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POTENTIOMETRIC-KINETIC METHOD FOR THE DETERMINATION OF MERCURY (II) BY USING ORTHO ANISIDINE

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ABSTRACT A new simple and sensitive extractive potentiometric method for the determination of mercury (II) with isonicotinic acid hydrazide (INH) has been developed. INH has been synthesized and characterized by elemental analysis. Mercury was complexed with INH to form reddish yellow color Hg-INH complex. Hg-INH complex extracts quantitatively (99.45%) into methanol (MeoH) from an aqueous solution of P^H The complex has maximum absorbance at 420nm (λmax). The molar absorbitivity and sandell's sensitivity of the complex was $2.609x10^{-3}$lit.mole^{-1}.cm^{-1} and $1.673x10^{-2}$µg/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: was applied for the determination of mercury in sewage waste and spiked water samples.

Key words: Potentiometric , Mercury**,** INH, O-Anisidine

INTRODUCTION

Mercury is a chemical element with the symbol Hg and atomic number 80. It is also known as quicksilver or hydrargyrum (from "hydr-" water and "argyros" silver). A heavy, silvery d-block element, mercury is the only metal that is liquid at standard conditions for temperature and pressure; the only other element that is liquid under these conditions is bromine, and metals such as caesium, francium, gallium, and rubidium melt just above room temperature. With a freezing point of −38.83 °C and boiling point of 356.73 °C, mercury has one of the narrowest ranges of its liquid state of any metal [1-3].

Mercury(II) salts form a variety of complex derivatives with ammonia. These include Milloin's base (Hg2N+), the one-dimensional polymer (salts of HgNH2+)n), and "fusible white precipitate" or [Hg(NH3)2]Cl2. Known as [[Nessler's reagent, potassium tetraiodomercurate(II) (HgI42-) is still occasionally used to test for ammonia owing to its tendency to form the deeply colored iodide salt of Millon's base.

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 concentration, mercury and its 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 potentiometric determination of mercury in water [4-15].

In the present investigation a sensitive potentiometric method for the determination of mercury with INH (HIPAPH) as a camplexing agent is described.

EXPERMENTAL METHODS

Shimedzu, UV- were used in the present investigation. INH was prepared by dissolving the required amount of the substance Fulka sample in triply distilled water and solution is standardized as per the method of vultrile[16]. All the reagents used are of analytical grade and all the solution is 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. 0.2% solution of INH prepared in distilled water.

GENERAL PROCEDURE:

An aliquot of the solution containing 5ml of Mercury (II) was taken. To these required amounts of Hydrochloric Acid is added to give desired concentration and 2.0mL of 0.1% INH are added and the total volume was diluted to 50mL by deionized double distilled water and the mixture was transferred into a 50ml separatory funnel. The yellowish red colour complex Hg(II)-INH formed was formed was extracted into 10mL of Methanol, after shaking vigorously for 30Seconds, the absorbance of Hg(II)-INH complex was measured at 420nm against the reagent blank.

RESULTS AND DISCUSSION

Methanol is chosen as solvent, since it was found that the metal complex effectively extracted. The Hg (II) complex was readily extractable into MeOH and no change was observed the extent of extraction when the mixture was shaken from 1.5 to 5.0 minutes. Hence 4.0 minutes of shaking time was enough for the complete extraction of complex in to MeOH. The optimum pH for the extraction of metal ion into the organic phase increase as the pH increase from 4.0 to 7.0 and again decrease from7.0 to10.0. It was observed that a ten fold excess of reagent was sufficient to produce maximum intensity of colour. This is equal to 1.0mL of 0.1% INH 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 to20.0 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 (1.7392) 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 0.016501. 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 2.609×10^{-3}lit.mol^{-1}.cm^{-1} and the molar obsorptivity of the complex is calculated as 1.67 3×10^{-2} μg/cm^{2}. Aliquots containing 9.0 mg/mL of Hg (II) gave a standard deviation of 0.9602×10^{-3} and co-efficient of variation is 0.2062 percent.

Composition of the absorbance:

Jobs method [17] of continuous variation and the molar ratio[18] method were applied to ascertain the stoichiometric composition of the comple. A Hg- dithizone (1:2) complex was indicated by both methods.

Effect of Foreign ion:

The effect of over 60 cations, anions and complexing agents on the determination of only I mgL^{-1}of Hg^{II} was studied. The criterion for interence was an absorbance value varying by more than 5% from the expected value for Hg^{II} alone. There was no interference from the following 1000 fold amount of EDTA or tartrate: a 500 foldamoutn of acetate, chloride, oxalate or ammonium (I). EDTA prevented the interference of 50 fold amounts of cerium (III) and (IV) or chromium (VI). During interference studies, if a precipitate was formed, it was removed by centrifugation. The amount mentioned is not the tolerance limit. But the actual amount studied. However, for those ions whose tolerance limit has been studied, their tolerance rations are mentioned in Table 1.

Table – 1 Tolerance limits of foreign ions, Tolerance ratio [Species(X)]/Hg^{II}(w/w)

Species x	Tolerance ratio x/Hg^{II}	Species x	Tolerance ratio x/Hg^{II}
Magnesium	100	Nickel(II)	100
Potassium	100	Strontium(II)	100
Thorium	100	Vanadium(V)	100
Barium	100	Bismuth	100
Cadmium	100	Ascorbicacid	200
Azide	200	Acetate	500
Bromide	200	Carbonate	200
Iodide	200	Nitrate	200
Lead(II)	50	Silver(I)	50
EDTA	1000	Tatrate	1000
Antimony	100	Aluminium	100
Sulphite	200	Sulphate	200
Palladium(II)	75	Mercury(I)	50
Chloride	500	ammonium	500
Uranium(IV)	500	Sn(II)	450

Tolerance ratio is defined as ratio that causes less than 5 % interference

APPLICATION OF THE DEVELOPED METHOD:

The developed extractive-potentiometric 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 Srikakulam Disctrictr of Andhra Pradesh. 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 9.6µg in sample-1, 7.8µg in sample-II and 5.6µg in sample-III. The results are compared with atomic absorption spectrophotometry and they are found to be in good agreement.

Table – 2 Determination of Hg (II) in seawage waste (10grams per sample)

S.No	Area of the seawage waste	Metal ion found		Recovery % present method
		Present method* (µg)	AAS method (µg)	
1	Rajam	9.6	9.5	98.9
2	Palakonda	7.8	7.9	98.7
3	Srikakulam	5.7	5.8	98.2

.Average value of three determinations

ANALYSIS OF ENVIRONMENTAL 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 showing that the developed method is applicable to analyse Environmental water sample with the percentage recovery for mercury is 99.8. This method was applicable for the analysis of real water samples.

Table – 3 Determination of Hg (II) in some Environmental water samples

Sample	Mercury / µgL		Recovery ± s,[a]%	Recovery ± s,[b]%
	Added	Found		
Tap water	0	1.5		
	100	101.5	99.9±0.2	0.21
	500	502.0	100±0.1	0.25
Well water	0	2.5		
	100	102.0	99.5±0.1	0.29
	500	505.0	100.3±0.2	0.15
Lake water	0	130.0		
	100	228.0	98.7±0.3	0.25
	500	635	100.5±0.5	0.27
River water(Sarada River)	0	5.0		
	100	103.0	99±0.2	0.13
	500	505.0	100±0	0.00
Sea water(Bay of Bengal)	0	3.5		
	100	104.0	100.5±0.5	0.08
	500	505.0	100.3±0.4	0.10

a) average of five replicate determinations

b) The measure precision is the relative standard deviation

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