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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on Tanks 30, 32, and 37 Surface Samples

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 eleventh shipment of samples was designated to include 3H evaporator system Tank 30, 32, and 37 surface samples. The Tank 30 surface sample (HTF-30-15-69) was taken 308.63 inches from the tank bottom and shipped to SRNL on June 29, 2015 in an 80 mL stainless steel dip bottle. The Tank 32 surface sample (HTF-32-15-67) was taken 268.35 inches from the tank bottom and shipped to SRNL on June 30, 2015 in an 80 mL stainless steel dip bottle. The Tank 37 surface sample (HTF-37-15-73) was taken 262.8 inches and shipped to SRNL on July 21, 2015 in an 80 mL stainless steel dip bottle. All samples were placed in the SRNL Shielded Cells and left unopened until intermediate dilutions were made on July 24, 2015 using 1.00 mL of sample diluted to 100.00 mL with deionized H₂O. A 30 mL Teflon[®] bottle was rinsed twice with the diluted tank sample and then filled leaving as little headspace as possible. It was immediately removed from the Shielded Cells and transferred to refrigerated storage where it remained at 4 °C until final dilutions were made on October 6. A second portion of the cells diluted tank sample was poured into a shielded polyethylene bottle and transferred to Analytical Development for radiochemical analysis data needed for Hazardous Material Transportation calculations. The initial Eurofins dilutions were not shipped due to procedural compliance issues in the Transportation Services Group. A second set of dilutions for Eurofins were prepared on October 13.

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).

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Separate dilutions of the Tank 32 surface sample were prepared for Purge & Trap activities conducted at SRNL. These 130 mL of these dilutions were purged with N₂ gas and the purge gas passed through either an activated carbon trap for dimethylmercury collection or a combination soda lime and dual gold trap for collection of Hg(0). The carbon and gold traps for this work were supplied by Eurofins. The traps were not sent to Eurofins with the bottles for Shipment #11, so the results are not included in this memorandum. The data will be added to this memo for comparison in Rev. 1 once it has been received back from 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 [CH₃Hg-X, where X is a counter anion], ethyl Hg [CH₃CH₂-Hg-X, where X is a counter anion], and dimethyl Hg [(CH₃)₂Hg]. 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 (dissolved) Hg; and 4) ionic Hg (Hg(I) and Hg(II)).

Details of the sample preparation and Purge & Trap activities are recorded in the SRNL E-Notebook system.ⁱⁱⁱ SRNL deionized water was employed as the blank. Prior to shipment, the cells-diluted tank 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, 48 aqueous samples were prepared on October 13, 2015 and shipped the following day by next-day air to Eurofins where 48 samples were received on October 15, 2015. Eurofins reported the aqueous sample results in units of ng Hg / L sample.

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 $\pm 20\%$ 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 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.^{iv} 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

ⁱⁱⁱ Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 11 & 12)", Experiment L2320-00194-04, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (June 2015).

^{iv} 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).

limit values reported for some species. For Tanks 30 & 32 the reported range includes the ethylmercury detection limit, but it is not included for the Tank 37 samples since there was not enough unaccounted for Hg to include the detection limit for ethylmercury. The recoveries for the Tank 30 and Tank 32 surface sample are 53 – 77% and 34 – 71%, respectively, while the Tank 37 surface sample is in the 79- 80 % range. The lower limit of the recoveries for Tank 32, i.e., assuming no ethylmercury present, are particularly low compared with similar sample sets.^v The Tank 37 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%.

^v Bannochie, C. J., *Results of Hg Speciation Testing on Tank 43 and 2H Evalpoartor Overhead Tank (OHT-2) Materials*, SRNL-L3100-2015-00115, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (June 2015).

**Table 1. Average Concentrations of various Hg species for Tank 30, 32, and 37 Surface 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 30 Surface	54.2 [4.4] (3)	47.4 [4.0] (3)	6.8*	0.740 [2.4] (3)	16.0 [20] (3)	5.22 [5.2] (3)	< 13	<0.0183	53 - 77%
Tank 32 Surface	33.0 [2.0] (3)	29.2 [6.7] (3)	3.8*	<0.0861	2.31 [31] (3)	5.20 [4.4] (3)	< 12	<0.0172	34 – 71%
Tank 37 Surface	17.9 [8.9] (3)	9.20 [3.8] (3)	8.7*	<0.101	3.47 [20] (3)	1.94 [1.8] (3)	<14*	<0.0202	79 - 80%

* Uncertainty in the total Hg and total soluble Hg measurements is $\pm 20\%$, the particulate value is the difference of these two measured values for the aqueous samples.

× 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 for Tank 37.

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