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Extractive spectrophotometric determination of Bi(III) in drugs & alloy samples by using sodium hexamethyleneimincarbodithioate

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Abstract

The reagent NaHMICdt.$2H_2O$ has found to be a good chelating agent for the spectrophotometric determination of various metal ions. The present investigation deals with spectrophotometric determination of Bi(III) by using NaHMICdt.$2H_2O$. The reagent reacted with Bi(III) to give yellow complex extractable into chloroform Bi(III) was extracted quantitatively in the pH range 1-3 Bi(III)-HIMCd complex showed λmax at 370 nm. The extracted species has 1:3 (M:L) stoicheometry. Beers law is obeyed in the range of 0.5-15 μg ml^{-1} of Bi(III). The molar absorptivity and the sandells sensitivity were found to be 1.04232 x 10^4 l $mol^{-1}cm^{-1}$ and 0.0202 μg mol^{-1} cm^{-2} respectively. The system has good reproducibility with standard deviation of 1.8 %. The effect of divers ion on the extraction of Bi(III) has been investigated. The proposed method is highly sensitive, selective, and simple and rapid has been applied for accurate determination of bismuth in synthesis mixtures and real samples.

Keywords: Bismuth, Sodiumhexamethyleneiminecarbodithioate, Extractive Spectrophotometry, Real Samples, Drug Samples, Synthetic mixture.

1. Introduction

Bismuth has been associated with medicine for more than 200 years. The element was first introduced in a pharmaceutical used in the treatment of syphilis [1]. Presently, bismuth is used in the cosmetics industry for the preparation of creams and hair dyes, while some of its colloidal salts due to their antiseptic, astringent and diuretic properties have important applications in pharmaceutical preparations and are employed as anti-ulcer, antibacterial, anti-HIV and radio therapeutic agents [2].

A literature survey reveals many extraction methods for bismuth. Solvent extraction separation of antimony and bismuth was carried out from aqueous acidic solutions with Cyanex 302 in toluene [3]. Extraction of bismuth with mixtures of acidic phosphorus extractants, di(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester, with some other extractants was also investigated including sec-octylphenoxyacetic acid, sec-nonylphenoxy acetic acid, 8-hydroxyquinoline, and 2,20-bipyridyl [4]. Extraction of the tetraiodobismuthate(III) anion with benzyltributylammonium cation was also reported [5]. Bismuth was determined spectrophotometrically at 485 nm after its adsorptive extraction from dilute sulfuric acid solution as tetrabutylammonium tetraiodobismuthate(III) on microcrystalline benzophenone followed by dissolution of the solid phase in ethyl acetate [6]. Separation and recovery of bismuth and molybdenum from a low grade bismuth glance flotation concentrate was studied by solvent extraction [7]. The influence of Arsenic initial concentration on the removal rate of Tin and Bismuth was investigated by adding As (III) ion in various concentrations to the solution containing H_2SO_4, Cu (II), Sb (III, V) and Bi (III) ions [8]. Other authors have proposed the extraction of Bismuth from acid or highly acidic solutions of HCl, HBr, HNO_3 and/or H_2SO_4 using Cyanex 925, Cyanex 921, 2-bromoalkanoic acid and Cyanex 302 as Extractant [9-12]. Bismuth (III) in alloy samples was determined extractive spectrophotometrically using 1-amino-4,4,6-trimethyl-(1H, 4H) pyrimidine-2-thiol [13].

Earlier methods used for the spectrophotometric determination of bismuth [14-23] has some limitations such as interference from some ions [14], critical pH [15-17], less stability [18,19], more extraction time [20], requires multiple extractions [21-23]. In the present method, analytical reagent hexamethylene-iminecarbodithioate was used for the extractive spectrophotometric determination of Bismuth (III). New analytical method can be employed for efficient determination of Bismuth (III) at µg level. The result of analysis obtained were employed with those obtained by known method with certify value of bismuth. The proposed method is sensitive rapid and free from many limitations.

2. Materials and Methods

2.1 Apparatus. All absorbance measurements were carried out on Bousch and Lomb spectronic 20 spectrophotometer. A digital elico pH meter (Model LI -120) with combined glass electrode was used to determine the pH of the solution. The stock solution of Bi(III) was prepared by dissolving calculated amount of $Bi(NO_2)_3$ in double distilled water containing 10 ml of concentrated nitric acid. The solution was diluted to 250 ml with doubly distilled water and standardized [24]. The reactant hexamethyleneimine brought from Lancaster was used without further purification. The ligand sodium salt of hexamethyleneiminecarbodithioate dehydrate was prepared by method reported in the literature stock solution of reagent [25].

2.2 Reagents. Stock solution of the reagent (0.20%) was prepared by dissolving $NaHMICdt.2H_2O$ (0.20 g) in ethanol. The buffer solution of pH 3.0 was prepared by using HCl and NH_3 solution of order. Cation and anion were prepared by dissolving there AR grade salts in doubly distilled water with a few drops of suitable acid. Synthetic mixtures were prepared by using standard solution of Bismuth and desired metal ions. Analytical grade chemicals were used unless otherwise stated. Doubly distilled water was used throughout the experimental work.

2.3 Recommended Procedure. To an aliquot containing 100 µg Bi(III), 1ml of 0.2 % HMICdt in ethanol was added. 1 ml 0.1N HNO_3 was then added. It was diluted to 10 ml with distilled water and the complex was extracted with chloroform (10ml) equilibrated mixture for 2 min organic extract was collected in 10 ml standard volumetric flask and made upto the mark with fresh solvent and absorbance was measured at 370 nm against similarly prepared reagent blank. The amount of Bi(III) was detected from the standard calibration curve.

3. Results and discussion

3.1 Absorption spectra

The yellow coloured complex shows absorbance maximum at 370 nm **(Figure.1)** where reagent has no significant absorbance. Hence all absorbance measurements were carried out at 370 nm against reagent blank.

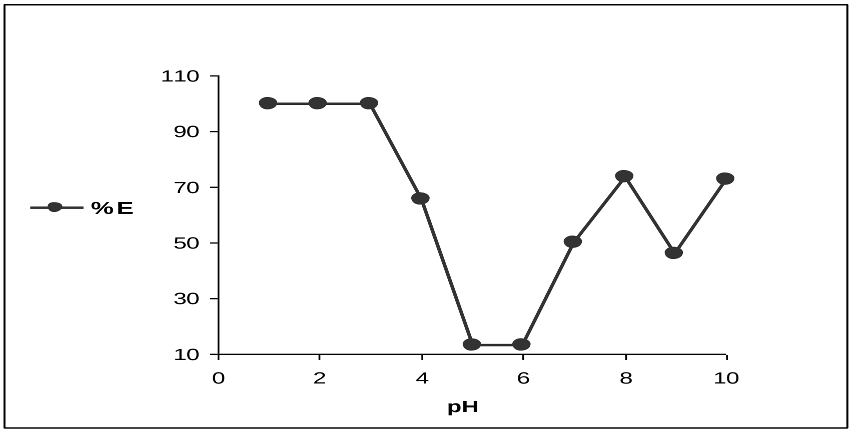

Fig. 1. Effect of pH on Extraction recovery of Bismuth

3.2 Effect of pH and Acidity. The extraction of Bismuth as function of pH Bi(III) was extracted by NaHMICdt. $2H_2O$ in chloroform over the pH range of 1-10 it was found that the complex would be quantitatively extracted in the pH range 1-3, where the percentage extraction was found to be over 99.99%. (**Figure 2)**

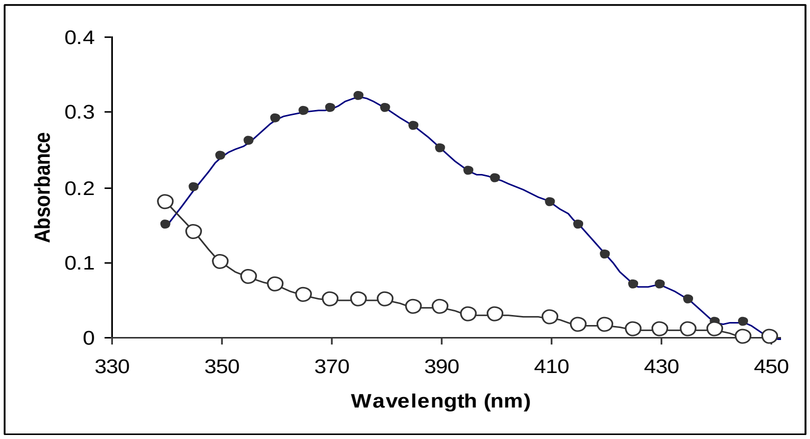

Fig. 2. Absorption spectra of reagent blank NaHIMCdt and Bi-HMIMcd complex in Chloroform

Therefore all extraction was carried out at pH 3.0. The extraction was also carried out in presence of various acid it was found that the extraction is quantitative in presence of 0.1N HNO_3 **(Table 1).**

Table 1. Recovery of Bismuth (III) in various acids

S. No.	Acids	Extraction Recovery (%)
1	0.1N HNO_3	99.78
2	1N HNO_3	96.50
3	0.1N HCl	98.55
4	1N HCl	95.58
5	0.1N H_2SO_4	89.80
6	1N H_2SO_4	65.17
7	0.1N CH_3COOH	85.37
8	1N CH_3COOH	69.17

3.3 Effect of Solvent. Various organic solvents were tried to get maximum extraction of Bi(III) with HMICdt. The result shows that among various solvent $CHCl_3$ was found to be the most suitable solvent for it quantitative extraction **(Table. 2).**

Table 2. Recovery of Bismuth (III) in various solvents

S. No.	Solvent	Extraction Recovery (%)
1	Chloroform	99.99
2	Toluene	91.00
3	Benzene	82.00
4	Iso- amyl alcohol	79.60
5	Iso -butyl alcohol	76.00
6	n-butyl alcohol	74.50
7	Methyl isobutyl ketone	72.00
8	Carbontetra Chloride	59.00
9	n-butyl acetate	38.72
10	Xylene	33.47
11	Nitrobenzene	20.00
12	Pentanol	11.97

3.4 Effect of HMICdt. Concentration. The effect NaHMICdt. $2H_2O$ concentration on extraction of Bi(III) was studied it was observed that 1 ml of 0.2% solution of NaHMICdt. $2H_2O$ was sufficient for quantitative extraction of Bi(III). Excess of reagent concentration did not effect on the extraction. Hence 1 ml of 0.2% reagent was used for further studies.

3.5 Effect of Equilibration time. The colour development was insisting, however shaking was varied from 10-180 second after reagent addition. The minimum shaking time required for quantitative extraction of Bi(III) was 120 second. While longer extraction time did not affect the % extraction. Hence 120 second of shaking time was fixed for further studies.

3.6 Colour Stability of the Extracted Species. The color stability of Bi(III) - NaHMICdt complex was studied by measuring absorbance at 370 nm at definite time interval. The complex was quantitative stable and remained constant for five days.

3.7 Calibration curve. The absorbance of the extracted species was a linear function of Bi(III) concentration in the range of 0.5-15 ppm at 370 nm. The optimum working range obtained from Ringbom's plot was found to be 2.5-12.5 ppm that confirms the beer's range. The molar absoptivity sandell's sensitivity of the method was found to be 1.0432×10^4 l mol^{-1} cm^{-1} & 0.0202 μg ml^{-1} cm^{-2} at 370 nm.

3.8 Effect of Foreign ions. The tolerance level for the divers ions investigated were as follows F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{-2}, $SO3^{-2}$, ClO_3^-, BrO_3^-, IO_3^-, $S_2O_3^{-2}$, $S_2O_5^{-2}$, $S_2O_8^{-2}$, SCN^-, Acetate , Citrate, Tartarate, Oxalate, Urea(20 mg each). Li(I) , Na(I), K(I), Ca(II), Mg(II), Se(IV), (10 mg each). Al(III), Ba(II), V(V), (7.5 mg each). Sb(III), Mo(VI), (5 mg each). Cr(III), Fe(III), (0.5 mg each). Cd (II) interferes masked with thiocyanate. The tolerance limit was set as the amount of foreign ion that causes an error of not more than +2 % in the recovery of metal ion.

3.9 Precision and Accuracy. The precision and accuracy of the method were determined the average of ten determination with 100 μg Bi(III) was found to be 99.9 μg with standard deviation 1.8529 & the deviation from mean at 95 % confident limit was ± 1.3066. The native of extraction complex was determined by job's continuous variation method and was found to be 1:3 (M:L) i.e Bi(III) - HMICdt was confirmed by mole ratio 1:3. The reaction of

$$Bi(III) + NaHMICdt \rightarrow Bi\ (HMICdt)_3.$$

4 Applications

4.1 Synthetic mixture. Procedure for the determination of Bismuth in synthetic mixture and real samples. A number of synthetic mixtures containing 50 μg bismuth and other commonly associated metal ions were prepared by mixing there solution and analyzed according to developed method **(Table. 3)**

Table 3. Determination of Bismuth (III) in various synthetic, Alloys and Drug Samples

Name of Sample	Bi Found by Present Method*	Certified Value	Recovery (%)
Synthetic Mixture#			
Bi^{+3}(50μg) + Sb^{+2}(100μg) + Pb^{+2}(100μg)	50	-	100
Bi^{+3}(50μg) + Al^{+3}(100μg) + Pb^{+2}(100μg)	49.98	-	99.96
Bi^{+3}(50μg) + Pd^{+2}(100μg) + Se^{+2}(100μg)	49.97	-	99.94
Bi^{+3}(50μg) + Al^{+3}(100μg) + Sb^{+2}(100μg)	49.97	-	99.94
Alloys Samples® (White Metal)			
Ita lab/1224	48.2	48.25	99.90
Ita lab/1225	30.75	30.80	99.84
Ita lab/1226	48.21	48.24	99.84
Drugs Samples #			
Trymotablet	106.64	107.64	99.07
Denol	106.64	107.64	99.07
Pylocid	134.53	134.54	99.99

Values are in μg, * Mean of Five determinations, ® Values in percentage

4.2 Analysis of alloys (White metal). Definite amount of alloy was dissolved in concentrated nitric acid and solution was evaporating to dryness. The dried residue was taken up in dilute nitric acid. The solution was filtered off and washed with hot dilute nitric acid and finally washed with hot water then filtrate was collected and dilute to 100 ml with distilled water. A definite aliquot of the above solution was used to extract and to determine bismuth by developed method. The result obtained were compared with those of AAS **(Table. 3)**

4.3 Analysis of Drug Samples. Tablet of Denol & pylocid which are used for the treatment of peptic ulcers were taken separately in beaker and dissolved in 10 ml of perchloric acid and evaporate nearly to dryness. The dried mass was dissolved in distilled water containing 1 ml of nitric acid. The solution was filtered through whatman filter paper No.42 and filtrate was diluted to 100 ml with distilled water. An aliquot of each above solution was taken for the estimation of bismuth by developed method. The result obtained were compared with those by AAS **(Table. 3)**

Conclusion

The proposed method can be used for determination of Bi at trace level. Method has advantage of reliability, reproducibility, and good sensitivity, simple instant color development and minimum interference. The method has been successively applied the separation of Bismuth at trace level in synthetic mixtures, pharmaceutical samples and real samples. The result obtained in the good agreement with the certify value and were compared with those obtained by known method.

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