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LIQUID-LIQUID EXTRACTION AND SEPARATION OF BISMUTH (III) WITH 4-METHYL-N-n-OCTYL ANILINE

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ABSTRACT

Various high molecular weight amines (liquid anion exchangers) are used for solvent extraction studies of metals. Extractive separation of Bi(III) from thiocyanate media using 4-Methyl-N-n-octyl aniline have been reported in this paper. Bi(III) was quantitatively extracted from 0.5M KSCN & 1.0M sulphuric acid with equal volume of 2% 4-Methyl-N-n-octyl aniline in xylene. It was stripped from the organic phase with acetate buffer & estimated complexometrically. The effects of acidity, thiocyanate concentration, reagent concentration, diluents, foreign ions and aqueous to organic phase volume ratio on the extraction have been discussed. Nature of extracted species and extraction mechanism is discussed. The method is applied to synthetic mixtures & alloy. It is fast, accurate & precise.

Keywords: Liquid anion exchangers, solvent extraction, 4-Methyl-N-n-octyl aniline,thiocyanate, xylene, extraction mechanism, synthetic mixtures alloy.

INTRODUCTION

High molecular weight amines are widely used in the extraction of various elements. The various amines, such as liquid anion exchangers used in the extraction of bismuth include tri-n-octylamine,Amberlite-LA-1[1-5]etc. Extraction with tri-n-octylamine from halide media cause interference of many metal ions spectrophotometrically[1-4]. The benzene solution of tri-n-octylamine, tri-iso-octylamine and aliquat 336 extract bismuth almost quantitatively from succinate medium at pH 6.5-7.0, but the method needs pre-equilibration of the reagent solution with sodium succinate solution[6]. The extraction of bismuth with N-n-Octyaniline from haloacid media is carried. The method is applied to determine bismuth from alloys, pharmaceuticals samples. In these methods benzene is used as diluent which is carcinogenic[7-9].

In contrast to the above mentioned drawbacks encountered in the extraction of bismuth(III) with various extractants, the proposed method is free from these limitations. The proposed method is relatively simple, rapid and does not required long period. The method is extended to determine bismuth in alloys.

EXPERIMENTAL

Reagents

Bismuth (III) solution

The stock solution of Bi (III) was prepared by dissolving 2.321 g of Bismuth nitrate pentahydrate in 5ml of conc. nitric acid & diluting to 100ml with distilled water. 10ml of this solution was diluted to 100ml with distilled water & standardised complexometrically[12]. It contained 1.0mg of Bi per ml.

EDTA Solution

A 0.002M EDTA solution was prepared by dissolving 0.744g of disodium salt of EDTA in demineralised water & diluting to one liter.

Thorium Nitrate Solution

A 0.002M solution was prepared by dissolving 1.140g. Thorium nitrate pentahydrate in demineralised water & diluting to one liter

Table-1: Percentage Extraction of Bi (III) with 4-Methy-N-n-octylaniline in xylene

Reagent %	KSCN M	Extraction %	D
1.0 %	0.1	12.3	0.14
	0.3	83.33	4.99
	0.5	83.33	4.99
	0.7	79.16	3.80
	1.0	58.33	1.40
	1.5	37.5	0.6
	2.0	16.66	0.20
	2.5	8.3	0.09
1.5%	0.1	8.3	0.09
	0.3	87.5	7.00
	0.5	95.83	22.98
	0.7	87.5	7.00
	1.0	75	3.00
	1.5	62.5	1.67
	2.0	29.16	0.41
	2.5	16.67	0.20
2.0%	0.1	12.5	0.14
	0.3	91.66	11.00
	0.5	99.7	332
	0.7	91.66	11.00
	1.0	79.16	3.79
	1.5	66.67	2.00
	2.0	45.83	0.85
	2.5	29.16	0.41

*Conditions as in general procedure except KSCN concentration. Bi (III) taken 1mg ; H_2SO_4 conc. 1.0 M Aqueous to Organic phase ratio 1:1

Table-2: Percentage Extraction of Bi (III) with 4-Methy-N-n-octylaniline in xylene

Reagent %	H_2SO_4 M	Extraction %	D
1.0 %	0.1	45.8	0.85
	1.5	58.3	1.39
	1.0	58.3	1.39
	1.5	58.3	1.39
	2.0	62.5	1.66
	2.5	62.5	1.66
	3.0	66.6	2.00
	4.0	00.0	0.00
1.5%	0.1	75.0	3.0
	1.5	75.0	3.0
	1.0	83.3	4.99
	1.5	83.3	4.99
	2.0	87.5	7.0
	2.5	87.5	7.0
	3.0	87.5	7.0
	4.0	00.0	0.0
2.0%	0.1	87.5	7.0
	1.5	87.5	7.0
	1.0	99.7	332
	1.5	99.7	332
	2.0	99.7	332
	2.5	99.7	332
	3.0	99.7	332
	4.0	4.16	0.04

*Conditions as in general procedure except H_2SO_4 concentration. Bi (III) taken 1mg ; KSCN conc. 0.5 M Aqueous to Organic phase ratio 1:1

Table-3: Effect of diluents on the extraction of Bi (III)

Diluents used	Dielectric constant	Extraction %
Xylene	2.30	99.7
Benzene	2.28	92
Carbon –tetrachloride	2.24	92
toluene	2.38	87.5
Nitrobenzene	34.8	83.3
Chloroform	4.81	58.3

*Bi (III) taken 1mg ; H_2SO_4 conc. 1.0 M,0.5 M KSCN 2% 4-Methyl-_N-n-octylanilineAqueous to Organic phase ratio 1:1

Table-4: Effect of Phase Volume ratio on the extraction of Bi (III)

Aqueous to organic phase ratio	Extraction %
1: 1	99.7
2: 1	99.7
3: 1	99.7
4: 1	99.7
5: 1	99.7
6: 1	95.4
10: 1	77.3

*Bi (III) taken 1mg ; H_2SO_4 conc. 1.0 M, 0.5 M KSCN , 2% 4-Methyl-_N-n-octylaniline in xylene

Table-5: Effect of foreign ions

Foreign ions	Added as	Tolerance limit, mg
Mg (II)	$Mg\ SO_4 . 7\ H_2O$	25
Mn (II)	$Mn\ SO_4 .\ H_2O$	20
Cu (II)	$Cu\ SO_4 . 5\ H_2O$	10
Cd (II)	$Cd\ Cl_2$	10
Ce (IV)	$Ce\ SO_4$	5
Hg (II)	$Hg\ Cl_2$	5
Th (IV)	$Th\ (NO_3\ ) . 5\ H_2O$	5
Cr (III) b	$Cr\ Cl_3 . 6\ H_2O$	10
Ni (II) a	$Ni\ Cl_2 . 6\ H_2O$	5
Fe (III) b	$Fe\ Cl_3$	5
Acetate	Sodium acetate	100
Ascorbate	Ascorbic acid	100
Succinate	Succinic acid	100
Oxalate	Oxalic acid	50
Tartarate	Tartaric acid	50
Citrate	Citric acid	Interference
Phasphate	Na_2HPO_4	Interference
Thiourea	Thiourea	Interference

*Bi (III) taken 1mg ; H_2SO_4 conc. 1.0 M, 0.5 M KSCN, 2% 4-Methyl-_N-n-octylaniline in xylene , Aq : Org phase ratio 1 : 1
a = masked with tartarate, b= masked with ascorbate

Table-6: Separation & determination of Bi (III) from synthetic mixtures :

Composition of the mixture	Bismuth found	
	mg	%
Mg (II), 5 ; Fe (III), 2 ; Bi (III), 1.0	0.99	99.7
Mn (II), 5 ; Cr (III), 2 ; Bi (III), 1.0	0.99	99.7

*2 % 4-Methyl – N-n-octylaniline in xylene, 1.0 M H_2SO_4, 0.5 M KSCN, Aqueous to organic Volume ratio 1:1

Table -7: Analysis of Bismuth alloy

Alloy	Percentage, Bi	
	Actual	Found
White metal	0.11	0.11

4-Methyl-N-n-octylaniline Solution
Solutions (%W/V) were prepared by using Xylene as diluent.

Acetate buffer solution
A solution was prepared by dissolving 27.2g of sodium acetate trihydrate in 400ml of demineralised water, adding 17 ml of glacial acetic acid and diluting it to one liter.

Xylenol orange
0.5g of indicator was dissolved in alcohol and diluted to 100ml with demineralised water.
All other chemicals used were of analytical grade. More dilute solution were prepared by accurate dilution.

Extraction procedure
To an aliquot of solution containing 1mg / ml of Bi(III), add sufficient quantity of sulphuric acid and potassium thiocyanate solutions to make the concentration 0.1 – 4.0M and 0.1-2.5M respectively, in a volume of 10 ml. transfer the solution to 125 ml separating funnel. Shake the flask for 5-6 minutes with 1-2% of 4-Methyl-N-n-octylaniline in xylene. Swirl the solution and allow to separate the two phases. Organic phase was stripped with 25ml of acetate buffer for 5 min. The amount of bismuth in stripped solution was determined comlexometrically[12], by adding excess of 0.002M EDTA and back titrating against 0.002M thorium nitrate, using xylenol orange as indicator. The end point is yellow to red.

RESULTS AND DISCUSSION

Effect of acidity, thiocyanate and reagent concentration
The concentration of KSCN was varied from 0.1-2.5M and that of H_2SO_4 from 0.1-4.0M, keeping the concentration of one constant and other varying. The concentration of 4-Methyl-N-n-octylaniline was varied from 1-2%. It was observed that bismuth was quantitatively extracted when the concentration of KSCN was 0.5M and that of H_2SO_4 1.0-3.0M [Fig.-1 and 2] with equal volume of 2% 4-Methyl-N-n-octylaniline in xylene [Table- 1 and 2]

Nature of extracted species and extraction mechanism
Log-log plot of the distribution ratio versus 4-Methyl-N-n-octylaniline concentration [Fig.-3] at 0.7M thiocyanate gave slopes of 1.4 indicating that metal to amine ratio in extracted species is 1 : 1 while at 2.0 & 2.5 M thiocyanate concentration the slopes were 2.07 & 2.0 respectively indicating that metal to amine ratio in the extracted species is 1 : 2. Hence, the probable extracted species at lower and higher thiocyanate concentrations are as $[RR^{I}NH_2^{+}Bi(SCN)_4^{-}]$ and $[(RR^{I}NH_2^{+})_2 Bi(SCN)_5^{2-}]$ respectively. The results show 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

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

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

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

Where $R = C_8H_{17}$ and $R^{I} = CH_3 - C_6H_5$

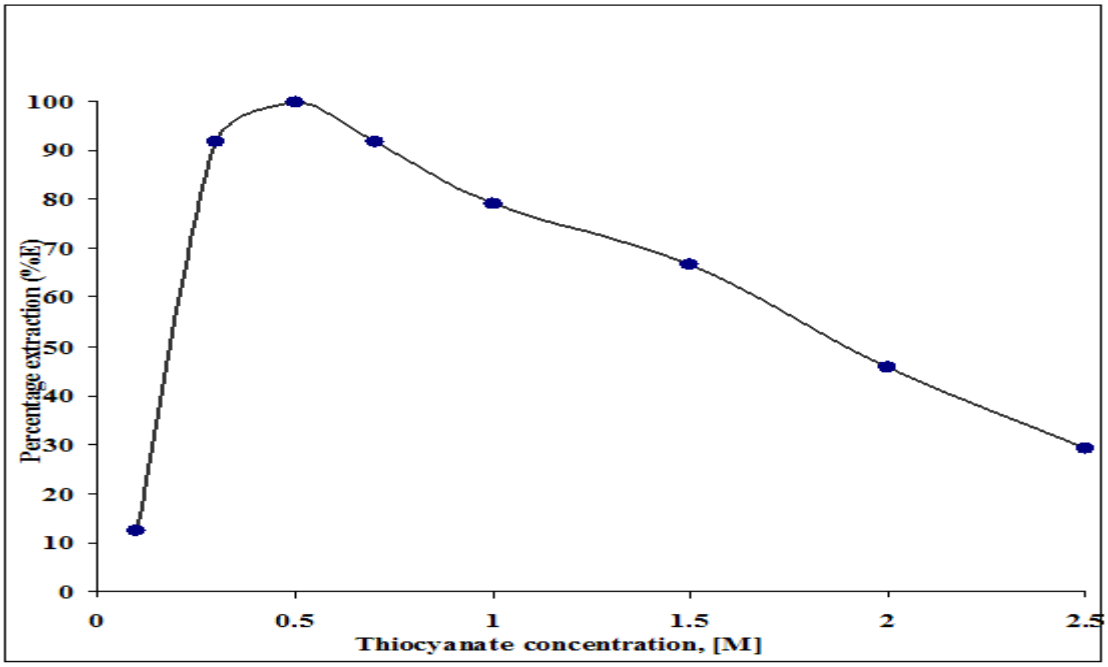

Fig. 1 The extraction of Bi (III) with 4-Methyl-N-n-octylaniline (2%) in xylene as function of Thiocyante conc. at 1.0 M sulphuric acid conc.

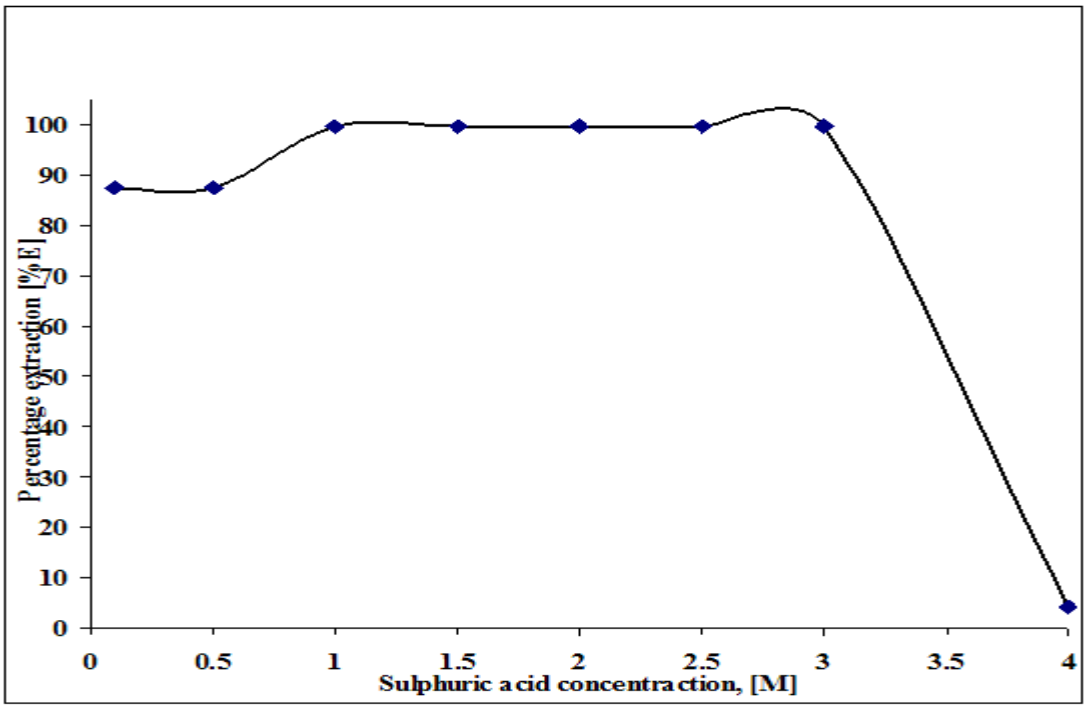

Fig. 2 The extraction of Bi (III) with 2% 4-Methyl-N-n-octylaniline in xylene as a function of Sulphuric acid conc. at 0.5M KSCN

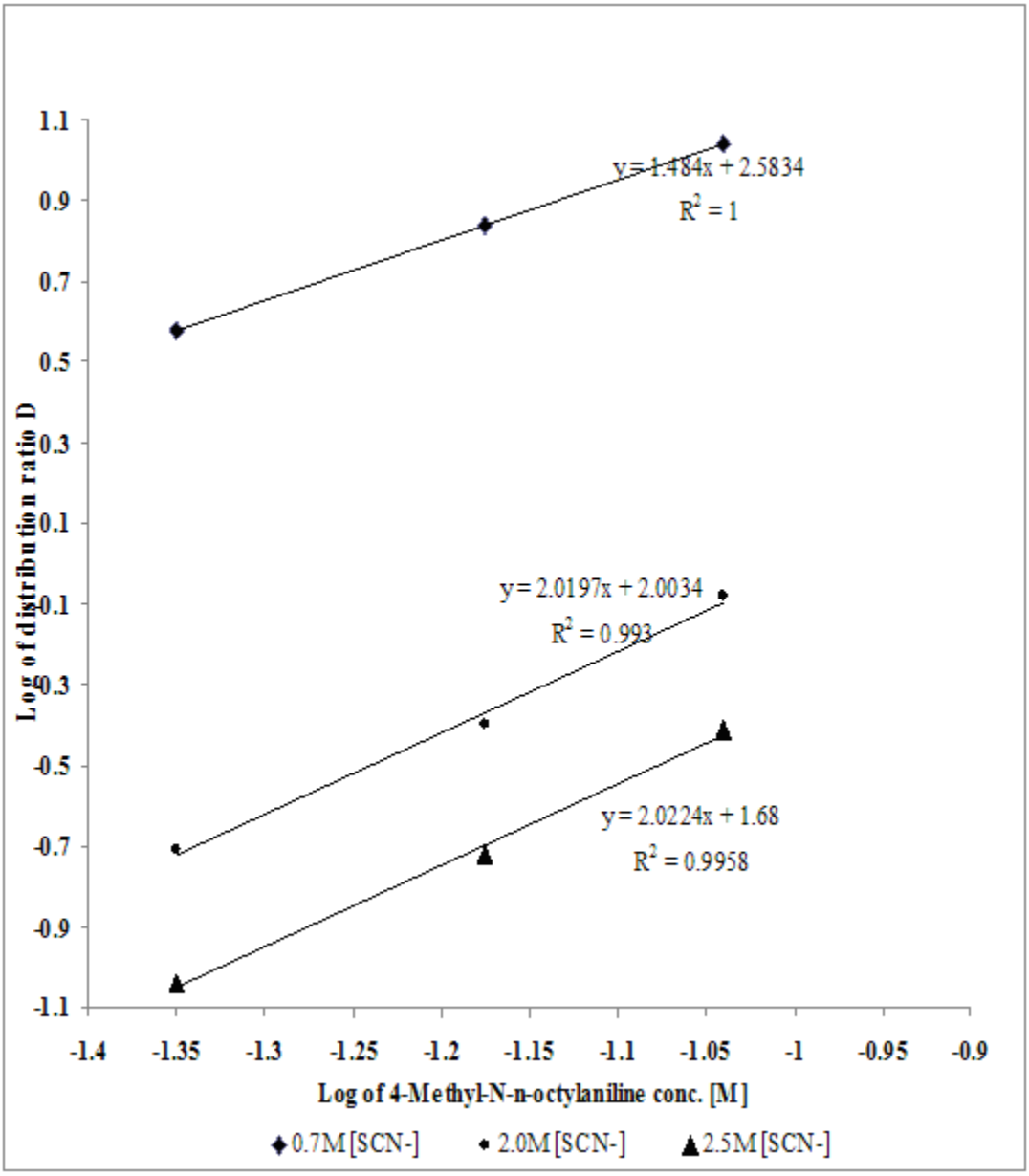

Fig. 3 Distribution ratio of Bismuth (III) as a function of 4-Methyl-N-n-octylaniline conc. at 0.7, 2.0, 2.5M Thiocyanate concentration

Effect of equilibration time

Variation of shaking time from 1 minute to 8 minute showed that a minimum of 5 minute of shaking time is needed for complete extraction of bismuth (III). To ensure the quantitative extraction of bismuth 6 min. time is recommended in the general extraction procedure. However the prolonged shaking had no adverse effect on the extraction of Bi (III) .

Effect of diluents

Various solvents such as xylene, toluene, benzene, cabon-tetrachloride, chloroform and nitrobenzene were tried as diluent for 4-Methyl-N-n-octylaniline [Table-3]. The extraction of bismuth (III) was quantitative with xylene, but other diluents found to be not giving quantitative extraction. Xylene was

selected as diluent as it gave quantitative extraction as well as clear-cut phase separation. The other diluents, may be attributed to the less stability of ion pair formed under conditions.

The effect of Aqueous:Organic volume ratio

Bi (III) was extracted from aqueous phase (10 ml to 100ml) containing 1.0M H_2SO_4 & 0.5 M KSCN. It was found that extraction of Bi (III) was remaining quantitative although Aq : Org volume ratio was changed upto 5:1, while it decreased beyond it. This indicated stability of ion pair was not affected under wide variations of Aq : Org phase volume ratio.

Effect of foreign ions

An interference study showed that a large number of cations and anions offer no interference (as shown by less than 1 % error in analyte recovery). The effect of foreign ions and their tolerance limits in the extraction of Bi (III) are reported in Table-5. For the extraction of 1 mg of Bi (III), 25 mg of Mg (II); 20 mg of Mn (II); 10mg each of Cu (II), Cd (II); 5 mg each of Ce (IV), Hg (II), Th (IV) were tolerated. The interference due to Ni (II) was removed by masking with tartarate. The interference due to Cr (III), Fe (III) was removed by masking with ascorbate. Among the anions, 100 mg each of acetate, succinate, ascorbate, 50 mg of tartarate, 20 mg of oxalate were tolerated. Citrate, phosphate, thiourea interfere seriously.

Determination of Bi (III) in synthetic mixture

Synthetic mixtures of various compositions were prepared and subjected for the extraction and determination of Bi(III). The results of triplicate analysis (Table-6) showed that Bi (III) could be separated and determined from synthetic multicomponent mixtures.

Separation of bismuth from alloys

Bismuth is separated and determined from the alloy like white metal by the proposed method.

0.5 g of alloy was dissolved in concentrated nitric acid. The solution was filtered to remove metastanic acid & antimonic acids from white metal. Filtrate was evaporated to dryness to remove excess of acid. The solid obtained was leached with 0.2 N hydrochloric acid and diluted to 100ml with distilled water. An aliquot from each sample was subjected for the extraction with 4-Methyl-N-n-octylaniline in xylene according to general procedure. Elements such as lead, copper and cadmium were not interfered, while nickel was co-extracted which was masked with citrate. Bismuth in organic phase was stripped with 0.1M HNO_3 and determined as in the general procedure. The results of triplicate analysis are given in Table-7.

CONCLUSION

The extraction of Bi (III) from thiocyanate media with 4-Methyl-N-n-octylaniline in xylene has been investigated. Effect of acidity, reagent concentration, diverse ion, shaking time, diluents, aqueous to organic phase ratio, nature of extracted species have been described. The method is simple, rapid and does not require long extraction period. The method proposed herewith permits the determination of Bi (III) in synthetic mixtures & alloys.

REFERENCES

1. B. Yu.Spivakov, V. I. Lebedev and V. M. Shkinev, *Zh. Anal. Khim.* ,**31 (4)**, 757, (1976).
2. M. A.Medkov, A. A. Smolkov, R. L. Davidovich, and N. A. Sedova, *Zh. Prikl. Khim. (Leningrad)* **59 (7),** 1604,(1986).
3. Tsukahara Iwao and Toshimi Yamamoto, *Anal. Chem.,* **64**, 3357(1973).
4. Moraes, Sergio de and Abrac, *Alcidio Anal. Chem.*, **46**, 1812, (1974).
5. W. Schade, *Chem. Tech. (Leipzig)* **,36,** 108, (1984).
6. S. D. Shete, and V. M. Shinde, *Microchim, Acta. I*, **63**, (1984).
7. G. N. Mulik, S. R. Kuchekar, and M. B. Chavan, *Ind. J. Chem.,* **25A**, 1073, (1986).
8. Mulik, G. N.; Kuchekar, S. R. and Chavan, M. B. J. Indian Chem. Soc. 64, 68, (1987).

9. Kadam-Patil N. B.; Sawant, S. S.; Mulik, G. N. and Chavan, M. B. Bull. Bismuth Inst. Suppl. 64, (1992).
10. Chandrashekar P. Mane, M. A. Anuse, *J. of the Chinese Chemical Society*, **155(4)**, 807(2008).
11. Yoshi Moriya, Mikic Sugai, Sin-ichi Nakata and Nobuaki Ogawa Analytical Science, **17(2)**, 297, (2001).
12. Vogel's Textbook of quantitative chemical analysis,sixth ed. Pearson Education, 381, (2004).

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