

Solvent extraction separation of bismuth(III) with hexaacetato calix(6)arene

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Bismuth(III) was quantitatively extracted from 0.1M HCl with 1×10^{-4} M of hexaacetato calix(6)arene in toluene. It was stripped with 2 M nitric acid and determined from the aqueous phase spectrophotometrically at 470 nm as its complex with thiourea. The various parameters such as pH, reagent concentration, kind of diluents, stripping agents, effect of diverse ions were studied to ascertain optimum conditions for the quantitative extraction of bismuth. Bismuth was separated from thorium(IV), iron(III), manganese(II), chromium(III), lead(II), palladium(II) and thallium(III) in multicomponent mixtures. The method was extended for the analysis of bismuth in real samples.

Amongst macrocyclic polyethers, 18C6 was used for the extraction of bismuth. A 0.05M of 18C6 in dichloroethane extracted it from 1M sulphuric acid containing 0.75M potassium iodide¹. The macrobicyclic polyethers are potential extractant for p-block metals but were never explored for extraction of bismuth². So also were the aza and thia crown ethers, proved poor extractants however calix(6)arene derivative proved to be promising extractant for bismuth. With hexaacetyl calix(6)arene, palladium³, iron⁴, cobalt⁵ were quantitatively extracted. Calixarenes have distinct advantage over macrocyclic polyethers for several reasons. Their capacity for complexation can be altered by effective substitution of upper rim with sulphato or lower rim with keto or acetyl group to render them water soluble. The cavity size for encapsulation of metal can be further enlarged by varying number of phenyl rings during synthesis of various homologues. The selection of optimum acidity for extraction renders the method useful. A new method is therefore proposed for bismuth. The extraction of bismuth from 0.1M hydrochloric acid with 0.0001M hexaacetyl calixarene followed by stripping with 2M nitric acid and determination of its thiourea complex at 470 nm is described in this paper. The method permitted separation of bismuth from large number of elements associated with it in industrial products and pharmaceutical preparations.

Experimental Procedure

A Jasco V-530 UV-Visible spectrophotometer with matched 10 mm quartz cuvetts and a digital pH

meter (Elico Pvt. Ltd. India, LI-120) with combined calomel and glass electrodes were used.

A stock solution of bismuth(III) was prepared by dissolving 0.580 g of bismuth nitrate in 250 mL of distilled water containing 0.1% acid. The solution was standardized complexometrically⁶ using xylenol orange as metallochromic indicator. The solution contained 1000 μ g /mL of bismuth(III). The diluted solution containing 100 μ g /mL of bismuth(III) was prepared by ten fold dilution of the stock solution. Hexaacetato *p*-tertiary butyl calix(6)arene was synthesized as per the procedure reported earlier⁵. 0.0001M solution of reagent in toluene and 12% aqueous solution of thiourea (A.R. grade) were used.

An aliquot of solution containing bismuth(III) (100 μ g) was taken. To this solution concentrated hydrochloric acid was added so as to have its concentration 0.1M in a total volume of 10 mL. It was then transferred into a separatory funnel and 10 mL, 0.0001M of hexaacetato calix(6)arene in toluene was added to it. The solution was then shaken for about three minutes. The two phases were allowed to settle and separate. The organic phase was carefully withdrawn and was once again shaken with 10 mL of 2M nitric acid to strip out bismuth. From this stripped solution bismuth was determined spectrophotometrically at 470 nm⁷ as its complex with thiourea against the reagent blank. The concentration of bismuth(III) was calculated from the calibration curve.

Results and Discussion

Extraction as the function of hydrochloric acid concentration-To ascertain optimum acidity for

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Table 1—Extraction of bismuth as the function of the hydrochloric acid

[HCl], M	%E	D
0.001	64.5	1.81
0.002	79.6	3.90
0.005	85.2	5.75
0.007	90.4	9.41
0.010	99.6	249
0.025	99.6	249
0.075	99.6	249
0.10	99.6	249
0.25	97.4	37.4
0.50	81.5	4.40

Table 2—Extraction of bismuth as the function of calixarene concentration

[Hexaacetyl calix(6)arene] 1×10^{-5} M	Extraction %E	Distribution ratio (D)
0.75	19.1	0.23
1.0	35.1	0.54
2.0	79.6	3.90
3.0	92.8	12.88
4.0	96.7	29.30
5.0	98.3	57.82
7.5	98.9	89.90
10-50	99.6	249

extraction, bismuth was extracted from 0.001M to 0.5 M hydrochloric acid. The extraction commenced at 0.005M (85.2%) while at 0.007M (90.4%), there was quantitative extraction from 0.01M to 0.1M hydrochloric acid concentration. The extraction showed decrease in magnitude beyond this acidity. Therefore for all practical purposes 0.1M hydrochloric acid was used for extraction of bismuth. In fact there was no apparent precipitation of oxychloride at this acidity, and as such the complex was quite stable (Table 1).

Effect of reagent concentration—Bismuth(III) was extracted from 0.1M hydrochloric acid with varying concentrations of hexaacetato calix(6)arene ranging from 0.0000075-0.0005M. The extraction was 79.6% with 0.00002M, 98.9% with 0.000075M and was quantitative at 0.0001M of the reagent. Hence 0.0001M of extractant was used for routine work. The application of high reagent concentration was not advisable, as there was no marked increase in the extraction of bismuth (Table 2).

Effect of diluents—Various polar and nonpolar solvents with varying dielectric constants were tested

Table 3—Extraction of bismuth with various diluents

Diluent	Dielectric constant	Extraction %E	Distribution ratio
Benzene	2.28	99.6	249
Xylene	2.38	99.6	249
Toluene	2.30	99.6	249
Carbon tetrachloride	2.24	99.6	249
Chloroform	4.80	89.4	8.43
Cyclohexane	2.00	91.2	10.36
Methylene chloride	9.08	60.5	1.53
Ethylene chloride	10.50	99.6	249

Table 4—Effect of stripping agents

Acid Molarity (M)	Extraction (% E)				
	0.5	1.0	2.0	3.0	4.0
HCl	96.4	99.6	99.6	82.5	61.7
HNO ₃	69.9	85.2	99.6	92.8	79.6
H ₂ SO ₄	79.6	92.8	99.6	88.2	80.1
HClO ₄	11.2	7.5	0.006	0.00	0.00
CH ₃ COOH	49.2	60.5	71.2	61.7	99.6

as the diluents. The extraction was more than 80% with chloroform, methylene chloride, cyclohexane while with benzene, toluene, xylene, carbon tetrachloride and ethylene chloride the extraction was quantitative. Toluene was used as the diluent as it not only facilitated clear-cut phase separation but it was less toxic in comparison to other diluents (Table 3).

Effect of stripping agents—After extraction of bismuth from 0.1M hydrochloric acid it was stripped with various mineral acids in varying concentrations from 0.5-4M. With 2M nitric, sulphuric or hydrochloric or 4M acetic acid the stripping was complete. Therefore for routine work 2M nitric acid was used as the stripping agent. It also facilitated spectrophotometric determination of bismuth (III) with thiourea⁷ (Table 4).

Period of equilibration—The extraction of bismuth(III) was carried out with varying periods of shaking ranging from 1-15 min. The extraction was quantitative within two minutes period of equilibration. The solution was therefore shaken for three minutes to achieve quantitative extraction.

Nature of extracted species—The composition of extracted species was ascertained as usual from the plot of $\log D$ versus $\log[\text{calixarene}]$ at fixed hydrochloric acid concentration. Since the slope was 2.87 the probable composition of extracted species is $[\text{Bi}(\text{calixarene})_3]$. The stereochemistry of the

Table 5—Effect of diverse ions, Bi=100 μ g

S N	Foreign ions	Amount taken (μ g)	Tolerance ratio
1	As ³⁺ , Sn ⁴⁺ , Sb ³⁺	Zero	Interference
2	Pd ²⁺ , Co ²⁺ , Ni ²⁺ , Tl ⁺ , Ag ⁺ , Au ³⁺	1000	1:10
3	Mg ²⁺ , Ca ²⁺ , Pb ²⁺ , Cu ²⁺ , Zn ²⁺ , Cr ³⁺ , Mn ²⁺	1200	1:12
4	Na ⁺ , K ⁺ , Li ⁺ , Cs ⁺ , Fe ³⁺ , Th ⁴⁺ , UO ₂ ²⁺	1500	1:15
5	Cl ⁻ , I ⁻ , Br ⁻ , SO ₄ ²⁻ , SO ₃ ²⁻ , NO ₃ ⁻ , NO ₂ ⁻	2000	1:20

Table 6—Separation from multicomponent mixtures

SN	Mixture	Concentration (μ g)	pH / [H ⁺] for extraction	Stripping agent (M)	% recovery
1	Th ⁴⁺	50	7.5	0.005M H ₂ SO ₄	98.6
	Tl ³⁺	50	3.0	2M HClO ₄	99.5
	Bi ³⁺	100	0.1M HCl	2M HNO ₃	99.6
2	Th ⁴⁺	50	7.5	0.005M H ₂ SO ₄	98.6
	Mn ²⁺	100	6.0	0.1M CH ₃ COOH	96.4
	Bi ³⁺	100	0.1M HCl	2M HNO ₃	99.6
3	Th ⁴⁺	50	7.5	0.005M H ₂ SO ₄	98.6
	Fe ³⁺	30	7.0	1M HNO ₃	99.6
	Bi ³⁺	100	0.1M HCl	2M HNO ₃	99.6
4	Th ⁴⁺	50	7.5	0.005M H ₂ SO ₄	98.6
	Mn ²⁺	100	6.0	0.1M CH ₃ COOH	96.4
	Fe ³⁺	30	7.0	1M HNO ₃	99.6
	Bi ³⁺	100	0.1M HCl	2M HNO ₃	99.6

complex is same as described earlier³. This complex involved no true covalent bond, but bismuth is expected to get encapsulated within calix(6)arene, cavity or annular space.

Separation from binary mixture—Bismuth(III) was extracted in the presence of several elements in binary mixture of ions (Table 5). The tolerance limit was set as the amount of foreign ion causing an error of \pm 1.2%. The common anions were tolerated in the ratio of 1:20, while alkali and alkaline earths were tolerated in the ratio 1:10, while p-block metals were tolerated in smaller proportions. However tin(IV), antimony(III) and arsenic(III) showed strong interference.

Separation of bismuth from multicomponent mixture—The difference in the acidity of extraction of bismuth as well as the kind of the stripping agents used for different elements was exploited to devise novel method of separation of many elements from the multicomponent mixtures. The advantage of

difference in stability of the complex was also taken in consideration. Some complexes were less stable while others were more stable. The weak complexes were therefore first stripped with dilute stripping agents, followed by stripping of other ions. The mixture of thorium, thallium and bismuth after extraction was resolved by stripping thorium with 0.005M sulphuric acid, thallium with 2M perchloric acid and bismuth with 2M nitric acid. The mixture of thorium(IV), manganese(II) and bismuth(III) was separated by stripping thorium with 0.005M sulphuric acid, manganese with 0.1M acetic acid and finally bismuth with 2M nitric acid.

After coextraction of thorium(IV), iron(III) and bismuth(III), thorium was stripped with 0.005M sulphuric acid, iron with 1M nitric acid and bismuth with 2M nitric acid.

Finally the quaternary mixture of thorium, manganese, iron and bismuth was isolated by stripping thorium with 0.005M sulphuric acid,

manganese with 0.1M acetic acid, iron with 1M nitric acid and bismuth with 2M nitric acid. The various separations are described in Table 6.

Analysis of bismuth(III) from pharmaceutical preparation—The sample of denol tablet was dissolved in 10mL hydrochloric acid. The solution was evaporated almost to dryness. It was laxivated with water and solution was made up to 500mL. An aliquot of solution was taken from which bismuth(III) was extracted and analysed as per general procedure. The amount of bismuth determined was comparable to the standard value of bismuth.

The proposed method is simple, rapid and selective. It permits separation and determination of bismuth from thallium, thorium, manganese, iron which are generally associated in just half an hour. The method is reproducible and relative standard deviation is $\pm 1.2\%$. As little as $10\mu\text{g/ml}$ of bismuth can be analyzed by proposed method. The method is

applicable to the real sample like pharmaceutical preparations.

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References

- 1 Vibhute R G & Khopkar S M, *Bull Bis Institute*, 55 (1998) 5.
- 2 Khopkar S M, *Analytical chemistry of macrocyclic and supramolecular compounds* (Narosa Publishing Co., New Delhi), 1999 (in press).
- 3 Mathew V J & Khopkar S M, *Talanta*, 45 (1997) 1697.
- 4 Khandwe R M & Khopkar S M, *Talanta*, 46 (1998) 521.
- 5 Gupta A & Khopkar S M, *Talanta*, 42 (1995) 1493.
- 6 Vogel A I, *Quantitative Inorganic Analysis*, 3rd edn (Wiley, New York), 1962.
- 7 Snell F D, *Photometric and Fluorimetric methods of analysis* (Wiley, New York), 1978.