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Extractive Spectrophotometric Determination of Mercury with Thiobenzoylacetone; Analysis of Waste Water

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Thiobenzoylacetone was used for the extraction and spectrophotometric determination of mercury(II). The complex quantitatively extracted at pH 4.0 with 10 ml of 0.001 M reagent in benzene. After removing the excess of the reagent with the buffer solution of pH 12.0, the complex was measured at 345 nm against reagent blank prepared similarly. The system adhered to Beer's law in the concentration range of 0.6 to 12.1 μg of mercury per ml. The molar extinction coefficient was 1.7×10^4 and the sensitivity was 0.011 μg/cm^2. The complex was stable for 48 h. The extraction was quantitative within 10 min of equilibbrium. It was possible to determine mercury in the presence of a large number of ions (1 : 1000). The method was found to be applicable to the analysis of waste water from chloro-alkali industries.

Many investigations have been made on the extractive photometric determination of mercury(II) with chelating ligands. 1-(2-Pyridylazo)-2-naphthol[1] was used for such purpose but the pH range of extraction was very narrow. The extraction involving dithizone[2] has been considered unsatisfactory because of its extreme sensitivity to variations in the laboratory conditions, while Bindschedler's Green[3] was used with some advantage but the dissolved chlorine in water showed a strong interference in such determinations. Brilliant Green[4] is not a good extractant as gold, and thallium interfered seriously. The extraction with Crystal Violet[5] was feasible within a narrow pH range of 1.3—1.6. In the Rhodamine-B[6] extraction, heavy metals showed strong interferences, and the colour has to be stabilised by the addition of potassium bromide.

Amongst β-diketones, extraction with acetylacetone and benzoylacetone[7] were not quantitative. The extractions with dibenzoylmethane[7] needed a long period of equilibration. Although thiothenoyltrifluoroacetone[8—10] was a good extractant, it was necessary to remove the excess of the reagent in order to improve sensitivity. With di(thiobenzoyl)methane[11] (II) as an extractant the absorbance was measured in the ultraviolet region. In this paper a simple, selective and sensitive method is described for solvent extraction and spectrophotometric determination of mercury(II) with thiobenzoylacetone. The method has been further extended to the determination of mercury from waste water.

Experimental

Apparatus and Reagent. A Spektromom 204 spectrophotometer with matched 10 mm quartz cuvettes, and a Cambridge pH meter with glass and calomel electrodes were used.

Thiobenzoylacetone (SBA) was synthesised from benzoylacetone (Fluka, A. G.) by the procedure described earlier.[12] About 0.001 M reagent was used in benzene. The reagent was preferably preserved in a refrigerator.

A stock solution of mercury was prepared by dissolving 1.356 g of mercury(II) chloride (B. D. H. AnalaR) in 1 litre of distilled water. The solution was standardised gravimetrically as thionalide.[13] It contained 3.872 mg of mercury per ml. The solutions of lower concentrations were prepared by volumetric dilution of the stock solution.

Buffer solution of pH 4.0 was prepared by dissolving 14.0 g of sodium acetate in 500 ml of distilled water and acidified with 0.2 M acetic acid.

Buffer solution of pH 12.0 was prepared by mixing 100 ml of 0.05 M Borax and 126.5 ml of a 0.1 M sodium hydroxide solution.

General Procedure. An aliquot of mercury(II) chloride solution containing about 48.4 μg of mercury was taken. Then 10 ml of buffer solution of pH 4.0 was added, and the total volume of the aqueous phase was made to 25 ml. The solution was then introduced into a separatory funnel, and shaken with 10 ml of 0.001 M SBA in benzene for 10 min. The layers were allowed to settle and separate. After separating out the aqueous phase, the organic phase was washed twice to remove excess of the free reagent with the buffer solution of pH 12.0. The organic phase was carefully withdrawn into a 10 ml volumetric flask. It was measured spectrophotometrically at 345 nm against a reagent blank prepared similarly. The amount of mercury was then calculated from the calibration curve.

Results and Discussion

Absorption Spectra. The absorption spectrum of the Hg(II)-SBA complex extracted at pH 4.0 against the reagent blank as a reference solution is shown

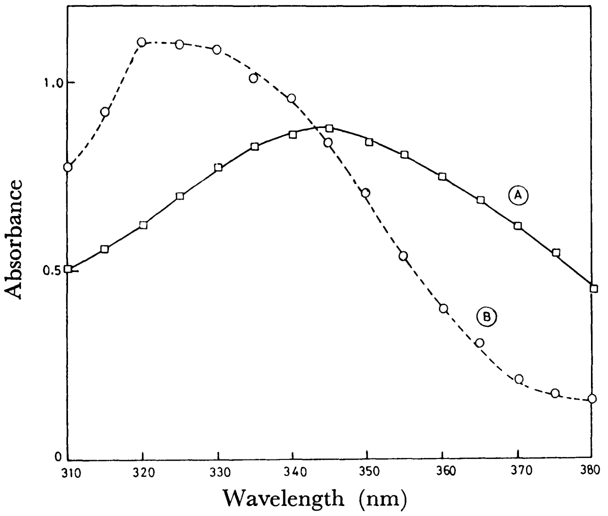

Fig. 1. Absorption of (A) mercury(II)-thiobenzoylacetone complex *vs.* reagent blank, and (B) reagent blank, and (B) reagent blank *vs.* benzene.
$[\mathrm{Hg}] = 4.84 \times 10^{-5}$ M, $\mathrm{SBA} = 1.0 \times 10^{-3}$ M, pH 4.0.

in Fig. 1. The spectrum of the reagent blank *vs.* benzene is also given. The difference in absorbance between the Hg(II)–SBA complex and the reagent blank appears to be maximum around 345 nm ; All absorbance measurements were therefore carried out at 345 nm. The molar extinction coefficient of the complex at 345 nm was 1.7×10^4 when the concentration of mercury was 48.4 μg/10 ml and the effective cell width was 10 mm. The sensitivity as per Sandell's definition was 0.011 μg/cm^2.

Extraction as the Function of pH. The exraction of mercury was studied as a function of pH(Fig. 2) from 1.0 to 11.0. Figure 2 shows that the extraction was quantitative between pH 0.2 to 9.0 ; the extraction started decreasing at pH 9.5 and at 11.0, it was 60.9%. Hence for all practical purposes pH 4.0 was employed for the purpose of extractions.

Adherence to Beer's Law. Different amounts of mercury(II) were taken and extracted at pH 4.0 and measured at various wavelengths, such as 335, 345 and 355 nm (Fig. 3). The Hg–SBA system conformed to Beer's law over the concentration range of 0.6 to 12.1 of mercury per ml at 345 nm only. Furthermore, at this wavelength there is a maximum slope for the absorbance-concentration plot. Hence all absorbance measurements were carried out at 345 nm.

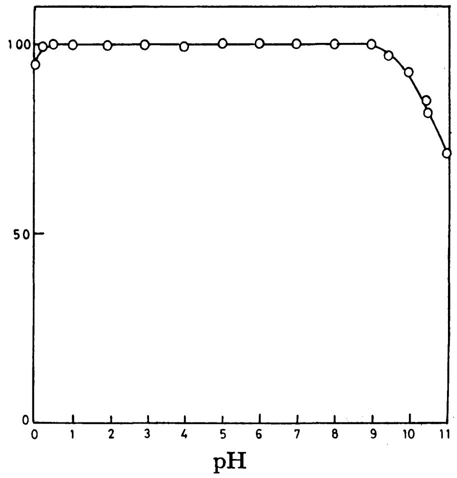

Fig. 2. Extraction of mercury as a function of pH.

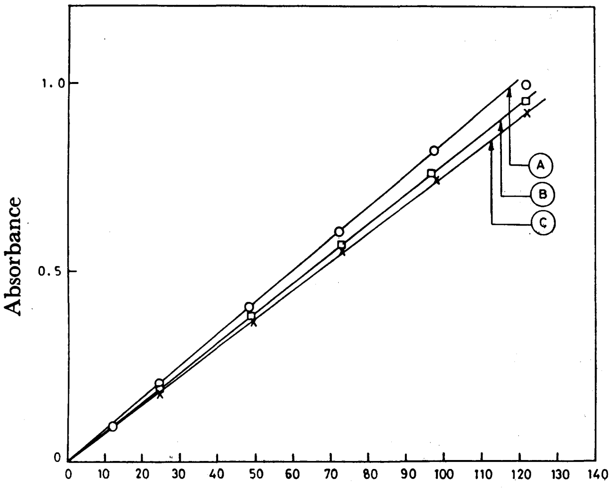

Fig. 3. Calibration curve at (A) 345 nm, (B) 335 nm, and (C) 355 nm.

Stability of the Colour of the Complex. As per the general procedure, the absorbance of the Hg(II) complex was measured at elapsed intervals of 0, 8, 16, 24, 48, 72, and 118 h. The absorbance of the complex was constant for 48 h. Hence the complex should be measured within 48 h of complexation.

Effect of Reagent Concentration. The extraction of mercury was carried out with varying concentration and varying volume of the reagent (Table 1). The result showed that a single extraction with 10 ml of 0.001 M reagent was adequate for quantitative extraction. There was insignificant enhancement in the extraction of mercury with greater concentration of reagent, and with dilute solutions the extraction was incomplete.

Table 1. Effect of reagent concentration
48.4 μg of Hg(II); 0.001 M SBA in benzene

SBA concentration $M\times10^{-4}$	SBA added, ml	Absorbance at 345 nm
2.0	10	0.165
4.0	10	0.280
5.0	10	0.380
6.0	10	0.410
8.0	10	0.410
10.0	10	0.410
	2.5[a)]	0.210
	5.0[a)]	0.380
	7.5[a)]	0.410
	15.0	0.290
15.0	10	0.410
20.0	10	0.415

a) Volume is made to 10 ml.

Effect of Salting-Out Agents. The chlorides of ammonium, lithium, sodium and calcium (1 to 3 M) were used as salting-out agents to study their effects on the extraction of mercury with 0.001 M SBA at pH 4.0 and 340 nm. The results showed that none of them had significant effects on extraction.

Period of Equilibration. The period of equilibration was varied from 2—30 min. It was observed that the extraction was quantitative after 7 min of equilibration. Hence for all purposes, 10 min equilibration period was employed.

Effect of Diverse Ions. The results in Table 2 show the effect of various ions the process of extraction. The tolerance limit was set at the amount of foreign ions required to cause a ±2% error in the mercury recovery. Alkali and alkaline earth metals, chloride, nitrite, nitrate, sulphate, acetate, perrhenate are tolerated in the ratio of 1 to 1000, whereas ions such as thallium(I), cadmium, antimony(V), bismuth(III), osmium(VI), platinum(IV), aluminium, thorium, cerium(IV), manganese(II), beryllium, sulphte, phosphate, fluoride and anions of organic dicarboxylic acids were tolerated in the ratio of 1 to 500. Other ions were tolerated in lesser ratios. Silver, lead, copper, pal-

TABLE 2. EFFECT OF DIVERSE IONS
Hg(II) = 48.4 μg; pH = 4.0; 10^{-3} M reagent

Forign ion	Added as	Tolerance limit, μg	Forign ion	Added as	Tolerance limit, μg
Ag^+	$AgNO_3$	Interferes	K^+	KCl	100000
Pb^{2+}	$Pb(NO_3)_2$	500[a)]	Rb^+	RbCl	100000
Tl^+	Tl_2SO_4	10000	Cs^+	CsCl	100000
Cd^{2+}	$Cd(NO_3)_2 \cdot 5H_2O$	10000	NH_4^+	NH_4NO_3	100000
Sb^{3+}	$Sb_2(SO_4)_3$	10000	Cl^-	NaCl	50000
Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	10000	Br^-	NH_4Br	100
Os^{6+}	Na_2OsO_4	13000	I^-	KI	100
Pt^{4+}	$H_2PtCl_6 \cdot 4H_2O$	10000	NO_3^-	KNO_3	50000
Ir^{3+}	$IrCl_3$	500	NO_2^-	KNO_2	50000
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	1000[b)]	SO_3^{2-}	$Na_2SO_3 \cdot 7H_2O$	25000
Pd^{2+}	$PdCl_2 \cdot 2H_2O$	1200[c)]	SO_4^{2-}	$Na_2SO_4 \cdot 10H_2O$	50000
Ru^{3+}	$RuCl_3$	200	PO_4^{3-}	$Na_2HPO_4 \cdot 12H_2O$	25000
Rh^{3+}	$RhCl_3$	2000	$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	100
Au^{3+}	$HAuCl_4 \cdot xH_2O$	50	SCN^-	KSCN	1000
Fe^{3+}	$Fe_2(SO_4)_3 \cdot 6H_2O$	6000	CN^-	KCN	Interferes
Cr^{3+}	$CrCl_3 \cdot 6H_2O$	6000	F^-	NaF	20000
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	15000	$tart^{3-}$	tartaric acid	20000
Th^{4+}	$Th(NO_3)_4$	18000	cit^{3-}	citric acid	15000
U^{6+}	$UO_2(NO_3)_2 \cdot 6H_2O$	5000	$oxal^{2-}$	oxalic acid	20000
Ce^{4+}	$Ce(SO_4)_2 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	15000	$ascorabate^-$	ascorbic acid	100
Zr^{4+}	$Zr(NO_3)_4$	1000	$malonate^{2-}$	malonic acid	20000
Be^{2+}	$Be(NO_3)_2$	20000	$EDTA^{4-}$	disodium salt of EDTA	5000
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	50000	$acetate^-$	sodium acetate	50000
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	40000	$thiourea^-$	thiourea	10000
Co^{2+}	$CoSO_4 \cdot 6H_2O$	800	ClO_4^-	$HClO_4$	25000
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	1000	WO_4^{2-}	$Na_2WO_4 \cdot 2H_2O$	20000
Ca^{2+}	$Ca(NO_3)_2 \cdot 6H_2O$	50000	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	25000
Ba^{2+}	$Ba(NO_3)_2 \cdot 4H_2O$	50000	AsO_3^{3-}	Na_2AsO_3	20000
Sr^{2+}	$SrCl_2 \cdot 2H_2O$	50000	ReO_4^-	$KReO_4$	50000
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	50000	CrO_4^{2-}	K_2CrO_4	10000
Li^+	Li_2SO_4	100000	VO_3^-	$NaVO_3$	25000
Na^+	Na_2SO_4	100000			

a) Selectively extracted with 0.25 M TTA in benzene at pH 4.0.[2)] b) Selectively extracted with 0.15 M TTA in benzene.[2)] c) Selectively extracted with 1% dimethylglyoxime in methanol into chloroform.

TABLE 3. DETERMINATION OF MERCURY FROM WASTE WATER WITH THIOBENZOYLACETONE (SBA) AND BINDSCHEDLER'S GREEN (BG)[3)]

Volume taken (in ml)	Absorbance		Amount found		Total amount of mercury present in 150 ml of waste water	
	SBA	BG	SBA	BG	SBA method in μg	BG method
2	0.065	0.240	8.24	8.24	1020.0	1031.0
4	0.135	0.470	16.30	16.40	1018.7	1025.0
6	0.205	0.700	24.30	24.50	1012.5	1020.0
10	0.340	—	40.4	—	1010.0	—

ladium and cyanide ions showed strong interference, but the interference of some of the ions was eliminated by selective extraction with 2-thenoyltrifluoroacetone[2)] for copper and lead, and dimethylglyoxime[2)] for palladium.

Analysis of Mercury in Waste Water. The method was applied on waste water containing ethyl mercury which was collected from chloro-alkali industry. About 150 ml of waste water was treated with 10 ml of concentrated sulfuric acid and 30 ml of 30% hydrogen peroxide. It was gently heated over a waterbath until the foaming ceased. The solution was allowed to cool and it was diluted to 250 ml.

A known volume of an aliquot of the solution was taken. Then 10 ml of buffer solution of pH 4.0 was added to it. The solution was extracted with 10 ml of 0.001 M SBA in benzene. The absorbance of mercury–thiobenzoylacetone complex was measured spectrophotometrically at 345 nm. For the purpose of comparison and testing the reproducibility the mercury in waste water was also determined by the extraction with Bindschedler's Green.[3] The results obtained are summarised in Table 3. It was seen that the proposed method compares favourably with existing methods for the separation and determination of mercury.

From ten determinations with 48.4 μg of Hg, the absorbance was found to be 0.410±0.010. The total operation requires about 45 min. The standard deviation was ±1.54%.

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