NEW ANALYTICAL TECHNIQUE FOR THE DETERMINATION OF MERCURY (II) BY EXTRACTION SPECTROPHOTOMETRIC METHOD WITH ISONITRISO P-ISOPROPYL ACETOPHENONE PHENYL HYDRAZONE 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 Isonitriso p-isopropyl Acetophenone Phenyl Hydrazone (HIPAPH) has been developed. Mercury was complexed with HIPAPH to form light yellow color Hg-(HIPAPH)$_2$ complex and was extracted in to methyl isobutyl ketone (MIBK). The complex has maximum absorbance at 395nm. The molar absorbitivity and sandell's sensitivity of the complex was 2.678×10^{-3} lit.mole^{-1}.cm^{-1} and $1.765 \times 10^{-2} \mu g/cm^2$ respectively. The developed method 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.

Keywords: Extraction Spectrophotometric, Isonitriso p-isopropyl Acetophenone Phenyl Hydrazone, Mercury (II), Sewage Wastes

INTRODUCTION

Mercury in water is toxic to living beings. The toxicity of mercury is increases in natural waters by the industrial water. Even at low ion concentrations, 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 with lesions in the cerebral context of man. In view of its toxicity methods capable of determine mercury in water are needed. Specrtrophotometry is one of the techniques for the determination of metals in water and there are methods reported for the spectrophotometric determination of mercury in water [1-11]. Rajesh and Hari [12] 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 HIPAPH as a complexing agent is described.

EXPERMENTAL METHODS

Shimadzu, PRI UV- visible – recording spectrophotometer, UV-240 and Elico digital pH meter L1-120 were used in the present investigation. Isonitriso p-isopropyl Acetophenone Phenyl Hydrazone was prepared by standard method [13]. All the reagents used are of analytical grade and all the solutions are 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 Isonitriso p-isopropyl Acetophenone Phenyl Hydrazone is dissolved in 1000mL of double distilled water (3×10^{-3}M solution).

GENERAL PROCEDURE

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 Isonitriso p-isopropyl Acetophenone Phenyl Hydrazone solution (HIPAPH) are 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 p-isopropyl Acetophenone Phenyl Hydrazone complex Hg (II) – HIPAPH formed was extracted into 10mL of MIBK, after shaking vigorously for 3.5 minutes, the absorbance of Hg (II)- HIPAPH complex was measured at 395nm against the reagent blank.

RESULTS AND DISCUSSION

Methyl isobutyl ketone (MIBK) is 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 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% HIPAPH 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) shown in figure-1. The exact concentration range was determined by constructing a Ringbom plot. Based on the slope of the Ringbom plot (1.3972) shown this ration 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 2.678×10^{-3}lit.mol^{-1}.cm^{-1} and the molar obsorptivity of the complex is calculated as 1.765×10^{-2} μg/cm^2. Aliquots containing 9.0 mg/mL of Hg (II) gave a standard deviation of 0.9432×10^{-3} and co-efficient of variation is 0.2263 percent.
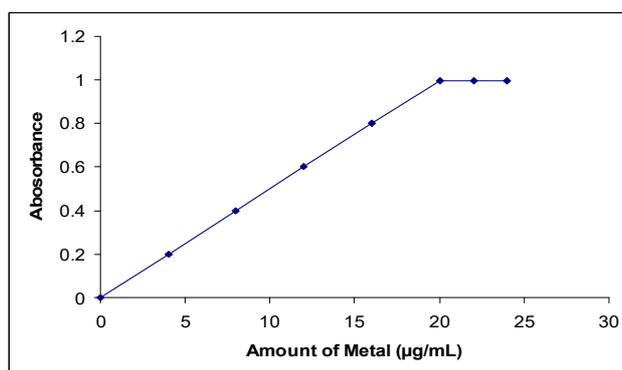

FIG.1: *APPLICABILITY OF BEER`S LAW Hg- (HIPAPH)₂ COMPLEX*

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 Edmonds and Birnbanm`s method.

The effect of diverse ion on the extraction and spectrophotometric determination of Hg (II) were studied and the results are presented in Table-1. From the Tabe-1 cations like Ba(II), Sr(II) and U(VI) do not have any effect on the extracts of Hg-(HIPAPH)$_2$ complex, when present up to 4,500µg 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 3,000µg. 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 5,000µg. 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 1000µg. The interference due to Fe (III), Cu (II) and Co (II) can be eleminated by using 1.0 mL of 0.4percent EDTA solution.

APPLICATION OF THE DEVELOPED METHOD
The developed extractive-spectrophotometric method was applied for the determination of mercury (II) in sewage waste and spiked water samples.

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 shown in Table-2. The results showed that the concentration of mercury (II) is 6.9µg in sample-1, 9.5µg in sample-II and 6.8µg in sample-II. 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-III showing that the developed method is applicable to analyse spiked water sample with the percentage recovery for mercury is 99.8. This method was applicable for the analysis of real water samples.

CONCLUSION

This method offers several interesting features such as simplicity,rapidity, and low cost besides sensitivity. The number of associated elements do not interfere in the determination. The selectivity of the reagents is also improved by the use of suitable masking agents to suppress the interference of metal ions like Fe (III), Cu (II) Co (II). Hence the proposed method is recommended for the determination of Hg(II) with HAPAPH by spectrophotometric method, at minor and trace levels, besides its use for analysis of real samples such as industrial effluents.

Table – 1 : *Effect of Foreign Ions on the extraction of Hg (II) – HIPAPH complex*

Foreign ion	Sources of the ion	Tolerance Limit (µg)
Ba (II)	$BaCl_2\ 2H_2O$	4500
Sr (II)	$Sr\ (NO_3)_2$	4500
U (VI)	$UO_2\ (CH_3COO)_2\ 2H_2O$	4500
Zn (II)	$ZnSO_4\ 7H_2O$	4000
Sn (II)	$SnCl_2$	4000
Pb (II)	$PbCl_2$	3000
Mn(II)	$MnSO_4\ H_2O$	3000
Fe (III)[*]	$FeCl_3$	3000
Cu (II)[*]	$CuCl_2$	3000
Co (II)[*]	$CoCl_2\ 6H_2O$	3000
Fluoride	NaF	5000
Chloride	KCL	5000
Acetate	CH_3COONH_4	3000
Tartrate	COOK. CHOH. CHOH. COONa. $4H_2O$	3000
Iodide	KI	3000
Sulphate	Na_2SO_4	1000
Bromide	KBr	1000
Bicarbonate	$NaHCO_3$	1000
Thiocyanate	NH_4SCN	1000

* Masked by using 1mL of 0.4% EDTA
Concentration of the metal ion Hg (II) – 20µg/mL
Concentration of the reagent (KBX)   – 2.0mL of 0.5%, pH-10.0, λ_{max} - 395

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	6.9	7.0	98.5
2	HPCL area	9.5	9.6	98.9
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} -: 395

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} .: 395

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