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LIQUID LIQUID EXTRACTION AND SEPARATION OF BISMUTH(III) WITH N-n-HEXYLANILINE

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ABSTRACT

N-n-hexylaniline in xylene was used for the extraction separation of Bi(III) from thiocyanate and sulphuric acid media. Bi(III) was extracted quantitatively with 10 mL 1.5% N-n-hexylaniline in xylene. It was stripped from the organic phase with (2x25cm^3) sodium acetate buffer and estimated titrimetrically.The effect of metal ion, acid, reagent concentration and various foreign ions was investigated.The method is applicable for the analysis of pharmaceuticals samples,alloys. It is fast, accurate and precise

Keywords: Bismuth trichloride ,solventextraction,Diluent, N-n-hexylaniline,Thorium nitrate ,EDTA ,Xylenol orange

INTRODUCTION

The principal consumer of bismuth is the manufacturers of pharmaceuticals chemicals nearly 70% of the production being used for this purpose. It is the least toxic of all the heavy metals. Subcarbonates and subgallates are used in the treatment of diarrhea, dysentery and radiology. Certian bismuth compounds were widely employed as an adjunct to the arsenic therapy and syphilis. Bismuth forms a number of low melting alloys which are widely used as a safety plugs in boilers, electrical fuses, solders ,magnets etc .Hence, it was thought worth while to develop a rapid, simple and selective method for its separation and determination in the presence of associated elements ,steel and alloys .The high molecular weight amines such as N-n-octylaniline has been used in this laboratory for the selective extraction of many metal ions from haloacid media[3-5] , N-n–hexylaniline is synthesized by using method similar to N-n-octylaniline by Gardlund's methods[1] , N-n-hexylaniline in xylene could be used for the anion exchange extraction of Bi(III) from KSCN and H_2SO_4 .The metal ion in the organic phase is stripped and determined titrimetrically.

There are reports on use of certain high molecular weight amines as liquid anion exchangers for solvent extraction of bismuth. These include 1622 hymine[6], amberliteL-A-1[7],tri-n-octylamine(TOA)[8-11],tri-iso-octylamine(TIOA)[8], aliquot 336[8],tris(2-ethylhexyl)amine[12] and $C_{10}C_{12}$ primary amines[13]. Extraction spectrophotometric determination of traces of bismuth in lead, copper ,nickel and in copper-base alloy with tri-n-octylamine[9] in benzene from hydrobromic acid media has been investigated and bismuth determination as its bromocomplex at 380 nm . The benzene solution of trioctylamine[8] ,tri-iso-octylamine[8] and aliquot 336[8] extract bismuth almost quantatively from sodium Succinate solution of pH 6.5-7.0 but the method needs the pre-equilibration of reagent solution with succinate solution of appropriate conc in addition to co-extraction of copper, selenium, tellurium, thorium, EDTA and phosphate .It also suffers from multiple extraction in extraction of bismuth with 1622 Hymine[6] in different solvents from nitric acid, mercury, thorium and uranium interfered seriously.

The proposed method is relatively simple, rapid and does not require long extraction period the method finds a wide range of applications in the analysis of commercial drug samples low fusible alloys.

EXPERIMENTAL

Reagents:

The stock solution of Bi (III) was prepared by dissolving 1.170g of bismuth nitrate (BDH) in 4 cm^3 of nitric acid and diluting to 100 cm^3 with water. The solution was standardized complexometrically [13]

N-n-hexylaniline solution : Solution (% ,v/v) were prepared by using xylene as the diluents .

Acetate buffer solution:It was prepared by dissolving 27.2g of sodium acetate trihydrate in 400 cm^3 water ,adding 17 $cm^3$of glacial acetic acid and diluting to 1 dm^3

Thorium nitrate solution: A 0.01 M solution was prepared by dissolving 5.881 gm of thorium nitrate tetrahydrate (BDH) in water and diluting to 1 dm^3

EDTA solution: A 0.01 M solution was prepared by dissolving 3.722 g disodium salt of EDTA in water and diluting to 1 dm^3

Working solutions were prepared by accurate dilution .All other chemicals used were of guaranteed grade

General procedure:

To an aliquot of solution containing up to 1mg/cm^3 of bismuth add sufficient quantity of sulphuric acid and potassium thiocyanate to make the concentrations 0.1-3M and 0.1-3M respectively in a volume of 10 cm^3 Transfer the solution to 125cm^3 seperating funnel .Shake it for 2 min with 10 cm^3 of 1.5% of N-n-hexylaniline in xylene. Swirl the separating funnel slightly. Separate the two layers and strip bismuth from the xylene layer by shaking with acetate buffer (2x 25 cm^3) for 2min. To the aqueous layer add sufficient 0.002 EDTA. Add 7 drops of 0.1% xylenol orange indicator and titrate excess of EDTA with 0.002 M Thorium nitrate The end point is yellow to red.

RESULTS AND DISCUSSION

Effect of acidity and reagent concentration:

The concentration of KSCN was varied from 0.1-3M and that of H_2SO_4 from 0.1-3M keeping the concentration of one constant other varying .The concentration of N-n-hexylaniline was varied from 0.5-1.5% . It was observed that bismuth was quantatively extracted when the concentration of KSCN was 0.3-0.7M and that of H_2SO_4 was 0.1-3M with equal volume of 1.5% N-n-hexylaniline in xylene (Table-1 and 2, Figure-1 and 2).

Nature of extracted species and extraction mechanism:

Log-log plot of distribution ratio versus N-n-hexylaniline concentration at 0.05 and 0.1M thiocyanate gave slopes of 0.9 and 1.0 respectively indicating that metal to amine ratio in extracted species is 1:1 while at 1 and 2M thiocyanate the slope were 1.9and 2.0 respectively indicating that metal to ion ratio in the extracted species is 1:2 {Figure no-3} Hence ,the probable extracted species at lower and higher thiocyanate conc are as $[RR'NH_2^+Bi(SCN)_4^-]$ and $[(RR'NH_2)_2Bi(SCN)_5^{2-}]$ respectively The results shows that at lower and higher thiocyanate concentration , Bismuth forms anions of the types $Bi(SCN)_4^-$ and $Bi(SCN)_5^{2-}$ respectively.

The extraction mechanism at lower thiocyanate concentration appears to be-

$$Bi(SCN)_3 + SCN^- = Bi(SCN)_4^- \quad \text{----------(1)}$$

$$[RR'NH]_{Org} + HSCN = [RR'NH_2^+(SCN)^-]_{Org} \quad \text{---------- (2)}$$

$$[RR'NH_2^+(SCN)^-]_{Org} + Bi(SCN)_4^- = [RR'NH_2^+Bi(SCN)_4^-] + (SCN)^- \quad \text{---------- (3)}$$

Where $R = C_6H_{13}$ and $R' = C_6H_5$

Effect of Equilibrium Time:

Variation of shaking time from 15 seconds to 5min showed that a minimum of 1min shaking is needed for complete extraction of bismuth (III).To ensure the quantitative extraction of bismuth 2min shaking time is recommended in general procedure However the prolonged shaking had no adverse effect on the extraction

Effect of Diluents:

Various other solvents such as xylene, benzene ,toluene chloroform and nitrobenzene were also tried as diluents .The extraction of bismuth was quantitative with benzene , xylene, toluene ,nitrobenzene as diluents .xylene was selected as the diluent as it gives clear-cut separation of the phases (Table no-3).

Table-1: Percentage extraction of Bi(III) with N-n-hexylaniline in xylene
Conditions as in the general procedure except KSCN Conc ,Bi(III) taken 1mg , H_2SO_4 Conc 3M

Reagent %	KSCN M	Extraction %	D
0.5%	0.05	26.92	0.3683
	0.1	42.30	0.7331
	0.3	69.23	2.2499
	0.5	69.23	2.2499
	0.7	69.23	2.2499
	1	65.38	1.8885
	2	23.07	0.2998
	3	11.53	0.1303

Reagent %	KSCN M	Extraction %	D
1%	0.05	46.15	0.8570
	0.1	61.53	1.5994
	0.3	92.30	11.9870
	0.5	92.30	11.9870
	0.7	92.30	11.9870
	1	88.46	7.6655
	2	50.00	0.0000
	3	24.00	0.3157

Reagent %	KSCN M	Extraction %	D
1.5%	0.05	57.69	1.3635
	0.1	73.07	2.7133
	0.3	100.0	∞
	0.5	100.0	∞
	0.7	100.0	∞
	1	95.45	20.9780
	2	69.23	2.2499
	3	45.45	0.8331

Table-2 : Percentage extraction of Bi(III) with N-n-hexylaniline in xylene :-
Conditions as in the general procedure except conc of Sulphuric acid ,Bi(III) taken 1mg , KSCN Conc 0.5M

Reagent %	Sulphuric acid M	Extraction %	D
0.5%	0.05	65.38	1.8885
	0.1	69.23	2.2499
	0.3	69.23	2.2499
	0.5	69.23	2.2499
	0.7	69.23	2.2499
	1	69.23	2.2499
	2	69.23	2.2499
	3	69.23	2.2499

Reagent %	Sulphuric acid M	Extraction %	D
1%	0.05	76.92	3.3327
	0.1	88.46	7.6655
	0.3	88.46	7.6655
	0.5	88.46	7.6655
	0.7	88.46	7.6655
	1	88.46	7.6655
	2	88.46	7.6655
	3	88.46	7.6655

Reagent %	Sulphuric acid M	Extraction %	D
1.5%	0.05	80.76	4.1975
	0.1	100.0	∞
	0.3	100.0	∞
	0.5	100.0	∞
	0.7	100.0	∞
	1	100.0	∞
	2	100.0	∞
	3	100.0	∞

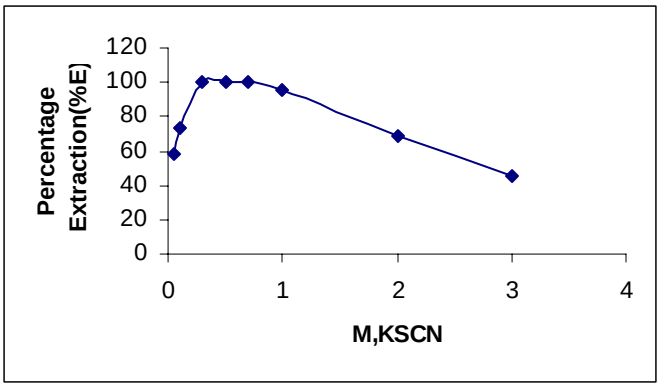

Fig.-1 : The extraction of Bi(III) with N-n-hexylaniline (1.5%) in xylene as a function of thiocyanate concentration at 3.0 M H_2SO_4

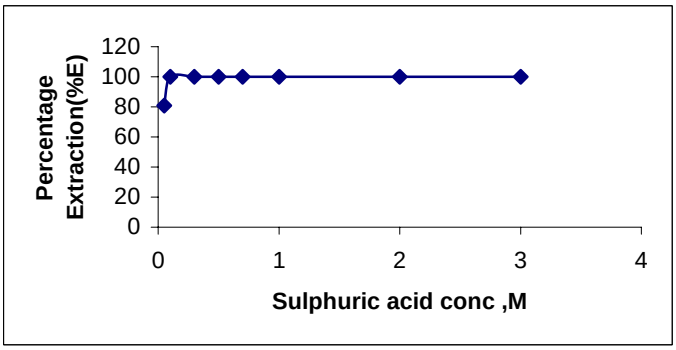

Fig.–2:The extraction of Bi(III) with 1% N-n-hexylaniline in xylene as a function of H_2SO_4 concentration at 0.5 M KSCN

Table – 3 : Effects of diluents

Diluents used	Dielectric constant	Extraction %
Xylene	2.30	100.0
Nitrobenzene	34.8	100.0
Benzene	2.28	100.0
Toluene	2.38	100.0
chloroform	4.81	75.00

Enrichment study on Bismuth (III):

Bismuth was extracted from aqueous ($10cm^3$ to $100cm^3$) of 0.5M OF KSCN and 1M H_2SO_4 with $10cm^3$ of 1.5% N-n-hexylaniline in xylene .Bi(III) was stripped and determined as described in the general procedure .It was found that extraction of Bi(III) was quantitative when aq:org volume ratio was only 1:1 and it decreased beyond it this may be attribute to the less stability of ion pair formed under conditions(Table -4).

Effect of foreign ions:

An interference study showed that a large of cations and anions offers no interference (as shown by less than 1% error in analysis recovery) the effect of foreign ions and their tolerance limits in the extraction Of bismuth are reported in(Table-5).

Separation of Bismuth from Alloy:

Bismuth is separated and determined from the alloys wood 's metal alloy by the proposed method. About 1g of alloy was dissolved in concentrated nitric acid .The precipitated metastanic acid from wood's metal were filtered off and filtrate were evaporated to dryness to remove excess of acids leached with 0.5M Hydrochloric acid and diluted to 100cm^3 with distilled water .An aliquot from each sample solution was extracted with N-n-hexylaniline in xylene according to general procedure.Elements such as lead, nickel, copper and cadmium in solution coextracted and were removed by washing the organic phase with with 15ml of 0.5 M hydrochloric acid and bismuth retained in organic phase was then stripped and determined as in the general procedure(Table -6).

Analysis of pharmaceuticals samples:

A tablet was dissolved in perchloric acid and solution was evaporated to near dryness.The residue was taken up in the minimum amount of perchloric acid and solution was evaporated to dryness again .The residue was then leached with water and diluted to 100ml with water .An aliquot was taken for the extraction and estimation of bismuth by the recommended procedure .The mean of six results is reported in (Table - 7).

CONCLUSION

The method proposed here permits the separation and determination of bismuth from its alloys with lead ,antimony and tin .The method can be used for determination of bismuth in Pharmaceutical preparation .The results are reproducible and accurate to ±0.4%.

REFERENCES

1. Z.S. Gardlunds, R.J. Curtius and G.W. Smith, *Liquid crystals and ordered fluids*, **2**, 541 (1973).
2. N.B. Kadam Patil, S.S. Sawant, G.N. Mulik and M.B. Chavan, *The Bulletin of Bismuth Institute,* **64**(1992).
3. G.N. Mulik, S.R. Kuchekar and M.B. Chavan, *Ind J.Chem*, **25A**, 1073 (1986).
4. G.N.Mulik, S.R. Kuchekar and M.B. Chavan, *J. Ind. Chem. Soc.*, **64**, 68 (1987).
5. G.N.Mulik and M.B. Chavan, Ph.D. Thesis, Shivaji University, Kolhapur (1986).
6. E.R.Schmid, E. Juenger and K. Pollak, *Mickrochim Acta,* **11**, 525 (1975).
7. W. Schade, *Chem. Tech (Leipzia)*, **36**, 18 (1984).
8. S.D.Shete,V.M. Shinde, *Microchim Acta,***I,** 63 (1984).
9. Tsukahara, Iwao, Yamamoto and Toshimi, *Anal.Chim.Acta,* **64**, 337 (1973).
10. B.Y. Spivakov, V.I. Lebedev, V.M. Shlinev, N.P. Krivenkova, T.S. Plotnikova, I.P. Kharlamov and Y.A. Zolotov, *Zh.Anal.Khim*, **31**, 757 (1976).
11. S. de Moraes, *Abrao and Alicidio,* **46**, 1812 (1974).
12. T.Suzuki, *Japan Analyst*, **15**,666 (1966).
13. I.A. Shevchuk, T.N. Simonova, Z.N. Kravtsova, T.I. Pluzhnik and N.I. Gorshkova, *Ukr. Khim. Zn*, **41**, 959 (1975).
14. J.C. Sheppard and R.Wamock*, J. Inorg. Nucl. Chem.,* **26**, 1421 (1964).
15. A.L.Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd Ed, Longmans Londons, p.442 (1961).

Table-4 : Enrichment study of Bismuth(III)

Aqueous to organic phase	Extraction %
1:1	100.0
2:1	87.50
3:1	54.16
4:1	29.16
5:1	20.83
10:1	20.83

Table-5: Effect of foreign ions
(Bi taken 1mg, 1.5% N-n- hexylaniline , KSCN-0.5M , H_2SO_4- 1M Aqueous to organic ratio 1:1)

Foreign Ions	Tolerance Limit,mg
Mg(II)	30
Mn(II	30
U(III)	30
Ca(II)	10
Cu(II)	5
Cr (III)	5
Sr (II)	5
$Ni(II)_{(a)}$	5
$Fe(III)_{(a)}$	5
$Al\ (III)_{(a)}$	5
$Cd\ (II)_{(a)}$	5
Ascorbic acid	200
Sodium acetate	200
Succinic acid	200
Tartaric acid	200
Oxalic acid	100
Citric acid	100
Sodium phosphate	50
Thiourea	None
a = masked with citric acid	

Table-6 :-Analysis of bismuth alloy

Alloy	Percentage Bi	
	Found	Actual
Woods metal	43.7	43.9

Table-7: Analysis of pharmaceutical samples

Sample	Manufacturer	Composition	Amount of Bismuth certified	Amount Found (Proposed Method)	AAS Method
Trymo Tabllet	Raptakos Breet Ltd.(India)	Colloidal Bismuth subcitrate calculated as Bi2O3	120mg (per tablet)	119.5 (per tablet)	119.7 (per tablet)

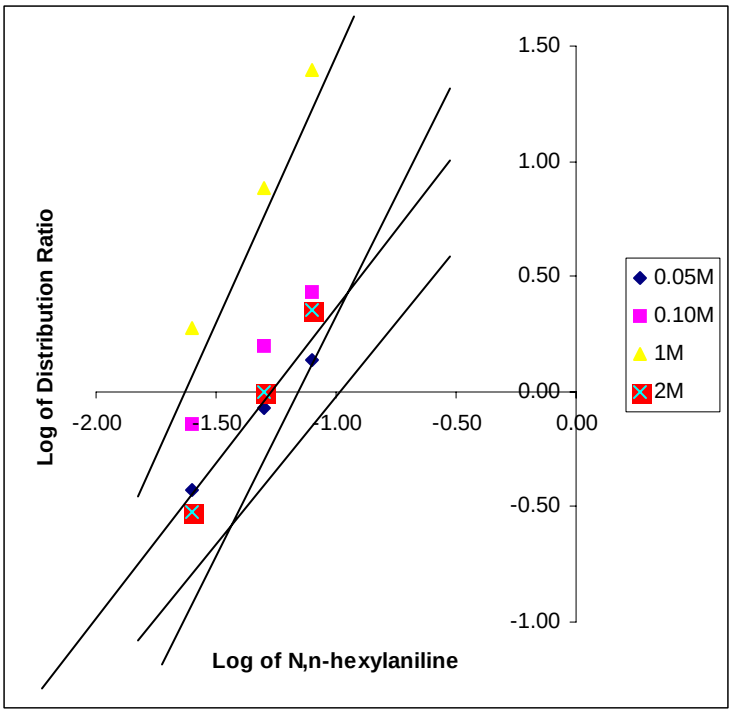

Fig. –3: Distribution ratio of Bi(III) as a function of N-n-hexylaniline conc at 0.05,0.1, 1 and 2M thiocyanate concentration

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