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Key WordsMercury  
Analysis  
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Bias**INTER-OFFICE MEMORANDUM**

SAVANNAH RIVER PLANT

DPSPU-85-272-34

March 27, 1985

TO: J. T. BUCKNER, JR., 703-F

FROM: H. P. HOLCOMB, 772-F *HPH*HIGH BIAS OF DCAP AND AA ANALYSES OF Hg(I)INTRODUCTION

Last November I issued a memorandum<sup>1</sup> to personnel in Laboratories, Health Protection, Naval Fuels, and SRL-ADD noting the problems that I had encountered with the analysis of solutions containing Hg(I). These analyses were conducted using Inductively Coupled Plasma (ICP) or Direct Current Argon Plasma (DCAP) spectrometers versus Hg(II) standards. Analyses of Hg(I) solutions were consistently high, sometimes more than twice their stoichiometric makeup. H. M. Forrest of Laboratories and A. R. Jurgensen of SRL-ADD have cooperated with me in trying to quantify this analytical discrepancy.

SUMMARY

This brief, but definitive, study indicates that the relatively new spectrometric techniques, DCAP and AA (Atomic Absorption), give high values for mercury when employed to analyze solutions that contain Hg(I) per se or that contain soluble mercury which is or has been subject to reducing conditions. I do not know if a similar problem exists with other multivalent, single ion systems, such as  $Fe^{+2}-Fe^{+3}$  or  $Ce^{+3}-Ce^{+4}$ , for example.

From a single stock source, solutions were prepared to contain 2 to 20 ppm ( $\mu\text{g}/\text{mL}$ ) of mercury, four as Hg(I) and four as Hg(II) with each respective pair containing the same total Hg concentration. The initial stock solution was prepared from reagent-grade mercurous nitrate monohydrate using standard quantitative gravimetric and volumetric techniques. Diluted, oxidized aliquots were prepared to contain only Hg(II). Separate diluted-only aliquots were prepared to contain only Hg(I). Samples of both sets of solutions were submitted for DCAP and AA spectrometric analyses.

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Positive bias for DCAP analysis of Hg(I) versus that found for Hg(II) averaged 48% for the 4 samples; for AA, the bias averaged 150%.

## EXPERIMENTAL

### Preparation of Hg(I) Stock Solution

0.350 g of "Baker Analyzed" reagent mercurous nitrate monohydrate,  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ , ( $<0.5\% \text{Hg}^{+2}$ ) was dissolved in weak nitric acid. Following dissolution, the solution was diluted to the mark in a 500-mL volumetric flask. The final solution yielded 500 ppm (or  $\mu\text{g/mL}$ ) Hg(I) and was 0.1M  $\text{HNO}_3$ .

### Preparation of Hg(I) Solutions For Analysis

Into four 25-mL volumetric flasks were pipetted, respectively, 1000  $\mu\text{L}$ , 500  $\mu\text{L}$ , 250  $\mu\text{L}$ , and 100  $\mu\text{L}$  of the 500 ppm Hg(I) stock solution. Following dilution to the mark with deionized water, the respective solutions contained 20, 10, 5, and 2 ppm Hg(I) with a maximum  $\text{HNO}_3$  concentration of 0.004M. Solutions of Hg(I) in weak  $\text{HNO}_3$  at room temperature are known to be fairly stable<sup>2</sup>; i. e., quite slow to oxidize to Hg(II) or to reduce to Hg(O).

### Preparation of Hg(II) Solutions For Analysis

Into vials containing 2.0 mL of 15.7M  $\text{HNO}_3$  were respectively pipetted the same size aliquots of 500 ppm Hg(I) stock solution used to prepare the Hg(I) solutions. The loosely capped vials were then placed in a boiling water bath for 1 hour. In previous studies to determine the fate of mercurous nitrate in Rocky Flats scrub alloy (RFSA) processing in F-Canyon, I had determined<sup>3</sup> that Hg(I) can be quantitatively oxidized to Hg(II) in the presence of a minimum of 5M  $\text{HNO}_3$  by heating for 5 minutes at boiling water temperatures.

Following the oxidation step, the contents of each vial was quantitatively transferred into a 25-mL volumetric flask and diluted to volume with deionized water. These four solutions therefore contained 20, 10, 5, and 2 ppm Hg(II), respectively, and were approximately 1.25M in  $\text{HNO}_3$ .

### Analysis of the Hg(I) and Hg(II) Solutions by DCAP and AA

Because of their previous involvement in analyzing my samples during which work the initial discrepancies were noted, both H. M. Forrest of Laboratories and A. R. Jurgensen of SRL-ADD were requested to analyze portions of the Hg(I) and Hg(II) solutions as prepared. My efforts in trying to quantitize the discrepancy were explained to them. Both graciously agreed to analyze the

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two sets of solutions to better define the analytical disparity. Their raw data are given in the following table.

TABLE 1DCAP and AA Analysis of Hg(I) and Hg(II) Solutions

ppm total Hg in solution as determined by gravimetric and volumetric preparation	Analysis Mode	ppm Hg		%Relative Difference (I) vs (II)
		Solutions of Hg(II)	Solutions Of Hg(I)	
20	DCAP	22.1	31.8	+44
	AA	23.7	54.5	+130
10	DCAP	11.1	17.3	+56
	AA	11.1	24.2	+118
5	DCAP	5.3	10.3	+94
	AA	3.0	12.1	+303
2	DCAP	2.3	2.3	0
	AA	1.0	1.5	+50
Average %Relative Difference				DCAP +48
				AA +150

DISCUSSION

The raw analytical data demonstrate the discrepancy in these two independent, relatively modern spectrometric techniques for analysis of Hg(I) vs Hg(II). As the Perkin-Elmer data sheet (attached to my 11/84 memorandum) on Hg analysis by AA indicated, the presence of Hg(I) can generate incorrectly higher results for mercury. The foregoing data and previous sample analyses also indicate that AA is not the only spectrometric technique affected by this problem. DCAP suffers the same malady, although not to as great an extent, based on just the foregoing single point analysis results.

To clearly define the discrepancy would necessitate a statistical study over a much broader concentration range than that investigated. Such is not the scope of my attention. I only wished to quantitatively document the problem and to issue the findings to those at SRP-SRL that should be aware of this analytical inconsistency. We already use Hg(I) in F-Canyon processing of RFSA, so it is not foreign to us. It could arise elsewhere as a process additive, as a result of reducing conditions in solution acting upon Hg(II)

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already there, or from environmental mercury concerns. The point is, however, Hg(I) can provide an analytical ambush if the analyst is unaware of its presence and has not taken proper precautions to negate its higher spectrometric sensitivity.

I do not know if this problem extends to other multivalent, single ion systems such as ferrous-ferric, cerrous-cerric, etc. Perhaps verification is needed of the presence or lack of bias in the analyses of these more common inorganic elements.

#### ACKNOWLEDGMENT

The assistance of H. M. Forrest of Laboratories and A. R. Jurgensen of SRL-ADD is gratefully acknowledged. Their cooperation and interest in helping to elucidate the problem of Hg(I) spectrometric sensitivity versus that of Hg(II) is appreciated.

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HPH/h