Note on the Flameless Atomic Absorption Response of Mercury Without Added Reducing Agent

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Since the ubiquitous presence of mercury in the environment became evident, a large number of papers have been published on the analysis of mercury in biological materials by various adaptations of the well known flameless atomic absorption analysis method of HATCH and OTT (2). This method is based on reduction of mercuric ion in acid solution to the atomic state with stannous ion followed by vaporization of volatile mercury with circulating air into the light path of an atomic absorption spectrophotometer and analysis. A version of this procedure was being used by the authors in which mercuric ion was reduced with stannous chloride in a 1 N sulfuric acid solution. While developing a standard curve, addition of stannous chloride was inadvertently omitted in one of the standards. It was observed, however, that a positive atomic absorption response to mercury was obtained although of somewhat lower magnitude than when stannous chloride was added. A response curve was developed for increasing quantities of mercury as mercuric chloride but with no stannous chloride used in the procedure. This is shown in Figure 1. It was found that the mercury response required a sulfuric acid concentration of at least 0.1 N and this response did not increase greatly as the acid concentration was increased to 6 N. A somewhat similar but lower mercury response was noted when phosphoric acid was substituted for sulfuric. The relation between the magnitude of the response and the quantity of mercury was more erratic with phosphoric acid. When no reducing agent was used a longer time of aeration was required before an equilibrium absorbance reading was obtained.

It is believed that the mechanism for the above observation may be as follows. Mercuric chloride is largely undissociated in acid solution and it is also volatile. The vapor pressure determined by dynamic method at 23^{o}C (296^{o}K) is 7.5 x 10^{-5}mm Hg; with nitrogen as the carrier gas 7 micrograms per liter was removed (4). Similar vapor pressure values were obtained using air (3). Upon aeration, mercuric chloride may therefore vaporize intact (sublime) into the light path whereupon it is photolytically decomposed to atomic mercury with subsequent absorption of the 2537 Å line. It was found that when mercuric chloride was present in sulfuric acid in mixture with either nitric acid or potassium permanganate (but without reducing agent) no atomic absorption response to mercury resulted upon aeration. This was probably due to oxidation of chloride and production of non-volatile mercuric sulfate.

Bulletin of Environmental Contamination & Toxicology,
Vol. 8, No. 3, 1972,

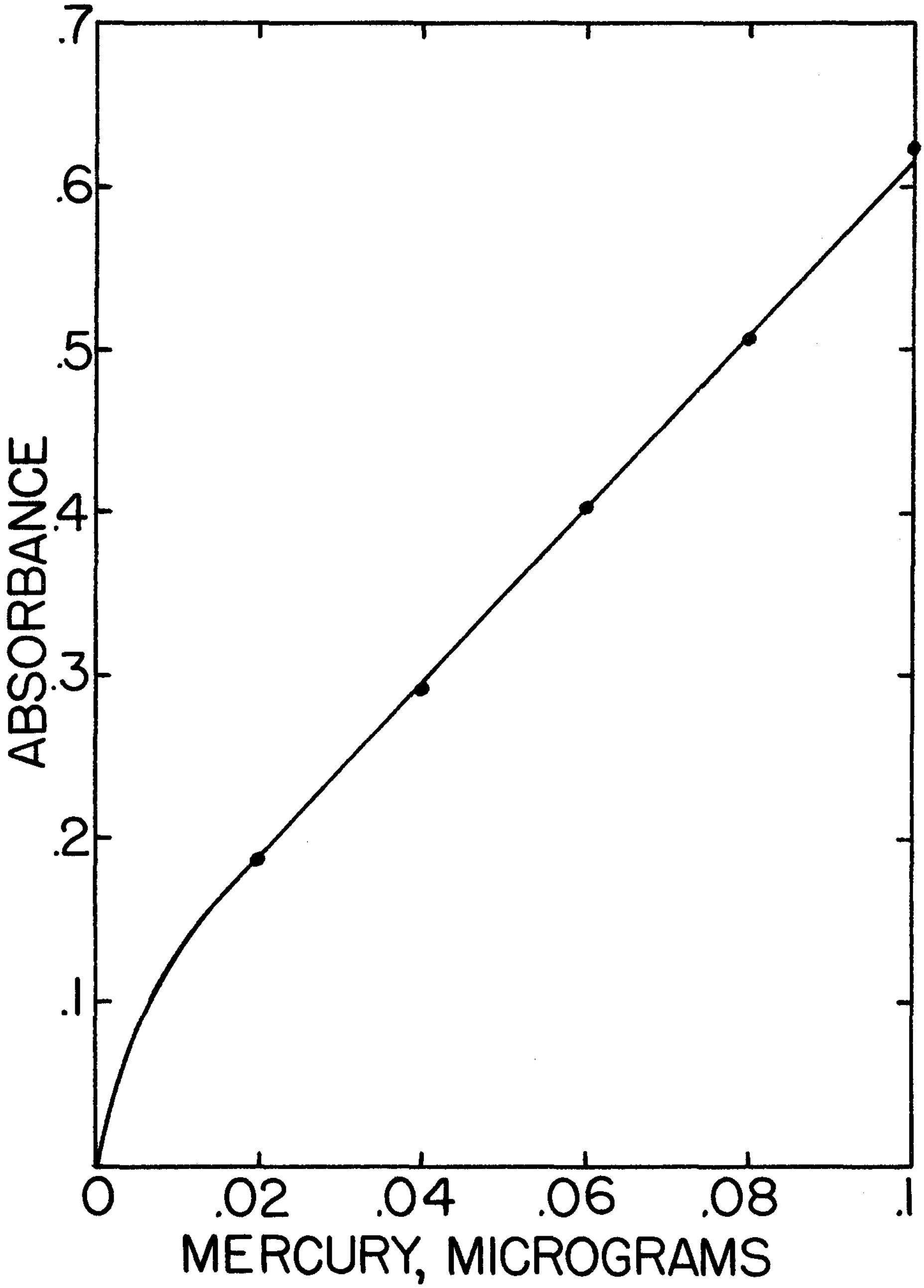

Figure 1. Flameless atomic absorption response of mercury evolved by aeration of mercuric chloride in 1 N sulfuric acid in the absence of a reducing agent.

The non-reduction procedure may not be applicable in hydrochloric acid media because the mercuric ion is stabilized as the relatively non-volatile $HgCl_2^{2-}$ complex (1).

References

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