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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on 2Q15 Tank 50 WAC and Cs-Decontaminated Tank 21 Waste 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. The fourth shipment of samples was designated to include 2Q15 Tank 50 WAC material (HTF-50-15-39) collected on April 7, 2015, and Tank 21 material (HTF-21-15-32, HTF-21-15-36, and HTF-21-15-37) the first collected on March 9 and the second two collected on April 6, 2015. The combined samples were subjected to Cs-decontamination through the use of MCU solvent. Samples were collected with the minimum possible free headspace and refrigerated prior to final dilution.

Eurofins supplied deionized water, 250 mL PETG bottles, 250 mL amber glass bottles, and preservative (1.2 mL concentrated HCl). Tank 50 and 21 samples were prepared in triplicate plus a blank. Each Tank 50 and 21 sample was analyzed for seven Hg species: total Hg, total soluble Hg, elemental Hg [Hg(0)], ionic 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] by calculation, 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 three separate bottles: 1) methyl Hg and ethyl Hg (after substracting ionic Hg determined from bottle #2); 2) dimethyl Hg, elemental Hg, and ionic Hg; and 3) total Hg and soluble total Hg. Initially it was communicated that Eurofins would determine Hg(0) and ionic Hg from bottle #3, but they were reported from bottle #2, hence this change is not reflected on the Chain of Custody (COC) forms for this shipment since the samples were

shipped prior to our receipt of this information from Eurofins. Due to the large number of analyses being conducted, Eurofins has suggested increasing from three to four sample bottles.

In total, 24 samples were prepared on April 15, 2015 and shipped by next-day air to Eurofins where they were received on April 17, 2015. Details of the sample preparation activities are recorded in the SRNL E-Notebook system.[i] SRNL deionized water was employed as the blank for the Tank 50 and 21 samples. The Tank 50 and 21 samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle #1 only) by nominally 1:3100 by volume (polybottles) or 1:2500 by volume (glass bottles).

Table 1 provides the Eurofins reported data corrected for dilutions performed by SRNL. All blanks, not shown in the table, were reported as Non Detect (ND). 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. In light of this measurement uncertainty, the difference in the values determined for total soluble Hg and total Hg are very small, indicating that there is likely little or no particulate Hg in these diluted Tank 50 or the diluted and treated Tank 21 samples. Previously reported[ii] data for Tank 21 prior to the Cs decontamination are repeated in the table for ease of reference.

The last column of Table 1 provides the percent of total Hg that the six measured species (elemental, ionic, methyl, ethyl, dimethyl, and particulate) represent. A range is provided to account for the uncertainty of the reported detection limit values. The recovery for both Tank 50 and treated Tank 21 are at 64 - 68% and 58 - 64%, respectively. The measured Hg(0) for the treated Tank 21 material varied considerably amongst the replicates, ranging from 0.975 mg/L to 3.87 mg/L, but not as variable as in some earlier samples.[iii] The species recovery is in the range of where the method uncertainties and the impact of combining results analyzed from three separately prepared dilutions may account for the difference between the sum and 100%. There could be additional organomercury species present, as has been previously noted, but commercial methods of detection are not readily available without further analytical method development.

These were the first samples with measureable ethyl mercury from the analysis where Eurofins only calibrates for the methyl mercuric species. It was recommended in Rev. 0 of this memorandum that SRR have Eurofins begin doing a separate calibration for this species. This has now been completed. Eurofins has looked at these stored samples using their calibrated ethyl Hg method and determined that ethyl Hg is <u>not</u> present in these samples. The previously reported ethyl Hg was a false positive resulting from their derivitization method for methyl Hg.

[i] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 4)", Experiment L2320-00016- 45, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (April 2015).
[ii] Bannochie, C. J., "Results of Preliminary Hg Speciation Testing on Tank 21 and Solvent Hold Tank (SHT) Material", SRNL-L3100-2015-00068, Rev. 1, Savannah River National Laboratory, Aiken, SC 29808 (September 2015).
[iii] Bannochie, C. J., "Results of Preliminary Hg Speciation Testing on Tank 22 and Waste Collection Hold Tank (WCHT) Material", SRNL-L3100-2015-00079, Rev. 1, Savannah River National Laboratory, Aiken, SC 29808 (May 2015).

Table 1. Concentrations of various Hg species for the 2Q15 Tank 50 WAC and Cs-Decontaminated Tank 21 Waste 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
2Q15 Tank 50	97.7 [5.0] (3)	94.3 [8.9] (3)	3.4	1.04 [16] (3)	4.86 [24] (3)	53.0 [2.9] (3)	<4.4	0.0235 [13] (3)	64 - 68%
Cs-Decon Tank 21	86.7 [3.6] (3)	85.0 [2.0] (3)	1.7	2.18 [69] (3)	5.72 [19] (3)	41.1 [5.8] (3)	<4.4	<0.000124	58 - 64%
Tank 21[ii]	101 [2.6] (3)	120 [5.4] (3)	ND*	<6.2	5.88 [11] (3)	58.2 [2.6] (3)	<22	0.0156 [5.6] (2)	58 - 83%

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20%, hence the difference between these values is very small thus indicating there is little or no particulate Hg.

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