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Spectrophotometric Determination of Mercury(II) by Solvent Extraction with Variamine Blue B[*1]

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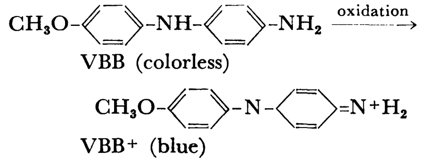
A new rapid, sensitive and selective method is proposed for the spectrophotometric determination of a trace of mercury(II) by solvent extraction. The method is based on the formation of an ion-pair complex between the tribromo-mercury(II) complex anion and the dyestuff cation obtained by oxidation of variamine blue B. The optimum pH range for the color reaction is 2.5—4. The blue complex can be extracted into nitrobenzene and has a maximum absorption at 605 mμ in the organic solvent. Beer's law holds in the range $3.2\times10^{-6}-2.2\times10^{-5}$ M of mercury(II) in the aqueous layer before the extraction, with a molar absorptivity of 4.03×10^4 mol^{-1}cm^{-1} l at 605 mμ. The color reaction is instantaneous and the complex remains stable 15 mintes in the nitrobenzene layer. Of the 22 cations and 11 anions examined, tin(II), tin(IV), antimony(III), iodide, cyanide, and thiocyanate showed serious interferences.

Many investigations[1] have been made on the spectrophotometric determination of mercury(II). The standard method based on the reaction with dithizone has been considered unsatisfactory because of its extreme sensitivity to variations in laboratory conditions, while the diphenylcarbazone method has serious drawbacks because of its extreme sensitivity to changes in acidity. A spectrophotometric method using thiocyanate has also been reported.[2] The method is limited by interference of halide and pseudohalide ions as well as such as silver.

Recently, rhodamine B,[3] phthalein complexone[4] and xylenol orange[5] were described as spectrophotometric reagents for mercury(II). The methods are sensitive, but suffer from a number of interferences. Another method based on the complex formation between mercury(II) ions and iodide ions has been described by Pappas and Powell.[6] A molar absorptivity of about 2.34×10^4 is claimed. 2,2′-dipyridyl-iron(II) chelate[7,8] was proposed for the spectrophotometric determination of mercury(II) by solvent extraction. Although this method is more reliable than the dithizone method, it is not sufficiently sensitive. The method proposed here has even greater sensitivity than the above techniques which have employed iodide ions or 2,2′-dipyridyl-iron(II) chelate.

Variamine blue B[9,10] (VBB) is known to be oxidized to form the blue dyestuff cation (VBB$^+$) as follows:



The tribromo-mercury(II) complex anion can be extracted into nitrobenzene with the VBB$^+$. This system was studied in detail to establish a method for the determination of mercury(II).

Experimental

Apparatus. Absorbance measurements were made using a Shimadzu Beckman Model QR-50 spectrophotometer with matched 1 cm quartz cells. A Toa Denpa Model HM-5A pH meter was used for pH measurements. An Iwaki Model KM shaker was used for the

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[*1] Presented at 18th Annual Meeting of the Japan Society for Analytical Chemistry, Hokkaido, October, 1969.

1) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Pub. Inc., New York (1965), p. 621.

2) G. E. Markle and D. F. Boltz, *Anal. Chem.*, **26**, 488 (1954).

3) H. Imai, *Nippon Kagaku Zasshi*, **90**, 275 (1969).

4) S. Komatsu and T. Nomura, *ibid.*, **88**, 542 (1967).

5) S. Komatsu, T. Nomura and M. Saito, *ibid.*, **88**, 1124 (1967).

6) A. J. Pappas and H. B. Powell, *Anal. Chem.*, **39**, 579 (1967).

7) K. Kotsuji, This Bulletin, **38**, 402 (1965).

8) Y. Yamamoto, S. Kikuchi, Y. Hayashi and T. Kumamaru, *Bunseki Kagaku*, **16**, 931 (1967).

9) L. Erdey and G. Rady, *Z. Anal. Chem.*, **149**, 250 (1956).

10) L. Erdey, *Chemist Analyst*, **48**, 106 (1959).

extraction.

Reagents. Guaranteed grade of mercuric chloride was dissolved in dilute sulfuric acid and diluted with deionized water to a concentration of 1.0×10^{-3} M of mercury(II). This standard solution was then diluted to the concentration required for the experiments.

Variamine blue B (VBB) solution, 10^{-3} M, was prepared by dissolving variamine blue B hydrochloride in deionized water.

A buffer solution was made 0.2 M from reagent grade sodium citrate and dilute sulfuric acid.

All the other reagents of a reagent grade were used without further purification.

Recommended Procedure. A solution was prepared by pipetting 2 m*l* of 0.1 M potassium bromide solution, 7 m*l* or less of a sample solution containing less than 0.016 g of mercury(II) per liter, 5 m*l* of 0.2 M citrate buffer solution (pH 2.9), 2 m*l* of 10^{-3} M VBB solution, and 2 m*l* of 0.1 M ammonium persulfate solution into 100-m*l* separatory funnel. This solution was brought to 25 m*l* with water. After adding 10 m*l* of nitrobenzene to the separating funnel, the contents were mixed thoroughly by a shaker for about one minute. After standing for five minutes, the nitrobenzene layer was drawn off into a glass tube with a glass stopper containing about 1 g of anhydrous sodium sulfate, and shaken to remove droplets of water. The absorbance of the extract is measured immediately at 605 mμ against a reagent blank or nitrobenzene.

Results and Discussion

Absorption Spectra. The absorption spectra shown in Fig. 1 were obtained for 0 and 1.6×10^{-5} M of mercury(II) solution through the recommended procedure. The presence of mercury(II) leads to a considerable increase in the absorbance (curve 1). The curve has a maximum value at 600 mμ. The absorbance maximum of the reagent blank (curve 2) in the nitrobenzene was at 500 mμ. The shift in the organic layer may be attributed to the effect of the association between the dyestuff cation and the complex anion. The maximum difference in the absorbance between curves 1 and 2 is found at 605 mμ. The absorbance is propotional the mercury(II) concentration at this wavelength.

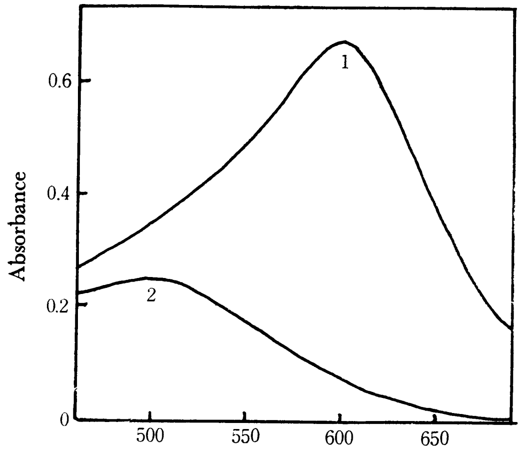

Fig. 1. Absorption spectra.
1: 1.6×10^{-5} M of Mercury(II)
2: Reagent blank
Reference: Nitrobenzene

Effect of pH. Figure 2 shows the typical pH dependence of the extraction system. The study was made by extracting 1.6×10^{-5} M of mercury(II) through the recommended procedure. The optimum pH was from 2.5 to 4.0. The pH of the solution was adjusted to 2.9 in this work.

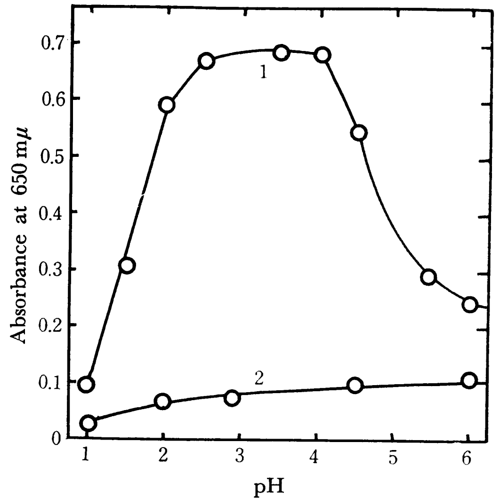

Fig. 2. Effect of pH.
1: 1.6×10^{-5} M of mercury(II)
2: Reagent blank
Reference: Nitrobenzene

A sodium citrate buffer was effective in keeping the solution at pH 2.9 as well as in masking metal ions. When the citrate concentration was less than 0.01 M in the aqueous layer, it took too long to separate the two layers. 0.01—0.08 M of citrate had no influence on the absorbance of the extract. At pH 2.9 no citrate-mercury(II) complex formation was apparent from this experiment.

Solvent for Extraction. Several organic so - vents have been examined for their ability to extract the bromo-mercury(II)-dyestuff ternary complex. The solvents investigated were benzene, butyl acetate, carbon tetrachloride, chloroform, cyclohexane, 1,2-dichloroethane, ether, ethyl acetate, *n*-hexane, isoamylalcohol, methyl isobutyl ketone, monochlorobenzene, nitrobenzene, and toluene. Among the solvents tested, only nitrobenzene was capable of extracting the complex while in the other cases a blue precipitate was slightly observed at the interface.

Effect of Reagents. In aqueous solution the tribromo-mercury(II) complex anion is in equilibrium with the mercury bromide and tetrabromomercury(II) complex anion. The distribution of the tribromo-mercury(II) concentration in the 8×10^{-3} M of potassium bromide is about 60%, from the formation constant ($\log\beta_1$: 9.05, $\log\beta_2$: 17.3, $\log\beta_3$: 19.7, $\log\beta_4$: 21.0). The absorbance in the nitrobenzene layer of a series of 1.6×10^{-5} M mercury(II) solution remained unchanged when the potassium bromide concentration was varied from 1.0×10^{-3} to 1.6×10^{-2} M. Mercury(II) seemed to be extracted as tribromo-mercury(II) through the equilibrium shift against the changes of bromide concentration.

Several kinds of oxidizing agents were tested to obtain the colored dyestuff cation. They were ferric sulfate, hydrogen peroxide, ammonium persulfate, potassium permanganate, ceric sulfate, potassium dichromate, manganic sulfate, potassium bromate, potassium iodate, calcium hypochlorite, chloramine T, and iodine. Of these, ammonium persulfate was chosen for the present work because it is the most effective in oxidizing the VBB and gives a lower absorbancy of the reagent blank. Maximum and constant color development required about a 5-fold molar excess of the ammonium persulfate to the VBB concentration. 2 m*l* of 0.1 M ammonium persulfate solution used in this work supplies the oxidizing reagent in a ratio of 100 to 1 against the 8×10^{-5} M of VBB.

Samples containing 1.6×10^{-5} M of mercury(II) were treated by the recommended procedure, except that the concentration of VBB was varied. Maximum color development in the nitrobenzene layer required more than about a 3-fold molar excess of VBB to mercury(II). 2 m*l* of 10^{-3} M VBB solution used in the procedure supplies a ratio of 5 to 1 if the sample contains 1.6×10^{-5} M of mercury(II).

Other Variable. In order to confirm complete extraction with nitrobenzene, a sample containing 1.6×10^{-5} M of mercury(II) was treated according to the procedure. The first extraction yielded an absorbance of 0.605 using a reagent blank as a reference. The aqueous solution was then extracted with another 10 m*l* portion of nitrobenzene. The measured absorbance of this organic layer was 0.003 against a reagent blank. From this experiment, it seems that the extraction rate using 10 m*l* of nitrobenzene is not less than 95%.

The stability of the color of the extracted organic layer was studied. Little or no error will be introduced if the absorbance is measured within fifteen minutes after extraction. After an hour, the absorbance decreased by 6.3%.

Color development in the nitrobenzene layer varied with the shaking time. For the condition in the present work, full color development took about thirty seconds. Continued shaking up to five minutes produced no further change in absorbance.

Calibration and Reproducibility. The system followed Beer's law in the range 3.2×10^{-6}—2.2×10^{-5} M of mercury(II). The molar absorptivity can be calculated to be 4.03×10^4 mol^{-1} cm^{-1}*l*.

Ten identical samples, each with a final mercury(II) concentration of 1.6×10^{-5} M, were treated and their absorbance were measured at 605 mμ using a reagent blank as a reference. The mean absorbance was 0.605, with a standard deviation of 0.007 absorbance unit.

Method of Continuous Variations. In order to investigate the structure of this colored complex, continuous variations plots were employed. The total concentration of mercury(II) plus VBB was 4×10^{-5} M. The continuous variations plots at 605 mμ and 560 mμ have a maximum 0.5 mole fraction of mercury(II), indicating a 1 to 1 mercury(II)-VBB ratio. The overall molar ratio of the mercury(II) : bromide : VBB is 1 : 3 : 1, and its formula can be suggested as $\mathrm{VBB^+\cdot[HgBr_3]^-}$.

Effect of Diverse Ions. The effect of diverse ions was studied for a sample containing 1.6×10^{-5} M of mercury(II). The tolerance to a given ion was defined as the maximum concentration which could be present without causing a deviation of 0.025 for the absorbance of the sample. Tolerances for diverse ions tested are listed in Table 1. Anions were added as solutions of their sodium, potassium or ammonium salts. Cations were added as solutions of their chlorides or sulfates. The citrate used as a buffering agent is also useful

TABLE 1. EFFECT OF DIVERSE IONS

Ion	Tolerance (M)	Ion	Tolerance (M)
Ag^+	1×10^{-3}	Sn^{2+}	5×10^{-7}
Al^{3+}	2×10^{-3}	Sn^{4+}	1×10^{-6}
Ba^{2+}	5×10^{-3}	Th^{4+}	1×10^{-4}
Be^{2+}	5×10^{-3}	Tl^+	1×10^{-4}
Bi^{3+}	2×10^{-4}	Zn^{2+}	5×10^{-3}
Ca^{2+}	5×10^{-3}	CH_3COO^-	2×10^{-3}
Cd^{2+}	5×10^{-4}	SO_4^{2-}	5×10^{-3}
Co^{2+}	1×10^{-3}	F^-	5×10^{-3}
Cr^{3+}	2×10^{-3}	I^-	1×10^{-5}
Cu^{2+}	2×10^{-3}	Cl^-	2×10^{-3}
Fe^{2+}	2×10^{-4}	NO_3^-	2×10^{-4}
Fe^{3+}	5×10^{-3}	$H_2PO_4^-$	5×10^{-3}
Mn^{2+}	5×10^{-4}	VO_3^-	1×10^{-3}
Mg^{2+}	5×10^{-3}	CN^-	5×10^{-7}
Ni^{2+}	2×10^{-3}	HCO_3^-	5×10^{-3}
Pb^{2+}*	1×10^{-3}	SCN^-	1×10^{-6}
Sb^{3+}	1×10^{-5}		

Mercury: 1.6×10^{-5} M. * Added as acetate.

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11) Assoc. of Offic. Agr. Chemists, "Official Methods of Analysis," 8th ed., Washington (1955), p. 76.

as a masking agent for many cations. Antimony(III) formed insoluble precipitates under these conditions, and only tin(II), (IV) among the cations tested showed serious effects.

Table 2. Application of the method

Sample No.	Mercury content (%)		Difference
	Proposed method	Official method	
1	2.21	2.14	+0.07
2	2.23	2.10	+0.13
3	2.20	2.09	+0.11

Application of the Method. By following the official method,[12] three solutions were prepared from agricultual medicines contained ethylmercuric phosphate. These solutions were analyzed by the official method and the proposed method. The results obtained are summarized in Table 2.

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