Extraction-spectrophotometric determination of traces of mercury (II) with bromide and rhodamine 6G

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Abstract

A very sensitive analytical method for the determination of mercury(II) after extraction of its bromide-rhodamine 6G complex into benzene has been developed. The optimum pH range for the extraction is 0.5-4.5. The molar absorptivity and Sandell sensitivity are 8.2×10^4 l.mole^{-1}. cm^{-1} and 2.5 ng cm^{-2} respectively. The interference of various ions has been studied. The method is applicable to the determination of mercury in coal and sea water.

Key words: Mercury (II) determination, solvent extraction, bromide, rhodamine 6G, benzene.

1. Introduction

The significance of mercury in the environment as a health hazard and in mineral prospecting has resulted in the large expansion of literature dealing with the determination of traces of mercury in recent years. Various instrumental techniques including atomic absorption, atomic fluorescence, neutron activation, etc., have been developed for the determination of mercury at p.p.m. and p.p.b levels and these have been adequately reviewed [1-5]. However, there is continued interest in extraction-spectrophotometric methods mainly because they are simple, inexpensive and can handle a large number of samples. The conventional technique of dithizone extraction though extemely sensitive, is less reliable due to variations of laboratory conditions [6], poor sensitivity in practice [7] and is subject to interference from other metal ions.

To achieve superior sensitivity and selectivity, extraction of ion association complexes of the type dye-Hg-x$^-$ /CN$^-$ /SCN$^-$ have been proposed. Several cationic dyes such as crystal violet [8], rhodamine B [9], brilliant green [10], pyrazolone [11] and methylene blue [12] have been studied among which tetrabromomercurate(II)-methylene blue system is the most sensitive. However, most of these systems are less sensitive than dithizone procedure though selectivity is improved considerably. In an attempt to critically evaluate ion association systems for mercury(II), it was found that traces of mercury could be extracted into benzene in the presence of rhodamine 6G and bromide. The present paper describes the development of a simple and rapid spectrophotometric technique based on this system. The method is sensitive, applicable over a wide pH range for the determination of mercury(II) at 0.01 p.p.m. level in the organic phase. The method works satisfactorily for the determination of mercury in coal and sea water.

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2. Experimental

Apparatus

A Shimadzu Graphicord UV-240 spectrophotometer with 10mm matched quartz cells was used for absorbance measurements. A Toshniwal pH meter with a combined glass electrode was used for pH measurements.

Reagents

All reagents used were of analytical grade unless otherwise stated. Distilled water was used throughout for dilution purposes.

Mercury(II) solution (1 mg/ml): prepared by dissolving 0.3385 g mercury(II) chloride in 250 ml distilled water. An appropriate volume of this solution was further diluted to get 1 p.p.m. solution of mercury(II).

Postassium bromide solution (1%): prepared by dissolving 1.0 g of potassium bromide in 100 ml water.

Acetate buffer pH 4.0 (0.1 M): prepared by dissolving 6.8 g sodium acetate trihydrate in 500 ml of water and adjusting the pH to 4.0 using glacial acetic acid.

EDTA solution (0.05 M): prepared by dissolving 1.8615 g of the acid in 100 ml distilled water.

Rhodamine 6G solution (0.05%): prepared by dissolving 0.05 g of the dye in 100 ml water and filtered.

Aminoacetic acid: used as obtained.
Benzene.

Recommended procedure

Transfer 1-15 μg of mercury(II) solutions to a series of 60 ml separating funnels. Add 2.0 ml potassium bromide, 1.0 ml EDTA, 5.0 ml buffer and 1.0 ml rhodamine 6G solution. Mix thoroughly, add 5.0 ml benzene and extract the complex for 1 minute. Measure the absorbance of the extracts against a reagent blank prepared under identical conditions at 528 nm.

Determine the concentration of the unknown by referring to the calibration curve.

(i) *Sea water:* Filter the sample to remove any suspended matter. Take an aliquot (5 ml) and develop the colour as described above. Determine mercury(II) concentration by referring to the calibration graph.

(ii) *Coal:* Mix 1.0 g coal sample with 25.0 ml nitric acid and 1.5 ml sulphuric acid. Leave overnight, reflux in a modified Bethge[13] apparatus until the digest becomes pale yellow. Add 10 ml of 45% perchloric acid and 0.4 g aminoacetic acid. Distil off the nitric acid until the sample volume is 5 ml. Distil the residue up to 340° C (until sulphuric acid starts fuming). Collect the distillate containing mercury(II), $HClO_4$, HNO_3 and dilute to 25 ml.

Determine mercury(II) by taking an aliquot and following the recommended procedure.
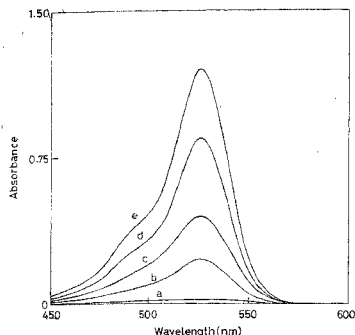
FIG. 1 Absorption spectra of mercury(II) - bromide - rhodamine 6G systems. a) Reagent blank - 1.0 ml EDTA (0.05 M), 1.0 ml bromide (1%) 1.0 ml rhodamine 6G (0.05%); Extracted at pH 4.0 into 5.0 ml benzene; 10 mm cells. Absorbance measured against benzene, b-e) Same as 'a' with 2.5, 5.0, 10.0 and 15.0 μg mercury(II) solutions.

3. Results and discussion

The reaction of mercury(II), bromide and rhodamine 6G produces a reddish complex which is not stable in aqueous medium. However, the complex could be easily extracted into benzene, toluene and chloroform. The organic extracts of mercury(II) showed an absorbance maximum at 528 nm while the reagent blank showed negligible absorbance. In view of the rapid and clear separation of phases when benzene was used, it was decided to use 5 ml of the solvent in future experiments.

Figure 1 shows the absorption spectra of varying concentrations of mercury(II), bromide-rhodamine 6G complex at pH 4.0 in benzene, from which it is evident that the complex has an absorbance maximum of 528 nm. Hence all further measurements were recorded at this wavelength.

Effect of experimental variables

The effect of acidity on the reaction system was investigated from 3N to 7.0 pH range. It was observed that the absorbance is practically constant over 0.5-4.5 pH range and hence a pH of 4.0 was maintained in all subsequent investigations by using 5.0 ml of 0.1 M acetic acid-acetate buffer. As the reaction was unaffected in the presence of EDTA, it was decided to add 1.0 ml of 0.05 M EDTA solution to all samples to suppress the interference of any other foreign metal.

The influence of the concentration of 0.4% bromide on the system was studied with fixed concentration of other reagents. Figure 2a indicates that 2.0 ml of bromide records maximum absorbance but in view of the low stability of the complex a slight excess of bromide (2 ml of 1%) concentration was maintained.

A similar experiment to determine optimum rhodamine 6G concentration (fig. 2b)
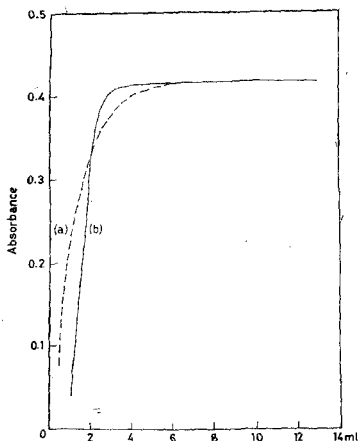
FIG. 2 Effect of reagents (a) Potassium bromide (0.04%) ----; (b) rhodamine 6G (0.01%) ——; Conditions as in fig. 1.c; at 528 nm.

revealed that 1 ml of 0.05% of the dye solution was sufficient for maximum colour development.

It was found that the reaction time and the order of addition were not critical. The complex could be completely extracted by equilibrating for one minute and the absorbance remained stable for more than 24 hours. The effect of change in aqueous volume to organic phase showed that at higher dilutions ($>$ 25 ml) the absorbance decreased, presumably due to the dissociation of the bromomercurate(II) complex. This problem could be avoided by maintaining higher bromide concentrations. In such cases blanks also showed a tendency for increased absorption. Hence it was decided to limit the aqueous phase to 15 ml for practical purposes.

Beer's law and precision

Beer's law was obeyed up to 0-20 μg of mercury(II) in 5 ml benzene extracts. The recommended concentration range is 1-15 μg in the aqueous phase.

The complex has molar absorptivity of 8.2×10^4 $l$mole^1. cm^{-1}. and Sandell sensitivity is 2.5 ng/cm^2. in the extract. The detection limit of mercury(II) corresponding to the aqueous phase is 0.7 ng/ml.

The relative standard deviations for ten determinations of different concentrations of mercury(II) are given in Table I.

Table I
Determination of mercury: Replicate analysis

Mercury(II) concentration (μg)	Mean of 10 determinations (μg)	Rel. Std. deviation (%)
2.5	2.52	1.3
5.0	5.02	0.5
7.5	7.48	1.0
10.0	10.04	2.0
15.0	15.00	1.3
20.0	19.87	0.7

Table II
Interference studies

Group	Interferent
I	Li(I), Cu(II), Ag(I)
II	Mg(II), Cu(II), Sr(II), Ba(II), Zn(II), Cd(II)
III	B(III), Al(III), Ce(III), Tl(I), Tl(III), U(IV), Th(IV)
IV	Sn(II), Sn(IV), Pb(II)
V	Sb(III), Bi(III), As(V), As(VII), V(IV), NH$_4$(I), nitrite, nitrate
VI	Cr(III), Cr(VI), Mo(VI), W(VI), Se(IV), Te(IV), sulphite, sulphate and thiosulphate
VII	Mn(II), flouride, chloride, bromide, iodide and iodate
VIII	Fe(III), Fe(III), Co(II), Ni(II), Pt(II), Pd(II), Pt(IV)
Miscellaneous	EDTA, citrate, tartrate, cyanide, thiocyanate

Nature of the complex

In the presence of large excess of bromide, mercury (II) forms tribromo and tetrabromo mercurates (II). These anionic species then react with rhodamine 6G to form neutral ternary complexes of the type R HgBr$_3$ and R HgBr$_4$ where R represents a rhodamine 6G cation.

The stoichiometry of mercury to rhodamine 6G was examined by mole ratio and Job's continuous variation methods. These studies indicated that mercury (II) to rhodamine 6G ratio is 1:1 in which case mercury (II) is a tribromo complex. That this was indeed so was verified by determining the stoichiometry of mercury (II) to bromide by the slope ratio method which showed evidence for 1:3 stoichiometry. Hence the empirical formulae of the complex is R HgBr$_3$.

Interference studies

The selectivity of the proposed method was investigated by determining 5 μg of mercury(II) in the presence of 1 mg of the interferrant ion by the recommended procedure. The species

Table III
Determination of mercury in coal/sea water

No. Sample	Mercury concentrations from replicate analysis (μg)				Mean	Std. devi- ation	% reco- very	Dithizone method (μg)
	1	2	3	4				
1. Coal A* (1.0g)	2.20	2.15	2.06	2.04	2.11	0.08	----	2.05
2. Coal B⁺ (1.0g)	0.75	0.82	0.76	0.76	0.77	0.03	---	0.75
3. Coal B + 2.5 μg mercury(II)	3.20	3.25	3.31	3.21	3.24	0.05	99.08	3.30
4. Sea water (10 ml)	---	---	---	---	---	---	----	---
5. Sea water (10 ml) + 2.5 μg mercury(II)	2.55	2.52	2.50	---	2.53	0.03	100.8	2.50
6. Sea water (10 ml) + 5.0 μg mercury(II)	5.01	5.025	5.05	5.01	5.02	0.02	100.5	5.05

* Obtained from the Central Fuel Research Institute, Dhanbad, India.

+ Obtained from the Regional Research Laboratory, Hyderabad, India.

Table IV
Ternary extraction systems for mercury(II)

No. System	Reaction conditions	Interferences	Molar absorptivity × 10⁵	Ref.
1. Hg-Br-methylene blue (CHCl₃, 605 nm)	1.3-3 M HCl	Au(III), Tl(III) Sb(III), Pb(II)	1.06	12
2. Hg-I-astrafloxin (CHCl₃, 570 nm)	2.5 M H₂SO₄	No data	1.0	15
3. Hg-I-brilliant green (CHCl₃, 640 nm)	0.7-1.6 pH	Fe(II)	1.0	16
4. Hg-Br-rhodamine 6G (Benzene, 528 nm)	0.5-4.5 pH	Pt(II)	0.87	Current work
5. Hg-Br-diantipyrinyl dyes (Benzene, 530 nm)	0.6 M H₂SO₄	Sn(II), Fe(III)	0.61	17
6. Hg-Br-Victoria blue (Benzene, 634 nm)	2.7 M H₂SO₄	Fe(III), Pb(II)	0.38	18

reexamined are presented in Table II. In these studies an absorbance difference of $\pm$ 0.03 was assumed to indicate the interference.

None of the common anions interfered seriously except cyanide, thiosulphate and thiocyanate. Iodide interfered by increasing the absorbance which could be overcome by the addition of 1 ml of 0.1 M sodium sulphite solution.

Among the cations, positive interference was observed in the presence of Tl(I), As(III) and W(VI) while Sn(II), Fe(III) and Pt(IV) interfered by decreasing the absorbance. Tl(I),

W(VI) and Fe(III) ions could be masked by the addition of 1.0 ml of 0.1 M sodium fluoride solution. Sn(II) interference was overcome by oxidising with bromine water and excess bromine removed by boiling. The tolerance limits for other interfering ions were found to be As(100 μ g) and Pt(5 Mg).

Applications of the method

The validity of the developed method to real samples was checked by analysing (a) coal and (b) sea water samples, by the standard addition technique. A pre-treatment procedure for coal was carried out according to Gardner's modified procedure[14] and analysis of mercury completed by the recommended procedure. For sea water no sample preparation was carried out except filteration to remove any suspended particulates. The analysis was further confirmed by the dithizone procedure. Results shown in Table III are in good agreement with the expected values.

4. Conclusions

The proposed method is simple, selective and rapid. The reaction can be carried out under moderate conditions as compared to similar ion-association systems as is evident from Table IV. It is less laborious and insensitive to light than dithizone. The few interferences (except As and Pt) can be effectively overcome by simple masking techniques. The method is applicable to coal and sea water analysis.

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