



New Analytical Technique for the Determination of Mercury (II) by Extraction Spectrophotometric Method with Potassium Benzyl Xanthate in Sewage Wastes and Spiked Water Samples

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ABSTRACT

A new simple and sensitive extractive spectrophotometric method for the determination of mercury (II) with potassium benzyl xanthate (KBX) has been developed. Mercury was complexed with KBX to form light yellow colour Hg-KBX complex and was extracted in to methyl isobutyl ketone (MIBK). The complex has maximum absorbance at 375nm. The molar absorbitivity and Sandell's sensitivity of the complex was $2.609 \times 10^{-3} \text{ L.mole}^{-1} \cdot \text{cm}^{-1}$ and $1.673 \times 10^{-2} \mu\text{g/cm}^2$ respectively. The developed method obeys Beer's law in the concentration range of 1.0 to 20 ppm. The composition of the complex (metal:ligand) was 1:2. The developed method was applied for the determination of mercury in sewage waste and spiked water samples.

INTRODUCTION

Mercury in water is toxic to living beings. The concentration of mercury increases in natural waters by the industrial wastes. Even at low ion concentration, mercury and it's compounds cause potential hazards due to enrichment in food chain. Damage by mercury pollution is chiefly in the cerebellum and sensory pathways of man. In view of its toxicity, methods capable of determining mercury in water are needed. Spectrophotometry is one of the techniques for determination of metals in water and there are methods reported for the spectrophotometric determination of mercury in water (Li 1985, Kumar et al. 2008, Yan et al. 2007, Ghaedi 2007, Jing et al. 2007, Hosseini & Moghaddam 2005, Khan et al. 2005, Reddy et al. 2008, Aswar & Joshi 2008, Maysam 2009). Danet & Barbuica (1980) determined mercury based on UV absorption of HgCl_4^{-2} or HgBr_4^{-2} .

In the present investigation a sensitive spectrophotometric method for the determination of mercury with potassium benzyl xanthate as a complexing agent is described.

MATERIALS AND METHODS

Schimedzu, PRI UV-visible-recording spectrophotometer, UV-240 and Elico digital pH meter L1-120 were used in the present investigation. Potassium benzyl xanthate was prepared by standard method (Vogel 1968, 1969). All the reagents used were of analytical grade and all the solutions were prepared in double distilled water. 1.353g of mercury (II) chloride was dissolved in deionized double distilled water and the solution was made up to 1000mL. Buffer of different pH values were prepared by standard procedure. Hydrochloric acid-potassium chloride buffer (pH 2.0 to 4.0), acetic acid-sodium acetate buffer (pH 4.0 to 7.0) and ammonium chloride and ammonium hydroxide buffer (pH

8.0 to 12.0) were prepared. 0.6639 g of potassium benzyl xanthate is dissolved in 1000mL of double distilled water to prepare 3×10^{-3} M solution.

An aliquot of the solution containing 10-200 μg of mercury (II) was taken. To this 3.0mL of ammonium chloride-ammonium hydroxide buffer and 2.0mL of benzyl xanthate solution (KBX) were added and the total volume was diluted to 10mL by deionized double distilled water and the mixture was transferred into a 50mL separatory funnel. The light yellow colour mercury potassium benzyl xanthate complex Hg (II) – KBX formed was extracted into 10mL of MIBK, after shaking vigorously for 3.5 minutes, the absorbance of Hg (II)-KBX complex was measured at 375nm against the reagent blank.

RESULTS AND DISCUSSION

Methyl isobutyl ketone (MIBK) was chosen as solvent, since it was found that the metal complex effectively extracted. The Hg (II) complex was readily extractable into MIBK and no change was observed in the extent of extraction when the mixture was shaken from 1.5 to 5.0 minutes. Hence 2.5 minutes of shaking time was enough for the complete extraction of complex in to MIBK. The optimum pH for the extraction of metal ion into the organic phase increase as the pH increase from 7.0 to 10.0 and again decrease from 10.0 to 14.0. It was observed that a twenty five-fold excess of reagent was sufficient to produce maximum intensity of colour. This is equal to 2.0mL of 0.5% KBX solution.

With the optimum conditions developed, the calibration curve was constructed. It was observed that Beer's law was obeyed for the constructed range of 1.0 to 20.0 ppm of Hg (II) as shown in Fig. 1. The exact concentration range was determined by constructing a Ringbom plot. Based on slope of the Ringbom plot (1.3972), the ratio between the relative error in concentration and photometric error is 1.5601. For a photometric error of one percent, AP = 0.01. Hence, the relative error in concentration is 0.015601. Mercury (II) can be determined accurately by these methods in the range of 3.0 to 17.0 ppm. Sandell's sensitivity of the reaction obtained from Beer's law is $2.609 \times 10^{-3} \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and the molar absorptivity of the complex is calculated as $1.7623 \times 10^2 \mu\text{g}/\text{cm}^2$. Aliquots containing 9.0 mg/mL of Hg (II) gave a standard deviation of 0.9502×10^{-3} , and co-efficient of variation 0.2062 percent.

The composition of mercury (II) complex was found to be 1:2 according to Job's method, molar ratio method and Asmn's method. The instability constant of the complex was found to be 1.4259×10^{-7} by

Table 1: Effect of foreign ions on the extraction of Hg (II)-KBX complex.

Foreign ion	Sources of the ion	Tolerance limit (μg)
Ba (II)	BaCl ₂ .2H ₂ O	4500
Sr (II)	Sr (NO ₃) ₂	4500
U (VI)	UO ₂ (CH ₃ COO) ₂ .2H ₂ O	4500
Zn (II)	ZnSO ₄ .7H ₂ O	4000
Sn (II)	SnCl ₂	4000
Pb (II)	PbCl ₂	3000
Mn(II)	MnSO ₄ .H ₂ O	3000
Fe (III)*	FeCl ₃	3000
Cu (II)*	CuCl ₂	3000
Co (II)*	CoCl ₂ .6H ₂ O	3000
Fluoride	NaF	5000
Chloride	KCL	5000
Acetate	CH ₃ COONH ₄	3000
Tartrate	CHOH, COONa.4H ₂ O	
	COOK, CHOH	3000
Iodide	KI	3000
Sulphate	Na ₂ SO ₄	1000
Bromide	KBr	1000
Bicarbonate	NaHCO ₃	1000
Thiocyanate	NH ₄ SCN	1000

*Masked by using 1mL of 0.4% EDTA; concentration of the metal ion Hg (II)-20 μg /mL; concentration of the reagent (KBX) -2.0mL of 0.5%; pH-10.0; λ_{max} -375

Table 2: Determination of Hg (II) in sewage waste (10.0g sample)

S.No.	Area of sewage waste	Metal ion found		Recovery (%) Present method
		Present method*(μg)	AAS method(μg)	
1	Steel plant area	7.6	7.8	97.4
2	HPCL area	8.8	8.9	98.8
3	Hindustan Zinc Ltd. Area	6.8	6.9	98.5

*Average value of three determinations; Reagent concentration: 2.0mL of 0.5%; pH: 10.0; λ_{max} : 375

Table 3: Determination of Hg (II) in spiked water samples.

S.No.	Amount of metal ion added (μg)	Metal ion found		Recovery (%) Present method
		Present method*(μg)	AAS method(μg)	
1	40	39.5	39.6	98.75
2	80	79.4	79.6	99.25
3	120	119.3	119.7	99.40
4	160	159.4	159.7	99.60
5	200	199.2	199.6	99.80

*Average value of three determinations; Reagent concentration: 2.0mL of 0.5%; pH:10.0; λ_{max} : 375

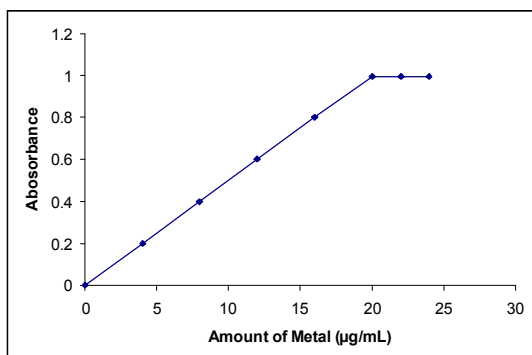


Fig.1: Applicability of Beer's law, Hg (KBX)₂ complex.

Edmonds and Birnbanm's method.

The effect of diverse ions on the extraction and spectrophotometric determination of Hg (II) was studied and the results are presented in Table 1. The cations like Ba(II), Sr(II) and U(VI) do not have any effect on the extracts of Hg (KBX)₂ complex when present up to 4,500 μg . Zinc (II) and tin (II) do not interfere in the determination of Hg (II) even when present up to 4,000 μg . Pb (II) and Mn (II) can be tolerated up to 3,000 μg . Fe (III), Cu (II) and Co (II) interfere in the determination of Hg (II) even when present in trace amounts.

Anions like fluoride, chloride and EDTA do not interfere when present up to 5,000 μg . Acetate, tartaric and iodide do not have any effect in the determination when present up to 3000 μg . Sulphate, bromide, bicarbonate, and thiocyanate can be tolerated up to 1000 μg . The interference due to Fe (III), Cu (II) and Co (II) can be eliminated by using 1.0 mL of 0.4 percent EDTA solution.

Determination of mercury (II) in sewage water: The proposed method was applied for the determination of mercury (II) in sewage water collected in different parts in Visakhapatnam city. 10.0g of the dried sample (sewage waste) was weighed and brought into solution by dry ash method. The results are given in Table 2. The results showed that the concentration of mercury (II) is 7.6 μg in

sample 1, 8.8 μg in sample 2, and 6.8 μg in sample 3. The results are compared with atomic absorption spectrophotometry and they are found to be in good agreement.

Analysis of spiked water samples: The developed method was applied for the determination of mercury (II) in spiked water samples. The recovery of mercury (II) from spiked water sample was examined using the general procedure. The results are given in Table 3, which show that the developed method is applicable to analyse spiked water sample with the percentage recovery for mercury at 99.8. This method was applicable for the analysis of real water samples.

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