



An Alternative Analytical Technique for Mercury Speciation in Radioactive Tank Waste at the Savannah River Site

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Introduction

Significant levels of mercury are present in the underground storage tanks at the US Department of Energy Savannah River Site (SRS) (Figure 1). Removal of the mercury from the radioactive liquid waste stored in these tanks (Figure 2) is a major concern and challenge for the federal government. The species of mercury in the tank wastes are suspected to have changed over time causing changes in the stabilization efficiency of mercury in the solid waste products, such as Saltstone.



Figure 1. The US Department of Energy Savannah River Site is located on the Savannah River on the border between the states of Georgia and South Carolina.



Figure 2. An aerial view of a tank farm similar to that at the Savannah River Site. The SRS has 51 underground storage tanks with a total mercury inventory of up to 70,000 kg of mercury.

It was originally believed that the mercury in the tank wastes was present as inorganic forms, such as HgO and Hg(II). However, a trend of increasing mercury concentrations from waste characterization analysis of the Saltstone triggered an investigation. Initial testing of the Saltstone waste feed showed a significant amount of organomercury species. As mercury speciation analyses were performed at additional individual tanks, poor mass balance (comparison of the total mercury concentration to the sum of the mercury species concentrations) was often observed, resulting in ambiguous interpretation of the results. Since the efficacy of the treatment process is dependent on the molecular forms of mercury present in the waste, the site contractor decided to investigate the situation by evaluating if alternative analytical techniques would yield better mass balance for mercury.

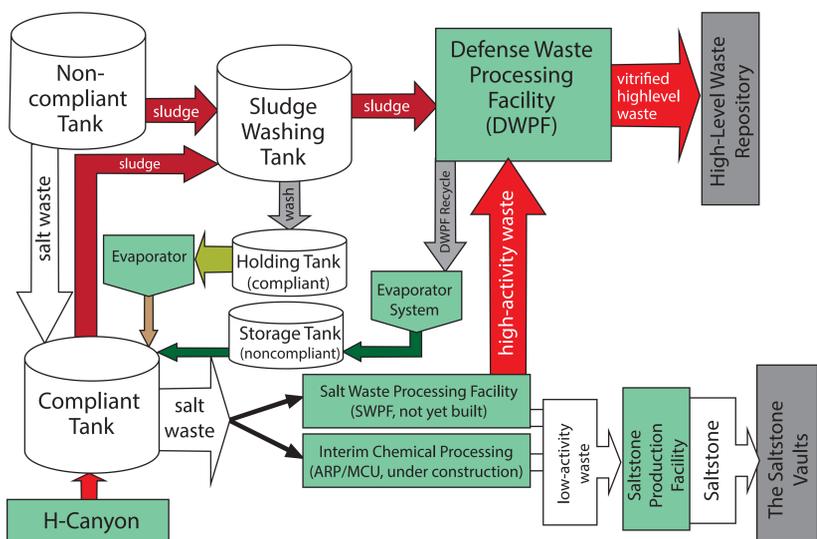


Figure 3. An example of the tank waste disposal process.

Methods

Diluted tank waste samples were analyzed for total Hg, dissolved Hg, volatile mercury (includes Hg₀ and DMeHg), methylmercury (MeHg), ethylmercury (EtHg), and dimethylmercury (DMeHg) by Brooks Applied Labs (BAL) using methods based on traditional cold vapor atomic fluorescence spectrometry (CV-AFS) technology. Additionally, BAL developed an alternative analytical technique for the simultaneous analysis of inorganic mercury [Hg(II)], MeHg, EtHg, and phenylmercury (PhHg) using ion pairing chromatography with cold vapor generation and inductively coupled plasma mass spectrometry detection (IP-CV-ICP-MS) and DMeHg by reverse phase chromatography (RP-ICP-MS). Results from the two methods are compared and discussed (Figure 4).

	Total Hg	Diss Hg	DMeHg	Volatile Hg	EtHg	MeHg	PhHg	Hg(II)
AFS	x	x	x	x	x	x		
ICP-MS			x		x	x	x	x

Figure 4. An overview of the mercury species determined by each method.

AFS

Total mercury and dissolved mercury (0.45-µm filtration) were determined following EPA Method 1631E using a Brooks Rand Instruments (BRI) MERX-T automated analysis system. Volatile mercury was determined by manually purging unaltered samples onto gold-coated glass bead pre-concentration traps for 45 minutes followed by thermal desorption and analysis with a BRI Amalgamation Control Module and Model III Detector. Volatile mercury can include both Hg₀ and DMeHg since both are volatile species and will adsorb to gold traps.



Figure 5. Brooks Rand Instruments MERX-M used for total and dissolved methylmercury analysis. A modification of the MERX-M system was also used for the automated analysis of dimethylmercury by AFS.

MeHg and EtHg were determined by EPA Draft Method 1630 (modified). The samples were first prepared by distillation. The distillate was then buffered for MeHg and derivatized with a sodium tetraethylborate solution prior to analysis on the BRI MERX-M (Figure 5). EtHg was prepared and analyzed in the same way, except sodium tetra-n-propylborate was used as the derivatization reagent.

For DMeHg, 40-mL of the sample was added directly to a septum-topped amber glass vial. No reagents were added. The samples were analyzed according to EPA Draft Method 1630, Appendix A (modified) on the MERX-M system using Carbotrap® preconcentration traps.

ICP-MS

BAL developed an analytical technique for the simultaneous analysis of inorganic Hg, MeHg, EtHg, and PhHg using IP-CV-ICP-MS (Figure 6 and 7) and DMeHg by RP-ICP-MS with analysis on a Perkin Elmer DRC II.

IP-CV-ICP-MS

- IP** • Species separation using ion pairing chromatography
- CV** • Oxidation with bromine monochloride
• Reduction to elemental mercury with borohydride
- ICP-MS** • Detection with inductively coupled plasma mass spectrometry

Figure 6. Overview of the steps of IP-CV-ICP-MS analysis of mercury species.

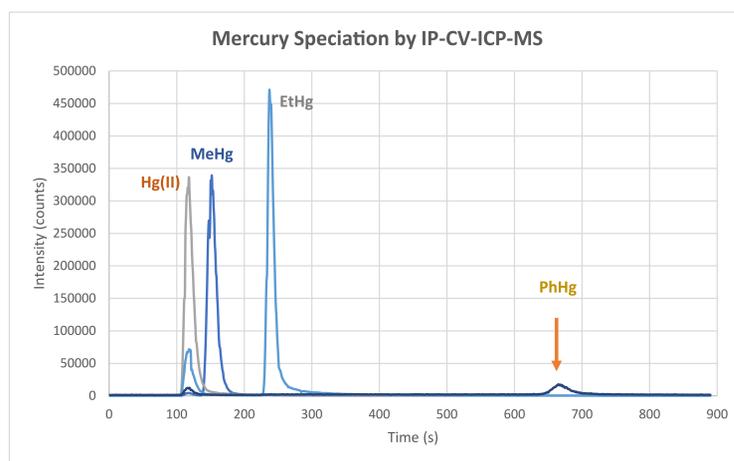


Figure 7. Example chromatogram of mercury species using IP-CV-ICP-MS.

Results and Discussion

Samples were taken from two tanks and large dilutions were made in triplicate to reduce the radioactivity to a level acceptable for transport and receipt by the laboratory. The triplicate samples were analyzed by AFS methods and ICP-MS methods and evaluated for mass balance (Figure 8).

Mass Balance (all results in ng/L)										
	THg	DHg	HgP	DMeHg*	TotVol Hg	EtHg	MeHg	Hg(II)	Sum of Species	% of THg
TK-22 (AFS)	416 ± 6	386 ± 12	31 ± 13	0.023 ± 0.004	36.3 ± 1.6	< 0.10	57 ± 4	343¥	436	105
TK-22 (ICP)				< 0.2	36.3¥	< 0.6	75.7 ± 3.8	343 ± 6	455	109
TK-38 (AFS)	1099 ± 13	1000 ± 13	99 ± 11	0.130 ± 0.038	186 ± 8	< 0.41	514 ± 13	314¥	1014	92
TK-38 (ICP)				< 0.2	186¥	10 ± 0	538 ± 10	314 ± 7	1048	95

Figure 8. Table of mean results for total mercury and mercury species. The sum of the species was calculated (sum of species includes DMeHg, volatile Hg, EtHg, MeHg, and Hg(II)) and compared to the total mercury result. No PhHg was detected. *DMeHg results by CV-AFS are possibly false positives due to elemental Hg in the samples. ¥Results were copied from a different method for mass balance calculation purposes.

The results from the two methods agreed well with one another, with the exception of MeHg from the TK-22 sample, which had an RPD between the methods of 28%. For EtHg and DMeHg, the differences between the results were largely due to the methods' different detection limits. Both methods yielded acceptable mass balance, with the sum of the species ranging from 92% - 109% of the total mercury concentrations.

Dimethylmercury Holding Time Study

The process to collect the tank waste samples, make serial dilutions, and send the samples to the laboratory commonly takes weeks to months. The serial dilutions for DMeHg were performed in Teflon™ bottles. DMeHg may have the ability to pass through the walls of plastic bottles; therefore, a holding time study was conducted to assess the potential loss of DMeHg from a Teflon™ bottle over time (Figure 9).

Study Design:

- 125-mL Teflon™ bottles filled with reagent water and no headspace
- 1000 ng/L DMeHg spiked to each bottle
- Stored at 4 °C in the dark
- Analyzed aliquots at 3 time intervals: 21, 45, and 77 days
- To account for potential analyte loss during opening of bottles at each time interval, 3 replicate bottles were used

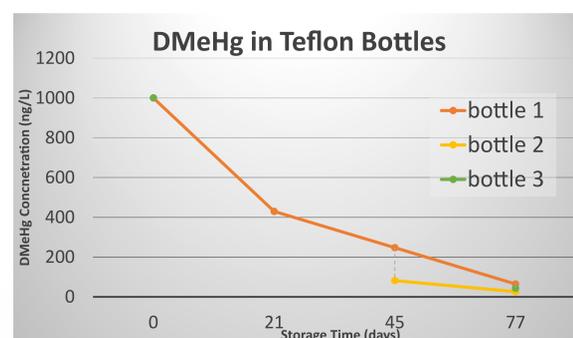


Figure 9. All three bottles were spiked with 1000 ng/L of DMeHg. Bottle 1 was analyzed at the first timepoint (21 days), while the other two bottles remained unopened. Bottles 1 and 2 were analyzed at the second timepoint (45 days), while Bottle 3 remained unopened. All three bottles were analyzed at the final timepoint (77 days). There was significant loss of DMeHg over the 77-day study, with less than 10% of the initial concentration remaining in both the opened and unopened bottles.

Conclusions

- Excellent mass balance was achieved on both sets of tank waste samples for both the AFS method and the ICP-MS method.
- The IP-CV-ICP-MS method effectively separated and directly quantitated all target non-volatile Hg species.
- The RP-ICP-MS method effectively separated DMeHg without elemental Hg interference.
- Samples for DMeHg, as well as samples for other Hg species, should always be collected in glass bottles and shipped to the lab immediately following collection.