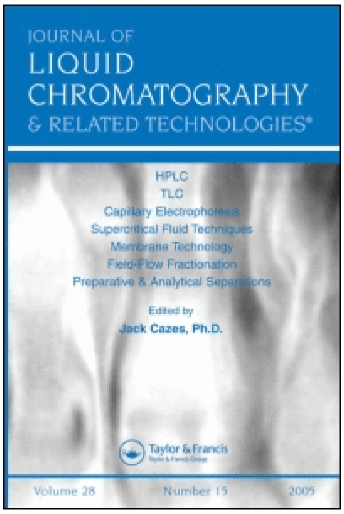

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REVERSED PHASE EXTRACTION CHROMATOGRAPHIC SEPARATION OF ANTIMONY(III) WITH TRIOCTYL PHOSPHINE OXIDE

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ABSTRACT

Antimony(III) was separated by extraction chromatography with trioctyl phosphine oxide as stationary phase on column of silica gel with 0.5 M hydrochloric acid as the mobile phase. It was stripped with 3 M hydrochloric acid. Antimony(III) was separated from large number of elements belonging to alkali and alkaline earths, transition and main groups in binary mixtures by selective extraction. It was possible to separate antimony(III) in multicomponent mixtures by exploiting differences in acidities at which various elements were eluted. The method was extended for the analysis of antimony from solder and brass.

INTRODUCTION

Although there are several methods for the extraction chromatographic separation of antimony from fission product elements, very few methods are available for the separation of antimony from commonly associated elements.

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Antimony was separated from lead by extraction chromatography utilizing tributyl phosphate (1) as the stationary phase. It was separated from indium with tributyl phosphate (2) from the chloride media. Antimony was separated from tin on silica gel coated with tributyl phosphate from hydrochloric acid (3). It was also separated from tin on Teflon-6 column with methyl isobutyl ketone as an extractant (4). Amberlite LA-2 was also utilized for the extraction chromatographic separation of antimony from tin (5). Antimony was separated from gold and thallium on cellulose column with trioctyl phosphine oxide as an extractant (6). It was also separated from arsenic on cellulose column coated with trioctyl phosphine oxide (7). However such a separation was possible from higher concentration of hydrochloric acid (1). The separation of antimony from indium was feasible by extraction chromatography with tributyl phosphate and acetylacetone (2). The separation of antimony and tin in tributyl phosphate was feasible from 11 M hydrochloric acid (3). The separation of tin from antimony on Teflon 6 column was not practicable as the extractant was stripped off (4). The systematic investigations on the reversed phase extraction chromatographic separation of antimony with trioctyl phosphine oxide as stationary phase are lacking. An endeavour is made in this paper to present such studies. The methods are given for the separation of antimony from binary and multicomponent mixtures with which it is commonly associated.

EXPERIMENTAL

Apparatus and reagents

The apparatus and chromatographic column was similar to the one described earlier (8).

The stock solution of antimony(III) was prepared by dissolving 2.11 g antimony(III) chloride (BDH AnalaR) in 25 ml of concentrated hydrochloric acid. It was then made upto 250 ml with distilled water. The solution on standardisation with chloramine T (9) contained 4.5 mg/ml of antimony(III). The diluted solution containing 60 µg/ml was prepared by appropriate dilution.

Silica gel (60-120 mesh BDH) was rendered hydrophobic by exposing it to the vapours of dimethyl dichlorosilane in an atmosphere of nitrogen for about three hours (10), then washed with anhydrous methanol and dried at 100°C. One ml of dimethyl dichlorosilane is adequate for 10 g of silica gel. Three grams of this gel was soaked in 5 ml of 0.1 M trioctyl phosphine oxide in toluene for 24 hrs. It was then centrifuged to obtain slurry of gel in water and packed in the column. The chromatographic column (0.8 x 20 cms) consisted of a pyrex tube fitted with glass wool plug at the bottom. The bed height of the column used was 8 cms. The bed was covered with opaque paper to avoid photochemical degradation of the extractant.

General procedure

An aliquot of solution containing 60 µg of antimony(III) was made to 0.5 M in hydrochloric acid in total volume of

2 ml. The solution was then passed through the column at the flow rate of 1 ml/min. Antimony which was extracted by trioctyl phosphine oxide on column, was stripped with various mineral acids and salts as eluants. Twenty fractions, each of 2 ml, were collected and subsequently analysed for antimony spectrophotometrically as its complex with phenylfluorone at 555 nm (11).

RESULTS AND DISCUSSION

In batch extraction antimony(III) was quantitatively extracted from 2-4 M hydrochloric acid with 0.1 M trioctyl phosphine oxide in cyclohexane (12), whereas antimony(V) was extracted from 8-10 M hydrochloric acid. However, it was possible to lower down the acidity to 0.5 M hydrochloric acid for the quantitative extraction of antimony(III) in the presence of aluminium trichloride as the salting out agent. The systematic studies of antimony(III) on the column with 0.25 to 4 M hydrochloric acid revealed that antimony was quantitatively extracted between 0.25 to 0.75 M hydrochloric acid. The ion association species of antimony(III) with trioctyl phosphine oxide and hydrochloric acid was dissociated at 1-4 M of hydrochloric acid. Therefore it was stripped off the column. Hence the optimum conditions for the extraction of antimony(III) was 0.5 M hydrochloric acid.

The systematic studies on the stripping of antimony were carried out with various eluants. 1-6 M of hydrochloric and nitric acid or 1-4 M of sulphuric acid quantitatively

TABLE - 1

Studies on Stripping of Antimony(III)

Eluant	Molarity (M)	V_{max} ml	V_t ml	% Recovery
HCl	1	12	24	100.8
	2-4	6	18	99.2
	5-6	4	14	99.5
HNO_3	1	14	20	99.2
	2	10	18	99.5
	3-5	6	14	100.8
	6	4	14	99.7
H_2SO_4	1-4	6	14	99.2

stripped off antimony(III) (Table 1). Although sulphuric acid was the best stripping agent with minimum volume of elution, it was not preferred as an eluant on account of problems encountered in the direct spectrophotometric determination of antimony. For almost similar reasons nitric acid was not preferred. The choice of was thus confined to 3 M hydrochloric acid as the eluting agent. All the salts proved to be poor eluting agents.

Separation of antimony(III) from binary mixtures

When antimony(III) was extracted at 0.5 M hydrochloric acid from column coated with 0.1 M trioctyl phosphine oxide foreign elements such as alkali and alkaline earths, transition and main group elements were not extracted by trioctyl phosphine oxide and therefore passed through the column (Table 2). Antimony(III) which was extracted on the column was later stripped with 3 M hydrochloric acid. It was possible to separate antimony(III) from commonly associated elements such as arsenic, lead, tellurium, rubidium etc. in binary mixtures in the concentration range of 1:100.

Separation of antimony(III) from multicomponent mixtures

It was interesting to note that various metals were extracted at various acidities with appropriate diluent(13). Thus bismuth, antimony(III), and tin were quantitatively extracted by trioctyl phosphine oxide from 0.5 M hydrochloric acid, whereas the metals such as tin, molybdenum(VI), chromium(VI) and gold were extracted with trioctyl phosphine oxide from 3 M hydrochloric acid. The elements such as copper, iron, titanium were extracted from 7-8 M hydrochloric acid. Thus it was possible to exploit the differences in acidities for extraction to develop the methods for separation. For instance, the metals which were not extracted from 0.5 M hydrochloric acid such as copper, arsenic, gallium, tellurium, lead, aluminium, zinc, germanium were stripped at this acidity, The extracted tin and gold were stripped off with 2 and 7 M nitric acid respectively. Thus the separation of antimony in multicomponent mixtures could be achieved by selective extraction and selective stripping of the extracted species on the column.

TABLE - 2

Separation of Antimony(III) from Binary Mixtures

Antimony(III) - 60 μg

Foreign ion	Foreign ion taken mg	Antimony found μg	Antimony recovery %
Li	10.6	60.5	100.8
Na	10.1	59.5	99.2
K	7.9	59.2	98.7
Rb	6.1	60.2	100.3
Be	9.5	59.7	99.5
Mg	8.4	59.7	99.5
Ca	9.6	59.5	99.2
Sr	9.8	59.2	98.7
Sc	10.6	60.2	100.3
Y	5.8	59.2	98.7
Ti	7.3	59.5	99.2
Th	8.7	59.5	99.2
V(IV or V)	6.9	60.5	100.8
Cr(III)	9.4	59.7	99.5
Mn	8.5	60.5	100.8
Fe(III)	10.5	59.7	99.5
Co	7.8	59.5	99.2
Ni	7.5	59.2	98.7
Pt	5.6	60.5	100.8
Cu	9.9	60.2	100.3
Cd	8.2	59.7	99.5
Al	10.4	59.7	99.5
As(III)	9.8	59.5	99.2
Pb	5.5	60.5	100.8
Se(IV)	9.0	60.2	100.3
Te(IV)	10.0	60.2	100.3

TABLE - 3

Separation of Antimony(III) from Multicomponent Mixtures

Element	Taken µg	Found µg	% Recovery	Eluant	Volume of eluant
1 Cu/As(III)	50	49.5	99	0.5 M HCl	8
Sb(III)	60	60.5	100.6	3 M HCl	14
Sn(IV)	59	59.2	100.3	2 M HNO_3	10
2 Al	70	71	101.4	0.5 M HCl	8
Sb(III)	60	59.5	99.2	3 M HCl	14
Au(III)	100	101	101	7 M HNO_3	10
3 Pb/Ga	75	76	101.3	0.5 M HCl	8
Sb(III)	60	59.7	99.5	3 M HCl	14
Mo(VI)	59	58.6	99.3	0.1 M HCl	16
4 Te(IV)	50	49.7	99.4	0.5 M HCl +1 M LiCl	8
Sb(III)	60	60.5	100.8	3 M HCl	14
In	75	74.1	98.8	0.1 M HCl	20
5 Zn	54	53.6	99.3	0.5 M HCl	8
Sb(III)	60	60	100	3 M HCl	14
Mo(VI)	50	49.5	99	0.1 M HCl	16
Cr(VI)	51	50	98	H_2O	22
6 Ge	22	21.8	99.1	0.75 M HCl + 2 M LiCl	8
Sb(III)	60	59.7	99.5	3 M HCl	14
Fe(III)	62.5	63	100.8	0.25 M HCl	16
Sn(IV)	59	60	101	2 M HNO_3	10
Au(III)	100	100.5	100.5	7 M HNO_3	10

The mixture of copper/arsenic(III), antimony(III) and tin(IV) in 0.5 M hydrochloric acid was passed through the column. As copper or arsenic(III) was not extracted by trioctyl phosphine oxide at this acidity they passed through the column. Antimony(III) and tin(IV) which were extracted, were eluted with 3 M hydrochloric acid and 2 M nitric acid respectively.

The mixture containing aluminium, antimony(III) and gold was passed on the column from 0.5 M hydrochloric acid when aluminium was not extracted and it passed through the column. The extracted antimony(III) was stripped with 3 M hydrochloric acid and gold with 7 M nitric acid.

The mixture containing lead, antimony(III) and molybdenum(VI) was made to 0.5 M hydrochloric acid and was passed on the column when lead was not extracted. The extracted antimony(III) and molybdenum(VI) were stripped with 3 M and 0.1 M hydrochloric acids respectively.

The mixture containing tellurium(IV), antimony(III) and indium was passed on the column from 0.5 M hydrochloric acid containing 1 M lithium chloride, when tellurium(IV) passed out as it was not extracted. Antimony(III) was then stripped with 3 M hydrochloric acid while extracted indium was stripped with 0.1 M hydrochloric acid.

The mixture of zinc, antimony(III), molybdenum(VI) and chromium(VI) in 0.5 M hydrochloric acid was passed through the column. Zinc was not extracted and hence it was washed with 0.5 M hydrochloric acid. The extracted antimony(III) was stripped with 3 M hydrochloric acid, molybdenum(VI) with 0.1 M hydrochloric acid and chromium(VI) with water.

The mixture of germanium, antimony(III), iron(III), tin(IV) and gold(III) was made to 0.75 M hydrochloric acid containing 2 M lithium chloride and was passed on the column when germanium was not extracted. Antimony(III) was stripped off with 3 M hydrochloric acid while iron(III), tin(IV) and gold(III) were retained on the column. They were when successively stripped with 0.25 M hydrochloric acid, 2 M nitric acid and 7 M nitric acid respectively.

Throughout the above separations, flow rate was maintained at 1 ml/min. All the elements after separation were determined spectrophotometrically with appropriate chelating ligands (14).

The method was extended for the analysis of antimony from solder and brass.

Separation of antimony from solder

About 0.1 g of the alloy was dissolved in concentrated hydrochloric acid. The solution was evaporated nearly to dryness and then made up to 500 ml containing 2% hydrochloric acid. An aliquot of solution containing tin, lead and antimony was passed on the column from 0.5 M hydrochloric acid. Since lead was not extracted at this acidity it passed through whereas tin and antimony were both extracted. Antimony was then stripped with 3 M hydrochloric acid followed by elution of tin with 2 M nitric acid. From the effluent lot antimony was determined spectrophotometrically. The amount of antimony was 4.52% against certificate value of 4.5%.

Separation of antimony from brass

About 0.2 g of the alloy was dissolved in concentrated hydrochloric acid. The solution was evaporated almost to dryness and extracted with water containing 2% hydrochloric acid and it was made up to 100 ml. An aliquot of solution containing copper, zinc, lead, tin and antimony was passed from 0.5 M hydrochloric acid on the column. Copper, zinc and lead were not extracted and they passed through the column leaving tin and antimony on the column. Antimony was then eluted with 3 M hydrochloric acid and tin with 2 M nitric acid. The amount of antimony was 0.1% against certificate value of 0.11%.

The separation of antimony from tin, lead, tellurium, copper, arsenic, aluminium is important as they are associated with it in various low fusible alloys. It was not possible to separate antimony from bismuth as both had identical conditions of extraction. The separation of antimony from copper, cadmium, arsenic, lead and tin is useful as they belong to the same group in qualitative analysis. The total time required for the separation and determination is 2 hrs. The results are reproducible.

REFERENCES

1. I. Akaza, T. Tajima and T. Kiba, Bull. Chem. Soc. Japan, 46, 1199 (1973).
2. I.P. Alimarin, T.A. Bolshova and G.A. Bakhareva, Zh. Anal. Khim., 28, 1300 (1973).
3. J. Mikulski and I. Stronski, Nukleonika, 6, 775 (1961).

4. G. Latwessen, Ph.D. Thesis, Iowa State University, IS-T-116 (1966).

5. I. Stronski, Radiochem. Radioanal. Letters, 5, 113 (1970).

6. J. Blouri and G. Revel, J. Radional. Chem., 10, 121 (1972).

7. E. Cerrai and C. Testa, Energia Nucleare, 8, 510 (1961).

8. R.B. Heddur and S.M. Khopkar, The Bull. of Bismuth Institute, 38, 6 (1982).

9. A.I. Vogel, 'Quantitative Inorganic Analysis', Longmann, London, 392 (1962).

10. E. Cerrai and G. Ghersini, Advances in Chromatography, 9, 60, 150 (1970).

11. S.G. Iyer, B.V. Kadam and Ch. Venkateshwarlu, Indian J. Chem., 11, 385 (1973).

12. J.C. White and W.J. Ross, U.S.A.E.C. Report, NAS-NS 3102 (1961), AA 1104, 9 (1962).

13. A.K. De, S.M. Khopkar and R.A. Chalmers, 'Solvent Extraction of Metals', Van Nostrand Reinhold, London (1970).

14. F.D. Snell, 'Photometric and Fluorometric Methods of Analysis', Wiley and Sons, New York (1978).