Determination of Mercury by Graphite Furnace Atomic Absorption Spectrometry after Ion-Pair Extraction with Zephiramine in Small Scale

Yasuaki Okamoto, Takahiro Kumamaru,* Shigeki Hara,† Hiroshi Matsuo,† and Mitsuo Kiboku††
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730
†Division of Interdisciplinary Studies of Natural Sciences, Faculty of Integrated Arts and Sciences, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730
††Department of Applied Chemistry, Faculty of Engineering, Kinki University, Hiro-machi, Kure 737-01

(Received December 24, 1986)

Synopsis. A simple procedure for the determination of mercury(II) by graphite furnace atomic absorption spectrometry is described. Mercury(II) was extracted as tetradecyldimethylbenzylammonium (Zephiramine) thiocyanatomercurate(II) into diisobutyl ketone (DIBK) by using a 10-cm^3 centrifuge tube, and an aliquot of the organic extract was directly pipetted out from the upper layer in the centrifuge tube and injected into the graphite furnace. The heating temperature program by ramp mode and the background correction by means of a 2-channel type atomic absorption spectrometer gave satisfactory results.

In the determination of volatile elements such as mercury by graphite furnace atomic absorption spectrometry (GF-AAS), losses of the analytes may occur during the ashing stage in the thermal cycle. Recently, a number of publications have described matrix modification or stabilization procedures by which analyte losses before atomization stage may be minimized or eliminated.[1–5] For example, the absorbance of mercury can be increased by addition of ammonium sulfide to the sample solution; this effect has been attributed to the formation of stable mercury(II) sulfide at the ashing temperature.[1] Kirkbright et al. have recommended a procedure in which the addition of potassium dichromate to the mercury sample in nitric acid solution allowed the use of ashing temperatures up to 250 °C without significant loss of mercury.[2] Filippelli reported a method for determining low levels of mercury by GF-AAS with preliminary preconcentration using ammonium 1-pyrolidinecarbodithioate (APDC)-chloroform extraction system.[3]

In this paper a method for the determination of mercury by GF-AAS combined with a small scale solvent extraction technique is described; mercury(II) was converted to thiocyanatomercurate and extracted into diisobutyl ketone (DIBK) as the ion-pair with tetradecyldimethylbenzylammonium (Zephiramine), and the extract was injected into graphite tube to measure the atomic absorption of mercury. This method is convenient and rapid, as the extraction is carried out by using a centrifuge tube and an aliquot of the organic phase in the upper layer can be directly pipetted out of the tube. This enables us to use much smaller amounts of samples and reagents compared with those in the conventional extraction, which serves to reduce laboratory-used mercury waste.

Experimental

Apparatus. A Nippon Jarrell-Ash Model AA-8200 two-channel atomic absorption spectrometer equipped with a Model FLA-100 graphite furnace atomizer was used. Background correction was accomplished by using a deuterium lamp. A Rikadenki Model B-381 strip chart recorder was used to monitor both the background-corrected atomic absorption and the background signals. Digital micropipettes of Gilson Model Pipetman P-20, P-200, P-1000, and P-5000 were used. The shaking for the extraction was carried out with a Taiyo Model SR-II shaker, where 10-cm^3 centrifuge tubes with ground stoppers were used instead of separatory funnels.

Reagents. Pure water from an Organo Miniclear Model DC-610 system was used. All chemicals were of analytical-reagent grade and were used without further purification. A 1000 μg cm^{-3} of mercury(II) standard stock solution was prepared by dissolving mercury(II) nitrate in dilute nitric acid. Solutions of suitable concentration were prepared by dilution with 0.1 mol dm^{-3} nitric acid before use. A 5.0×10^{-2} mol dm^{-3} Zephiramine solution was prepared by dissolving 2.02 g of Zephiramine chloride dihydrates (Wako Pure Chemicals) to 100 cm^3 with water. A 2.0 mol dm^{-3} potassium thiocyanate solution was prepared by dissolving 19.4 g of potassium thiocyanate (Wako Pure Chemicals) to 100 cm^3 with water.

Standard Procedure. Transfer an aliquot of the mercury(II) solution containing not more than 80 ng mercury(II) into the centrifuge tube. Add 200 mm^3 of the potassium thiocyanate solution and 80 mm^3 of the Zephiramine solution, and dilute the mixture to 5 cm^3 with water. Then, add 1 cm^3 of DIBK. Shake the centrifuge tube for ca. 5 min by means of the mechanical shaker. After standing for ca. 15 min, inject an aliquot of 20 mm^3 of the upper organic phase into the graphite furnace and measure the atomic absorption peak signal of mercury. The instrument operating conditions are listed in Table 1.

Results and Discussion

Optimization of Instrument Operating Conditions. In order to avoid the loss of mercury before the atomization stage and to separate the atomic absorption peak signal from the background signal, a moderate elevation of temperature throughout the heating cycle was very essential. Experiments were carried out to determine the loss of mercury during the drying and ashing stages of the heating program by recording signals from 20-mm^3 aliquots containing 1.6 ng mercury(II). A setting of 60 °C-50 s for the drying stage was suitable. No appreciable loss of mercury from the furnace was observed at the ashing temperature of up to ca. 300 °C with the ramp mode which avoided abrupt vaporization. The background signal decreased significantly with increase in the ashing temperature. The

Table 1. Instrument Operating Conditions

Atomizer (FLA-100)	
Sample injection	20 mm^3
Drying (Ramp mode)	6 A (60 °C) for 50 s
Ashing (Ramp mode)	25 A (300 °C) for 120 s
Atomization (Maximum ramp mode)	95 A (1300 °C) for 5 s
Clean up	280 A (2900 °C) for 3 s
Purge argon gas flow	2.5 dm^3 min^{-1}
Spectrometer (AA-8200)	
Wavelength	
Atomic absorption (HCL)	253.7 nm (Hg I)
Background correction (D$_2$)	253.0 nm
Damping	1 (0.1 s time constant)
Recorder range	100 mV/full scale

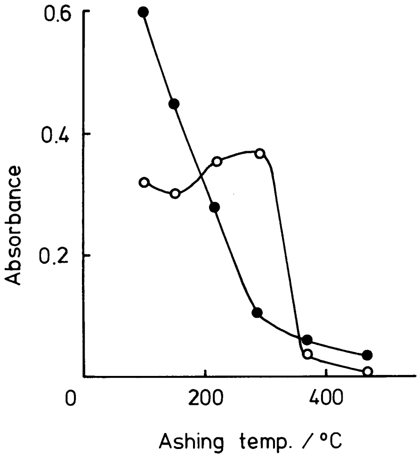

Fig. 1. Effect of ashing temperature on atomic absorption and background peak signals. Mercury(II): 1.6 ng, ○: mercury atomic absorption, ●: background. See Table 1 for conditions.

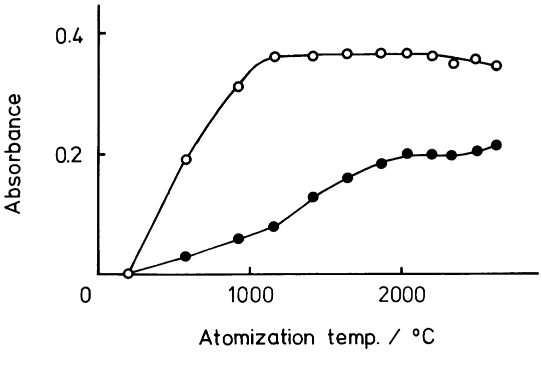

Fig. 2. Effect of atomization temperature on atomic absorption and background peak signals. Mercury(II): 1.6 ng, ○: mercury atomic absorption, ●: background. See Table 1 for conditions.

results are shown in Fig. 1. Therefore, the ashing condition of 300 °C-120 s was selected for the standard procedure. The effects of atomization temperature with the maximum ramp mode on the atomic absorption and background peak signals are shown in Fig. 2. The atomic absorption peak signal was maximum and constant over the temperature range of 1200—2200 °C, whereas the background signal increased as the temperature increased. So that, the atomization

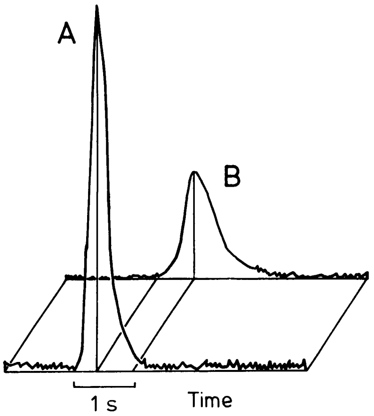

Fig. 3. Signal vs. time profiles. Mercury(II): 1.6 ng. A: Mercury atomic absorption, B: background. See Table 1 for conditions.

temperature of 1300 °C was chosen. Under the conditions, the atomic absorption signal of mercury appeared first, followed by the background peak signal ca. 0.6 s later. The signal vs. time profiles obtained for both the atomic absorption and background are shown in Fig. 3.

Optimization of Conditions of Solvent Extraction. In liquid-liquid extraction, the organic solvent should have a high distribution coefficient for the analyte and be insoluble in water. Moreover, it is preferable for the organic solvent to float on the aqueous phase so that the organic extract can be directly pipetted out of the centrifuge tube without separating the organic layer. DIBK was confirmed to be a favorable solvent in these respects.

The effect of pH on the extraction was investigated by extracting mercury(II) from a series of aqueous solutions containing 400 ng mercury(II) buffered at various pH values, while other variables in the standard procedure were kept constant. The maximum extraction of the ion-pair of Zephiramine thiocyanatomercurate(II) was obtained, when the acidity of the aqueous phase lay within the range of 1 mol dm^{-3} in nitric acid to pH 7.

The effects of the concentration of potassium thiocyanate and Zephiramine in the aqueous phase on the extraction were also examined according to the standard procedure. When the concentration of mercury(II)

Table 2. Analytical Results of Mercury in Several Waste Water Samples

Sample	Mercury found/ng cm^{-3}	
	Calibration curve method	Standard addition method
Raw sewage water A[a]	1.8±0.2	2.0±0.3
Raw sewage water B[a]	N.D.[b]	N.D.[b]
Raw mercury waste water A	14.3±0.3	14.7±0.3
Raw mercury waste water B	28.6±0.4	28.8±0.3
Raw mercury waste water C	9.8±0.3	12.0±0.2

a) Acid digestion sample.[6] b) N.D.: Not detected.

in the aqueous phase was kept at 80 ng cm^{-3}, it was necessary for the maximum and constant extraction that the concentrations of potassium thiocyanate and Zephiramine were at least 1×10^{-2} and 2×10^{-4} mol dm^{-3}, respectively. In order to minimize the background peak signal which was mainly caused by an excess Zephiramine extracted with the ion-pair, we selected 8×10^{-2} and 8×10^{-4} mol dm^{-3} as the initial concentrations of potassium thiocyanate and Zephiramine in the aqueous phase, respectively.

Extraction Percentage. The extraction efficiency was estimated to be 99% from the results obtained by the successive extraction of mercury(II) in the aqueous phase according to the standard procedure in which the initial concentration of mercury(II) in the aqueous phase was kept at 80 ng cm^{-3}.

Detection Limit and Working Curve. The detection limit was 0.5 ng cm^{-3} on the basis of the above results. The detection limit was defined as the concentration in the aqueous phase required to give a signal three-fold greater than the standard deviation of the base line fluctuation. The calibration curve was linear up to 80 ng cm^{-3} mercury(II) initially present in the aqueous phase. The relative standard deviation for 10 replicate determinations was 1.0% for 40 ng mercury(II). As to the stability of the extract, no appreciable change in the absorbance was observed over the period of 48 h, even when the organic phase was kept standing with the aqueous phase.

Application to Determination of Mercury in Waste Water Samples. Some waste water samples were analyzed for mercury contents by the standard procedure. As a check, the samples were also analyzed by standard addition method. As can be seen from the results given in Table 2, both data are in satisfactory agreement.

References

1) R. D. Ediger, *At. Absorpt. Newsl.*, **14**, 127 (1975).
2) G. F. Kirkbright, H. C. Shan, and R. D. Snook, *At. Spectrosc.*, **1**, 85 (1980).
3) M. Filippelli, *Analyst (London)*, **109**, 515 (1984).
4) R. F. Sanzolone and T. T. Chao, *Analyst (London)*, **108**, 58 (1983).
5) Z. Slovak, *Anal. Chim. Acta*, **115**, 111 (1980).
6) Japanese Industrial Standard, K 0102 (1986).