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To: R. E. Edwards

From: C. J. Bannochie

Results Hg Speciation Testing on Tank 21 and Solvent Hold Tank (SHT) Material

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. The second shipment of samples was designated to include Tank 21 material (HTF-15-21-32) collected on March 9, 2015 and Solvent Hold Tank (SHT) material (MCU-15-28, -29, and -30) collected on March 10, 2015. Samples were collected with the minimum possible free headspace.

Eurofins supplied deionized water, 250 mL PETG bottles, 250 mL amber glass bottles, 40 mL volatile organic analysis (VOA) vials, and preservative (1.2 mL concentrated HCl). Tank 21 and SHT samples were prepared in triplicate plus a blank. Each Tank 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 Tank 21 analytes were determined from samples in three separate bottles: 1) methyl Hg and ethyl Hg; 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 sample volume shortfalls, the added total soluble Hg analysis was not determined from bottle #2 but rather from bottle #3. Due to the large number of analyses being conducted, Eurofins has suggested increasing from three to four sample bottles.

In total, 16 samples were prepared on March 18, 2015 and shipped by next-day air to Eurofins where they were received on March 20, 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 21 samples, and "clean" Isopar L was submitted as the blank for the SHT samples. The Tank 21 original samples were intially diluted with deionized water in the SRNL Shielded Cells by nominally 1:100 to reduce the radiation dose. These diluted Tank 21 samples were then further diluted in the radiochemical hood with deionized water and preservative by nominally 1:3000 (polybottles) or 1:2500 (glass bottles). Thus the Tank 21 samples sent for analyses were diluted nominally in the range of 1:250,000 or 1:300,000.

The Hg species reported for the SHT samples were all collected from samples diluted by nominally 4X into reagent grade *n*-hexane into vials. The results reported by Eurofins were reported on a mass basis (ng Hg/g sample). The SHT density used to convert these to a mg/L volume basis was 0.835 g/mL @ 25 °C[ii].

Eurofins reported that it was not possible to determine the dimethyl Hg content of the SHT samples. Injection of the material caused back pressure and column performance issues that they were unable to overcome. This is likely caused by the high boiling points of the Cs extractant: MaxCalix; the suppressor: 1,2,3-tris(3,7-dimethyoctyl)guanidine; and the modifier: 1-(4-(*sec*-butyl)phenoxy)-3-(2,2,3,3-tetrafluoropropoxy)propan-2-ol, which likely thermally degrade before boiling and hence cannot be run through a GC column successfully. Hence the percent Hg recovery for the SHT material is missing the contribution of this species. This was unfortunate because one could expect any dimethyl Hg present in the salt feed to the Modular Caustic-Side Solvent Extraction Unit (MCU) to concentrate in the Isopar solvent since, as a nonpolor species, dimethyl Hg should have greater affinity in this phase than in the aqueous phase.

Table 1 provides the 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 in the measurement of total Hg and total soluble Hg, which are used to determine the particulate Hg value, i.e. the value for Hg species adsorbed to particulate matter in the samples. In light of this measurement uncertainty, the difference in the values determined for total soluble Hg and total Hg are very small or even negative, indicating that there is likely little or no particulate Hg in these highly diluted Tank 21 samples and the minimal diluted SHT samples. The value for total Hg in Tank 21 and SHT material should be the average of the measured values for total soluble Hg and total Hg. Therefore, for **Tank 21: 111 mg/L total Hg** [RSD 10%] and for the **SHT: 13.9 mg/L total Hg** [RSD 4.6%].

Eurofins indicated that there is 50% low bias in the determination of methyl Hg from an organic matrix and recommended that SRNL double the reported value of this species for the SHT samples. Hence, the value reported in Table 1 is double that reported by Eurofins.

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[i] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 2)", Experiment L2320-00016- 41, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (March 2015).

[ii] Fondeur, F. F., Taylor-Pashow, K. M. L., *Solvent Hold Tank Sample Results for MCU-15-556-557-558: March 2015 Monthly Sample*, SRNL-STI-2015-00206, Draft, Savannah River National Laboratory, Aiken, SC 29808 (April 2015).

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 average total Hg values list in the previous paragraph were utilized for this calculation. Since the initial issuance of the memorandum, Eurofins has examined these samples utilizing their calibrated ethyl Hg method and reported that no ethyl Hg above the reporting limit was observed. This update is now reflected in the Table 1.

Table 1. Concentrations of various Hg species for Tank 21 and SHT 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 21	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%
SHT	14.2 [6.0] (2)	13.5 [0.44] (2)	ND*	0.272 [35] (3)	3.44 [27] (3)	3.72 [1.1] (2)	--	Indeterminate	53+%

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

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