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**Results of Hg Speciation Testing on DWPF SMECT-1, SMECT-3, and SMECT-5 Samples**

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 thirteenth shipment of samples was designated to include Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Condensate Tank (SMECT) from Sludge Receipt and Adjustment Tank (SRAT) Batch 736 and 738 samples. The various sample designations for the three samples analyzed are provided in Table 1. The Batch 736 'Baseline' SMECT sample was taken following a long DWPF outage related to the Potential Inadequacy in the Safety Analysis (PISA) regarding antifoam during which extensive flushing of the SMECT occurred to remove antifoam degradation products. The Batch 736 'End of Cycle' SMECT sample was taken following the completion of all SRAT processing including formic/nitric acid addition and concentration. The Batch 738 'After PRFT (Precipitate Reactor Feed Tank) Addition' is similar to a baseline sample but follows the end of caustic boiling during which the PRFT material is added to the contents of the SRAT vessel, after the vessel cools it is sampled for acid calculation analyses and prior to the start of formic/nitric acid addition and concentration. Batch 738 experienced a sludge slurry carryover event, so there was sludge solids in the SMECT sample received by SRNL. Hence, only the supernate phase of this sample was diluted and sent to Eurofins for analysis.

[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).

**Table 1 Sample Designations for DWPF SMECT Samples Analyzed by Eurofins**

| SRNL Sample ID | DWPF Description | DWPF Sample ID | DWPF LIMS No. |
|---|---|---|---|
| SMECT-1 | SRAT 736 Baseline | 1 | 200020712 |
| SMECT-3 | SRAT 736 End of Cycle | 3 | 200020775 |
| SMECT-5 | SRAT 738 After PRFT Addition | 11 | 200020844 |

SRNL removed the samples from the doorstops on October 19 and repackaged them for transfer to B-103 refrigerated storage. The SMECT-5 sample was particularly hot and visibly brown due to the sludge excursion into the off-gas system during Batch 738. They were subsampled in a radiological hood and the subsamples sent to Analytical Development for radionuclide analyses needed for Hazardous Material Transportation calculations, with the balance of the sample returned to refrigerated storage, where it remained at 4°C until final dilutions were made on November 3. It was decided that the SMECT-5 sample would be allowed to settle and the final dilution for Eurofins Hg speciation drawn from the supernate phase.

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)).

Prior to shipment, the samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:2500 by mass. SRNL deionized water was employed as the blank. 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 November 3, 2015 and shipped the following day by next-day air to Eurofins where 48 samples were received on November 5, 2015. Eurofins reported the initial aqueous sample results in units of ng Hg / L sample on December 3, 2015.

Separate dilutions of all three samples were prepared for Purge & Trap (P&T) activities conducted at SRNL. Portions of these dilutions, 130 mL, were purged with $N_2$ gas and the purge gas passed through either an activated carbon trap for dimethylmercury collection or a combination soda lime and dual gold traps in series for collection of Hg(0). The carbon and gold traps for this work were supplied by Eurofins. Details of the sample preparation and P&T activities are recorded in the SRNL E-Notebook system.[iii] This work is still scoping in nature and designed to determine whether we can reduce the variability, especially for Hg(0), seen in replicate measurements

[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).

made by Eurofins on the solution samples they have received. The traps were sent by next-day air to Eurofins on December 1, 2015. Eurofins reported the trap results in units of ng Hg / trap on December 18, 2015.

Table 2 provides the average concentrations of Hg species in the aqueous samples derived from Eurofins reported data corrected for dilutions performed by SRNL. All but one blank, not shown in the table, were reported at the reporting limits, or 'RL' values. The exception was one SMECT-5 blank analyzed for total Hg, but its measured value was five orders of magnitude lower than the samples analyzed along with it. 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 high elemental Hg in the three SMECT samples, a species which may be removed when the aqueous samples are filtered for total soluble Hg; hence, the reported particulate values have been corrected by subtracting out the contribution from Hg(0). The elemental Hg values reported were determined from the ionic Hg bottles (Set #4) because it was clear that analyzing the Hg(0) after sampling the Set #2 bottles for dimethylmercury led to a significant loss of Hg(0) to the headspace created in the sample bottle. Eurofins will no longer use the Set #2 bottles for Hg(0) measurements and SRNL will change its Chain of Custody form requests to reflect this modification to the protocol.

Eurofins purged the Hg(0) from the ionic Hg bottles prior to determining ionic Hg, as they had implemented for Shipment #12 following our discussion about the data sets that contain high elemental Hg as noted in our previous memo.[iv] This led to an appreciable decrease in the reported ionic Hg, and for one sample, a more consistent replicate set of data.

For the first time ethyl Hg was measured in a SRR sample. It was detected in all three SMECT-1 samples, but was only above the RL limit for two of the three replicates. Due to the initial dilutions employed to avoid interferences in the SMECT-3 (250,000x) and SMECT-5 (125,000x) samples compared to the 2500x dilution for the SMECT-1 sample, ethyl Hg was not measured above the detection limit in these two samples. Eurofins attempted to reanalyze these two samples at lower dilutions, but due to the instrument's automatic detector protection system this was not possible. Initially, they believed this was caused by high inorganic Hg, but upon further discussion, they agree that it is the higher methyl Hg in the SMECT-3 and SMECT-5 samples as compared to the SMECT-1 samples that is the root issue. Methyl Hg is also propylated in the method for ethyl Hg determination, and the instrument is purging any samples that are too high in methyl propyl Hg so as not to damage the detector. Ethyl Hg is likely present in these samples too, but ethyl propyl Hg cannot be quantified at the dilution the instrumentation will accept. There was no dimethyl Hg in these samples above the reporting limit of the analytical method.

Comparing the baseline Batch 736 SRAT cycle sample SMECT-1 to the end of cycle Batch 736 SRAT sample SMECT-3, it is clearly shown that methylmercury is being produced and collected in the SMECT as a result of SRAT operations. The value rises from less than 1 mg/L to 136 mg/L in the SMECT following SRAT operations.

[iv] Bannochie, C. J., *Results of Hg Speciation Testing on Tanks 30, 32, and 37 Depth Samples*, SRNL-L3100-2015-00206, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (November 2015).

Additionally, it is clear from Table 2 that the SMECT contains a variety of Hg species (particulate, Hg(0), ionic Hg, and methyl Hg) at appreciable concentrations.

The last column of Table 2 provides the percent of total Hg that the six measured species (particulate, elemental, ionic, methyl, ethyl, and dimethyl) represent. Only about 60% of the SMECT-1 Hg species are accounted for, which is lower than determined for the other two samples. A range is provided for the SMECT-3 and SMECT-5 samples to account for the uncertainty of the detection limit values reported for the ethyl Hg species. The recoveries for the SMECT-3 and SMECT-5 analyses are 75 – 89% and 75 – 80%, respectively. 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%.

Table 3 provides data that was obtained from traps SRNL collected from dilutions of each sample. Due to the high concentration of elemental Hg in these particular samples, the amount of Hg(0) exceeded the capacity of the two sequential Au traps. This was evidenced by the relatively high amount of Hg(0) detected in the second trap, indicative of Hg(0) breakthrough from the first trap; therefore, the values for Hg(0) in Table 3 are labeled as indeterminate. At the time of the collection, the amount of Hg(0) in these three samples was not known, so it was not possible to predict the dilution factor that would be necessary to not exceed the trap capacity. The dimethyl Hg collected on the activated carbon traps was below the reporting limit established by Eurofins and is thus consistent with data they obtained on the bottle samples they received.

**Table 2. Average Concentrations of various Hg species for DWPF SMECT 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 |
|---|---|---|---|---|---|---|---|---|---|
| **SMECT-1** | 504 [4.5] (3) | 257 [2.0] (3) | 68*‡ | 179 [2.0] (3) | 53.4 [1.2] (3) | 0.979 [NA] (1) | 0.885 [4.2] (2) | < 0.000241 | 60% |
| **SMECT-3** | 588 [10] (3) | 343 [0.2] (3) | 50*‡ | 195 [8.0] (3) | 60.9 [6.8] (3) | 136 [2.2] (3) | < 84 | < 0.000242 | 75 – 89% |
| **SMECT-5** | 721 [8.2] (3) | 516 [5.6] (3) | ~0*‡ | 362 [2.5] (3) | 131 [2.9] (3) | 44.9 [1.5] (3) | < 42 | < 0.000238 | 75 – 80% |

* 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 these samples inflates the particulate Hg values. The particulate value is corrected by the subtracting the value of the Hg(0) from the difference between the total and total soluble Hg values.

**Table 3. Concentrations of Hg(0) and Dimethyl Hg in DWPF SMECT Samples After SRNL Purge & Trap expressed as mg Hg/L (ppm) [%RSD] (No. Replicates)**

| Sample | Elemental Hg [Hg(0)] | Dimethyl Hg |
|---|---|---|
| **SMECT-1** | Indeterminate | < 0.000334 |
| **SMECT-3** | Indeterminate | < 0.000332 |
| **SMECT-5** | Indeterminate | < 0.000332 |

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