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To: R. E. Edwards

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Results of Hg Speciation Testing on DWPF Batch 735 RCT and OGCT Samples

Approved by:

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INTRODUCTION

Eurofins Frontier Global Sciences, Inc. in Seattle, WA on behalf of the Savannah River Remediation (SRR) Mercury Task Team tasked the Savannah River National Laboratory (SRNL) with preparing and shipping samples for Hg speciation. The fifth shipment of samples was designated to include Defense Waste Processing Facility (DWPF) samples from Batch 735 including two Recycle Collection Tank (RCT) samples and one Off Gas Condensate Tank (OGCT) sample; both are described fully in Table 1. This work was requested by DWPF in a Technical Assistance Request (TAR)[i].

Table 1. DWPF Sample Designation

Bottle ID	Label	Description	Batch Number	Date Pulled
261	RCT-5	SMECT Condensate from SRAT Cycle	4589	21 Mar 15
437	RCT-5/RCT-8	SMECT Condensate after SME Cycle	4593	30 Mar 15
232	OGCT-4	During Batch 735 Operation	~4594	2 Apr 15

Samples were collected with the minimum possible free headspace in Teflon bottles but were not refrigerated nor kept in the dark prior to transfer to SRNL on April 29 and 30. Two samples of each of the above materials were

[i] Fellinger, T. L., *Shipment and Preparation of DWPF Samples for Hg Speciation and Analysis*, X-TAR-S-00002, Savannah River Remediation, Aiken, SC 29808 (April 23, 2015).

sent to SRNL; the sample of each pair with the lowest activity was brought upstairs to B-wing and refrigerated prior to preparing final dilutions.

Eurofins supplied deionized water, 250 mL clear and amber glass bottles, and preservative (1.2 mL concentrated HCl). RCT and OGCT samples were prepared in triplicate plus a blank. Each RCT and OGCT sample was analyzed for seven Hg species: total Hg, total soluble Hg, elemental Hg [Hg(0)], ionic or 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: 1) methyl Hg and ethyl Hg; 2) dimethyl Hg, elemental Hg, and ionic Hg (Hg(I) and Hg(II)); 3) total Hg and soluble total Hg; and 4) a set used for density determination. This was the first set of samples to utilize a measured ethyl Hg technique rather than the calculated technique employed on earlier shipments.[ii]

In total, 48 samples were prepared on May 12, 2015 and shipped by next-day air to Eurofins where they were received on May 14, 2015. Details of the sample preparation activities are recorded in the SRNL E-Notebook system.[iii] SRNL deionized water was employed as the blank for the RCT and OGCT samples. The RCT and OGCT samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:2500 by volume.

Table 2 provides the average concentrations of various 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.

The proportions of particulate Hg for these samples are all relatively high compared to previous Hg speciation analyses performed on tank waste samples, but the value is inflated due to the high levels of elemental Hg present (Hg(0)). Some of this elemental Hg is removed in the filtration step and thus this solution species removal gets attributed to particulate Hg. Eurofins has indicated that they could examine the filters collected and attempt to determine a 'truer' particulate contribution for mass balance purposes, but this has not yet been done.

The high elemental Hg content of these DWPF samples also impacts the ionic or inorganic Hg determination. Since the ionic/inorganic Hg was determined on unfiltered samples, Eurofins now believes that all of the Hg reported as ionic is actually due to Hg(0), so including the ionic Hg in the Hg balance would double count the Hg(0) contribution to the total. Hence, the last column of Table 1 provides the percent of total Hg from five measured species (elemental, methyl, ethyl, dimethyl, and particulate) rather than six. The recovery for the RCT (SRAT), RCT (SME) and OGCT samples are very good at 105%, 85%, and 95%, respectively. There is significant variability in the elemental Hg analyses.

[ii] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on 2Q15 Tank 50 WAC and Cs-Decontaminated Tank 21 Waste Samples*, SRNL-L3100-2015-00084, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (May 2015).
[iii] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 5)", Experiment L2320-00016- 46, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (April 2015).

As previously noted, these were the first samples where ethyl mercury was measured rather than calculated from the methyl mercury calibration, but no detectable ethyl mercury above the reporting limits of the analytical method was observed. Similarly, no dimethyl Hg above the reporting limit was determined. Methyl Hg was much lower in these DWPF samples, both in absolute terms and as a percentage of total Hg in the sample, than was observed in Tank 21[ii, iv], 22[v], 49[vi], or 50[ii, vii].

[iv] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on Tank 21 and Solvent Hold Tank (SHT) Material*, SRNL-L3100-2015-00068, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (April 2015).
[v] 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).
[vi] Bannochie, C. J., Crawford, C. L., *Results of Hg Speciation Testing on 2Q15 Tank 50 and Tank 21 TCLP Extraction Fluid Samples and Tank 49 Material*, SRNL-L3100-2015-00106, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (June 2015).
[vii] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on 4Q14 Tank 50, 1Q15 Tank 50, and SRNL 14-Day TCLP Leachate*, SRNL-L3100-2015-00054, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (April 2015).

Table 2. Average Concentrations of various Hg species in DWPF samples from the RCT (SRAT-only), RCT (end of SME cycle) and OGCT 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
RCT (SRAT-only)	266 [11] (3)	198 [18] (3)	68*	203 [29] (3)	154 [7.0] (3)‡	7.96 [2.8] (3)	< 0.926	< 1.40E-03	105%
RCT (SME-end)	193 [2.9] (3)	156 [5.6] (3)	37*	122 [36] (3)	90.8 [9.6] (3)‡	5.10 [3.2] (3)	< 0.886	< 1.34E-03	85%
OGCT	191 [2.7] (3)	131 [4.3] (3)	60*	121 [43] (3)	105 [6.5] (3)‡	< 0.279	< 0.880	< 1.36E-03	95%

* The value for particulate Hg is inflated by the unknown fraction of elemental Hg [Hg(0)] that is removed when the sample is filtered.

‡ Due to the high concentration of elemental Hg [Hg(0)] in these samples and the fact that ionic Hg was determined on unfiltered samples, Eurofins believes the ionic Hg value reported is due entirely to elemental Hg, thus this species is NOT included in the calculation of the species fraction value.

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