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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on 3Q15 Tank 50, Salt Solution Feed Tank (SSFT), and Solvent Hold Tank (SHT) Materials

Approved by:

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INTRODUCTION

The Savannah River National Laboratory (SRNL) was tasked with preparing and shipping samples for Hg speciation by Eurofins Frontier Global Sciences, Inc. in Seattle, WA on behalf of the Savannah River Remediation (SRR) Mercury Task Team.[i,ii] The ninth shipment of samples was designated to include 3Q15 Tank 50, Modular Caustic Side Solvent Extraction Unit (MCU) Salt Solution Feed Tank (SSFT), and MCU Solvent Hold Tank (SHT) materials. The 3Q15 Tank 50 variable depth sample (HTF-50-15-92) was subsampled into a Teflon® bottle immediately following transfer of the sample in the SRNL Shielded Cells on July 13, 2015 and refrigerated in 773-A, B-119 at 4 °C the same day. The MCU SSFT (MCU-15-688) sample was pulled on June 11, 2015. While the MCU SHT samples were pulled on June 15, 2015 and consisted of three peanut vials (MCU-15-713, -714, and -714), each of which served as a replicate for mercury speciation testing. All MCU samples were received at SRNL on June 16, 2015. The SHT samples were moved the same day to refrigeration, while the stainless steel dip bottle containing the SSFT sample was placed in the Shielded Cells. On July 9, 2015 it was opened and an aliquot diluted 1:100 with Eurofins deionized water and a portion of the diluted sample transferred to a Teflon® bottle prior to moving it to refrigeration that same day. All samples were kept in the dark and refrigerated until final dilutions were prepared for shipment to Eurofins.

[i] Sudduth, C. B., *Mercury Speciation*, X-TTR-G-00002, Savannah River Remediation, Aiken, SC 29808 (May 2015).
[ii] Crawford, C. L., Bannochie, C. J., *Task Technical and Quality Assurance Plan for Mercury Speciation Analyses in Savannah River Site Liquid Waste Systems*, SRNL-RP-2015-00320, Savannah River National Laboratory, Aiken, SC 29808 (May 2015).

Eurofins supplied deionized water, 250 mL clear and amber glass bottles, and preservative (1.2 mL concentrated HCl). Triplicate samples of each material were prepared for this shipment. Each replicate was analyzed for seven Hg species: total Hg, total soluble (dissolved) Hg, elemental Hg [Hg(0)], ionic (inorganic) Hg [Hg(I) and Hg(II)], methyl Hg [CH_3Hg-X, where X is a counter anion], ethyl Hg [CH_3CH_2-Hg-X, where X is a counter anion], and dimethyl Hg [$(CH_3)_2Hg$] (Tank 50 and SSFT only). The difference between the total Hg and total soluble Hg measurements gives the particulate Hg concentration, i.e. Hg adsorbed to the surface of particulate matter in the sample but without resolution of the specific adsorbed species. The analytes were determined from samples in four separate bottles: 1) methyl Hg and ethyl Hg; 2) dimethyl Hg and elemental Hg; 3) total Hg and soluble total Hg; and 4) ionic Hg (Hg(I) and Hg(II)).

Details of the sample preparation activities are recorded in the SRNL E-Notebook system.[iii] SRNL deionized water was employed as the blank for the Tank 50 and SSFT samples, and "clean" Isopar L was submitted as the blank for the SHT samples. Prior to shipment, the Tank 50 and SSFT samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:3000 by mass. The Hg species reported for the SHT samples were all collected from samples diluted by nominally 4X into vials containing reagent grade *n*-hexane. All containers were filled close to the maximum allowable volume to minimize headspace within the sealed samples. In total, 32 aqueous and four organic samples were prepared on July 21, 2015 and shipped the following day by next-day air to Eurofins where they were received on July 23, 2015. Eurofins reported the SHT results on a mass basis (ng Hg / g sample) and the aqueous samples were reported in units of ng Hg / L sample. The SHT density used to convert to a mg/L volume basis was 0.835 g/mL @ 25 °C.[iv]

Table 1 provides the average concentrations of Hg species derived from Eurofins reported data corrected for dilutions performed by SRNL. All blanks, not shown in the table, were reported at the reporting limits, or 'RL' values, except for two SHT analyses where in the blank gave a value of 0.002% of the samples (Hg(II) analysis) and 2% of the samples (Hg(0) analysis). The RL values given by Eurofins are typically 1X to 7X higher than the associated detection limits, or 'DL' values. The RL values typically are associated with the 'quantification' limit for a given analyte and analytical method. There is a ± 20% uncertainty that Eurofins reports in the measurement of total Hg and total soluble Hg, which are used to determine the particulate Hg value for aqueous samples. There was relatively little elemental Hg in the SSFT sample, a species which may be removed to an unknown extent when the aqueous samples are filtered for total soluble Hg; hence, the reported particulate value should not be inflated as was observed for the DWPF RCT and OCGT samples.[v] The elemental Hg was about 16% of the particulate value for the 3Q15 Tank 50 sample, so this particulate value could be inflated to some degree. Only one SHT sample showed any particulate Hg, and Eurofins feels it is unlikely that there is any particulate matter in these samples; hence the single measurement was not included in the species fraction calculation. There was no ethyl Hg(II) in these samples above the reporting limit of the analytical method.

[iii] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 9 & 10)", Experiment L2320-00194- 03, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (June 2015).
[iv] Fondeur, F. F., Taylor-Pashow, K. M. L., *Solvent Hold Tank Sample Results for MCU-15-661-662-663: April 2015 Monthy Samples*, SRNL-STI-2015-00307, Savannah River National Laboratory, Aiken, SC 29808 (July 2015).
[v] Bannochie, C. J., *Results of Hg Speciation Testing on DWPF Batch 735 RCT and OGCT Samples*, SRNL-L3100-2015-00105, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (June 2015).

Eurofins reported again[vi] that it was not possible to determine the dimethyl Hg content of the SHT samples. Apparently, too much Isopar L is purging from the sample along with the dimethylmercury and collecting on the activated carbon trap, which is then being released along with the dimethylmercury into the GC column. They are definitely seeing dimethylmercury, but they are thus far unable to quantify it.

The last column of Table 1 provides the percent of total Hg that the six measured species (particulate, elemental, ionic, methyl, ethyl, and dimethyl) represent. A range is provided to account for the uncertainty of the detection limit values for ethyl Hg(II). The recoveries for the Tank 50 sample is in the 70-74% range, while the SSFT sample is in the 75-88% range, the higher variability due to the larger detection limit for ethyl Hg(II). These species recoveries are in the range of where the method uncertainties and the impact of combining results analyzed from four separately prepared dilutions could account for the difference between the sum and 100%.

The recovery for the SHT sample is very close to the value determined previously (53%)[vi] and is likely low due to the unaccounted for dimethylmercury. This species would be expected to extract into the organic phase in MCU. Eurofins is exploring whether there are alternative methods for selectively extracting it from our matrix.

Total Hg measured by SRNL via aqua regia dissolution, followed by CV-Hg Atomic Absorption (AA) analysis found 102 mg/L in the 3Q15 Tank 50 sample[vii]. A separate SSFT sample (MCU-15-667) received in June along with the one analyzed here by Eurofins had a total Hg measurement of 120 mg/L.[viii] This sample was not subjected to an aqua regia dissolution but was digested at the instrument per Analytical Development procedure.[ix] Both these total Hg results compare well with those reported in Table 1 considering the ± 20% uncertainty in the method.

[vi] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on Tank 21 and Solvent Hold Tank (SHT) Material*, SRNL-L3100-2015-00068, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (April 2015).
[vii] Crawford, C. L., "3Q CY15 Tank 50 WAC", Experiment B9108-00026-23, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (June 2015).
[viii] Peters, T. B., unpublished data, August 13, 2015.
[ix] Brown, L. W., "Procedure for Cold Vapor/Hydride Generation Atomic Absorption", Manual L16.1, Procedure ADS-1557, Rev. 7, Savannah River National Laboratory, Aiken, SC 29808 (May 2013).

Table 1. Average Concentrations of various Hg species for 3Q15 Tank 50, MCU SSFT, and MCU SHT Samples expressed as mg Hg/L (ppm) [%RSD] (No. of Replicates)

Sample	Total Hg	Total Soluble Hg	Particulate Hg	Elemental Hg [Hg(0)]	Ionic Hg [Hg(I) & Hg(II)]	Methyl Hg	Ethyl Hg	Dimethyl Hg	Species Fraction of Total Hg
Tank 50	113 [2.5] (3)	99.6 [1.1] (3)	13.4*	2.20 [4.2] (3)	10.2 [10] (3)	53.3 [12] (3)	< 4.3	0.143 [9.9] (3)	70 - 74%
SSFT	105 [1.2] (3)	92.0 [3.7] (3)	13.0*	0.616 [5.4] (3)	9.15 [6.4] (3)	56.2 [13] (3)	< 13	0.0938 [0.4] (3)	75 - 88%
SHT	11.1 [7.5] (3)	12.3 [12] (3)	0.636 [NA] (1)‡	0.252 [32] (3)	3.10 [0.7] (3)	2.30 [11] (3)	< 0.032	Indeterminate	51%

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20%, the particulate value is the difference of these two measured values for the aqueous samples and a separate calculation for the SHT samples.

‡ Eurofins believes there is likely no particulate Hg in the SHT samples, so this single value has not been included in the fraction calculation.

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