

Determination of trace levels of mercury in aqueous solutions by inductively coupled plasma atomic emission spectrometry: Elimination of the ‘memory effect’

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Abstract

The measurement of mercury in aqueous solutions by ICP-AES is adversely affected by the memory effect wherein mercury accumulates within the sample introduction system and is slowly released over time to give increasing response signals at the same initial mercury concentration. The memory effect is obviated by the addition of Hg(II) complexants: thiourea and gold(III) chloride are both effective in preventing mercury sorption and vapor buildup with the latter being preferred because the memory effect vanishes more rapidly. Conditions are described wherein it is possible to quantify low levels of mercury(II) in aqueous solutions by ICP-AES under routine operating conditions that can be applied to other metal ions by adding 1 mg of gold(III) chloride per 3 mg of mercury(II) to those solutions.

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1. Introduction

The toxicity of mercury at very low levels has led to its stringent control with a maximum contaminant level of 2 µg/L being set by the US Environmental Protection Agency [1]. This has led to the development of techniques for accurate monitoring of mercury levels [2] via cold vapor atomic absorption spectrometry [3,4], plasma atomic emission spectrometry [5], atomic fluorescence spectrometry [6,7], inductively coupled plasma (ICP) optical emission spectrometry [8] and ICP-mass spectrometry [9–11].

Despite methods with good sensitivity and selectivity, few can directly measure Hg(II) in aqueous solutions under routine operating conditions as can be done with other ions [12]. Mercury accumulates in instruments irrespective of its initial concentration in solutions, leading to a memory effect whereby there is a gradual increase of the mercury signal strength with time, a non-linear calibration, and a long wash-out time [13]. Mercury contamination of the instruments may be attributed to

its adsorption on the transfer tubing, spray chamber and nebulizer [14].

Mercury in solution exists as an equilibrium of Hg(0), Hg(I), and Hg(II). Since only Hg(0) is volatile, one method of eliminating the memory effect entails complete reduction of the mercury to Hg(0) with the reducing agents stannous chloride and sodium borohydride [15]. The mercury vapor is then purged from solution into an absorption cell. This cold vapor technique [16] is frequently used for mercury determination in solution when coupled with atomic absorption or atomic fluorescence spectrometry. The standard EPA mercury determination method is based on this technique [17]. The generation of mercury vapor does, however, require additional equipment for its generation and measurement. An alternative technique involves the stabilization of mercury in solution as Hg(II). Gold(III) chloride and potassium dichromate are typical stabilizing agents that give complete conversion to Hg(II) thus obviating volatilization [18]. The technique has been applied to the measurement of mercury via ICP-mass spectrometry (MS) [19]. The addition of chelants that bind Hg(II) also stabilizes it within aqueous solutions and limits loss through volatilization. Thus the addition of Triton X-100, ammonia and EDTA allows for the accurate measurement

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Table 1
ICP-AES operating conditions

Plasma power (w)	1200
Coolant flow (L/min)	15.0
Auxiliary flow (L/min)	0.5
Nebulizer flow (L/min)	1.0
Fast preflush time (s)	12
Total preflush time (s)	20
Sample aspiration flow (mL/min)	2.0
Wash time between samples (min)	1–2

of mercury in aqueous solutions by ICP-MS [20]. The use of 2-mercaptoethanol reduces the memory effect to the point that ICP-MS gives a detection limit for mercury of 5.1 $\mu\text{g/L}$ [21].

Techniques have been developed to allow the use of cold vapor coupled atomic absorption spectrometry (CV AAS) [22] and ICP-MS for mercury determination. The detection limits are 10 $\mu\text{g/L}$ for the former and 3 $\mu\text{g/L}$ for the latter [23]. While ICP is thus an excellent technique for mercury determination, its extension to the more commonly available ICP-atomic emission spectroscopy (AES) remains problematic due to the memory effect [24]. It is reasonable to expect that mercury-stabilizing agents added to solutions would eliminate the memory effect in ICP-AES as they have with ICP-MS. The use of a 2% L-cysteine solution containing Hg(II), but only at a very low level (1 $\mu\text{g/L}$), obviates the memory effect in ICP-AES [25]. We now report a rapid and accurate method for the determination of total mercury in aqueous solutions at the mg/L level using ICP-AES through a comparative study of gold(III) chloride, triethylamine, ethylenediaminetetraacetic acid (EDTA), disodium ethylenediaminetetraacetate (Na_2EDTA) and thiourea.

2. Experimental section

2.1. Reagents

Mercury solutions are prepared by diluting a 1000 mg/L mercury(II) nitrate reference solution containing 1.8% nitric acid. Au(III) solutions are prepared from a 1000 mg/L gold atomic absorption standard solution in 0.5 M HCl. Triethylamine, ethylenediamine tetraacetic acid (EDTA), disodium EDTA (Na_2EDTA), and thiourea (analytical grade) were purchased from Acros and used directly without purification. Nanopure water with resistivity $>18\text{ M}\Omega$ was used from a Barnstead ultrapure water system.

2.2. Instrumentation

A Spectroflame M120E (Spectroanalytical Instruments) inductively coupled atomic emission spectrometer (ICP-AES) controlled by Spectro Smart Analyzer Vision software was used for analysis of the mercury in solution. Sample solutions were introduced by peristaltic pump. Ultra-pure argon from Airgas was used. The wavelength of analysis was set at 184.956 nm. The operating conditions (also appropriate for the analysis of other transition metal ions) are detailed in Table 1. Measurement was initiated immediately after the preflush.

2.3. Analytical procedure

Mercury(II) solutions with 2.0 mg Hg(II)/L were prepared in 50 mL volumetric flasks also containing one of the following: Au(III) at 1.0 mg/L, 0.1% triethylamine, EDTA (saturated solution), 0.1% Na_2EDTA , or 0.1% thiourea (following reports in the literature with ICP-MS, 0.1% Triton X-100 was added to the amine and thiourea solutions as a wetting agent). One set of solutions was allowed to stand for 1 h before analysis and a second set was allowed to stand for 17 h. Au(III) solution at 1.0 mg/L was made by successive dilutions of a 1000 mg/L standard reference solution. Triethylamine, Na_2EDTA and thiourea solutions were prepared by dilution of their 1% stock solutions. Due to its low solubility (0.5 g/L), the EDTA solution was prepared by adding 0.05 g directly to the Hg(II) solution in a 50 mL volumetric flask and then using only the supernatant for the ICP measurement. Mercury standard solutions at levels up to 10.0 mg/L containing up to 10.0 mg Au(III)/L were prepared by successive dilution of 1000 mg/L Hg(II) and Au(III) reference solutions.

After the plasma was ignited, nanopure water acidified with 1% nitric acid was used to wash the sample introduction system and the instrument allowed to stabilize for 15–20 min. The optics were then refiled, the sample solution aspirated into the ICP-AES, and measurement initiated immediately after a 20 s preflush. Three measurements were taken as the solution was continuously aspirated and averaged. Nitric acid solutions (1 M) containing 1.0 mg Au(III)/L were used to rinse the sample introduction system between samples for 1–2 min.

3. Results

The memory effect increases the mercury count and leads to erroneous results for the concentration of mercury in successive samples. Fig. 1 shows the changes in mercury signal intensity measured at different times when Hg(II) standard solution at 0.2 mg/L is aspirated into the ICP-AES. The same result is seen

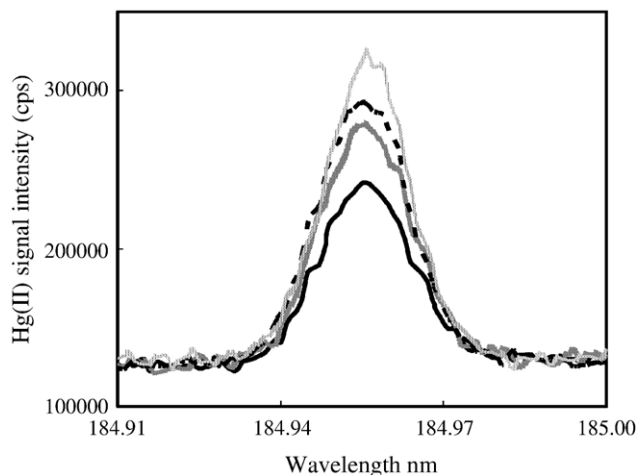


Fig. 1. Changes in continuous signal intensity measurements of Hg(II) (0.2 mg/L) in aqueous solution (the lowest (black solid) line is the first measurement followed by the second, third and fourth measurements).

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