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A Combined Solvent Extraction-Spectrophotometry for the Determination of Bismuth(III)

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A method has been proposed for the extraction of bismuth(III) at microgram level from bromide media using mesityl oxide as an extractant. The bismuth–bromo complex formed in the concentration range of 0.05—0.3 mol dm^{-3} hydrobromic acid showed quantitative extraction into mesityl oxide. Various experimental conditions such as acid concentration, mesityl oxide concentration, period of equilibration, stripping agents, and diverse ions have been studied. Bismuth ion after stripping is determined by thiourea spectrophotometrically. The method is applicable to the analysis of pharmaceutical samples, alloy samples, and synthetic mixtures.

Bismuth is an important element because of its intermediate or metalloid character. It is chiefly employed for the preparation of hard and easily fusible alloys which are useful as safety plugs in boilers, electrical fuses, solders, and type metal for printing. Trivalent bismuth salts are used medicinally to control diarrhoea and other gastrointestinal distresses. Bismuth salts are also used as radio-contrast agents. In view of this separation of bismuth from associated elements for the determination is desired.

Literature survey reports a very few extraction methods for bismuth(III). Amongst the ion-association systems, polar solvents such as tributyl phosphate (TBP), methyl isobutyl ketone (MIBK), isopentyl alcohol, isopentyl acetate, and diethyl ether have been used for the extraction of bismuth from iodide, perchlorate and thiocyanate media.[1–5] High molecular weight amines have also been used for extraction of bismuth from iodide, chloride, thiocyanate, bromide, and succinate media.[6–11] *N*-*m*-Tolyl-*p*-chlorobenzohydroxamic acid has been used to extract bismuth.[12] However the existing methods suffer from limitations such as longer extraction time,[3,12] critical pH,[12] centrifugation,[11] and large number of interferences.[2,3,6] The proposed method is free from these limitations and affords separation for the determination of bismuth in some samples. The method is reproducible and rapid.

Experimental

Apparatus and Reagents. Mesityl oxide (bp 128 °C, Fluka) was used after double distillation.

Thiourea; 10% solution was used for the determination of bismuth.[13]

The stock solution of bismuth(III) was prepared by dissolving 0.58 g of bismuth nitrate (AR grade) in distilled water containing 2 cm^3 of concentrated nitric acid and diluting to 250 cm^3. The solution was standardised by known method[14] and diluted as required for working solution. All other reagents used were of analytical reagent grade.

Absorbance measurements were made on a Unicam SP 500 spectrophotometer with 1 cm (silica) cells.

General Extraction Procedure. To an aliquot of solution containing 200 μg of bismuth(III), hydrobromic acid was added so that its concentration is 0.2 mol dm^{-3} in a total volume of 10 cm^3. The solution was transferred into a separatory funnel and extracted with 5 cm^3 of undiluted mesityl oxide for 30 s. After separating the aqueous layer, bismuth from the organic layer was stripped with two 5 cm^3 portions of 0.2 mol dm^{-3} nitric acid and determined with thiourea spectrophotometrically at 460 nm.[12]

Results and Discussion

Extraction Conditions. The concentration of hydrobromic acid was varied from 0.05 to 1.0 mol dm^{-3} and that of mesityl oxide from 50 to 100% (v/v) by dilution

Table 1. Extraction of Bismuth(III) as a Function of Hydrobromic Acid Concentration and Mesityl Oxide Concentration. Bi(III)=200 μg

Mesityl oxide concn/%	[HBr] / mol dm^{-3}	Extraction / %	Distribution ratio, D
50	0.2	13.8	0.32
60	0.2	25.0	0.67
70	0.2	42.6	1.48
80	0.2	58.7	2.84
90	0.2	72.6	5.30
100	0.05—0.3	99.9	1998
100	0.4	83.7	10.26
100	0.5	73.1	5.43
100	1.0	57.5	2.70

with toluene. The results (Table 1) showed that the quantitative extraction of bismuth occurs with undiluted mesityl oxide from the solution containing 0.05 to 0.3 mol dm^{-3} hydrobromic acid. Variation of shaking time from 5 to 60 s showed that an equilibration for 30 s was enough for complete extraction of bismuth into organic phase. However prolonged shaking had no adverse effect on the extraction of bismuth.

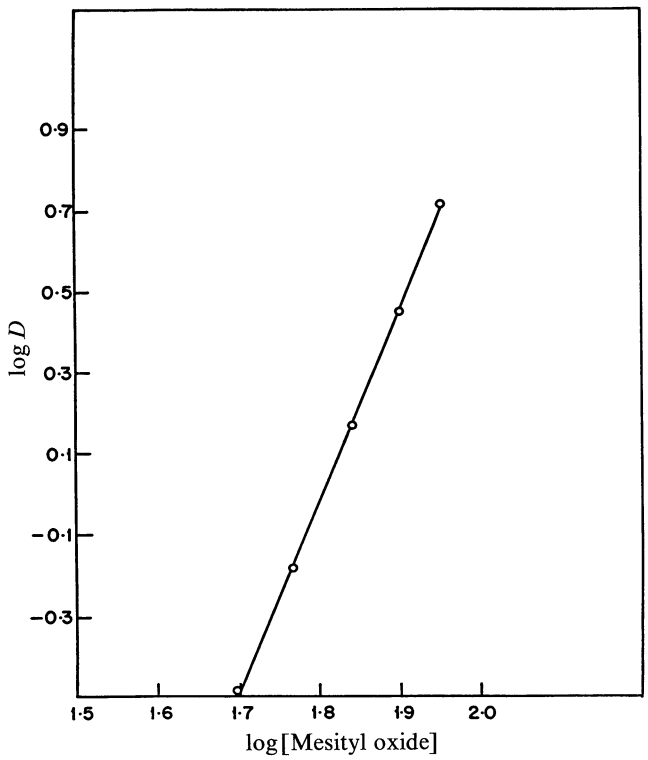

Fig. 1. Plot of log(distribution ratio, D) vs. log(Mesityl oxide concentration, %) at 0.2 mol dm^{-3} hydrobromic acid concentration.

Nature of the Extracted Species. The nature of the extracted species was established using log–log plot. A plot of log of distribution ratio (D) versus log of mesityl oxide concentration (at 0.2 mol dm^{-3} hydrobromic acid concentration) gave a slope of 2.3 indicating a molar ratio of 1 : 2 with respect to the extractant (Fig. 1).

Effect of Strippng Agents. Different stripping agents were tried for back extraction of bismuth. Nitric acid was suitable stripping agent because with other agents such as hydrochloric acid, perchloric acid, sulphuric acid, ammonium hydroxide, and sodium hydroxide the recovery of bismuth was not quantitative. Water do not strip bismuth from the organic phase. The results are reported in Table 2.

Effect of Foreign Ions. Varying amounts of foreign ions were added to a fixed amount of bismuth (200 μg) to study interference in the recommended procedure. The tolerance limit was set at the amount required to cause ±1% error in bismuth recovery. There was no interference from 8000 μg each of Cu(II), Zn(II), Fe(III), Mn(II), and Ni(II); 6000 μg each of Mo(VI), Co(II), Mg(II), citrate, and tartrate; 4000 μg each of Be(II), Pb(II), Th(IV), As(III), and fluoride; 2000 μg each of W(VI), Sb(III), V(V), Ba(II), Ti(IV), U(VI), thiourea, oxalate, sulfate, nitrate, nitrite, phosphate, chloride, and ascorbic acid; 1000 μg each of Cd(II), Hg(II), Sn(II), Cr(VI), Au(III), Ag(I), and Pd(II); 400 μg of thiosulfate and 200 μg of EDTA.

Analysis of Synthetic Mixture. The proposed method was applied for the extraction and determination of

Table 2. Effect of Stripping Agents.[a] Bi(III)=200 μg

Stripping agent	Concentration / mol dm^{-3}	Extraction / %	Distribution ratio, D
HNO_3	0.1	77.8	7.01
	0.15—0.5	99.9	1998
	2.0	92.3	23.97
HCl	0.01	7.4	0.16
	0.1	74.1	5.72
	0.2	70.4	4.76
	2.0	40.7	1.37
H_2SO_4	0.01	59.3	2.91
	0.05—0.4	98.1	103.26
	1.0	92.3	23.97
$HClO_4$	0.05	59.3	2.91
	0.1	70.4	4.76
	0.2	96.3	52.05
	0.3—0.8	97.8	88.91
	2.0	88.9	16.02
NaOH	0.1	60.5	3.06
	0.2	70.4	4.76
	1.0—2.0	Interference[b]	
NH_4OH	0.2	37.0	1.17
	2.0	40.7	1.37
	4.0	Interference[b]	

a) Water do not strip bismuth from the organic phase. b) Interference in the color development.

Table 3. Analysis of Synthetic Mixture

Composition	Bismuth found[a]	Relative error
μg	μg	±,%
Bi, 200.0; Ti, 1000.0; Mo, 1000.0; V, 1000.0; Fe, 1000.0	200.0	0.0
Bi, 200.0; As, 600.0; Sb, 600.0; Sn, 600.0; Pb, 600.0	198.0	1.0

a) Average of triplicate analysis.

bismuth in different synthetic mixtures. The results showed that the recovery of bismuth was ⩾99%. The results are reported in Table 3.

Analysis of Alloys. A known amount of bismuth was added to leaded brass (BCS 385), leaded bronze (BCS 364), and leaded gunmetal (BCS 183/4) and bismuth was recovered by the proposed method. The procedure is detailed below.

Weigh accurately 100 mg each of leaded brass, leaded bronze, and leaded gunmetal, add 3 cm^3 of concentrated nitric acid and evaporate to almost dryness. The residue is taken up with water and the precipitate of metastannic acid is filtered off. The precipitate is first washed with hot dilute nitric acid and then thoroughly with hot water. To the filtrate add solution containing 2.5 mg of bismuth and dilute to 25 cm^3. 2 cm^3 of this solution is taken for extraction and determination of bismuth by the proposed method. The results are reported in Table 4.

40 mg of Woods alloy was taken and dissolution was carried out as described above. Then the filtrate was diluted to 100 cm^3 and 1 cm^3 of this solution was taken for extraction and determination of bismuth by the proposed method. The result is reported in Table 4.

Analysis of Pharmaceutical Samples. Bismuth containing drugs such as Denol were analysed by the proposed method. A Denol tablet was dissolved in 10 cm^3 of perchloric acid, evaporated to almost dryness, taken up in water, filtered and the filtrate was diluted to 500 cm^3. Agrawal and Bhatt have determined bismuth in

Table 4. Analysis of Standard Alloys for Extraction of Bismuth(III)

Alloy	Composition	Bismuth found[a]/mg	Relative error
	%		±,%
Leaded brass (BCS[b] 385)	Cu, 58.7; Pb, 2.24; Fe, 0.15; Zn, 38.5; Sn, 0.27; Ni, 0.13; Al, 0.005; Mn, 0.005; Sb, 0.005+2.5 mg Bi	2.49	0.4
Leaded bronze (BCS 364)	Cu, 80.6; Sn, 9.35; Pb, 9.25; Ni, 0.28; Sb, 0.18; Zn, 0.13; As, 0.065; P, 0.056; Al, 0.002 Si, 0.002+2.5 mg Bi	2.48	0.8
Leaded gunmetal (BCS 183/4)	Cu, 84.06; Pb, 3.15; Sn, 7.27; Zn, 3.47; Ni, 1.0; P, 0.090; Fe, 0.056; Sb, 0.23; As, 0.13; S, 0.11+2.5 mg Bi	2.48	0.8
Woods alloy (Indalloy 158) Indium Corporation of America	Bi, 50.0; Pb, 26.7; Sn, 13.3; Cd, 10.0	19.99	0.1

a) Average of triplicate analysis. b) BCS=British Chemical Standard.

Table 5. Analysis of Drugs

Name of drug	Composition	Certified value or added value of Bi	Bismuth found[a]
Denol (Elder Pharmaceuticals, India)	Colloidal bismuth subcitrate, calculated as Bi_2O_3 120 mg	107.64 mg	107.63 mg
Pectomycin suspension (Lyka Labs. Limited, India)	Each 15 cm^3 contains, light kaolin. I.P. 2.5 mg Pectin I.P. 50 mg Streptomycin sulphate I.P. ≅0.5 mg streptomycin Flavoured syrupy base q.s.+2.5 mg Bi	2.5 mg	2.5 mg

a) Average of triplicate analysis.

Pectomycin suspension[12] (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 was added to 5 cm^3 of Pectomycin suspension and dissolved in 10 cm^3 of 2.5 mol dm^{-3} H_2SO_4 the solution was filtered and diluted to 50 cm^3. 1 cm^3 and 4 cm^3 aliquot of Denol and Pectomycin suspension were respectively taken for extraction and determination of bismuth by the proposed method. The results are reported in Table 5.

The method is selective and permits a rapid separation and determination of a microgram amount of bismuth. The average recovery of bismuth was 99.0±1%. Each determination took a total of 20—25 min.

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