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CHEMICAL ENHANCEMENT METHOD FOR THE DETERMINATION OF MERCURY BY SPECTROPHOTOMETRY AFTER IODIDE EXTRACTION

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Summary—A selective and sensitive spectrophotometric method for the determination of 0.08–2.5 ppb of mercury(II) is described. Mercury is extracted as tetraiodomercury(II)–Cd–phenanthroline ion-pair into benzene and selectively stripped into EDTA. The iodide associated with mercury present in the stripping is oxidized to iodate and then treated with excess iodide to give iodine. The iodine formed is extracted into benzene and equilibrated with iodate in acidic medium in the presence of chloride and Rhodamine 6G for the formation of ICl_2^- species and its extraction as ion-pair with Rhodamine 6G. Determination is completed by measuring the absorption of the extract at 535 nm. The coefficient of variation is 1.5% for 10 determinations of 200 ng of mercury. The method has been applied to establish the mercury content of natural waters and chloralkali plant effluent.

Although the methods for the spectrophotometric determination of mercury based on the formation of ternary complexes[1–5] possess superior sensitivity and selectivity when compared to the widely used dithizone method,[6] they do not lend themselves well to the direct determination of mercury at levels occurring in natural waters without resorting to a preconcentration step.

The formation of anionic iodine complex and its extraction as an ion-pair with cationic dyes into benzene has been found useful in the determination of variety of species at trace levels.[6–10] Recently a method was described for the spectrophotometric determination of arsenic after its selective separation as AsI_3.[11] In the presence of chloride and acid, reaction of arsenic(III) and the associated iodide with excess iodate caused the oxidation of the liberated iodine and its stabilization as ICl_2^- species.

$$2I_2 + IO_3^- + 6H^+ + 10Cl^- \rightarrow 5ICl_2^- + 3H_2O. \quad (1)$$

Determination was completed after extraction of the anionic iodine complex as ion-pair with Rhodamine 6G into benzene. It seemed to us that other metal ions that form extractable species with iodide could be determined similarly to arsenic and the sensitivity of method can be considerably improved by first oxidizing the iodide present as metal iodide to iodate with bromine water

$$I^- + 3Br_2 + 3H_2O \rightarrow IO_3^- + 6HBr \quad (2)$$

and then reacting with excess iodide in acid medium to produce iodine.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O. \quad (3)$$

The six iodine atoms released for each iodide ion present as the metal iodide can be made to react, after separation, with iodate in the presence of chloride and acid for the formation of the anionic iodine complex for subsequent determination by spectrophotometry. Systematic study on these lines showed that as low as 0.08 ppb of Hg(II) can be determined with high degree of selectivity after its separation as HgI_4^{2-} by extracting as ion-pair with Cd-phenanthroline cation into benzene. The method has been found useful for the rapid and precise determination of mercury levels of natural waters and chloralkali plant effluent by spectrophotometry.

EXPERIMENTAL

Apparatus

Absorbances were measured using a Carl-Zeiss PMQ II Spectrophotometer with 10 mm quartz cells.

Reagents

Standard mercury(II) solution, 1.0 mg/ml. Prepared by dissolving 0.1354 g of mercuric chloride in 10 ml of nitric acid and diluting to volume with water in 100 ml standard flask. A suitable

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volume of this solution was diluted to obtain working standards.

Cd-phenanthroline solution (10^{-5}M). Prepared by mixing solution of 0.02 g of $3CdSO_4 . 8H_2O$ and 0.2 g of 1,10-phenanthroline and diluting to 250 ml.

The following solutions were prepared by dissolving appropriate amounts of the reagents in distilled water.

Potassium iodide solution	: 0.1*N*
EDTA (disodium salt)	: 0.004*M*
Bromine water	: 5%
Potassium iodate solution	: 0.01%
Sodium chloride solution	: 15%
Sulphosalicylic acid	: 0.5%
Sulphuric acid	: 5*N*, 0.5*N*
Rhodamine 6G	: 0.02%

Benzene (thiophene free) for extraction purposes.

Procedure

Transfer the sample solution (< 150 ml) containing not more than 400 ng of mercury(II) in a separatory funnel. Add enough sulphuric acid and potassium iodide solutions to make their concentration 1*N* and 0.02*N*, respectively followed by 1 ml of $10^{-5}M$ Cd-phenanthroline solution. Shake the solution for 1 min with 10 ml of benzene. Separate the organic phase and equilibrate for 1 min with 5 ml of 0.004*M* EDTA. Allow the layers to separate and discard the organic layer.

Determination

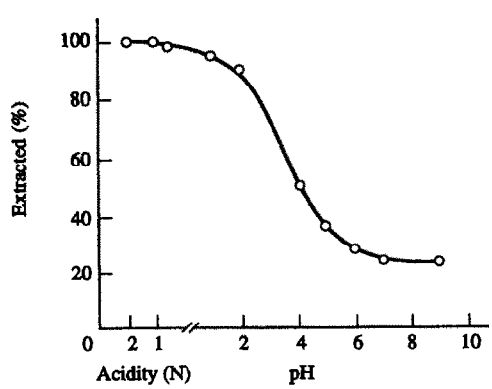
Treat the stripping with sufficient bromine water until a slight excess is present (pale yellow colour). Stir well and add 1 ml of 0.5% sulfosalicylic acid followed by 1 ml each of 0.1*M* KI and 0.5*N* H_2SO_4 and dilute to 10 ml. Equilibrate the solution with 5 ml of benzene for 1 min. Wash the organic phase twice with 5 ml of water to remove any residual potassium iodide solution. Separate the organic layer and shake with 25 ml of aqueous solution containing 2 ml each of 0.01% KIO_3, 5*N* H_2SO_4, 15% NaCl and 0.02% Rhodamine 6G for 1 min. After the separation of the layers, transfer the benzene layer into a dry test tube and add about 1 g of anhydrous sodium sulfate. Measure the absorbance of the extract at 535 nm in 10 mm cells against the reagent blank, run through the entire procedure. Establish the concentration of mercury by reference to the calibration graph prepared with 15–400 ng of mercury(II) and following the above procedure.

RESULTS AND DISCUSSION

Extractive separation of mercury as HgI_4^{2-}

Although tetraiodomercury(II) is known to extract as ion-pair with cationic dyes, in order to avoid complications arising due to the colour imparted to the extract, it was decided to examine the use of Cd-phenanthroline complex for the extraction of tetraiodomercury(II). Iron(II)–phenanthroline was not considered, as bromine addition after stripping would result in the formation of Fe(III) that would also react with iodide to produce iodine. Initial studies were performed using 3 ml of $10^{-5}M$ Cd-phenanthroline solution from 10 ml of aqueous solution made 0.03*M* with respect of KI. Cold vapour AAS was used to establish the extent of extraction by determining the amount of mercury remaining in the aqueous phase. The aqueous layer was rendered alkaline before reduction with $SnCl_2$ to overcome the influence of iodide on mercury determination.[13]

Variation of the acidity of the aqueous layer, as shown in Fig. 1, revealed that the extraction was maximum and constant when the overall acidity was greater than 0.5*N* with respect to H_2SO_4. For quantitative extraction 1 ml of $10^{-5}M$ Cd-phenanthroline solution and overall concentration of 0.01*N* KI was found necessary. Addition of higher concentrations of KI and Cd-phenanthroline complex than the recommended amounts had no effect on the extraction of mercury. The formation of ion-pair was



$([Hg^{2+}] = 200$ ng, [KI] = 2 x 0.1N, [cd - phenanthroline]$^{2+}$= 1 x 10^{-5}M, total volume = 10 ml, volume of benzene = 10ml)

Fig. 1. Effect of acidity on the extraction of $[HgI_4^{2-}$-(Cd-phenanthroline)$^{2+}]$ ion pair.

found to be instantaneous and mixing the phases for about 30 sec was found sufficient for its quantitative extraction into benzene.

Benzene, toluene, xylene, hexane, cyclohexane, carbon tetrachloride, chloroform and isoamylacetate were investigated as extraction solvents. However only benzene proved to be satisfactory, as the extraction of the ion-pair was found to be maximum in this solvent and provided low blank absorbance.

Extraction was not affected when the aqueous to organic phase volume ratio was 30:1 and as low as 15 ng of Hg^{2+} could be extracted from an aqueous phase volume of 150 ml into 10 ml of benzene.

Water, 0.1*M* NaCl, 0.1*M* Na_2CO_3, 0.1*M* NH_3–NH_4Cl buffer and 0.1*M* EDTA were investigated for stripping the ion-pair from the organic layer. Only EDTA however, was found to be effective to strip the ion-pair quantitatively at pH values greater than 6.0. Equilibration for 1 min with 5 ml of 0.004*M* EDTA was found adequate to strip the ion-pair from the organic layer.

Determination with Rhodamine 6G

As the final measurement step involved the determination of iodine resulting from reaction of iodide with iodate, the suitability of the method based on the formation of ICl_2^-–Rh 6G was examined after extraction of the liberated iodine into benzene. Preliminary studies were made using 5 ml of benzene for the extraction of iodine produced by reacting 1 μg of IO_3^- with 2 ml of 0.01*M* KI in a sample volume of 10 ml.

As recommended,[11] after extraction, the benzene layer was equilibrated with 2 ml each of KIO_3 (0.01%), H_2SO_4 (5*N*), NaCl (15%) to strip the iodine as ICl_2^- species into the aqueous layer. To the stripping 2 ml of 0.02% Rhodamine 6G was added and made up to 25 ml before extracting into benzene for the measurement of absorbance at 535 nm. It was established that stripping of iodine into the aqueous layer as ICl_2^- species and its re-extraction as the ion–pair into benzene can be combined and that the determination can be more conveniently carried out by simply equilibrating for 1 min the benzene layer containing iodine with a mixture solution containing 2 ml each of 0.01% KIO_3, 5*N* H_2SO_4, 15% NaCl and 0.02% Rhodamine 6G in a final volume of 25 ml.

Having developed a satisfactory procedure for the determination of iodine after extraction into benzene, studies were made to establish the favourable conditions for the oxidation of iodide to iodate. Though both bromine and chlorine have found application for this purpose,[12] the use of bromine was taken up for detailed study since the removal of excess bromine can be accomplished by chemical means without recourse to boiling. Reagents examined for this purpose included sulphosalicylic acid, formic acid and phenol. Only sulphosalicylic acid and formic acid were found to be suitable as the blank was found to be high when phenol was used. The presence of excess sulphosalicylic acid or formic acid showed no effect on the formation and determination of iodine by the method described.

Systematic examination of the conditions most suitable for oxidation of iodide with bromine water indicated that oxidation was quantitative at acidity greater than 0.05*N* H_2SO_4. Addition of bromine water until the solution acquired a pale yellow colour was found adequate for oxidation purposes. Subsequent treatment of the solution with 1 ml of 0.5% solution of sulphosalicylic acid or 1 ml of 5% solution of formic acid was found sufficient to destroy the excess bromine. The iodate formed was determined after treatment with 1 ml each of 0.1*M* KI and 0.5*N* H_2SO_4, following the procedure described.

Conditions were optimized independently for the formation of iodine by reaction of iodide with iodate. One μg of iodate was treated with 2 ml of 0.01*N* KI and the acidity for the reaction was varied from 0.01*N* to 0.2*N* H_2SO_4. A minimum acidity of 0.05*N* H_2SO_4 was found necessary for the reaction. The acidity required for the oxidation of iodide to iodate with bromine water and the reaction of iodate with iodide were therefore identical.

On the basis of the above findings, it was decided to apply the method for the determination of Hg(II) after its extraction as HgI_4^{2-}–Cd–phenanthroline complex into benzene and stripping the ion-pair into EDTA. Since each atom of Hg(II) combines with four atoms of iodide to form HgI_4^{2-}, as is apparent from equation (4)

$$5HgI_4^{2-} + 4IO_3^- + 24H^+ \rightarrow 5Hg^{2+} + 12I_2 + 12H_2O \quad (4)$$

the treatment of the EDTA stripping with iodate in acid medium will yield 4.8 atoms of iodine for each atom of mercury. On the other hand, if the stripping were to be treated with

bromine water to form iodate and then treated with excess iodide to give iodine in accordance with equations (5) and (6), each atom of

$$HgI_4^{2-} + 12Br_2 + 12H_2O \rightarrow 4IO_3^- + 24HBr + Hg^{2+} \quad (5)$$

$$4IO_3^- + 20I^- + 24H^+ \rightarrow 12I_2 + 12H_2O \quad (6)$$

mercury will yield 24 atoms of iodine thus giving a five-fold increase in the yield of iodine. Actual experiments with 200 ng of Hg(II) showed a five-fold enhancement in sensitivity as the absorbance was found to be 0.290 (as against 0.06) when bromine water treatment formed an integral part of the procedure. In this instance the absorbance was identical to that obtained when 3.00 μg of iodine in benzene was subjected to determination. As 3.04 μg of iodine would result from 200 ng of Hg(II) (equations (2) and (3)), it was concluded that the reaction sequence involved leads to the release of stoichiometric amount of iodine to take part in the final measurement step.

When the recommended procedure was followed the calibration graph was linear over the range 15–400 ng mercury. From the slope of the calibration graph the molar absorptivity was found to be 5.3×10^5 l/mole/cm. The coefficient of variation established by carrying out 10 determinations of 200 ng of Hg(II) was found to be 1.5%.

Effect of interfering metal ions

The interference of 1 mg each of the following ions on the determination of 200 ng of mercury were studied. The ions examined, classified according to their mode of reaction with iodide included:

(1) those that oxidized iodide to iodine: Sb(V), Cu(II), Fe(III) and As(V);
(2) those that formed insoluble precipitates with iodide: Ag(I), Tl(I), Pb(II) and Bi(III);
(3) those that formed anionic complex similar to that of Hg(II): Pd(II), Pt(II) and Cd(II);

Table 1. Analysis of water samples

Sample	Volume used for analysis (*ml*)	Amount added (*ng*)	Amount found (*ng*)	Concentration (*ng/l*)	% recovery
Tap water 1440 ng/l*	80	—	110,121,114 (115)†	1435	—
	80	100	200,200,200 (200)		93.02
	80	150	255,248,262 (255)		96.22
	80	200	300,300,300 (300)		95.23
	100		145,145,145 (145)	1450	—
	100	100	241,235,255 (244)		99.59
	100	150	310,306,314 (310)		105.08
	100	200	345,338,364 (349)		101.15
Sea water 2700 ng/l*	80	—	214,207,217 (212.6)	2660	—
	80	100	306,314,314 (311)	—	99.59
	80	150	345,348,361 (348)		96.13
	80	200	410,410,410 (410)		99.51
	100	—	281,278,284 (281)	2810	—
	100	100	358,364,361 (361)		94.75
		150	400,393,410 (401)		94.00
		200	476,472,479 (476)		98.96

*By cold vapour AAS method.
†Values in parentheses give the average of the amount found.

(4) those that formed neutral complexes: Zn(II), As(III), and Sb(III).

There was no interference from Sb(V), Cu(II), Fe(III) and As(V) because the iodine formed did not strip into EDTA. Similarly Ag(I), Tl(I), Pb(II) and Bi(III) showed no interference as their iodides were not extracted into benzene. Pt(II), Pd(II), As(III), Sb(III) and Zn(II) were not found to extract under conditions optimal for Hg(II). Cadmium(II) interfered when Cd-phenanthroline solution containing stoichiometric amounts of Cd(II) and phenanthroline was used for extraction purposes. The interference however could be overcome by addition of excess of phenanthroline prior to extraction. Consequently it was decided to incorporate a slight excess amount of phenanthroline in the Cd-phenanthroline solution meant for extraction purpose.

Application of the method to water samples

Tables 1 and 2 presents the results of the analysis of tap water and sea water (collected from Madras coast, Bay of Bengal, India) and the effluent of the chloralkali plant. The samples were analysed with and without added standard by the proposed procedure. The samples were acidified to pH ~ 1.5 with HNO_3 and filtered through 0.45 μm millipore membrane filter before analysis. Suitable aliquots were subjected to determination. The waste water originating from chloralkali plant may contain mercury both in elemental as well as ionic form. The effluent from the chloralkali industry was analysed after treating the effluent with permanganate to ensure the oxidation of any elemental mercury, if present, to ionic mercury.[14] The samples were also analysed by standard cold vapour AAS. The results clearly show that the method developed works satisfactorily for the analysis of mercury in natural and effluent water samples.

CONCLUSION

The method described provides a simple and reliable means of determination of trace amounts of mercury by spectrophotometry. It is more sensitive ($\epsilon = 5.3 \times 10^5$ l/mole/cm) than the widely used method based on reaction with dithizone ($\epsilon = 3.9 \times 10^4$ l/mole/cm). The method also has the advantage of virtual freedom from interference from extraneous ions and can therefore serve as an alternative to the widely used flameless AAS for the rapid and precise determination of trace amounts of mercury in natural water and effluent samples.

Table 2. Analysis of treated chloralkali plant effluent

Sample	Volume used for analysis (*ml*)	Amount added (μg)	Amount found (μg)	Concentration ($\mu g/l$)	% recovery
Chloralkali plant effluent (99.3 μg/l)*	1	—	95,95,95 (95)†	95	—
	1	50	140,145,148 (144)		99.31
	1	70	158,160,160 (159)		96.36
	1	80	166,176,172 (171)		97.71
	2	—	197,200,203 (200)	100	—
	2	50	241,248,255 (248)		99.2
	2	70	259,262,266 (262)		97.03
	2	80	270,278,275 (274)		97.85
	3	—	300,300,300 (300)	100	—
	3	50	344,344,347 (345)		98.43
	3	70	361,364,370 (365)		95.64
	3	80	380,393,300 (387)		100.2

*By cold vapour AAS method.
†Values in parentheses give the average amount found.

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