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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on Tank 43 and 2H Evaporator Overhead Tank (OHT-2) 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 eighth shipment of samples was designated to include two Tank 43 (2H Evaporator System Feed Tank) samples: a surface sample (HTF-43-15-52) and a variable depth sample taken at 161" (HTF-43-15-54).[iii] The third sample submitted was from the 2H Evaporator Overhead Tank (OHT) #2. All samples were received by SRNL on May 11, 2015. The OHT-2 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 43 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 3, 2015. Following initial dilution in the Shielded Cells, the diluted Tank 43 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 32 and OHT-2 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 43 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 43 and OHT-2 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 43) and 1:82 by mass (OHT-2). 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 9, 2015 and shipped the following day by next-day air to Eurofins where they were received on June 11, 2015. Unlike shipment #7, no samples were received frozen by Eurofins.[v]

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. 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.[vi] 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 the Tank 43 samples are in the 90+% range, while the OHT-2 sample is 139%. The latter high recovery is due to there being more methyl Hg measured on these samples than total Hg, which implies that all the Hg in this Overhead Tank is methyl Hg. 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 241 mg/L on a separate surface sample and 218 mg/L on a separate subsurface sample.[vii] A

[iv] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 8)", Experiment L2320-00016- 49, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (May 2015).
[v] Bannochie, C. J., *Results of Hg Speciation Testing on Tank 38 and 2H Evaporator Overhead Tank (OHT-1) Materials*, SRNL-L3100-2015-00113, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (June 2015).
[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] Oji, L. N., unpublilshed data.

comparison of methyl Hg in Tank 22 (the DWPF recycle collection tank) that feeds Tank 43 (2H Evaporator feed tank) can be made. Methyl Hg was about 26% of the total Hg measured in Tank 22[viii], while for Tank 43 it has increased to between 47-57% of the total Hg; it was 40% in Tank 38 (2H Evaporator bottoms tank). Since material from Tank 38 is often returned to Tank 43 for subsequent passes through the evaporator, there is comingling of the waste making it more difficult to conclude that the Evaporator is a major source of the methyl Hg production, though this seems to be a reasonable conclusion based on the data collected to date.

In light of the relatively high particulate Hg in the Tank 43 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.

[viii] 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 1. Average Concentrations of various Hg species for Tanks 38 [v] and 43 and 2H Evaporator OHT-1[v] and OHT-2 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%
Tank 43 Surface	286 [2.7] (3)	208 [0.75] (3)	78	1.44 [18] (3)	44.0 [5.6] (3)	135 [12] (3)	< 8.72	0.00468 [0.32] (2)	93%
Tank 43 Subsurface	234 [1.8] (3)	186 [1.3] (3)	48	3.46 [20] (3)	30.5 [2.1] (3)	134 [8.1] (3)	< 8.45	0.613 [24] (3)	96%
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%
2H OHT-2	4.80 [6.8] (3)	4.64 [1.6] (3)	0.16	0.0636 [20] (3)	0.224 [61] (3)‡	5.58 [10] (3)	< 0.570	0.00536 [8.0] (3)	139%

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

‡ One replicate was 4-5x smaller than the other two. If it is excluded, the average = 0.302, %RSD = 11.

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