Direct Nebulization of Sample Solution Containing Reductant for the Determination of Mercury by Inductively Coupled Plasma-Atomic Emission Spectrometry

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Synopsis. In order to enhance the sensitivity of mercury, the most effective reductant, tin(II) chloride was added to a mercury solution, and the mixture was immediately introduced into the plasma through a conventional pneumatic nebulizer. The attainable detection limit for mercury was improved from 79 ng ml^{-1} in the untreated solutions to 1.3 ng ml^{-1} when tin(II) chloride was added. The present method was successfully applied to the determination of trace concentrations of mercury in several samples of waste water.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is the current method of choice for the determination of a great number of elements. However, for normal pneumatic nebulizers, the transport efficiency in the sample introduction system of ICP-AES is very low (i.e., less than 5%).[1] If the analyte is present in solution in a volatile form, the transport efficiency dramatically increases. Such a phenomenon has been described for some elements that may be present in solution in a volatile form, e.g., boron by flame atomic absorption spectrometry,[2] osmium and mercury,[3] molybdenum,[4] and iodine[5,6] by ICP-AES. Summerhays et al.[3] have presented quite a few preliminary results for mercury. However, no comprehensive study has been completed yet. In this work, therefore, we examined in detail a further method for enhancing the sensitivity of mercury by conventional ICP-AES with use of several reductants, and applied the present method to the determination of trace concentrations of mercury in some samples of waste water.

Experimental

Apparatus. A Nippon Jarrell-Ash Model ICAP-50SM inductively coupled argon plasma emission spectrometer equipped with a normal pneumatic nebulizer of cross-flow type was used in combination with a Rikadenki R-21 strip chart recorder.

Reagents. All the reagents were of analytical-reagent grade and were used as received from commercial sources. High-purity water (Milli-Q water) was obtained by a Milli-Q ion exchange and membrane-filter purification system (Millipore Corporation, Bedford, MA, USA). A 1000 μg ml^{-1} mercury stock standard solution was prepared by dissolving mercury(II) chloride in Milli-Q water.

Procedure. The present procedure, referred to as reductant addition method, consisted of mixing the sample solution and reductant solution. The treated sample was then nebulized into the ICP source through a normal nebulizer. In the optimization of the operating conditions, all emission intensities, when stabilized, were integrated at least in triplicate over a fixed period of time. Background emission intensity, integrated over the same time period, was subtracted from all line emission data to obtain the net line emission intensities for mercury. The experimental conditions used are described in Table 1.

Table 1. Optimized Experimental Conditions for the Determination of Mercury

Wavelength	Hg(I)253.652 nm
RF power forward	1.0 kW
Coolant gas flow rate	17.0 l min^{-1}
Plasma gas flow rate	0.40 l min^{-1}
Carrier gas flow rate	0.52 l min^{-1}
Observation height (above load coil)	18.0 mm
Sample uptake rate	1.32 ml min^{-1}
Reductant ($SnCl_2$) concentration	1.0 w/v% in 1.0 v/v%HCl

Results and Discussion

In an attempt to obtain a maximum line-to-background intensity ratio, I_n/I_b (I_n, net analyte emission intensity; I_b, background emission intensity) for mercury, various operating parameters were optimized individually, while the other parameters were kept at their optimum values (i.e., univariate search technique). Standard solutions containing 5 and 0.1 μg ml^{-1} of mercury for conventional solution nebulization and reductant addition method, respectively, were used to obtain the best experimental parameters. The optimized operating conditions are summarized in Table 1.

Selection of Reductant. The influence of various reducing agents, at their concentration range of 0.05—5 w/v%, on the mercury emission intensity was briefly investigated. Each solution containing mercury and a reductant was acidified with hydrochloric acid to give a final acidity of 0.1—10 v/v%. The reducing agents examined were tin(II) chloride, sodium sulfite, hydroxylamine, and sodium tetrahydroborate. As a result, tin(II) chloride gave rise to the largest enhancing effect, and the mercury emission intensity in the presence of tin(II) chloride was increased by a factor of approximately 50 in comparison with that obtained by conventional nebulization with the addition of no reductant. The great improvement in emission intensity of mercury produced by reduction of the mercury ion to elemental mercury vapor using tin(II) chloride in the following reaction:

$$Hg^{2+} + Sn^{2+} \longrightarrow Hg^0 + Sn^{4+},$$

may result from increased efficiency of the analyte transport to the ICP source. Consequently, tin(II) chloride was selected as the most suitable reductant for mercury and used under the optimized concentration and acidity (Table 1) for the continuation of this study. There was no significant difference in background emission intensity between a blank solution of tin(II) chloride and Milli-Q water.

Calibration Curve and Detection Limit. Calibration graphs were established for mercury with and without the addition of tin(II) chloride under the optimized experimental conditions described in Table 1 and are shown in Fig. 1. The data points are the means of five replicate measurements each. At higher concentrations of mercury the enhancement by the addition of the reducing agent was gradually smaller, resulting in an increased curvature in the calibration graph. This curvature might be attributed to a decrease in the transport efficiency of the elemental mercury and/or an increased loss of mercury vapor from solutions (see below) at higher concentrations of mercury.

The detection limits for mercury obtained with and without the addition of tin(II) chloride were 1.3 and 79 ng ml^{-1}, respectively. The detection limit reported here corresponds to the concentration of the analyte required to give a net intensity, i.e., background-corrected emission intensity, equal to three times the standard deviation of the background emission intensity with the use of the IUPAC recommendation.[7] The short-term precisions expressed as a relative standard deviation (RSD) for 10 replicate measurements are 2.76% at 10 ng ml^{-1} of mercury with this reductant addition method and 2.86% at 500 ng ml^{-1} of mercury with the conventional nebulization.

Loss of Volatile Elemental Mercury from Solutions. It can be expected that after the addition of tin(II) chloride to mercury solutions, produced elemental mercury may be lost as mercury vapor from the mercury solutions to the atmosphere. Therefore, the loss of the elemental mercury formed after the addition of the reducing agent was examined at various standing times. As a consequence, the losses of elemental mercury from a mercury solution of 100 ng ml^{-1} were 0, 0, 7.9, 42.6, and 60.0% at standing times of 2, 5, 10, 20, and 30 min, respectively. The mercury was not lost at least within 5 min standing after the reductant addition. Thus it was necessary to nebulize the mercury solutions mixed with tin(II) chloride as soon as possible after the mixing.

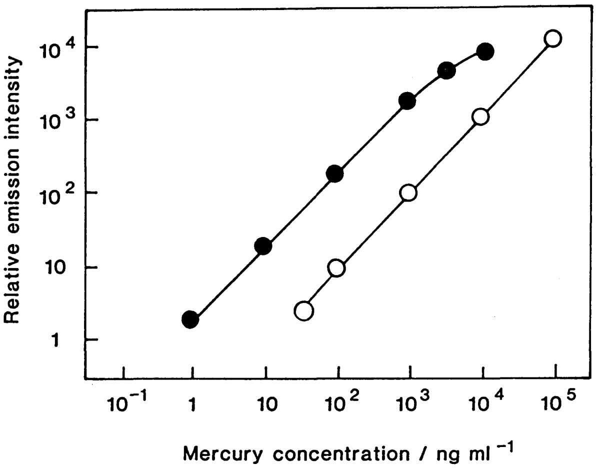

Fig. 1. Calibration curves for mercury by reductant addition method (●) and conventional nebulization (○).

Memory Effect. In the present procedure it was particularly found that the clean-up time was increased when compared with the conventional nebulization as shown in Fig. 2. The time scale on the abscissa of the figure was defined as the period of time elapsed after the sample solution was exchanged for Milli-Q water. The larger memory effect was related to the time required for the solution to be wasted out of the nebulizer chamber. In order to alleviate this large memory effect, 1.0 v/v% hydrochloric acid as a clean-up solution was nebulized for about 1 min in between spraying of the sample solutions into the nebulizer chamber.

Effect of Diverse Elements. Although spectral interferences such as background enhancement and line overlap on the Hg 253.652-nm line are small, some chemical interferences might arise, in principle, from the effect of concomitant elements (i.e., ions) in the present reductant addition method. Under the experimental conditions listed in Table 1, the presence of various diverse elements at concentrations 100-fold greater than mercury was first investigated. The results of depressing or enhancing interferences from some elements are

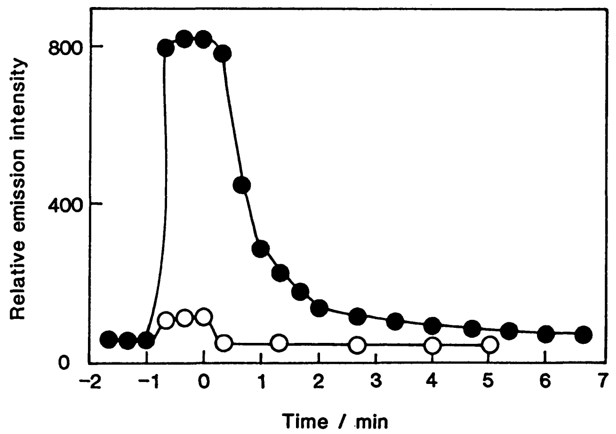

Fig. 2. Memory effect in reductant addition method (●) and conventional nebulization (○) with a mercury solution of 100 ng ml^{-1}.

Table 2. Interferences from Diverse Elements

Element$^{a)}$	Added as	Relative intensity$^{b)}$	Tolerance limit$^{c)}$
Al	Metal in HCl	1.83	1.0
Au	$HAuCl_4$	0.34	0.01
Bi	$Bi(NO_3)_3$	1.54	1.0
Ca	$CaCl_2$	0.43	1.0
Ce	$Ce(SO_4)_3$	1.97	1.0
Cu	$CuSO_4$	0.23	1.0
Ge	GeO_2 in NaOH/HCl	1.50	1.0
Pd	$PdCl_2$	0.37	0.01
Pt	H_2PtCl_6	0.03	0.1
Sb	Metal in HNO_3/HCl	1.58	0.1
Sr	$Sr(NO_3)_2$	0.47	1.0
Te	Na_2TeO_3	0.06	1.0
Zr	$ZrCl_4$	0.41	1.0

a) Added at level of 100-fold ratio of mercury (100 ng ml^{-1}). b) Relative to 1.00 for the emission intensity of mercury alone. c) Maximum concentration (μg ml^{-1}) with no significant interference.

Table 3. Determination of Mercury in Several Samples of Waste Water

Sample	Mercury concentration (ng ml^{-1})	
	Present method[a]	MIP-AES[b]
Feb. 9, 1990	1.46±0.06 (5)	1.44
Feb. 13, 1990	1.81±0.08 (5)	1.85
Feb. 14, 1990	1.55±0.12 (4)	1.50
Feb. 16, 1990	1.41±0.05 (6)	1.44
Feb. 17, 1990	1.74±0.08 (5)	1.70
Feb. 19, 1990	1.61±0.09 (5)	1.58

a) The mean±standard deviation (number of determinations). b) The mean of three determinations.

shown in Table 2. Interference was considered to have occurred when the analyte emission intensity changed by more than ±5% from that for mercury alone. It was also confirmed that some of the interferences shown in Table 2 were observed in the conventional solution nebulization (i.e., without the addition of the reducing agent). Next, the tolerance limits for the interferences were examined and are shown also in Table 2.

Application to the Determination of Mercury in Waste Waters. To demonstrate its accuracy and precision, the present reductant addition method was applied to the determination of mercury in some samples of waste water taken at the inlet of the Wastewater Treatment Facility of the University of Osaka prefecture. A sample taken was immediately filtered through a No. 2 filter paper (Toyo Roshi Kaisha, Ltd.), and the filtrate was analyzed for mercury by the method of standard additions. The results obtained are given in Table 3. At the same time, the mercury concentrations in the samples were determined by means of atmospheric-pressure helium microwave induced plasma-atomic emission spectrometry (MIP-AES) coupled with cold-vapor generation technique,[8] and the results obtained by MIP-AES are also shown in Table 3. It should be noted in Table 3 that the results obtained by the present method with ICP-AES are in good agreement with those obtained by MIP-AES.

In conclusion, trace concentrations of mercury can be determined satisfactorily by using ICP-AES in combination with a simple addition of tin(II) chloride to the mercury solution. The detection limit of this reductant addition method for mercury is greatly improved over the conventional nebulization with untreated sample solutions. The technique described here has successfully been applied to the determination of mercury in several samples of waste water. Finally, because of the rapid loss of elemental mercury from the solutions, the present procedure would be more usefully coupled with a flow injection system.

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