Extraction and Separation Studies of Bismuth(III) and Antimony(III) with Tris(2-ethylhexyl)phosphate

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Separation of bismuth(III) from lead, antimony, gold, and tellurium and that of antimony(III) from copper, bismuth, and lead is achieved by selective extraction of bismuth(III) and antimony(III) from halide solutions into tris(2-ethylhexyl)phosphate (TEHP) dissolved in toluene or xylene. The extracted species are evaluated by log D–log C plots. The method is applicable to the analysis of some 'real' samples. The separation and determination takes only 20 minutes.

Both bismuth and antimony are important from commercial point of view. Hence their separation and determination from associated elements is desired.

Neutral extractants such as bis(2-ethylhexyl)phosphate,[1—3] tributyl phosphate,[4—6] isopentyl acetate,[7] 18-crown-6,[8] mesityl oxide,[9] isobutyl methylketone,[10] and high molecular weight amines such as dodecenyltrialkyl ammonium chloride[11] and tris(2-ethylhexyl)-amine[12] are used for extraction studies of bismuth(III) from halide media, whereas polar solvents such as tributyl phosphate,[13] mesityl oxide,[14] trioctylphosphine oxide,[15] isobutyl methyl ketone,[16] butyl acetate,[17] phosphoro dithioate derivatives,[18,19] 18-crown-6,[20] and a few high molecular weight amines are used for the extraction of antimony from chloride, iodide and sulfate media.[21—24] Hydroxamic acid derivatives are also used to extract antimony.[25,26] However existing methods of bismuth and antimony suffer from limitations such as longer extraction time,[4,7,16,20,22,25] strict temperature controlling,[7,22] multiple extraction,[16] use of high concentrations of salting out agents,[13] and critical pH range.[5,6,10,12]

Tris(2-ethylhexyl)phosphate (TEHP) has been earlier used in this laboratory for the extraction studies of uranium(VI),[27] thorium(IV),[28] and tellurium(IV).[29] An extension of this work has shown that the TEHP can also be used for extraction and separation of bismuth-(III) and antimony(III) from associated elements. The method is simple, fast and applicable for the analysis of some 'real' samples.

Experimental

Apparatus and Reagents. Spectronic 20 D (Milton Roy Co.) spectrophotometer and control dynamics digital pH meter are used for the absorbance and pH measurements.

The stock solutions of bismuth(III) and antimony(III) are prepared by dissolving 0.58 g of bismuth nitrate in 250 cm^3 of distilled water containing 2 cm^3 of concentrated nitric acid and dissolving 0.100 g of powdered antimony metal in 25 cm^3 of concentrated sulfuric acid and diluting to 100 cm^3. Both the solutions of bismuth(III) and antimony(III) are standardized by known methods[30,31] and are further diluted as required for working solution.

A 50% solution of tris(2-ethylhexyl)phosphate (TEHP) obtained from Aldrich chemicals (bp 215°C) is used as an extractant.

Thiourea; 10% solution is used for the determination of bismuth.[32]

Potassium iodide; 20% solution is used for the determination of antimony.[33]

All other reagents used are of analytical reagent grade.

General Extraction Procedure for Bismuth(III) and Antimony(III). Bismuth(III) and antimony(III) are extracted from halide media into tris(2-ethylhexyl)phosphate under the optimum extraction conditions given in Table 1. After stripping from TEHP phase bismuth and antimony are spectrophotometrically determined with thiourea[32] and potassium iodide[33] respectively.

The bismuth and antimony contents are computed from earlier drawn calibration plots.

Results and Discussion

Extraction Conditions. The extraction of bismuth(III) and antimony(III) are studied at various concentrations of hydrochloric acid (0.025—8 mol dm^{-3}) and hydrobromic acid (0.025—7 mol dm^{-3}) with different concentrations of TEHP (10.0—50.0% dissolved in toluene or xylene). The results given in Tables 2 and 3 show that two 5 cm^3 portions of 50% TEHP in xylene extracts antimony(III) quantitatively from 2.0—3.0 mol dm^{-3} hydrochloric acid solution whereas from hydrobromic acid solution its extraction is incomplete. The quantitative extraction of bismuth(III) from 0.09 to 0.3 mol dm^{-3} hydrobromic acid solution is feasible with 5 cm^3 of 50% TEHP in toluene; from hydrochloric acid media, extraction of bismuth is incomplete.

Period of Extraction: Variation of shaking period from 5 to 60 s showed that 20 s and 45 s equilibration time is adequate for quantitative extraction of antimony and bismuth from chloride and bromide media respectively. However, prolonged shaking has no adverse effect on the extraction of both antimony(III) and bismuth(III).

Effect of Diluent: The effect of various solvents such as xylene, toluene, benzene, chloroform, and carbontetrachloride on the extraction of antimony(III) and bismuth(III) using the proposed method is investigated. A 50% solution of TEHP in diluents such as xylene, toluene, and benzene provides quantitative extraction of antimony and bismuth. The extraction is,

Table 1. Optimum Extraction Conditions for Bismuth(III) and Antimony(III) with Tris(2-ethylhexyl)phosphate

Metal ion / μg		Halide concentration	(TEHP)/ diluent	Period of extraction	Back extraction	Estimation procedure
Bi (III),	50—200	0.09 to 0.3 mol dm^{-3} HBr in a total volume of 10 cm^3	5 cm^3 of 50% TEHP in toluene	45 s	2×5 cm^3 of 0.1 mol dm^{-3} HNO_3	Thiourea at 460 nm[32]
Sb (III),	75—300	2.0 to 3.0 mol dm^{-3} HCl in a total volume of 10 cm^3	2×5 cm^3 of 50% TEHP in xylene	20 s	8 cm^3 of water	Potassium iodide at 425 nm[33]

Table 3. Extraction of Antimony(III) and Bismuth(III) as a Function of Hydrochloric Acid/Hydrobromic Acid Concentration[a]

	[HCL] / mol dm^{-3}	Extraction / %	Distribution ratio/D	[HBr] / mol dm^{-3}	Extraction / %	Distribution ratio/D
Sb (150 μg)	0.2	45.59	1.68	2	16.00	0.38
	0.5	72.06	5.16	3	27.08	0.74
	1.0	91.18	20.68	4	64.00	3.56
	2.0—3.0	99.90	∞	5	64.00	3.56
	4.0	92.65	25.21	6	68.00	4.25
	5.0	76.47	6.49	7	68.00	4.25
	6.0	64.71	3.66	—	—	—
	7.0	57.35	2.68	—	—	—
	8.0	41.18	1.40	—	—	—
Bi (200 μg)	0.025	11.11	0.25	0.025	55.55	2.49
	0.075	18.51	0.45	0.75	96.29	51.90
	0.100	40.74	1.37	0.09—0.3	99.90	∞
	0.200	51.85	2.15	0.50	96.29	51.90
	0.300	48.14	1.85	0.65	33.33	0.99
	0.5—0.75	33.33	0.99	0.75	25.92	0.69
	0.900	25.92	0.69	0.90	22.22	0.57
	3.000	14.81	0.34	3.00	11.11	0.25
	4.000	7.40	0.16	4.00	11.11	0.25

a) (TEHP) : 2×5 cm^3 dissolved in xylene for Sb(III), 1×5 cm^3 dissolved in toluene for Bi(III).

Table 2. Extraction of Bismuth(III) and Antimony-(III) as a Function of TEHP Concentration[a]

	[TEHP]%	Percentage extraction	Distribution ratio/D
Sb (150 μg)	10	41.18	1.40
	20	64.71	3.66
	30	83.82	10.36
	40	92.65	25.21
	50	99.90	∞
Bi (200 μg)	10	11.11	0.25
	15	25.92	0.69
	20	33.33	0.99
	30	62.96	3.39
	40	85.18	11.49
	50	99.90	∞

a) Aqueous plase: 2.0—3.0 mol dm^{-3} HCl for Sb(III) and 0.09—0.3 mol dm^{-3} HBr for Bi(III).

Table 4. Effect of Stripping Agents[a]

Stripping agents	mol dm^{-3}	Percentage extraction	Distribution ratio/D
HNO_3	0.05	96.29	51.90
	0.1—0.2	99.90	∞
	0.3—1.0	96.29	51.90
	0.02	88.88	15.98
H_2SO_4	0.05—0.2	99.90	∞
	0.3	92.59	24.99
	1.0	81.48	8.79
HCl	0.05	70.37	4.74
	0.1	92.59	24.99
	0.2—0.4	62.96	3.39
$HClO_4$	0.05	92.59	24.99
	0.1—0.3	99.99	∞
	1.0	85.18	11.49

a) Water does not strip bismuth from organic phase.

however, incomplete with other diluents.

Nature of Extracted Species: The nature of the extracted species is established using the log–log plots of distribution ratio versus TEHP concentration for antimony (at 2.0 mol dm^{-3} hydrochloric acid concentration) and bismuth (at 0.1 mol dm^{-3} hydrobromic acid concentration). The slope of 1.7 indicates the metal to TEHP ratio of 1:2 in the extracted species. Hence, the extracted species is an ion association complex formed by solvation. The possible species are $HSbCl_4 \cdot 2TEHP/HBiBr_4 \cdot 2TEHP$.

Effect of Stripping Agents: Various stripping agents are tried to back extract bismuth from organic phase. The results in Table 4 show that nitric acid (0.1—0.2 mol dm^{-3}), sulfuric acid (0.05—0.2 mol dm^{-3}) and perchloric acid (0.1—0.3 mol dm^{-3}) are suitable for stripping bismuth quantitatively. Water do not strip bismuth from TEHP phase although it strips antimony quantitatively.

Effect of Various Foreign Ions: Varying amounts of foreign ions are added to a fixed amount of antimony (150 μg) or bismuth (200 μg) to study interference in the recommended procedure. The tolerance limit is set at the amount required to cause ±2% error in metal recovery. The results are reported in Table 5.

Binary Separation of Bismuth(III) from Antimony(III), Lead(II), Gold(III), and Tellurium(IV). Bismuth is often found in association with lead, antimony, gold, and tellurium. Hence, separation of bismuth from binary mixtures is tried by the proposed method. Bismuth and antimony are separated by extracting antimony from 3 mol dm^{-3} hydrochloric acid solution with 50% TEHP dissolved in toluene. It is then stripped with water (8 cm^3) and determined in the aqueous phase spectrophotometrically using the iodide method.[33] Bismuth which remains quantitatively in water phase is determined using thiourea.[32] Lead and bismuth are separated as lead does not show any extraction and remains quantitatively in the aqueous phase. It is determined in the aqueous phase spectrophotometrically using 4-(2-pyridylazo)resorcinol (PAR).[34] Gold is coextracted with bismuth. However, they are separated by selective stripping of bismuth with nitric acid. Gold is not stripped and the amount is determined in the organic phase itself by measuring the absorbance of the yellow complex at 400 nm. Tellurium and bismuth are separated by extracting bismuth from 0.1 mol dm^{-3} hydrobromic acid solution with 50% TEHP dissolved in toluene. Tellurium which remains quantitatively in the aqueous phase is determined spectrophotometrically with tin(II) chloride.[29] The recovery of bismuth and that of other ions in the binary mixture is ⩾99.0%.

Binary Separation of Antimony(III) from Copper(II), Bismuth(III), and Lead(II). The method permits separation and determination of antimony(III) from binary mixtures containing either copper, bismuth or lead. Separation of antimony and bismuth is described above. Antimony is separated from copper and lead by it's extraction with 50% TEHP dissolved in xylene from 2 mol dm^{-3} hydrochloric acid solution. Under these conditions copper and lead remain quantitatively in the aqueous phase where they are determined spectrophotometrically using 1-(2-pyridylazo)-2-naphthol (PAN)[35] and 4-(2-pyridylazo)resorcinol (PAR),[34] respectively. Antimony is stripped from the organic phase with water and determined spectrophotometrically using potassium iodide. The recovery of antimony and that of other ions in the binary mixture is ⩾99.0%.

Table 5. Effect of Various Foreign Ions[a]

Ions	Tolerance limit/μg	
	Bi(III)	Sb(III)
Ag(I)	1000	750
Hg(II)	4000	1000
Pb(II)	5000	5000
Ni(II)	2500	5000
Cu(II)	5000	5000
Mn(II)	5000	5000
Ba(II)	2000	5000
Ca(II)	5000	5000
Cd(II)	5000	5000
Sn(II)	500	150
Mg(II)	5000	5000
Zn(II)	5000	5000
Co(II)	5000	5000
As(III)	2000	2000
Al(III)	1000	2000
Fe(III)	5000	2000
Bi(III)	—	500
Sb(III)	500	—
Au(III)	3000	150
Ti(IV)	1500	2000
Te(IV)	1000	150
Th(IV)	5000	1000
Se(IV)	1000	500
V(V)	1000	1000
W(VI)	2000	300
Cr(VI)	5000	None
U(VI)	2000	2000
Mo(VI)	4000	1000
Citrate	5000	750
Tartrate	5000	750
Oxalate	4000	750
Nitrite	2000	750
Sulphate	2000	4000
Nitrate	2000	4000
Chloride	2000	5000
Phosphate	2000	5000
Ascorbate	2000	2000
Thiourea	2000	1000
Thiosulphate	200	1000
EDTA	None	2000

a) Bi(200 μg); aqueous phase: 0.1 mol dm^{-3} HBr; Extractant: 5 cm^3 50% TEHP in Toluene. Sb(150 μg); aqueous phase: 2.0 mol dm^{-3} HCl; Extractant: 2×5 cm^3 50% TEHP in Xylene.

Table 6. Analysis of Standard Alloys and Drugs

Sample	Composition	Bi added or certified value of Bi/Sb	Recovery of Bi/Sb %	Standard deviation	Coefficient of variation %
Alloy					
Leaded brass (BCS[a] 385)	Cu, 58.7%; Pb, 2.24%; Fe, 0.15%; Zn, 33.5%; Sn, 0.27%; Ni, 0.13%; Al, 0.005%; Mn, 0.005%; Sb, 0.05 %	2.5 mg Bi	99.20	0.008	0.32
Leaded bronze (BCS 364)	Cu, 80.6%; Sn, 9.35%; Pb, 0.25%; Ni, 0.28%; Zn, 0.13%; As, 0.065%; P, 0.056%; Al, 0.002%; Si, 0.003	2.5 mg Bi	99.20	0.006	0.25
Leaded gunmetal (BCS 183/4)	Cu, 84.06%; Pb, 3.15%; Sn, 7.27%; Zn, 3.47%; Ni, 0.13%; S, 0.11%	2.5 mg Bi	99.60	0.015	0.60
Woods alloy (Indalloy 158)	Pb, 26.7%; Bi, 50%; Sn, 13.3%; Cd, 10.0%	20 mg Bi	99.80	0.042	0.21
Drugs					
De-nol (Elder Pharmaceuticals, India)	Colloidal bismuth subcitrate, calculated as Bi_2O_3 120 mg	107.64 mg Bi	99.80	0.016	0.01
Pectomycin suspension (Lyka Labs, Limited, India)	Each 15 ml contains, light kaolin I. P. 2.5 mg, Pectin I. P. 50 mg; Streptomycin sulphate I. P. 0.5 mg; Streptomycin flaboured Syrupy base q. s.	2.5 mg Bi	99.60	0.004	0.15
Sodium antimony gluconate Inj. I. P.	Each ml. contains Sodium Antimony gluconate I. P. 0.333 g (Equivalent to 100 mg of total antimony) Phenol I. P. 0.5% w/v	200 mg Sb	99.80	0.07	0.03

a) BCS = British Chemical Standard.

Analysis of Alloys and Pharmaceutical Samples. Since bismuth containing alloy samples are not available, known amount of bismuth is added to standard alloy solution and the proposed method is used for the recovery of bismuth.

100 mg each of leaded brass, leaded bronze and leaded gunmetal is dissolved in 3 cm^3 of concentrated nitric acid. Metastannic acid is filtered off and to the filtrate is added 2.5 mg of bismuth. Dilute to 25 cm^3 and a 2 cm^3 aliquot of this solution is taken for extraction and determination of bismuth by the proposed method.

Woods alloy (40 mg) containing bismuth is dissolved as described above and diluted to 100 cm^3. A 1 cm^3 aliquot of the solution is taken for extraction and determination of bismuth.

De-nol tablet is dissolved in 10 cm^3 of perchloric acid, (continuous heating is avoided to eliminate the probability of spurting) evaporated to dryness, the residue is taken up in water, filtered and the filtrate is diluted to 500 cm^3. Agrawal and Bhatt have determined bismuth in pectomycin suspension[36] manufactured by Lyka Labs, India. The sample of pectomycin available in the Bombay market, however, does not contain bismuth and hence, 2.5 mg of bismuth is added to 5 cm^3 of pectomycin suspension. The suspension is dissolved in 10 cm^3 of 2.5 mol dm^{-3} sulfuric acid; the solution is filtered and diluted to 50 cm^3. A 1 cm^3 and 4 cm^3 aliquot of de-nol and pectomycin solution is taken for the extraction and determination of bismuth by the proposed method.

A 1 cm^3 of sodium antimony gluconate injection containing 100 mg of antimony(V) is evaporated to dryness, the residue is decomposed with perchloric acid, leached and diluted to 500 cm^3 with 0.5 mol dm^{-3} sul-

furic acid. A 1 cm^3 of this solution containing 200 μg of antimony is treated with ascorbic acid to reduce antimony. Antimony is extracted and determined as per the recommended extraction procedure.

The results of analysis are reported in Table 6.

The methods are accurate and permit rapid separation and determination of micro amounts of antimony(III) and bismuth(III). The average recovery of antimony and bismuth is ⩾99.0%. Each determination takes a total of 15—20 min.

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