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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on Tank 38 and 2H Evaporator Overhead Tank (OHT-1) Materials

Approved by:

C. L Crawford, Technical Reviewer per E7, 2.60 Date

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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 seventh shipment of samples was designated to include two Tank 38 (2H Evaporator System Drop Tank) samples: a surface sample (HTF-38-15-48) and a variable depth sample taken at 265" (HTF-38-15-50).[iii] The third sample submitted was from the 2H Evaporator Overhead Tank (OHT) #1. All samples were received by SRNL on May 11, 2015. The OHT-1 was not placed in the SRNL Shielded Cells but was instead placed in a refrigerator in 773-A, B-wing upon receipt and kept at 4°C. The Tank 38 samples were left in their stainless steel dip bottles until they were opened and an aliquot of each diluted 1:10 with Eurofins deionized water on June 1, 2015. Following initial dilution in the Shielded Cells, the diluted Tank 38 samples were immediately moved to refrigeration and kept in the dark until 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 Tank 38 and OHT#1 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)

[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).
[iii] Sudduth, C. B., Email: "Tank 38/43 Sample Designations", Savannah River Remediation, Aiken SC 29808 (May 12, 2015).

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 [$(CH_3)_2Hg$]. 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.[iv] SRNL deionized water was employed as the blank. The Tank 38 samples were diluted in the SRNL Shielded Cells 1:10 by volume prior to cell exit and storage in refrigeration. Prior to shipment, the Tank 38 and OHT-1 samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:2500 by mass (Tank 38) and 1:82 by mass (OHT-1). All bottles were filled close to the maximum allowable volume to minimize headspace within the sealed samples. In total, 48 samples were prepared on June 3, 2015 and shipped the following day by next-day air to Eurofins where they were received on June 5, 2015.

Eurofins reported that several of the coolers arrived below 0°C resulting in frozen samples and broken bottles due to the expansion of the frozen matrix and the lack of headspace in the containers. Eurofins indicated they were able to recover the samples since they were still frozen. The impacted samples were primarily the amber bottles prepared for dimethyl and elemental Hg, as well as one clear bottle prepared as a total and total soluble Hg blank. The specific samples impacted are listed in Table 1. The cause of the frozen samples has been identified as resulting from changes implemented in the packaging configuration to ensure all samples arrived at or below 4°C: 1) smaller profile bubble wrap, 2) ice packs added within the double poly bag cooler liner, and 3) additional ice packs per cooler. These changes coupled with the shipment being designated as “non-rad per DOT” and therefore not subject to the use of the 95 kPa pressure bags that are normally required for air shipments, resulted in a significant reduction in the amount of insulation between the samples and the enclosed ice packs. Two changes to the procedure were implement for the following and all future shipments to address the frozen samples issue experienced with this shipment: 1) 95 kPA pressure bags are to be used for insulation purposes even when they are not required by regulation and 2) a consistent amount of ice packs will be utilized in each cooler.

Table 1. Frozen samples recovered by Eurofins

Bottle ID	Sample Number	Analytes
G14646	38s48-DME-1	dimethyl and elemental Hg
G14647	38s48-DME-2	dimethyl and elemental Hg
G14649	38s48-DME-B	dimethyl and elemental Hg blank
G14650	38d50-DME-1	dimethyl and elemental Hg
G14651	38d50-DME-2	dimethyl and elemental Hg
G14652	38d50-DME-3	dimethyl and elemental Hg
G14653	38d50-DME-B	dimethyl and elemental Hg blank
G14620	OHT1-TSM-3	total and total soluble Hg blank

[iv] Bannochie, C. J., “Eurofins Sample Preparation for Hg Speciation (Part 7)”, Experiment L2320-00016- 48, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (May 2015).

Table 2 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. There was relatively little elemental Hg, which may be removed to an unknown extent when the 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] There was no ethyl 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. The RL limit is included for the ethyl Hg species in the sum since there would be at most this amount in the samples analyzed. The recoveries for all the samples are in the 80-90% range. All 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%.

Total Hg measured by SRNL via aqua regia dissolution, followed by CV-Hg Atomic Absorption (AA) methods was around 374 mg/L on a separate surface sample and 340 mg/L on a separate subsurface sample.[vi] Comparison of methyl Hg in Tank 22 (the DWPF recycle collection tank that feeds Tank 43 which feeds the 2H Evaporator) with Tank 38 (2H Evaporator bottoms tank) can be made. Methyl Hg was about 26% of the total Hg measured in Tank 22[vii], while for Tank 38 it has increased to 40% of the total Hg. A comparision with the Tank 43 will be made when that data is released by Eurofins.

In light of the high particulate Hg in the Tank 38 samples analyzed by Eurofins and the relatively low elemental Hg level (as previously stated, a high elemental Hg level can inflate the particulate value), it is recommended that Eurofins examine the Hg speciation on the particulate solids that they collected. The company has been preserving the filters in the event SRR wanted to examine them further.

[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).
[vi] Oji, L. N., unpublilshed data.
[vii] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on Tank 22 and Waste Concentrate Hold Tank (WCHT) Material*, SRNL-L3100-2015-00079, Rev. 1, Savannah River National Laboratory, Aiken, SC 29808 (May 2015).

Table 2. Average Concentrations of various Hg species for the Tank 38 and 2H Evaporator OHT-1 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 38 Surface	496 [2.6] (3)	325 [2.5] (3)	171	3.58 [46] (3)	29.8 [7.1] (3)	200 [6.2] (3)	< 35.1	0.148 [52] (3)	89%
Tank 38 Subsurface	476 [14] (3)	316 [1.3] (3)	160	4.07 [90] (3)	31.6 [4.7] (3)	160 [6.8] (3)	< 34.3	0.0525 [48] (3)	82%
2H OHT-1	3.78 [6.5] (3)	3.65 [7.5] (3)	0.13	0.0587 [9.9] (3)	0.505 [1.0] (3)	2.45 [3.6] (3)	< 0.115	0.000899 [42] (3)	86%

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20%, the particulate value is the difference of these two measured values.

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