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Extraction Studies of Trivalent Bismuth Using Tributylphosphine Oxide as an Extractant with Applications to Alloys and Pharmaceutical Samples

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Abstract—**Extraction studies of Bismuth are undertaken from salicylate media using Tributylphosphine oxide (TBPO) as an extractant. Optimum extraction conditions are evaluated. The nature of extracted species is ascertained with logD-logC plots. Extraction mechanism is discussed, which is found to proceed through formation of solvated species. The basicity of TBPO solvates the Bismuth salicylate and transfers it to the organic phase. The method permits separation of bismuth from associated elements and has also been applied to the separation and determination of bismuth from synthetic mixtures.**

Index Terms—**Tributylphosphine oxide, Extraction, Bismuth, sodium salicylate**

I. INTRODUCTION

Bismuth is an important element due to its intermediate or metalloid character. It is used for the preparation of hard and easily fusible alloys, which are used as safety plugs in boilers, electrical fuses, automatic sprinklers, solders and type metal for printing. Trivalent metal salts are used medicinally to control diarrhea and other gastrointestinal distresses. They are also use as radiocotrasting agents. Bismuth also displays toxic effects and leads to decreased appetite, weakness and rheumatic pain. In view of this, separation and purification of bismuth is greatly desired.

Various solvent extraction methods have been used for the separation of bismuth. The neutral extractants such as Tri-n-butyl phosphate [1,3], Bis(2-ehtylhexyl) phosphate [4,5], Isopentyl acetate [6], 18-crown-6 [7], methyl isobutyl ketone [8] and Tri-n-octylphosphine oxide [9] are used for the extraction of bismuth from halide, thiocyanate and perchlorate media. Amongst the high molecular weight amines Tris (2-ehtylhexyl) amine [10], Dodecenyltrialkyl ammonium chloride [11], Tri-n-octyl-amine [12], Tri-iso-octyl amine [12] and Aliquat-336 [12] have been used for the extraction studies of bismuth from halide and succinate media.

In our laboratory Mesityl oxide [13,14], Tris (2-ehtylhexyl) phosphate (TEHP) [15], Triphenylphosphine oxide (TPPO) [16] and Triphenyl arsine oxide (TPAsO) have been extensively used for the extraction studies of bismuth from halide and salicylate media. However, the existing methods suffer from limitations such as longer extraction period [1,6], strict controlling of temperature [6], multiple extraction [16], critical pH range [2,8,10], large interferences [6,8] and high concentration of extractants [13,14,16].

In the present communication we propose study of solvent extraction behavior of trivalent bismuth from salicylate media with Tributylphosphine oxide (TBPO) as an extractant. Tribuytlphosphine oxide has already been used in our laboratory for extraction of Uranium, Thorium [17}, tellurium [18] lead, copper [19] scandium, yttrium and lanthanum [20]. The method is also free from above mentioned drawbacks and facilitates separation and determination of bismuth from associated elements, synthetic mixtures, alloys and pharmaceuticals. The method is highly selective and reproducible.

II. EXPERIMENTAL

Apparatus:

Absorbance and pH measurements are carried out on Spectronic 20 D (Milton Roy and Co.) and Control Dynamics Digital pH meter with combined glass electrode respectively.

Reagents:

The stock solution of bismuth is prepared by dissolving 0.58 g of bismuth nitrate (AR grade) in distilled water containing 2cm^3 of concentrated nitric acid. The solution is standardized by known method [21] and diluted further as required.

Tributylphosphine oxide (TBPO) (Aldrich) are used for the extraction studies.

10% aqueous solution of thiourea is used for the spectrophotometric determination of bismuth [22].

All other chemicals used are of Analytical Reagent grade.

General extraction procedure for bismuth:

To an aliquot of solution containing microgram (100-200 μg) amount of bismuth, sodium salicylate is added to obtain the desired molarity in total volume of 25cm^3. The pH of the solution is adjusted to the desired value using 0.1 mol dm^{-3} with sodium hydroxide and nitric acid respectively. The solution is then transferred to the separatory funnel and shaken for the required time with appropriate quantities of TBPO dissolved in toluene. (The optimum extraction conditions are reported in Table no 1). After separating the two layers, bismuth is back extracted from the organic phase with two 5 cm^3 portions of 0.2 mol dm^{-3} nitric acid and determined spectrophotometrically with Thiourea [22] at 460 nm.

III. RESULTS AND DISCUSSION

The extraction of bismuth is studied at various pH values (1.5 to 7.0) (fig. 1), sodium salicylate concentrations (6.25 x 10^{-3} to 1 x 10^{-3} mol dm^{-3}) with using TBPO dissolved in toluene as an extractant. It is found that bismuth (III) gets quantitatively extracted from 8.75 x 10^{-2} mol dm^{-3} sodium salicylate at pH 3.2 – 3.7 with 5 cm^3 of 0.1% (w/v) TBPO dissolved in toluene.

Variation in the shaking period from 5 sec to 120 sec indicates that a shaking period of 45 sec. is adequate for quantitative extraction of bismuth. However, prolonged shaking has no adverse effect on the extraction.

Various diluents like toluene, xylene, benzene and carbon tetrachloride are tried for their suitability as diluents. It is observed that the extraction is quantitative with toluene only. Under the optimized conditions the extraction is incomplete with other diluents.

Several stripping agents like nitric acid, hydrochloric acid, sulphuric acid, ammonium hydroxide and sodium hydroxide are used for the back extraction of bismuth. It is found that 0.2-2 mol dm^{-3} nitric acid, 0.1-0.5 mol dm^{-3} of hydrochloric acid, 0.05-0.2 mol dm^{-3} sulphuric acid back extract bismuth quantitatively. Water does not back extract bismuth from the organic phase.

Nature of extracted species:

The composition of the extracted species is ascertained using log-log plots. The plot of log of distribution ratio verses log of sodium salicylate concentration (at fixed pH, fixed TBPO concentrations) gives slope of 3.01 (fig.2). This indicates a molar ration of 1:3 of the metal ion with respect to salicylate. Similarly, the plot of log of distribution ratio verses log of extractant concentration (at fixed pH and salicylate concentration) gives straight lines with a slope 2.14 for (fig.3). The slope predicts the number of extractant molecules coordinated with the metal ion. Thus, the probable extracted species that for is $Bi(Hsal)_3.2TBPO$, where Hsal stands for the salicylate ion. Bismuth salicylate is solvated by the TBPO extractant and transferred into the organic phase. From the coordination number of the extractant with the metal it is evident that higher basicity of TBPO facilitates the extraction on bismuth salicylate into organic phase by removing water from the coordination site of the metal ion forming unhydrated adducts, which favours the extraction into organic phase.

Effect of diverse ions:

Varying amounts of foreign ions are added to the fixed amount of Bi (III) to study their interference in general extraction and subsequent determination of bismuth. The tolerance limit is set at the amount of the foreign ion causing ±2% error in the recovery of the bismuth. The results are reported in Table 2.

IV. APPLICATIONS

Binary separation of bismuth (III) from copper (II), lead (II), iron (III), antimony (III), tellurium (IV), vanadium (V) and chromium (VI):
Under the optimum extraction conditions of bismuth, the metal ions Cu, Pb, Fe, Sb, Te, V and Cr do not show any extraction into TBPO phase. This facilitates their separation from the binary mixtures. Bismuth from the organic phase is back extracted with 0.2 mol dm^{-3} nitric acid and determined as described in the general extraction procedure. Unextracted copper (II), lead (II) and vanadium (V) are determined in the aqueous phase spectrophotometrically with 4(2-pyridylazo) resorcinol (PAR) [23,24] method. Iron (III) is determined with thiocyanate [17] method and antimony (III) is determined with iodide [24] method, while tellurium (IV) and chromium (VI) are determined with stannous chloride [24] and diphenyl carbazide (DPC) [25] methods, respectively.
The method also facilitates separation and determination of bismuth from synthetic mixtures. The results are reported in the Table 3.

Analysis of alloys:
The proposed methods are applied to the various commercial alloy samples such as leaded bronze (BCS-364), leaded gunmetal (BCS-183/4) and woods alloy. The detail procedure is given below.
Weigh 100 mg of each of leaded bronze and leaded gunmetal alloy, dissolve it in 3 cm^3 of concentrated nitric acid and evaporate to dryness. The residue is taken up with water and precipitate of metastannic acid is filtered off. The precipitate is first washed with hot dilute nitric acid and then with hot water. To the filtrate add 2.5 mg bismuth solution and dilute to 25 cm^3. A 2 cm^3 of aliquot of this solution is taken up for the extraction and determination of the bismuth by the proposed method. The results are reported in Table 4.
Weigh 40 mg of woods alloy and dissolve it in 2cm^3 of concentrated nitric acid. The solution is prepared as described above and filtrate is diluted to 100 cm^3. A 1 cm^3 aliquot of this solution is taken up for the analysis of the bismuth by the proposed method. The results are reported in Table 4.

Analysis of pharmaceutical sample:
Bismuth containing drug "Denol" is analyzed by the proposed method. A denol tablet (Elder pharmaceuticals, India) is dissolved in 10cm^3 of perchloric acid, evaporated to dryness and taken up in water. The solution is filtered and filtrate is diluted to 500 cm^3. A 1 cm^3 aliquot of this solution is taken for the extraction and determination of the bismuth by the proposed method. The results are reported in Table 4.

V. CONCLUSIONS

The reported paper indicates a simple and novel method for extraction of Bismuth from salicylate media. It can be applied as a novel extractant for various metal extraction studies from varied systems. The proposed methods for bismuth have several distinct advantages over those discussed in the introduction.

1. The methods are simple, rapid and precise.
2. It needs no pre-equilibration or use of salting out agents.
3. Extraction occurs in single step.
4. The methods are highly reproducible and the total analysis time is only about 20 minutes.
5. The method is highly selective; they provide the separation and quantitative determination of bismuth from commonly associated elements, multicomponent mixtures, alloys and pharmaceutical sample.

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Statements and Declarations
On behalf of all authors, the corresponding author states that there is no conflict of interest for this manuscript.

Data Availability Statement
The data for the manuscript submitted will available freely on request.

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Table 1: Optimum Extraction conditions for Bi (III)

Bi (III)	Aqueous phase, [Salicylate] mol dm^{-3}	pH	Organic phase, 5cm^3 toluene	Extraction period, sec.	Stripping solution	Estimation procedure
(100-200) μg	8.75x10^{-2}	3.2-3.7	0.1% TBPO	45	0.2 mol dm^{-3} HNO_3 (2x5cm^3	Spectrophotometrically by Thiourea [18]

Table 2: Diverse ion effect

Aqueous Phase :	8.75X10^{-2} mol dm^{-3} sodium salicylate at pH 3.2 – 3.7
Organic Phase :	0.1 %TBPO in toluene

Foreign ions	Tolerance limit, μg
Cu(II)	200
Pb(II)	5000
Mn(II)	2000
Ba(II)	2500
Zn(II)	2000
Cd(II)	3000
Co(II)	500
Mg(II)	2000
Sb(III)	2500
Al(III)	3000
La(III)	500
Fe(III)	200
Y(III)	1000
EDTA	none
Th(IV)	1000
Zr(IV)	1000
Hf(IV)	1000
Ti(IV)	None
Ce(IV)	500
Te(IV)	200
V(V)	1000
U(VI)	1500
Cr(VI)	500
Mo(VI)	500
SO_4^{2-}	1000
Cl^-	1000
$NO3^-$	1000
SCN^-	500

*not tolerated

Table 3 : Separation of Bi(III) from binary and multicomponent mixtures.

Composition of the mixture, µg	Percent recovery, %	Relative error, ∗%	Estimation procedure for the added ion
Bi, 200; Cu, 50	99.5 99.2	0.5 0.8	PAR[19]
Bi, 200; Pb, 50	99.7 99.1	0.3 0.9	PAR[20]
Bi, 200; Fe, 100	99.1 99.6	0.9 0.4	Thiocyanate[17]
Bi, 200; Sb, 200	99.2 99.3	0.8 0.7	Iodide[20]
Bi, 200; Te, 200	99.3 99.3	0.7 0.7	$SnCl_2$[20]
Bi, 200; V, 50	99.4 99.6	0.6 0.4	PAR[20]
Bi, 200; Cr, 50	99.7 99.6	0.3 0.4	DPC[21]
Bi, 200; Pb, 100 Fe, 100; Ni, 200 V,50	99.2	0.8	
Bi, 200; Sb, 200 Te, 100; U, 100 Cd,100	99.1	0.9	

∗ Average of triplicate analysis

Table 4: Estimation of Bi(III) in alloys and pharmaceutical samples

Sample	Composition (%)	Bi (III) added or Certified value, mg	Recovery of Bi (III), mg	R.S.D, %
Leaded bronze (BCS-364)	Cu,80.6;Sn,9.35; Pb,1.25; Ni,0.28;Zn,0.13; As.0.065; P,0.56 Al,0.002; Si,0.002; + 2.5 mg Bi (III)	2.5	2.48	0.51
Leaded gunmetal (BCS-183/4)	Cu,84.06; Sn,7.27; Pb,3.15; Ni,1.0; P,0.09; Fe,0.056; Sb,0.23; As,0.13; S,0.11; + 2.5mg Bi(III)	2.5	2.48	0.23
Woods alloy (Indalloy 158), Indium corporation of America	Bi,50; Pb,26.7; Sn,13.3; Cd,10	20	19.9	0.58
Denol tablet, (Elder pharmaceuticals India)	Colloidal bismuth subcitrate, calculated as Bi_2O_3, 120 mg	107.64	107.14	0.40

∗Average of triplicate analysis

BCS- British Chemical Standard

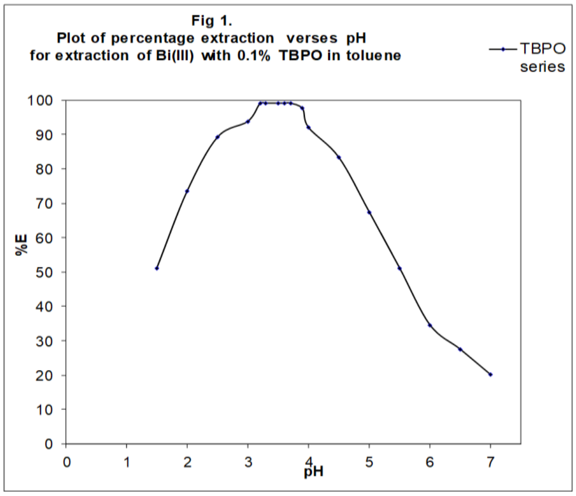

Fig 1.
Plot of percentage extraction verses pH
for extraction of Bi(III) with 0.1% TBPO in toluene

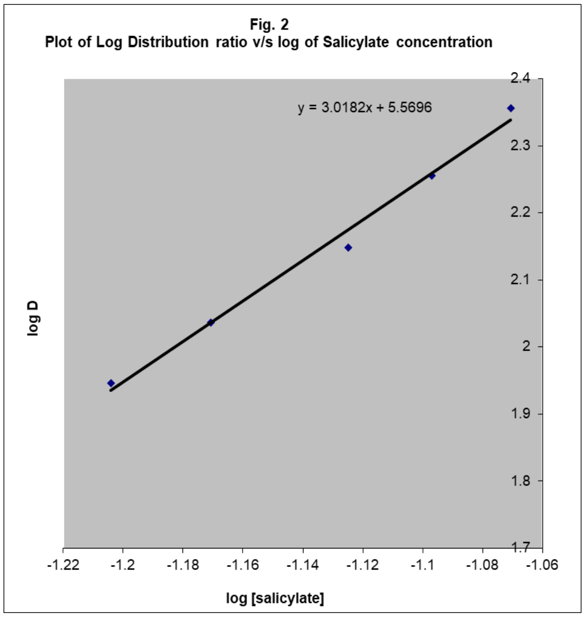

Fig. 2
Plot of Log Distribution ratio v/s log of Salicylate concentration

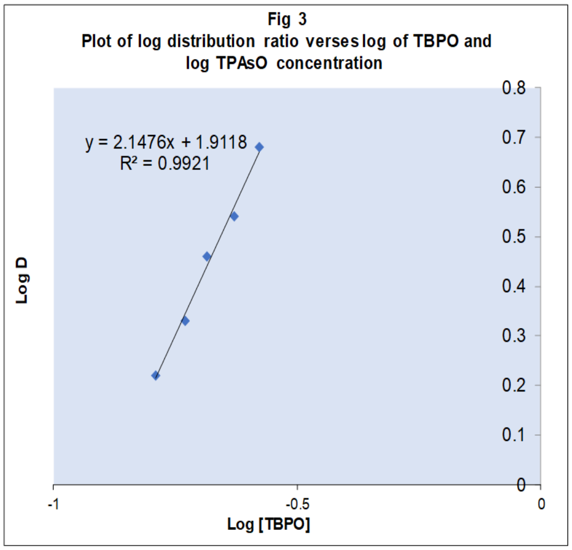

Fig 3
Plot of log distribution ratio verses log of TBPO and
log TPAsO concentration