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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on MCU Strip Effluent Hold Tank (SEHT) and Decontaminated Salt Solution Hold Tank (DSSHT) 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 tenth shipment of samples was designated to include Modular Caustic Side Solvent Extraction Unit (MCU) Strip Effluent Hold Tank (SEHT) and MCU Decontaminated Salt Solution Hold Tank (DSSHT) materials from processing Salt Batch 7b. The MCU SEHT (MCU-15-722) and DSSHT (MCU-15-709) samples were pulled on June 15, 2015. All MCU samples were received at SRNL on June 16, 2015. The DSSHT sample was moved the same day to refrigeration, while the SEHT 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.

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

[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).

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 (except as noted below): 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,iv] SRNL deionized water was employed as the blank for the SEHT and DSSHT samples. Prior to shipment, the DSSHT and cells-diluted SEHT samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:3000 by mass. All containers were filled close to the maximum allowable volume to minimize headspace within the sealed samples. In total, 32 aqueous samples were prepared on August 4, 2015 and shipped the following day by next-day air to Eurofins where 24 samples were received on August 6, 2015. Due to an HMTR labeling issue, FedEx returned two of the six parcels to SRS on August 6, these corresponded to the acid preserved samples. The parcel temperatures were checked by SRNL and found to be <4 °C, so the ice was refreshed, correct labels applied, and the parcels shipped again on August 6 to Eurofins. The acid preserved SEHT samples arrived on August 7 in Seattle, but the DSSHT acid preserved samples did not leave Memphis until Sunday evening and were delivered to Eurofins on August 10 at ambient temperature. No explanation for the shipping failure in Memphis by FedEx has been received as of this writing. Since the samples were acid preserved for methyl and ethyl Hg measurements, Eurofins felt the ambient temperature would have little or no impact on the results, but the situation is noted here for completeness. Eurofins reported the aqueous sample results in units of ng Hg / L sample. The DSSHT density used to convert mass to volume was 1.244 g/mL @ 10.1 °C.[iv]

During analysis of the data, it was learned that the set of triplicate DSSHT samples prepared for total and soluble total Hg, were actually further SEHT samples, and gave identical results to those obtained from the SEHT dilutions.[v] To obtain a DSSHT sample total soluble Hg value, Eurofins measured the DSSHT bottles they originally analyzed for elemental and dimethyl Hg. To determine the total Hg they analyzed the DSSHT bottles originally analyzed for ionic Hg. The total Hg and total soluble Hg values shown for DSSHT material in Table 1 are from these measurements.

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. 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

[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] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 10) [Continued]", Experiment L2320-00194- 07, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (August 2015).
[v] The duplicate samples caused by the introduction of the DSSHT sample to the radiohood prior to the completion of all dilutions with the SEHT sample. This was a break in the dilution protocol used to date to prepare these samples, but Eurofins has sufficient sample redundancy and were able to obtain the required data.

elemental Hg in the either 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.[vi] There was no ethyl Hg(II) nor dimethyl Hg in these samples above the reporting limit of the analytical method.

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 SEHT sample is 100%, while the DSSHT sample is in the 74-81 % range, the higher variability due to the large detection limit for ethyl Hg(II) once dilutions are applied. 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%.

A separate composite DSSHT sample (MCU-15-706, -707, -708) had a SRNL total Hg measurement of 118 mg/L, and a separate composite SEHT sample (MCU-15-719, -720, -721) had a SRNL total Hg measurement of 34 mg/L.[vii] Both samples were digested by aqua regia before analysis by Cold Vapor Atomic Absorption (CVAA). The samples analyzed at SRNL had been received in June along with the ones analyzed by Eurofins described in this memorandum. Both these total Hg results compare reasonably well with those reported in Table 1 considering the ± 20% uncertainty in the method.

[vi] 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).
[vii] Peters, T. B., unpublished data, August 13, 2015.

Table 1. Average Concentrations of various Hg species for MCU SSFT[viii], SHT[viii], SEHT and DSSHT Samples from Salt Batch 7b 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
SSFT	105 [1.2] (3)	92.0 [3.7] (3)	13*	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)‡ (measured)	0.252 [32] (3)	3.10 [0.7] (3)	2.30 [11] (3)	< 0.032	Indeterminate	51+%
DSSHT	123 [5.1] (3)	125 [1.6] (3)	0*	0.744 [8.1] (3)	12.2 [6.0] (3)	77.7 [2.8] (3)	<8.6	<0.00154	74 – 81%
SEHT	21.7 [1.8] (6)	20.5 [1.9] (6)	1.2*	0.574 [31] (3)	3.50 [4.2] (3)	16.3 [6.0] (3)	<18ˣ	<0.128	99 – 100%

* 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. Organic sample particulate measurements are measured and not done by difference between the total Hg and total soluble Hg.

ˣ There is not enough unaccounted for Hg to use this reporting limit as an upper bound for the amount of potential ethyl Hg, so it is not included in the fraction calculation.

[viii] Bannochie, C. J., *Results of Hg Speciation Testing on 3Q15 Tank 50, Salt Solution Feed Tank (SSFT), and Solvent Hold Tank (SHT) Materials*, SRNL-L3100-2015-00144, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (August 2015).

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