated by comparing the baseline standard and filtered solution. The data are summarized in Figure 5. A detailed discussion of the test protocol, the raw data and example instrument reports are provided in Appendix C.

The testing indicated that the quartz fiber columns are effective for collecting large particles (particles $\geq 50 \mu\text{m}$ diameter were $>99\%$ removed from solution); however, the setup does not effectively remove small particles (removing only 20 to 30% of the 1.5 μm particles). Thus, the quartz fiber filter column is not equivalent in performance to a standard membrane filter. Nonetheless, the quartz fiber column filters are compatible with the DMA-80 and could be used as a prefilter (in front of a membrane filter) for turbid samples that contain large particles (to minimize the potential for clogging a membrane filter). The resulting quartz columns and membrane filters can be combined (filter rolled and placed inside column) and placed on the DMA-80 for composite quantification of total mercury in the particulate phase.

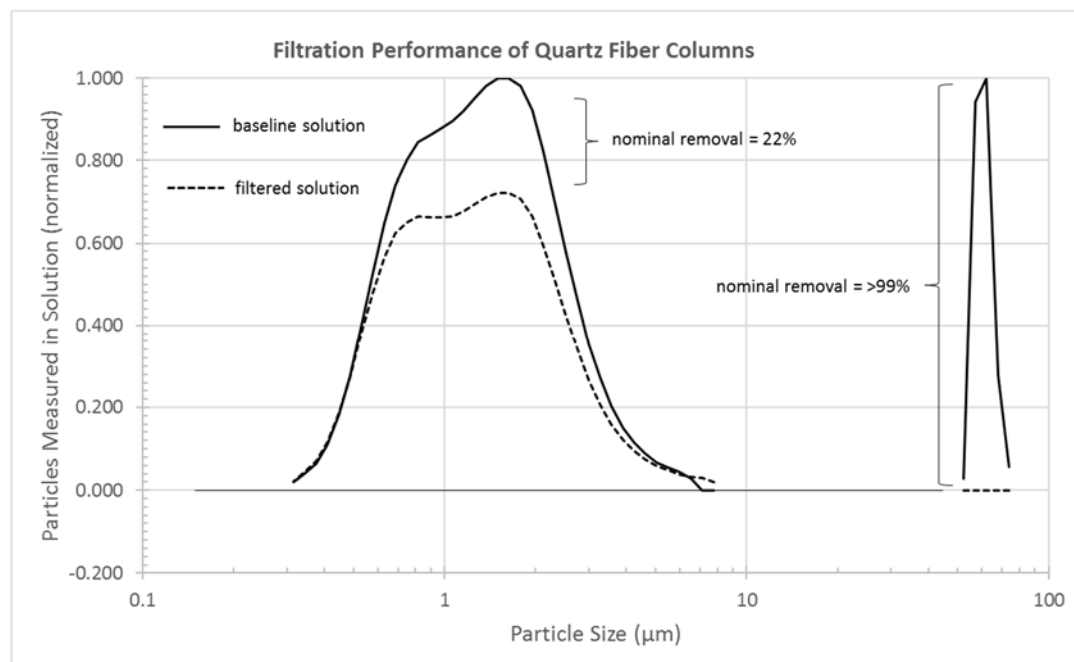


Figure 5 Summary of Particulate Removal Performance for “Small” and “Large” Particles by SRNL-Fabricated Quartz Fiber Filters

3.2 Deployment Testing for LWS System (Radioactive) Samples

SRNL analyzed soluble and particulate samples on a DMA-80 instrument housed in a contamination area (CA) containment unit/fume hood, shown in Figure 6. The DMA instrument rests on a platform¹¹ with low profile locking wheels that allow the option of moving the instrument to any location on the hood floor for customizing space for sample analysis and other radiological activities. Thus, the same hood was used to dilute, filter, and analyze Liquid Waste System (LWS) samples.

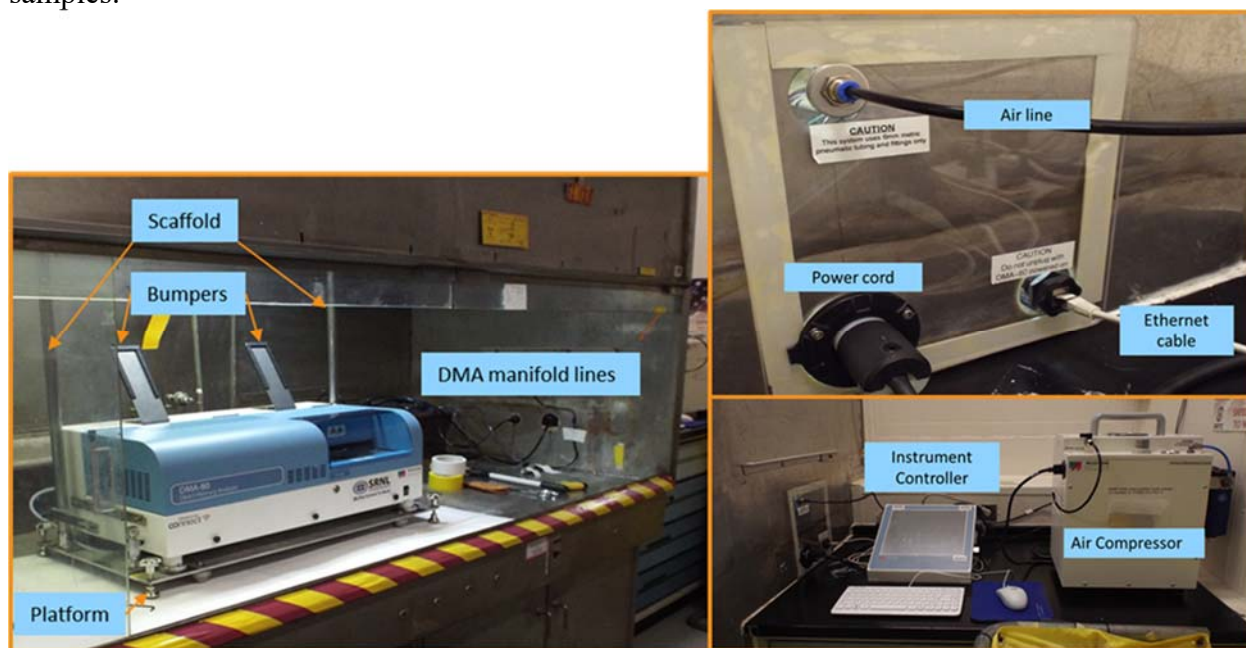


Figure 6: Radiological Containment Unit (CU) Housing a DMA-80 for Analyzing Radioactive Mercury Samples and Work Area for Sample Preparation.

The first (Cust. ID = 1Q19 WAC Tk 50) and second quarter (Cust. ID = 2Q19 Tk 50) Tank 50 LWS sample was quantified according to schema shown in Figure 7. The LWS samples were diluted with deionized water (1:100, Appendix B; R&D directions) to within the calibration curve (0.01 to 1 mg/L) and/or to a radiological dose level that is safe for handling (<5 mRem/hr WB). From the diluted sample, a 0.5 mL of LWS sample was passed through a premoistened filter paperⁱⁱⁱ to trap particulate mercury followed by 4.5 mL of DI water (DF 1:10) rinse. This rinse does not significantly change the pH which remains basic but it does remove soluble mercury and most particulates below 0.45 μm . The filter paper containing the particulate mercury was carefully placed into a sample boat while an aliquot (0.1 mL) of filtrate was absorbed onto Additive B^{iv} preloaded in a sample boat. Figure 7 shows the loaded sample boats. Table 2 summarizes the results of same day triplicate analyses (n = 3) for total, soluble and particulate mercury from SRNL and an outside laboratory.

ⁱⁱⁱ The 0.45 μm cellulose based filter paper is rated to trap 98% of particles nominally at 0.45 μm . Additionally, particles are trapped in the fibrous layers allowing for strong particle retention during manipulation of the filter paper from the filter holder to the sample boat.

^{iv} See page 4.

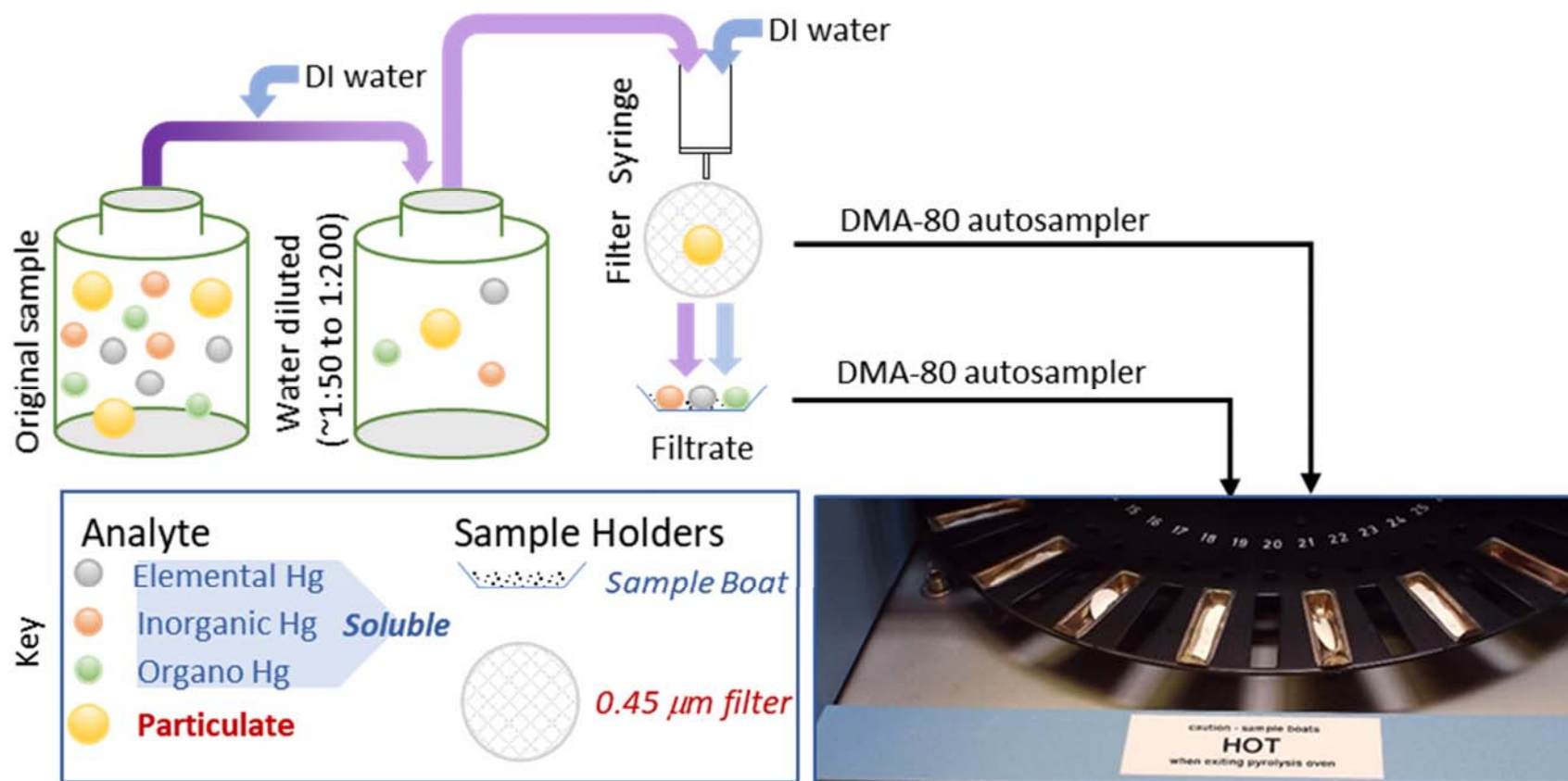


Figure 7: Sample Analysis Schema for Particulate and Soluble Mercury Analysis on the Radiologically Contained DMA-80.

Tank 50 is an in-use tank that received decontaminated salt solution from the Modular Caustic Side Solvent Extraction Unit (MCU) and feeds the liquid to the Saltstone Production Facility (SPF). Quarterly measurements of soluble and calculated particulate mercury concentration of Tank 50 samples by the offsite laboratory Eurofins (2015 to 2019) show ranges for each mercury analysis. Our measured values fall well within these ranges. As summarized in Table 3, the calculated particulate mercury values range from 3.5% to 29.2% of the measured total mercury values and the measured soluble mercury values range from 70.6% to 96.5% of the measured total mercury values.

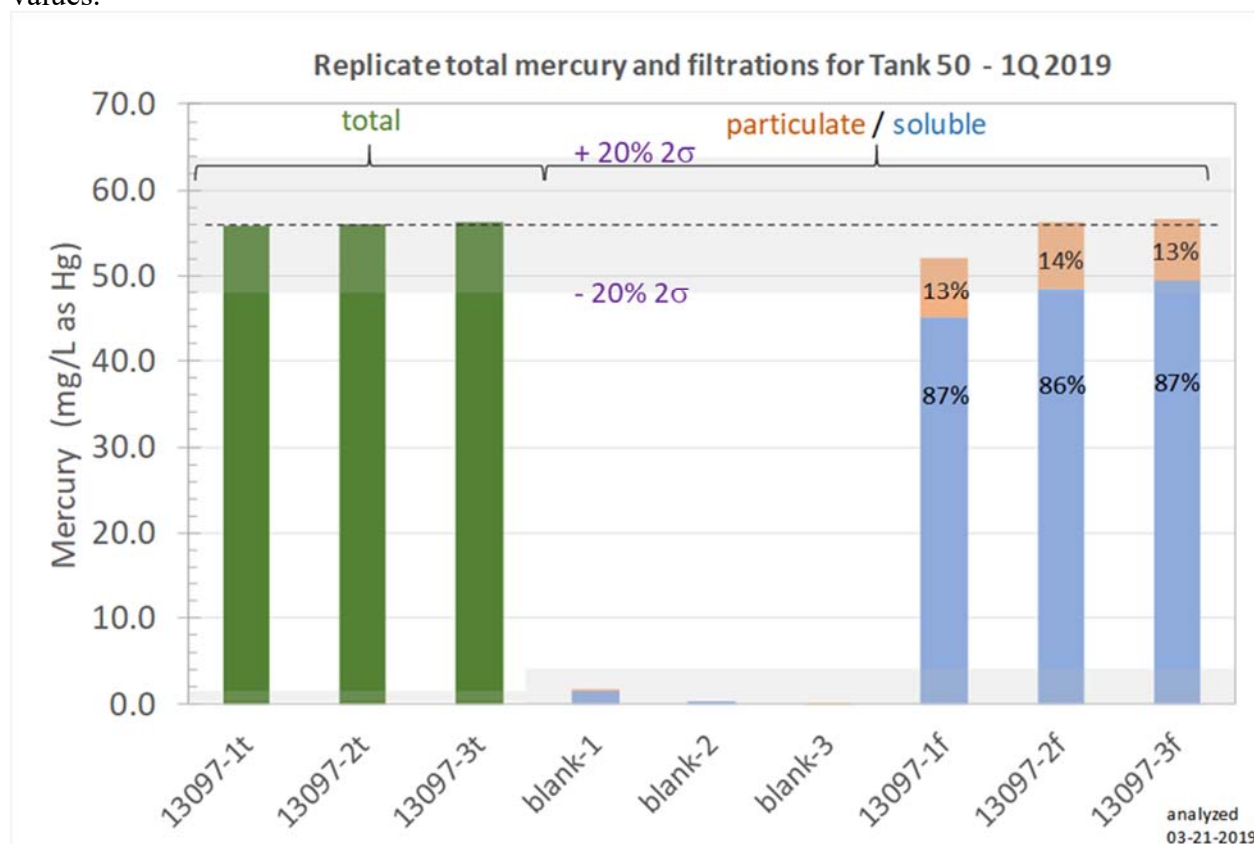


Figure 8: Triplicate Same Day Analyses ($n = 3$) of Tank 50 for Soluble, Particulate, and Total Hg. Note blank 1 is slightly elevated due to trace mercury carryover from a sample analysis.

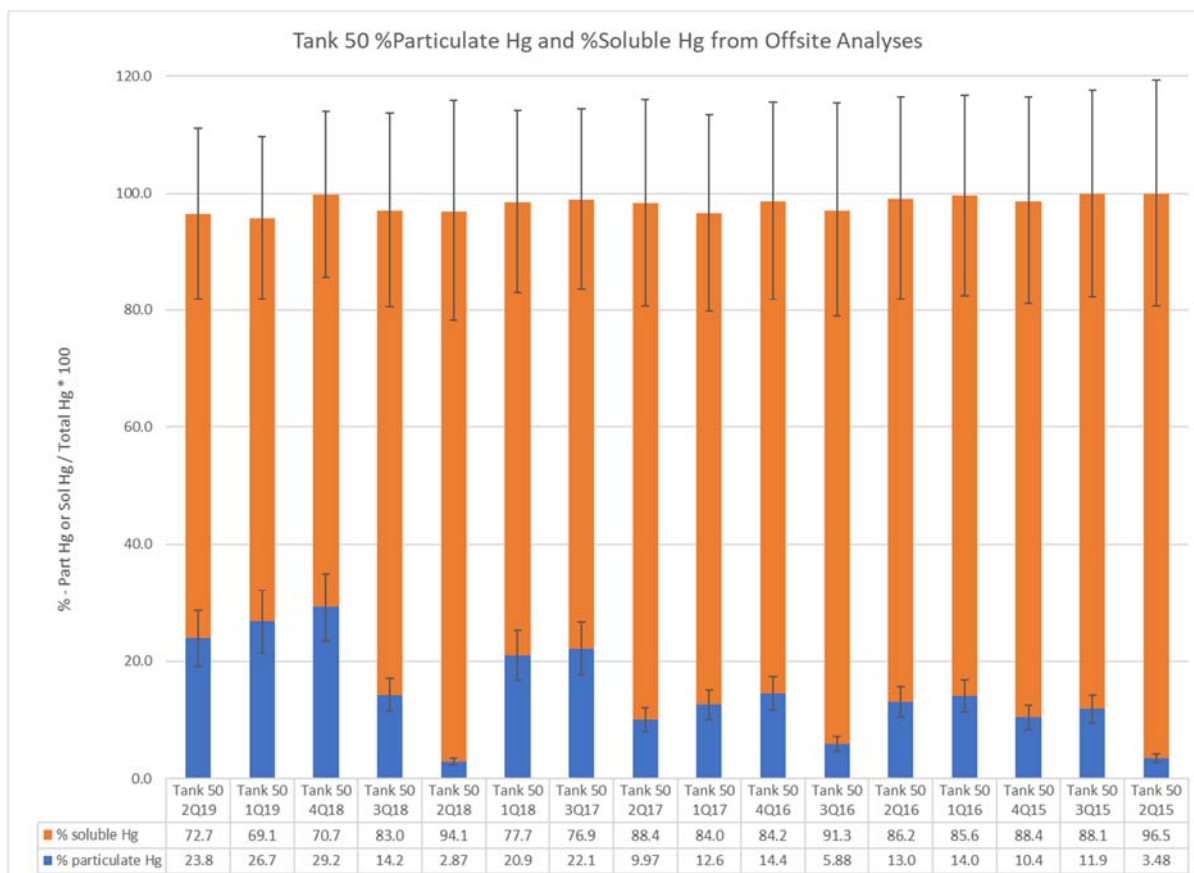
More convincingly, the SRNL soluble and particulate mercury values when summed (55.1 mg Hg/L) closely match the measured SRNL total mercury value (55.0 mg Hg/L). This summation method is one way to quality check the soluble mercury and particulate mercury data where the calculated total mercury value should be within $\pm 20\%$ (2σ) of measured total mercury value⁹. Additionally, the offsite measured¹² soluble Hg value of 46.6 mg Hg/L ($\pm 20\%$ 2σ) for first quarter 2019 Tank 50 closely matched the SRNL measured soluble mercury value of 47.8 ($\pm 20\%$ 2σ). SRNL measured particulate value of 7.26 mg Hg/L ($\pm 20\%$ 2σ) was lower than the calculated particulate value derived from the offsite data of 18 mg Hg/L. The 18 mg Hg/L particulate mercury value was calculated from three measurements with uncertainties of $\pm 20\%$ 2σ and the true accuracy is not readily found as described in Appendix A. All mercury results are summarized in Table 2.

Table 2: SRNL and Offsite Laboratory Analysis of Mercury ($\pm 20\% 2\sigma$)

1 st Quarter 2019 Tank 50 Hg, mg Hg/L				
#	Total	Soluble (filtrate)	Particulate (filter)	Soluble + Particulate Total (Calculated)
1	55.9	45.5	6.89	52.4
2	56.1	48.6	7.69	56.3
3	56.2	49.5	7.21	56.7
AD Mean	56.1	47.9	7.3	55.1
Eurofins Mean	67.4	46.6	18 (calculated)	64.6

2 st Quarter 2019 Tank 50 Hg, mg Hg/L				
#	Total	Soluble (filtrate)	Particulate (filter)	Soluble + Particulate Total (Calculated)
1	63.9	53.7	7.86	61.6
2	62.2	58.4	6.87	65.3
3	64.5	57.6	6.76	64.4
AD Mean	63.5	56.6	7.2	63.7
Eurofins Mean	63.0	45.8	15 (calculated)	60.8

Table 3: Tank 50 %particulate Hg (calculated) and %soluble Hg (measured) by Eurofins



4.0 Conclusions

A facile and robust method was developed, tested and deployed for quantifying particulate total mercury and soluble total mercury in dilute liquid samples such as the samples generated by diluting the SRS LWS. The deployed methods rely on direct mercury analysis – and the associated capability for matrix independent quantification of total mercury in solids and/or liquids (i.e., any sample that can be introduced into the instrument oven for pyrolysis to release all mercury for measurement). The matrix independence allows for measurement of the starting sample, the collected particulates and the filtrate liquid, thus facilitating a mass balance quality check. Dependable total mercury measurements have been previously demonstrated with an uncertainty of $(\pm 20\% 2\sigma)^9$ and are used in this report as a quality check for the summation of directly measured soluble and particulate mercury.

Key features of the particulate-soluble method deployed for radioactive sample analyses include:

- Uses small volumes of sample -- minimizing generation of waste
- Minimizes sample processing steps and sample handling -- protective of workers (ALARA) and improved data quality
- Uses syringe filters -- avoiding vacuum filtration and the potential loss of volatile species
- Uses small diameter filters (13 mm nominal to 25 mm if needed to avoid clogging) that minimize waste
- Uses small disposable poly filter holders -- eliminates the need to clean filter holders and assist in waste control and minimization
- Provides flexibility for a range of starting concentrations, particulate-soluble ratios, and sample matrix conditions

The deployed particulate-soluble mercury method is supported by extensive scoping studies and related documentation. These studies demonstrated that such physical process with the following characteristics can be leveraged to measure particulate and soluble mercury by direct analysis: a) effectively separates particulates from soluble species, b) filter media does not sorb or capture soluble mercury, and c) filter media is compatible with DMA-80 autosampler carousel (e.g., column) or sample boat (e.g., filter membrane). The research demonstrated that the selected membrane filters do not sorb soluble inorganic mercury or soluble monomethylmercury. The research documented that fabricated quartz fiber columns do not provide the filtration performance of a membrane filter, but the columns do provide an option for prefiltration of turbid samples that minimizes the potential for filter clogging. This method of analysis is recommended for determining the concentrations of soluble and particulate mercury in LWS samples with trace amount of solids based on study results and comparison with an outside laboratory.

5.0 References

1. Brown, M. K. *Waste Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility*; X-SD-Z-00001_Rev 18; 2018; p 42.
2. Bannochie, C. J.; Fellingner, T. L.; Garcia-Strickland, P.; Shah, H. B.; Jain, V.; Wilmarth, W. R., Mercury in Aqueous Tank Waste at the Savannah River Site: Facts, Forms, and Impacts. *Separation Science and Technology* **2017**, 53 (12), 1935-1947.
3. Boggess, A. J.; White, T. L.; Jones, M. A.; Bannochie, C. J. *Task Technical and Quality Assurance Plan: Speciation of Mercury in SRS Tank Samples*; SRNL-RP-2016-00788, Revision 1; Savannah River National Laboratory: Aiken, SC, 2018.
4. De La Rosa, K.; Looney, B. B. *Mercury Speciation via Direct Mercury Analyzer*; Florida International University (FIU): Florida International University (FIU), 2018; pp 1-21.
5. White, T. L., Electronic Notebook Particulate and Soluble Hg. In *Particulate and Soluble Hg*, 2019.
6. *Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry*; US Environmental Protection Agency: Washington, DC, 2007.
7. Gray, R. J. *SRNL Mercury Speciation Capability Development*; X-TTR-H-00069_Revision 1; 9/13/2018, 2018.
8. White, T. L. *Electronic Laboratory Notebook: Total Hg Studies*; ELN-a0169-00057-06; Savannah River National Laboratory: Aiken, SC, 2018.
9. White, T. L.; Brown, L. W.; Looney, B. B.; Jones, M. A. *Total Mercury Analysis Comparison*; SRNL-STI-2019-00056; Savannah River National Laboratory: 2019; pp 1-21.
10. Savannah River National Laboratory *Procedure for Operating Non-radioactive and Radioactive Microtrac S3500 Particulate Size Analyzers*; L16.1 ADS-1126 revision 4; Savannah River National Laboratory, 2019; pp 1-14.
11. White, T. L.; Brown, L. W.; Looney, B. B. *Total Mercury Analysis in Radioactive Wastes using a Direct Mercury Analyzer with Additive*; SRNL-L4130-2019-00005; Savannah River National Laboratory, 2019.
12. Bannochie, C. J. *Results of Hg Speciation Testing on the 1Q19 Tank 50 Sample*; SRNL-L3300-2019-00018 Rev. 0; Savannah River National Laboratory, 2019.

Appendix A: Basis for SRNL Schema Development Strategy: Particulate and Soluble Mercury

For most LWS samples, the baseline method of calculating the particulate concentration by difference between total and filtrate is a strategy that relies on subtracting two large numbers to obtain a small number. Given the expected RSD of the two large numbers, the estimated particulate fractions by difference could vary widely. Furthermore, the vacuum filtration step requires additional assumptions about loss of purgeable species such as elemental and dimethyl mercury. A more robust method would quantitatively collect enough particulate material for direct measurement.

For example: if a LWS sample (circa 100 mg/L total Hg diluted 500x to 0.2 mg/L or 200 ng/mL) containing 2% each particulate/elemental/dimethyl is analyzed by the baseline approach, the particulate would be calculated (in units of ng/mL) as:

Assuming total mercury in dilution is measured as 200 ng/mL

Assuming purgeable (elemental and dimethylmercury) in the dilution have been independently measured as 8 ng/mL

Therefore:

$$\begin{aligned}\text{Particulate concentration in dilution} &= \text{total} - \text{soluble} + \text{purgeable} \\ &= 200(+/- \text{error}) - 188(+/- \text{error}) + 8(+/- \text{error})\end{aligned}$$

(note that these concentrations would be multiplied by DF to relate to the original solution...)

Alternatively:

If 10 mL of the diluted sample is pressure-filtered through a 0.45 um filter and 40 ng was collected on the filter. (easily and accurately measured on the DMA-80). The resulting particulate value would be 4(+/- error) ng/mL. The filtrate would also be measured as a standard liquid sample (adjusted for any additional dilution by filter rinse water). This approach would improve data quality and minimize the assumptions related to volatile mercury forms and would allow for an independent mass balance quality check. The RSD error on the particulate fraction would be independent of the other measurements and scaled to the measured value (e.g., if the particulate fraction is small, its RSD would be equally small). This is the SRNL preferred strategy.

If there is reason to do any of the fractions by difference, improved performance would be provided by calculating the soluble fraction, i.e., soluble = total – particulate. In this case the calculation is simplified, as it is based on subtracting a typically small number from a large number with minimal assumptions about volatile mercury forms. The relatively small RSD error for the particulate fraction would not impact the quality of data for the much larger soluble fraction.

Appendix B: R & D Directions for Soluble and Particulate Mercury

R&D Directions → → → → → → → →		Reference: PS-PL-AP-4006
1. → PI: Brian Looney/Leigh Brown → → 2. → Task Title: Particulate and Soluble		
3. → Date: → Customer Name: → Analyst: → Speed Chart: 0203lat81		
4. → Work Group and Location: Analytical Development, Bldg. 773A, Lab B143		
5. → Applicable Reference Documents: L1 Manual, AD procedure L16.1 ADS-1580, HAS SRNL-ACT-0677		
Equipment — 5.0 mL gas tight luer lock syringe for pipetting through a polypropylene filter holder with a 13 mm diameter filter (Millipore SX0001300 or equivalent), other pipettes, vial holder/block, stand/clamp, glass vial, and DMA sample boat		
Chemicals — DI water, optional dilute (2-5%) nitric acid solution		
Hazards —		
Step	Hazards	Controls
Sample Prep and Instrument Operation	Possible splash, spill and/or exposure to vapors outside of containment.	Sample aliquot not to exceed 1.0 mL unless directed by Task Supervisor. Handle pipetting through filter operation in the containment unit behind the 6 inch zone with proper PPE. Pay attention and use caution when pressing the syringe plunger looking for leaks.
Particulate		
→ Label 16 mL glass vial		
→ Load 13 mm filter membrane into filter holder (outside hood if possible) by: <ul style="list-style-type: none"> a. → Add a drop of DI water onto filter holder screen b. → Using tweezers, place filter membrane centered onto screen in filter holder c. → Check filter holder top to make sure silicone "O-ring" seal is in place d. → Assemble filter holder — visually check to make sure filter membrane stayed in place 		
→ Out side hood use a 5 mL syringe to rinse the filter paper with 4.5 mL of DI water (preloads dead volume) <ul style="list-style-type: none"> a. → Remove plunger from syringe and attach barrel to filter holder b. → Pipette 4.5 mL of water into syringe barrel c. → Reinsert plunger and gently press to force liquid through the filter d. → Disconnect syringe from filter holder 		
→ Set up labelled receiving vial and stage filter holder and syringes (Loading sample) <ul style="list-style-type: none"> a. → Remove plunger from 2.5 mL syringe and attach barrel to filter holder b. → Pipette 0.5 mL of sample into syringe barrel (adjust volume as appropriate) and collect any filtrate in vial c. → Reinsert plunger and gently depress plunger until sample is through the filter. <i>use caution — if sample is not flowing or stops flowing, do not try to force by pressing hard (stop work — clean up and start over with larger 25 mm filters. If the solution is still requiring you to press hard, stop work and contact task supervisor).</i> d. → Disconnect 2.5 mL syringe from filter holder and set aside for cleaning 		
→ Remove plunger from 5 mL syringe, attach 5 mL syringe barrel to filter holder, and pipette 4.5 mL of DI water into the syringe body (adjust as appropriate)		
→ Reinsert and gently depress plunger until rinse water is pushed through filter — <i>use caution — if sample is not flowing or stops flowing, do not try to force by pressing hard (stop work — clean up and develop an alternative plan).</i>		
→ Prepare filter for analysis: <ul style="list-style-type: none"> a. → Remove syringe b. → Open filter holder c. → Using tweezers, fold filter in half (trapping particulates inside fold) d. → Using tweezers roll the folded filter and place in a clean nickel sample boat e. → Place boat and filter in a labeled bag f. → Analyze boat on the DMA — if filter blanks are similar to additive a blanks, then use the standard 3mL liquid sample calibration. The concentration is related to the original sample as follows: particulate concentration (ng/mL) = original DF from the tank * ng on the filter / volume of sample filtered (e.g. for method above → 100DF * ng on filter from DMA / 0.5 mL) 		

____ Repeat for all samples and blanks. Analyze samples same day. ¶

¶

Soluble¶

____ Analyze filtrate on the DMA using the standard SRNL method for liquid samples — adjust dilution for added
~~rinse water~~ (e.g., if initial DF from the tank was 100 and we add a DF of 10 (0.5 mL in 5 mL), then the final DF would be
1000)¶

Appendix C: Particle Size Analyzer used to Generate Data for the Quartz Fiber Column Tests

The Microtrac S3500 particle size analyzer uses a wet sample delivery controller (re-circulator) to disperse the sample uniformly in a fluid and deliver the sample to the analyzer. This wet sample delivery controller in its basic form consists of a reservoir where the sample is introduced, a fluid pump, a valve to the drain system, and the necessary tubing connections to the analyzer. The flow through the analyzer sample cell is always from the bottom to the top. The analyzer consists of the sample cell and three lasers (improves resolution) and two silicon photodiode array detectors. The figure depicts the top-down view showing the positions of the lasers and detectors

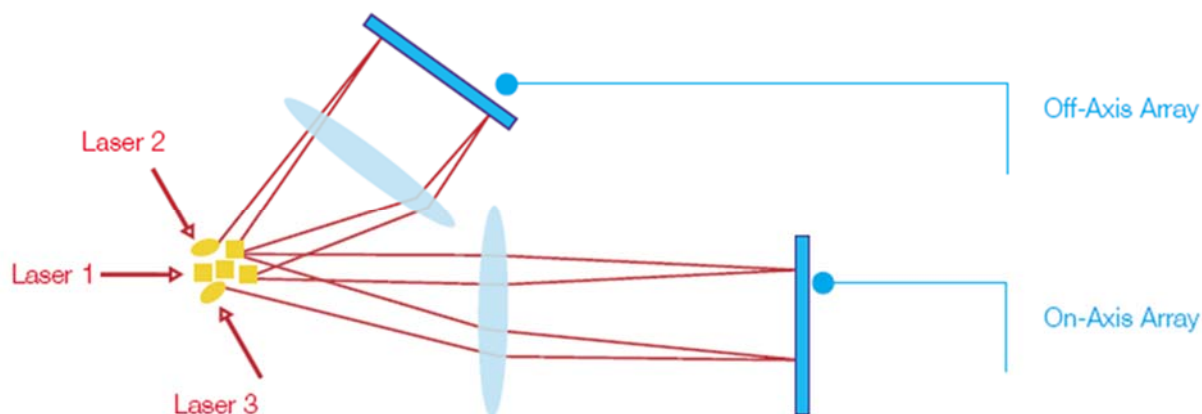


Figure 9: Top-Down View Showing the Optical Configuration of the Microtrac S3500

A laser beam is projected through the sample cell that contains a stream of moving particles suspended in a liquid. Light rays that strike a particle are scattered (Mie scattering, where the particle radius \approx laser wavelength.). The scattered light forms an angular pattern which is measured by the two photodiode arrays. Electrical signals proportional to the measured light intensities are then processed by the computer using modified Mie calculations for non-spherical particles to form a multichannel histogram of the particle size distribution.

The required mass to obtain an average sample loading index on the Microtrac S3500 varies with particle size, i.e., the finer the particles size distribution, the smaller the mass needed. A complete list of all the instrument operating parameters can be found in the following table.

Table 4: Microtrac S3500 Instrument Parameters for the Two Microtrac Standards

	BCR66 Microtrac STD	Glass-1 Microtrac STD
Transparency	Transparent	Transparent
Particle Shape	Irregular	Spherical
Particle Refractive Index	1.54	1.51
Number of Channels	100	100
Progression	Geom 8 Root	Geom 8 Root
Residuals	Disabled	Disabled
Filter	Enabled	Enabled
Fluid	Water	Water

Two filtration performance test campaigns were run. The first scoping test installed the quartz fiber filter column in-line within the Microtrac S3500 flow system. The flow rate for this scoping test (>40 mL/second) was higher than realistic operating flow rates. A second reference run was performed using realistic flow rates (1 to 2 mL/second) on the benchtop and the resulting solutions were run on the Microtrac 3500 (unmodified without the in-line filter setup).

Scoping Test

The Microtrac 3500 was modified by flaring the tubing (SRNL glass shop). This configuration allows the option of installing the quartz fiber filter in-line as shown in Figure 10. The filter was placed on the return line from the sample cell back to the re-circulator. The flowrate of the re-circulator for the sample delivery system was set at 42.25 mL/sec.



Figure 10: Photograph of Modified Circulation Line to Incorporate Option to Install Quartz Fiber Filter Column

Two standard solutions containing glass particles were used for the testing – BCR66 and Glass-1. BCR66 contained relatively smaller particles (1.26 μm median diameter) and Glass-1 contained relatively larger diameter particles (58 μm median diameter). Following the baseline runs, both standards were analyzed with the in-line quartz fiber filter. The removal effectiveness was calculated based on a change in the loading factor (which represents the overall mass of particles present). As shown below, the quartz fiber filter column removed approximately 18 to 27% of the small particles and 96% of the larger particles when ran at a high flow rate in the re-circulator. Sequential quantification of the BCR66 sample indicated that, after the initial filtration, the filter reached a steady state as the recirculating flow continued.

SCOPING TEST USING HIGH FLOWRATE RECIRCULATOR

	loading factor	overall removal efficiency (%)	notes:
BCR 66			
baseline	0.011	na	standard solution
recirculating filter (sample 1)	0.009	18	initial removal performance by filter in recirculator
recirculating filter (sample 2)	0.008	27	second analysis of recirculating sample
recirculating filter (sample 3)	0.008	27	third analysis of recirculating sample
Glass 1			
baseline	0.204	na	standard solution
recirculating filter	0.009	96	removal performance by recirculating filter

For the Benchtop testing, the quartz fiber filter column was operated at approximately 1 to 2 mL/sec. The two standards were applied to separate filter columns and rinsed with DI water (similar to a hypothetical analysis protocol). A separate baseline solution was prepared by diluting the standard using an equivalent quantity of DI water. The removal effectiveness was calculated by comparing the filtered samples and diluted standards based on the changes in loading factor. As shown below, the quartz fiber filter column removed approximately 22% of the small particles and >99% of the larger particles.

BENCHTOP FILTRATION AT LOW FLOWRATE

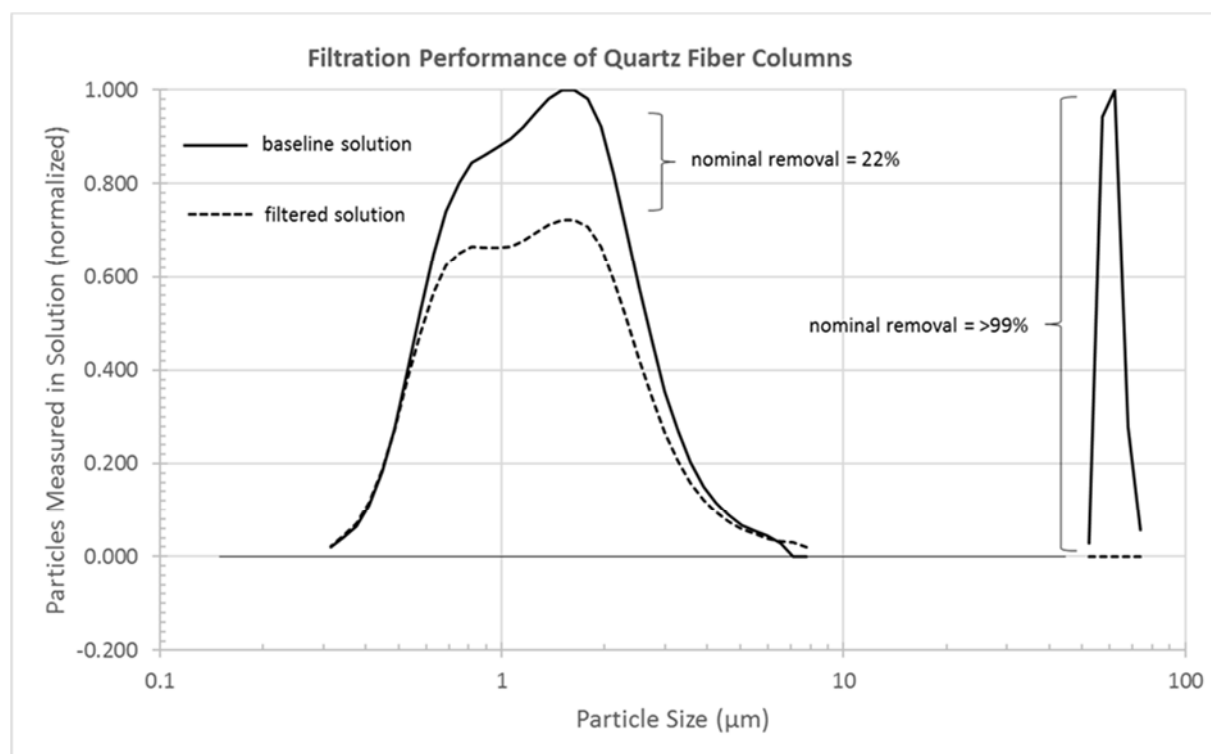
	loading factor	overall removal efficiency (%)	notes:
BCR 66			
baseline	0.009	na	standard solution - dilution matched to filter
benchtop filter	0.007	22	removal performance by benchtop filter application
Glass 1			
baseline	0.191	na	standard solution - dilution matched to filter
benchtop filter	0.000	> 99	removal performance by benchtop filter application

Appendix D: Summary of Quartz Fiber Column Filtration Tests

The testing indicates that the quartz fiber filter columns are effective for large particles (removing almost 100% if particles > approximately 50 μm) but the configuration does not effectively remove small particles (removing only 20 to 30% of the 1.5 μm particles). Thus, the quartz fiber filter column is not equivalent in performance to a standard membrane filter such as a 0.45 μm MCE or PES filter. Nonetheless, the columns are compatible with the DMA-80 and analysts could use the quartz fiber filter as a prefilter (in front of a membrane filter) for turbid samples that contain large particles (to minimize the potential for clogging a membrane filter). The resulting quartz columns and membrane filters can be combined (filter rolled and placed inside column) for composite quantification of total mercury in the particulate phase.

The interpretive spreadsheet and example raw instrument data are appended below.

As shown in the spreadsheet, the summary values graphed in the body of the report (and below) are from the benchtop filtration. The data are normalized based on the mass in the size bin with the highest fraction in each of the original standards (this bin is arbitrarily set to a graph value of 1 so that the two standards can be graphed on the same scale and to help the reader assess removal fraction when comparing the quantities of particles in each bin in the filtered sample compared to the baseline sample).



Note: same as Figure 5 in the text body.

The example raw data presented are for the Benchtop tests for the Glass-1 and BCR66 materials, respectively. The diluted baseline and filter data are presented for each standard. Raw data for all runs are maintained in the SRNL ELN T6751-00351-13.

BENCHTOP TEST

Nominal 1 um particles

loading factor = 0.007

Filtered			filtered normalized graph value
size	% in bin	raw norm	
7.78	0.14	0.11	0.020
7.13	0.21	0.16	0.029
6.54	0.23	0.18	0.032
6	0.27	0.21	0.038
5.5	0.34	0.26	0.048
5.04	0.42	0.33	0.059
4.62	0.53	0.41	0.074
4.24	0.68	0.53	0.095
3.89	0.87	0.68	0.122
3.57	1.13	0.88	0.158
3.27	1.47	1.14	0.206
2.999	1.9	1.48	0.266
2.75	2.43	1.89	0.340
2.522	3.03	2.36	0.424
2.312	3.68	2.86	0.515
2.121	4.25	3.31	0.595
1.945	4.75	3.69	0.664
1.783	5.06	3.94	0.708
1.635	5.16	4.01	0.722
1.499	5.17	4.02	0.723
1.375	5.09	3.96	0.712
1.261	4.98	3.87	0.697
1.156	4.84	3.76	0.677
1.06	4.76	3.70	0.666
0.972	4.74	3.69	0.663
0.892	4.74	3.69	0.663
0.818	4.75	3.69	0.664
0.75	4.66	3.62	0.652
0.688	4.46	3.47	0.624
0.63	4.04	3.14	0.565
0.578	3.42	2.66	0.478
0.53	2.74	2.13	0.383
0.486	1.94	1.51	0.271
0.446	1.33	1.03	0.186
0.409	0.83	0.65	0.116
0.375	0.51	0.40	0.071
0.344	0.32	0.25	0.045
0.315	0.16	0.12	0.022

loading factor = 0.009

Baseline			baseline normalized graph value
size	% in bin	raw norm	
7.78	0	0	0.00
7.13	0	0	0.00
6.54	0.16	0.16	0.03
6	0.25	0.25	0.04
5.5	0.3	0.3	0.05
5.04	0.37	0.37	0.07
4.62	0.49	0.49	0.09
4.24	0.64	0.64	0.12
3.89	0.84	0.84	0.15
3.57	1.13	1.13	0.20
3.27	1.5	1.5	0.27
2.999	1.97	1.97	0.35
2.75	2.56	2.56	0.46
2.522	3.21	3.21	0.58
2.312	3.93	3.93	0.71
2.121	4.57	4.57	0.82
1.945	5.12	5.12	0.92
1.783	5.45	5.45	0.98
1.635	5.56	5.56	1.00
1.499	5.56	5.56	1.00
1.375	5.45	5.45	0.98
1.261	5.3	5.3	0.95
1.156	5.11	5.11	0.92
1.06	4.98	4.98	0.90
0.972	4.88	4.88	0.88
0.892	4.79	4.79	0.86
0.818	4.69	4.69	0.84
0.75	4.46	4.46	0.80
0.688	4.12	4.12	0.74
0.63	3.61	3.61	0.65
0.578	2.92	2.92	0.53
0.53	2.24	2.24	0.40
0.486	1.53	1.53	0.28
0.446	1.01	1.01	0.18
0.409	0.61	0.61	0.11
0.375	0.36	0.36	0.06
0.344	0.22	0.22	0.04
0.315	0.11	0.11	0.02

Nominal 50 um particles

LF = 0

Filtered			filtered normalized graph value
size	% in bin	raw norm	
74	0.26	0	0.000
67.86	0.14	0	0.000
62.23	0.05	0	0.000
57.06	0.16	0	0.000
52.33	0.65	0	0.000

0.191

Baseline			baseline normalized graph value
size	% in bin	raw norm	
74	2.44	2.44	0.06
67.86	12.08	12.08	0.28
62.23	43.39	43.39	1.00
57.06	40.86	40.86	0.94
52.33	1.23	1.23	0.03



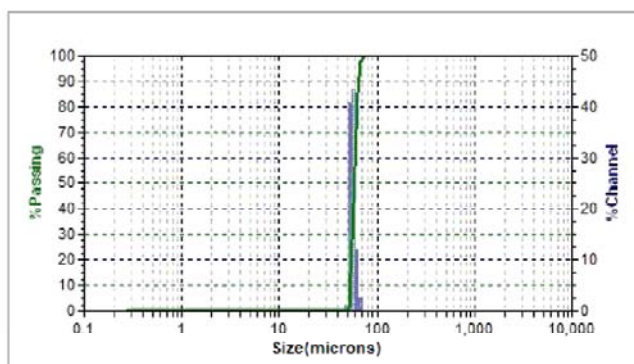
10.3.0
S3000/S3500

- Particle Size Analysis -

Glass-1
159242 Diluted

Data Acquired: 12/20/2018 - 10:10

Calculated: 12/20/2018 - 10:10



Peak Summary

Dia	Vol%	Width
57.89	100.0	7.75

Size(um)	%Tile

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
1408	0.00	100.00	74.00	2.44	100.00	3.89	0.00	0.00			
1291	0.00	100.00	67.86	12.08	97.56	3.57	0.00	0.00			
1184	0.00	100.00	62.23	43.39	85.48	3.27	0.00	0.00			
1086	0.00	100.00	57.06	40.86	42.09	2.999	0.00	0.00			
995.6	0.00	100.00	52.33	1.23	1.23	2.750	0.00	0.00			
913.0	0.00	100.00	47.98	0.00	0.00	2.522	0.00	0.00			
837.2	0.00	100.00	44.00	0.00	0.00	2.312	0.00	0.00			
767.7	0.00	100.00	40.35	0.00	0.00	2.121	0.00	0.00			
704.0	0.00	100.00	37.00	0.00	0.00	1.945	0.00	0.00			
645.6	0.00	100.00	33.93	0.00	0.00	1.783	0.00	0.00			
592.0	0.00	100.00	31.11	0.00	0.00	1.635	0.00	0.00			
542.9	0.00	100.00	28.53	0.00	0.00	1.499	0.00	0.00			
497.9	0.00	100.00	26.16	0.00	0.00	1.375	0.00	0.00			
456.5	0.00	100.00	23.99	0.00	0.00	1.261	0.00	0.00			
418.6	0.00	100.00	22.00	0.00	0.00	1.156	0.00	0.00			
383.9	0.00	100.00	20.17	0.00	0.00	1.060	0.00	0.00			
352.0	0.00	100.00	18.50	0.00	0.00	0.972	0.00	0.00			
322.8	0.00	100.00	16.96	0.00	0.00	0.892	0.00	0.00			
296.0	0.00	100.00	15.56	0.00	0.00	0.818	0.00	0.00			
271.4	0.00	100.00	14.27	0.00	0.00	0.750	0.00	0.00			
248.9	0.00	100.00	13.08	0.00	0.00	0.688	0.00	0.00			
228.2	0.00	100.00	12.00	0.00	0.00	0.630	0.00	0.00			
209.3	0.00	100.00	11.00	0.00	0.00	0.578	0.00	0.00			
191.9	0.00	100.00	10.09	0.00	0.00	0.530	0.00	0.00			
176.0	0.00	100.00	9.25	0.00	0.00	0.486	0.00	0.00			
161.4	0.00	100.00	8.48	0.00	0.00	0.446	0.00	0.00			
148.0	0.00	100.00	7.78	0.00	0.00	0.409	0.00	0.00			
135.7	0.00	100.00	7.13	0.00	0.00	0.375	0.00	0.00			
124.5	0.00	100.00	6.54	0.00	0.00	0.344	0.00	0.00			
114.1	0.00	100.00	6.00	0.00	0.00	0.315	0.00	0.00			
104.7	0.00	100.00	5.50	0.00	0.00	0.2890	0.00	0.00			
95.96	0.00	100.00	5.04	0.00	0.00	0.2650	0.00	0.00			
88.00	0.00	100.00	4.62	0.00	0.00						
80.70	0.00	100.00	4.24	0.00	0.00						

Summary

Data Item	Value
MV(um):	58.34
MN(um):	57.59
MA(um):	58.08
CS:	1.03E-01
SD:	3.87

Percentiles

%Tile	Size(um)
10.00	53.49
20.00	54.77
30.00	55.81
40.00	56.84
50.00	57.89
60.00	58.95
70.00	60.12
80.00	61.48
90.00	63.80
95.00	66.08

Distribution:	Volume	Run Time:	30 Sec	Fluid:	WATER		
Progression:	Geom 8 Root	Run Num:	Avg of 3	Fluid Ref. Index:	1.333	Loading Factor:	0.191
Upper Edge:	1408	Particle:	PM	Above Residual:	0	Transmission:	0.94
Lower Edge:	0.243	Transparency:	Transparent	Below Residual:	0	RMS Residual:	2.69E-03
Residuals:	Disabled	Part. Ref. Index:	1.51			Flow:	65 %
Num. Channels:	100	Part. Shape:	Spherical	Cell ID:	0595	Usonic Power:	N/A
Analysis Mode:	S3000					Usonic Time:	N/A
Filter:	Enabled	DB Record:	9058	Recalc Status:		Serial Num:	S3754
Analysis Gain:	N/A	Database:	C:\Program Files (x86)\Microtrac FLEX 10.3.0\Databases\psd-2012.MDB				

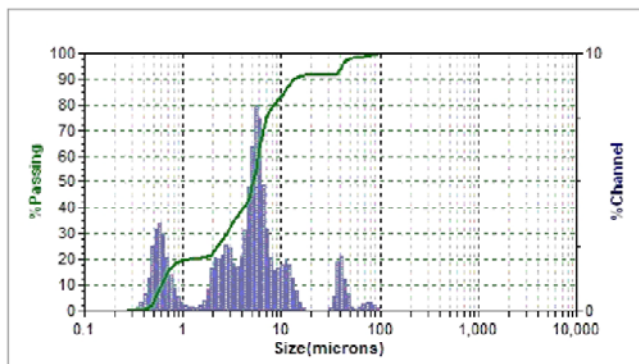


10.3.0
S3000/S3500

- Particle Size Analysis -

Glass-1
159242 Filtered

Data Acquired: 12/20/2018 - 10:22
Calculated: 12/20/2018 - 10:22



Peak Summary

Dia	Vol%	Width
0.00000	0.0	0.00
0.00000	0.0	0.00
0.00000	0.0	0.00
0.00000	0.0	0.00

Size(um)	%Tile

Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
1408	0.00	100.00	74.00	0.26	98.95	3.89	1.75	38.43			
1291	0.00	100.00	67.86	0.14	98.69	3.57	1.84	36.68			
1184	0.00	100.00	62.23	0.05	98.55	3.27	2.44	34.84			
1086	0.00	100.00	57.06	0.15	98.50	2.999	2.57	32.40			
995.6	0.00	100.00	52.33	0.65	98.34	2.750	2.17	29.83			
913.0	0.00	100.00	47.98	1.23	97.69	2.522	2.02	27.66			
837.2	0.00	100.00	44.00	2.14	96.46	2.312	2.08	25.64			
767.7	0.00	100.00	40.35	1.91	94.32	2.121	1.67	23.56			
704.0	0.00	100.00	37.00	0.54	92.41	1.945	0.83	21.89			
645.6	0.00	100.00	33.93	0.10	91.87	1.783	0.40	21.06			
592.0	0.00	100.00	31.11	0.00	91.77	1.635	0.20	20.68			
542.9	0.00	100.00	28.53	0.00	91.77	1.499	0.13	20.46			
497.8	0.00	100.00	26.16	0.00	91.77	1.375	0.15	20.33			
456.5	0.00	100.00	23.99	0.00	91.77	1.261	0.19	20.18			
418.6	0.00	100.00	22.00	0.00	91.77	1.156	0.22	19.99			
383.9	0.00	100.00	20.17	0.00	91.77	1.060	0.35	19.77			
352.0	0.00	100.00	18.50	0.11	91.77	0.972	0.56	19.42			
322.8	0.00	100.00	16.96	0.33	91.66	0.892	0.91	18.86			
296.0	0.00	100.00	15.56	0.78	91.33	0.818	1.37	17.95			
271.4	0.00	100.00	14.27	1.26	90.55	0.750	2.06	16.58			
248.9	0.00	100.00	13.08	1.81	89.29	0.688	3.02	14.52			
228.2	0.00	100.00	12.00	1.99	87.48	0.630	3.38	11.50			
209.3	0.00	100.00	11.00	1.79	85.49	0.578	3.19	8.12			
191.9	0.00	100.00	10.09	1.66	83.70	0.530	2.50	4.93			
176.0	0.00	100.00	9.25	1.58	82.04	0.488	1.31	2.43			
161.4	0.00	100.00	8.48	2.09	80.46	0.446	0.65	1.12			
148.0	0.00	100.00	7.78	3.18	78.37	0.408	0.33	0.47			
135.7	0.00	100.00	7.13	4.89	75.19	0.375	0.14	0.14			
124.5	0.00	100.00	6.54	7.45	70.31	0.344	0.00	0.00			
114.1	0.00	100.00	6.00	7.97	62.85	0.315	0.00	0.00			
104.7	0.12	100.00	5.50	6.39	54.88	0.2890	0.00	0.00			
95.96	0.22	99.88	5.04	4.83	48.49	0.2650	0.00	0.00			
88.00	0.35	99.66	4.62	3.11	43.66						
80.70	0.36	99.31	4.24	2.12	40.55						

Summary

Data Item	Value
MV(um):	8.43
MN(um):	0.587
MA(um):	2.035
CS:	2.948
SD:	4.76

Percentiles

%Tile	Size(um)
10.00	0.607
20.00	1.161
30.00	2.766
40.00	4.15
50.00	5.16
60.00	5.82
70.00	6.52
80.00	8.31
90.00	13.68
95.00	41.42

Distribution:	Volume	Run Time:	30 Sec	Fluid:	WATER		
Progression:	Geom 8 Root	Run Num:	Avg of 3	Fluid Ref. Index:	1.333	Loading Factor:	0.000
Upper Edge:	1408	Particle:	PM	Above Residual:	0	Transmission:	1.00
Lower Edge:	0.243	Transparency:	Transparent	Below Residual:	0	RMS Residual:	2.18E-02
Residuals:	Disabled	Part. Ref. Index:	1.51			Flow:	65 %
Num. Channels:	100	Part. Shape:	Spherical	Cell ID:	0595	Usonic Power:	N/A
Analysis Mode:	S3000					Usonic Time:	N/A
Filter:	Enabled	DB Record:	9062	Recalc Status:		Serial Num:	S3754
Analysis Gain:	N/A	Database:	C:\Program Files (x86)\Microtrac FLEX 10.3.0\Databases\psd-2012.MDB				

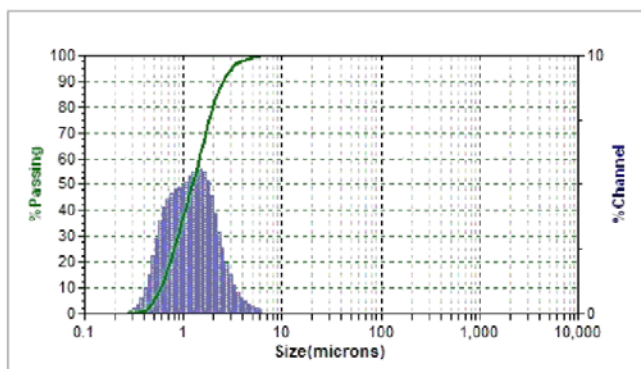


10.3.0
S3000/S3500

- Particle Size Analysis -

BCR66
159236 Dilute

Data Acquired: 12/20/2018 - 09:35
Calculated: 12/20/2018 - 09:35



Peak Summary

Dia	Vol%	Width
1.242	100.0	1.51

Size(um)	%Tile

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
1408	0.00	100.00	74.00	0.00	100.00	3.89	0.84	97.79			
1291	0.00	100.00	67.86	0.00	100.00	3.57	1.13	96.95			
1184	0.00	100.00	62.23	0.00	100.00	3.27	1.50	95.82			
1086	0.00	100.00	57.06	0.00	100.00	2.999	1.97	94.32			
995.6	0.00	100.00	52.33	0.00	100.00	2.750	2.56	92.35			
913.0	0.00	100.00	47.98	0.00	100.00	2.522	3.21	89.79			
837.2	0.00	100.00	44.00	0.00	100.00	2.312	3.93	86.58			
767.7	0.00	100.00	40.35	0.00	100.00	2.121	4.57	82.65			
704.0	0.00	100.00	37.00	0.00	100.00	1.945	5.12	78.08			
645.6	0.00	100.00	33.93	0.00	100.00	1.783	5.45	72.96			
592.0	0.00	100.00	31.11	0.00	100.00	1.635	5.56	67.51			
542.9	0.00	100.00	28.53	0.00	100.00	1.499	5.56	61.95			
497.8	0.00	100.00	26.16	0.00	100.00	1.375	5.45	56.39			
456.5	0.00	100.00	23.99	0.00	100.00	1.261	5.30	50.94			
418.6	0.00	100.00	22.00	0.00	100.00	1.156	5.11	45.64			
383.9	0.00	100.00	20.17	0.00	100.00	1.060	4.98	40.53			
352.0	0.00	100.00	18.50	0.00	100.00	0.972	4.88	35.55			
322.8	0.00	100.00	16.98	0.00	100.00	0.892	4.79	30.67			
296.0	0.00	100.00	15.56	0.00	100.00	0.819	4.69	25.88			
271.4	0.00	100.00	14.27	0.00	100.00	0.750	4.46	21.19			
248.9	0.00	100.00	13.08	0.00	100.00	0.688	4.12	16.73			
228.2	0.00	100.00	12.00	0.00	100.00	0.630	3.61	12.61			
209.3	0.00	100.00	11.00	0.00	100.00	0.578	2.92	9.00			
191.9	0.00	100.00	10.09	0.00	100.00	0.530	2.24	6.09			
176.0	0.00	100.00	9.25	0.00	100.00	0.486	1.53	3.84			
161.4	0.00	100.00	8.48	0.00	100.00	0.448	1.01	2.31			
148.0	0.00	100.00	7.78	0.00	100.00	0.409	0.61	1.30			
135.7	0.00	100.00	7.13	0.00	100.00	0.375	0.36	0.69			
124.5	0.00	100.00	6.54	0.16	100.00	0.344	0.22	0.33			
114.1	0.00	100.00	6.00	0.25	99.84	0.315	0.11	0.11			
104.7	0.00	100.00	5.50	0.30	99.59	0.2890	0.00	0.00			
95.96	0.00	100.00	5.04	0.37	98.29	0.2650	0.00	0.00			
88.00	0.00	100.00	4.62	0.49	98.92						
80.70	0.00	100.00	4.24	0.64	98.43						

Summary

Data Item	Value
MV(um):	1.45
MN(um):	0.656
MA(um):	1.062
CS:	5.65
SD:	0.752

Percentiles

%Tile	Size(um)
10.00	0.593
20.00	0.733
30.00	0.881
40.00	1.051
50.00	1.242
60.00	1.455
70.00	1.701
80.00	2.015
90.00	2.539
95.00	3.11

Distribution:	Volume	Run Time:	30 Sec	Fluid:	CURRENT CARRIER		
Progression:	Geom 8 Root	Run Num:	Avg of 3	Fluid Ref. Index:	1.333	Loading Factor:	0.009
Upper Edge:	1408	Particle:	BCR66	Above Residual:	0	Transmission:	0.93
Lower Edge:	0.243	Transparency:	Transparent	Below Residual:	0	RMS Residual:	1.72E-02
Residuals:	Disabled	Part. Ref. Index:	1.54			Flow:	65 %
Num. Channels:	100	Part. Shape:	Irregular	Cell ID:	0595	Usonic Power:	N/A
Analysis Mode:	S3000					Usonic Time:	N/A
Filter:	Enabled	DB Record:	9050	Recalc Status:		Serial Num:	S3754
Analysis Gain:	0	Database:	C:\Program Files (x86)\Microtrac FLEX 10.3.0\Databases\psd-2012.MDB				

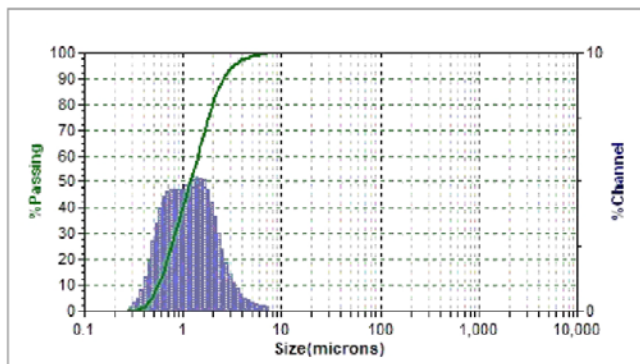


10.3.0
S3000/S3500

- Particle Size Analysis -

BCR66
159236 Filtered

Data Acquired: 12/20/2018 - 09:49
Calculated: 12/20/2018 - 09:49



Peak Summary

Dia	Vol%	Width
1.193	100.0	1.55

Size(um)	%Tile

Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
1408	0.00	100.00	74.00	0.00	100.00	3.89	0.87	97.18			
1291	0.00	100.00	67.86	0.00	100.00	3.57	1.13	96.31			
1184	0.00	100.00	62.23	0.00	100.00	3.27	1.47	95.18			
1086	0.00	100.00	57.06	0.00	100.00	2.999	1.90	93.74			
995.8	0.00	100.00	52.33	0.00	100.00	2.750	2.43	91.81			
913.0	0.00	100.00	47.98	0.00	100.00	2.522	3.03	89.38			
837.2	0.00	100.00	44.00	0.00	100.00	2.312	3.68	86.35			
767.7	0.00	100.00	40.35	0.00	100.00	2.121	4.25	82.67			
704.0	0.00	100.00	37.00	0.00	100.00	1.945	4.75	78.42			
645.8	0.00	100.00	33.93	0.00	100.00	1.783	5.06	73.67			
592.0	0.00	100.00	31.11	0.00	100.00	1.635	5.16	68.61			
542.9	0.00	100.00	28.53	0.00	100.00	1.499	5.17	63.45			
497.8	0.00	100.00	26.16	0.00	100.00	1.375	5.09	58.28			
456.5	0.00	100.00	23.99	0.00	100.00	1.261	4.98	53.19			
418.6	0.00	100.00	22.00	0.00	100.00	1.156	4.84	48.21			
383.9	0.00	100.00	20.17	0.00	100.00	1.060	4.76	43.37			
352.0	0.00	100.00	18.50	0.00	100.00	0.972	4.74	38.61			
322.8	0.00	100.00	16.96	0.00	100.00	0.892	4.74	33.87			
296.0	0.00	100.00	15.56	0.00	100.00	0.818	4.75	29.13			
271.4	0.00	100.00	14.27	0.00	100.00	0.750	4.66	24.38			
248.9	0.00	100.00	13.08	0.00	100.00	0.688	4.46	19.72			
228.2	0.00	100.00	12.00	0.00	100.00	0.630	4.04	15.26			
209.3	0.00	100.00	11.00	0.00	100.00	0.578	3.42	11.22			
191.9	0.00	100.00	10.09	0.00	100.00	0.530	2.71	7.80			
176.0	0.00	100.00	9.25	0.00	100.00	0.488	1.94	5.09			
161.4	0.00	100.00	8.48	0.00	100.00	0.446	1.33	3.15			
148.0	0.00	100.00	7.78	0.14	100.00	0.409	0.83	1.82			
135.7	0.00	100.00	7.13	0.21	99.86	0.375	0.51	0.99			
124.5	0.00	100.00	6.54	0.23	99.65	0.344	0.32	0.48			
114.1	0.00	100.00	6.00	0.27	99.42	0.315	0.16	0.16			
104.7	0.00	100.00	5.50	0.34	99.15	0.2890	0.00	0.00			
95.95	0.00	100.00	5.04	0.42	98.81	0.2650	0.00	0.00			
88.00	0.00	100.00	4.62	0.53	98.39						
80.70	0.00	100.00	4.24	0.68	97.86						

Summary

Data Item	Value
MV(um):	1.442
MN(um):	0.622
MA(um):	1.019
CS:	5.89
SD:	0.773

Percentiles

%Tile	Size(um)
10.00	0.562
20.00	0.692
30.00	0.831
40.00	0.997
50.00	1.193
60.00	1.416
70.00	1.675
80.00	2.007
90.00	2.576
95.00	3.23

Distribution:	Volume	Run Time:	30 Sec	Fluid:	CURRENT CARRIER		
Progression:	Geom 8 Root	Run Num:	Avg of 3	Fluid Ref. Index:	1.333	Loading Factor:	0.007
Upper Edge:	1408	Particle:	BCR66	Above Residual:	0	Transmission:	0.95
Lower Edge:	0.243	Transparency:	Transparent	Below Residual:	0	RMS Residual:	9.93E-03
Residuals:	Disabled	Part. Ref. Index:	1.54			Flow:	85 %
Num. Channels:	100	Part. Shape:	Irregular	Cell ID:	0595	Usonic Power:	N/A
Analysis Mode:	S3000					Usonic Time:	N/A
Filter:	Enabled	DB Record:	9054	Recalc Status:		Serial Num:	33754
Analysis Gain:	0	Database:	C:\Program Files (x86)\Microtrac FLEX 10.3.0\Databases\psd-2012.MDB				

Distribution:

timothy.brown@srnl.doe.gov
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
c.diprete@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
nancy.halverson@srnl.doe.gov
erich.hansen@srnl.doe.gov
connie.herman@srnl.doe.gov
patricia.lee@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
bill.wilmarth@srnl.doe.gov
charles.crawford@srnl.doe.gov
thomas.peters@srnl.doe.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
roberto.gonzalez@srs.gov
tony.polk@srs.gov
patricia.suggs@srs.gov
mary.whitehead@srnl.doe.gov
Kevin.Brotherton@srs.gov
Richard.Edwards@srs.gov
terri.fellinger@srs.gov
eric.freed@srs.gov
jeffrey.gillam@srs.gov
barbara.hamm@srs.gov
bill.holtzscheiter@srs.gov
john.iaukea@srs.gov
Vijay.Jain@srs.gov
Jeremiah.Ledbetter@srs.gov
Jocelin.stevens@srs.gov
chris.martino@srnl.doe.gov
jeff.ray@srs.gov
paul.ryan@srs.gov
Azadeh.Samadi-Dezfouli@srs.gov
hasmukh.shah@srs.gov
aaron.staub@srs.gov

Records Administration (EDWS)

Thomas02.whit@srnl.doe.gov
Brian02.looney@srnl.doe.gov
Leigh.brown@srnl.doe.gov
david.missimer@srnl.doe.gov