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To: R. E. Edwards

From: C. J. Bannochie

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

Approved by:

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

W. R. Wilmarth, SRNL Mercury Task Lead Date

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 twelfth shipment of samples was designated to include 3H evaporator system Tank 30, 32, and 37 depth samples. The Tank 30 depth sample (HTF-30-15-70) was taken at 190 inches from the tank bottom and the Tank 32 depth sample (HTF-32-15-68) was taken at 89 inches from the tank bottom and both were shipped to SRNL on June 29, 2015 in an 80 mL stainless steel dip bottles. The Tank 37 surface sample (HTF-37-15-94) was taken around 253.4 inches from the tank bottom 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 H_2O. 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 20. 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.

Separate dilutions of all three Tank depth samples were prepared for Purge & Trap activities conducted at SRNL. A portion of these dilutions, 130 mL, were purged with N_2 gas and the purge gas passed through either an

[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).

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 #12, 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 (1.0 mL 50% H_2SO_4). 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 [$(CH_3)_2Hg$]. 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 20, 2015 and shipped the following day by next-day air to Eurofins where 48 samples were received on October 21, 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 ± 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 Tank 30 or 37 samples, a species which may be removed to an unknown extent when the aqueous samples are filtered for total soluble Hg; hence, the reported particulate values should not be inflated as was observed for the DWPF RCT and OCGT samples.[iv] There was a sizable Hg(0) measurement for Tank 32, so this will contribute to the large particulate value shown in the table. 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 reported for some species. Due to the high Hg(0) in the Tank 32 depth sample, the percent of total

[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).

Hg figure was derived from the sum of the particulate Hg value minus the Hg(0) value, plus the Hg (0), plus the re-measured ionic Hg value, along with the methyl, ethyl and dimethyl Hg contributions.

Eurofins also reanalyzed the samples for ionic Hg after purging the samples to remove Hg(0). As expected there was only a small change in the ionic Hg value for the Tank 37 sample (relatively little Hg(0)), slightly more change in the Tank 30 samples, and a relatively large change in the Tank 32 samples (high Hg(0)). The measured averages for the purged samples were (mg/L) [%RSD]: 10.0 [14.3], 58.5 [5.7], and 6.94 [14.3] for Tank 30, 32, and 37 samples, respectively. These replicate measurements agree reasonably well with the original data set after correcting it for the amount of Hg(0) present. The replicate measurements are shown in Table 1 as "re-measured/corrected" data. From here on, Eurofins has been asked to measure the ionic Hg after purging the samples for Hg(0). There should be a fair amount of elemental Hg in the upcoming DWPF samples.

What is not clear from the data is why no concentration factor is seen for ionic Hg or total Hg following evaporator operations. While Hg(0) and dimethyl Hg would be expected to volatilize across the 3H evaporator, ionic Hg, and the total Hg after subtracting these two species, should concentrate. One possible explanation is the solubility of ionic Hg is lower in the more concentrated salt solution in the drop tanks. However, it should be noted that a concentration of ionic Hg was seen in the surface samples recently analyzed.[v] This explanation would be consistent for the total Hg value found in Tank 30 since the Tank 32 total Hg value minus the Tank 32 Hg(0) value, minus the difference between ionic Hg in Tank 32 and Tank 30 gives a value of 36.4 mg/L, which is within the 20% uncertainty of the reported 47.2 mg/L total Hg in Tank 30.

For Tanks 30 & 32 the reported range includes the ethyl mercury 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 ethyl mercury. The recoveries for the Tank 30 and Tank 32 depth samples are 61 – 86% and 85 – 95%, respectively, while the Tank 37 surface sample is around 78 %. These 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 Tanks 30, 32, and 37 Surface Samples*, SRNL-L3100-2015-00202, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (November 2015).

Table 1. Average Concentrations of various Hg species for Tank 30, 32, and 37 Depth 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 32 Depth	122 [3.6] (3)	79.1 [2.0] (3)‡	42.9*‡	37.1 [14] (3)	72.0 [1.3] (3)‡	2.57 [3.0] (3)	< 12	< 0.0168	NA
Tank 32 Depth corrected/re-measured			*5.8*	*37.1*	*58.5 [5.8] (3)*	*2.57*	*<12*	*<0.0168*	*85 – 95%*
Tank 30 Depth	47.2 [3.4] (3)	32.5 [3.7] (3)	14.7*‡	0.930 [25] (3**)	12.2 [4.6] (3)	4.09 [4.7] (3)	< 12	< 0.0168	NA
Tank 30 Depth corrected/re-measured			*13.8*	*0.930*	*10.0 [14.3] (3)*	*4.09*	*< 12*	*< 0.0168*	*61 – 86%*
Tank 37 Depth	20.5 [3.6] (3)	12.7 [8.6] (3)	7.8*‡	0.340 [8.8] (3)	7.37 [8.3] (3)	1.29 [6.1] (3)	< 14ˣ	< 0.0193	NA
Tank 37 Depth corrected/re-measured			*7.5*	*0.340*	*6.94 [14.3] (3)*	*1.29*	--	*< 0.0193*	*78%*

* 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.

‡ The Hg(0) measured for this sample is likely to inflate both the particulate and ionic Hg values. The particulate value is corrected by the subtracting the value of the Hg(0).

** One of the three replicates was 40% lower than the other two, leading to the high percent relative standard deviation (%RSD).

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 for Tank 37.

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