

Selective liquid-liquid extraction of antimony(III) from hydrochloric acid media by *N-n*-octylaniline in xylene

B. M. SARGAR, M. M. RAJMANE and M. A. ANUSE

*Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur-416 004, India
(e-mail: maanuse@rediffmail.com)*

(Received 2 June 2003)

Abstract: *N-n*-Octylaniline in xylene was used for the extraction separation of antimony(III) from hydrochloric acid media. Antimony(III) was extracted quantitatively with 10 mL 4 % *N-n*-octylaniline in xylene. It was stripped from the organic phase with 0.5 M ammonia and estimated photometrically by the iodide method. The effect of metal ion, acid, reagent concentration and various foreign ions was investigated. The method affords binary and ternary separation of antimony(III) from tellurium(IV), selenium(IV), lead(II), bismuth(III), tin(IV), germanium(IV), copper(II), gold(III), iron(III) and zinc(II). The method is applicable for the analysis of synthetic mixtures, alloys and semiconductor thin films. It is fast, accurate and precise.

Keywords: antimony(III), *N-n*-octylaniline, solvent extraction.

INTRODUCTION

Antimony it is commonly found in copper, silver and lead ores. The abundance of antimony in the earth's crust is 0.20 ppm.

Antimony and its compounds are industrially important because of their usefulness in the manufacture of alloys, paints, paper, plastics, textiles, glass, clay products and rubber. In recent years high purity antimony has been used in the production of the semiconductor compound indium antimonide and in the formulation of bismuth telluride type compound used for thermoelectric applications.

The determination of antimony species is fundamental in environmental and clinical studies because of its implications for human health. Also its toxicity and biological behaviour depend on its oxidation state. Although antimony is a potentially significant element for plants, it does not have any known essential function in animals. On the contrary, its toxicity has been demonstrated. However, a systemic antimonial therapy is still recommended for multiple lesions caused by human leishmaniasis (kala azar or black fever) disease. As pentavalent antimonials are much less toxic than the trivalent antimonials, they are used for this type of

therapy. Hence the separation and determination of antimony(III) is of analytical importance.

High molecular weight amines (HMWA) have been used for the extraction of antimony(III). The bromo complex of antimony(III) was extracted with 3 % trioctylamine in isobutyl methyl ketone (MIBK)¹ and determined by the AAS technique. The extractability of antimony(III) and (V) with tridodecylamine from various aqueous solutions has been reported.² It was found that a high concentration of acid was required for extraction. Antimony(III) and (V) were quantitatively extracted with 1 % capriquat in xylene from 0.1 M potassium iodide and 0.5 M sulphuric acid solution. This method was applied for the determination of antimony from plant materials.³ Octyltrimethylammonium chloride in chloroform was used for the extraction of antimony(V). A metal:ligand ratio of 1:1 was investigated.⁴ LIX 1104 SM reagent was found to be an effective extractant for antimony(III) from sulphuric acid solution.⁵ The extraction reaction was exothermic. The co-extraction of arsenic and iron were minimized by high antimony loading in the organic phase.

Various organophosphorus compounds have been found to be sensitive for the extraction of antimony(III). Antimony(III) was selectively extracted from halide solutions into tris-(2-ethylhexyl) phosphate dissolved in xylene.⁶ This method was applied for the separation of antimony(III) from lead, gold, tellurium in the analysis of real samples. The solvent extraction and ion exchange methods were used for the removal of antimony from copper sulfate-sulfuric acid solution using 2EHAP₄ as the extractant.⁷ Bismuth and arsenic were separated from antimony by using LIX 1104 SM, 2EHAP₄, tributyl phosphate(TBP), DPPP, DBBP, KELEX 100. The methods were employed for the analysis of copper refinery electrolytes.⁸ The solvent extraction of antimony(III) from aqueous hydrochloric acid by bis-(2,4,4-trimethylpentyl) phosphinodithioic acid (cyanex 301) in kerosene + 10 % (v/v) *n*-decanol was investigated.⁹ Quantitative extraction of antimony(III) was observed in 0.1–1.0 M sulfuric acid and 0.1–2.0 M hydrochloric acid with 8.5×10^{-2} M Cyanex 302 in toluene.¹⁰ This method was successfully applied to a real sample. A review of the extractants used for the recovery of antimony from copper electrolyte has been presented. The extractants used for this process were TBP, an ester of phosphoric acid, mono-(2-ethylhexyl) phosphoric acid, D2EHPA acid and mono-(iso-octadecyl) phosphoric acid, DS-5834, esters of alkylphosphonic acids, trialkylphosphine oxide, Cyanex 923, hydroxamic acids, LIX 1104, alcohols (2-ethylhexanol and others), hydrophobic diols and alkylpolyphenols.¹¹ 2-Ethylhexyl-phosphonic acid mono-2-ethylhexyl ester was used as an extractant for antimony(III) from 0.1 M hydrochloric acid media.^{12,13} The method was applied for the separation of metal ions from commonly associated ions and real samples. The solvent extraction of antimony(III) from aqueous acid media was investigated using tri-*n*-octylphosphine oxide (TOPO) in toluene.¹⁴ However EDTA, Te(IV), Sn(II) interfered. Triphenylphosphine oxide (TPPO) in toluene was used for the extraction of

antimony(III) from 2–2.5 M hydrochloric acid media.¹⁵ Tellurium(VI), Sn(II) and EDTA interfered.

Ethyl ether,¹⁶ diisopropyl ether¹⁶ and ethyl acetate¹⁷ were used as extractants for antimony(V) from hydrochloric acid solution. Under these conditions, Fe(III) was co-extracted, while Sn(II), Cd(II) and Co(II) were moderately extracted.

A novel extractant, *N-n*-octylaniline, has been used in our Laboratory as an extractant for the extraction separation of some platinum group metals (PGMs).^{18–21} An extension of this work has shown that *N-n*-octylaniline could also be used for the extraction separation of antimony(III) from chloride media. This method is rapid and provides separation of antimony(III) from tellurium(IV), selenium(IV), lead(II), bismuth(IV), tin(IV), germanium(IV), copper(II), gold(III), iron(III) and zinc(II).

EXPERIMENTAL

Apparatus

An Elico digital spectrophotometer (model SL-171) with 1 cm quartz cells was used for the absorbance measurements. pH measurements were carried out using a Elico digital pH meter model LI-120.

Reagents

Antimony(III) solution. A stock solution was prepared by dissolving 0.468 g of pure (99.9 %) antimony trichloride (s.d. Fine Chemical Ltd.) in 6 M hydrochloric acid and diluting to 250 mL in a standard flask to give 1 mg/mL Sb(III) concentration. The solution was standardized volumetrically using the potassium bromate method.²² The working solution was prepared by appropriate dilution of the stock solution with 0.1 M hydrochloric acid.

N-n-octylaniline. A 4 % (v/v) solution of *N-n*-octylaniline²³ dissolved in xylene was used as an extractant.

Potassium iodide (40 % solution). Potassium iodide (40 g) was dissolved in 100 mL distilled water.

Ascorbic acid (2 % solution). Ascorbic acid (2 g) was dissolved in 100 mL distilled water.

Sulphuric acid (1:1). An equimolar concentration of sulphuric acid and water was prepared.

General extraction procedure

An aliquot of a solution containing antimony(III) (300 µg) was pipetted into a 25 mL volumetric flask. To this, a sufficient amount of concentrated hydrochloric acid was added to give a final acid concentration of 3.0 M. The final volume of the solution was made up to 25 mL with distilled water. Then the solution was transferred to a 125 mL separating funnel. Then 10 mL of 4 % *N-n*-octylaniline in xylene was added and the mixture was shaken for 1 min. The two layers were allowed to separate and the aqueous layer was discarded. Antimony(III) from the organic phase was stripped with two 10 mL portions of 0.5 M ammonia. Antimony(III) from the aqueous phase was determined spectrophotometrically as its complex with iodide²⁴ at 425 nm. The amount of antimony(III) was computed from the calibration curve.

RESULTS AND DISCUSSION

Effect of acidity

The extraction of 300 µg of antimony(III) was carried out from different acid media with 4 % *N-n*-octylaniline in xylene keeping the aqueous to organic volume ratio constant at 2.5:1. The extraction was found to be quantitative from 2.5 to 4 M hydrochloric acid but on increasing the concentration of hydrochloric acid further,

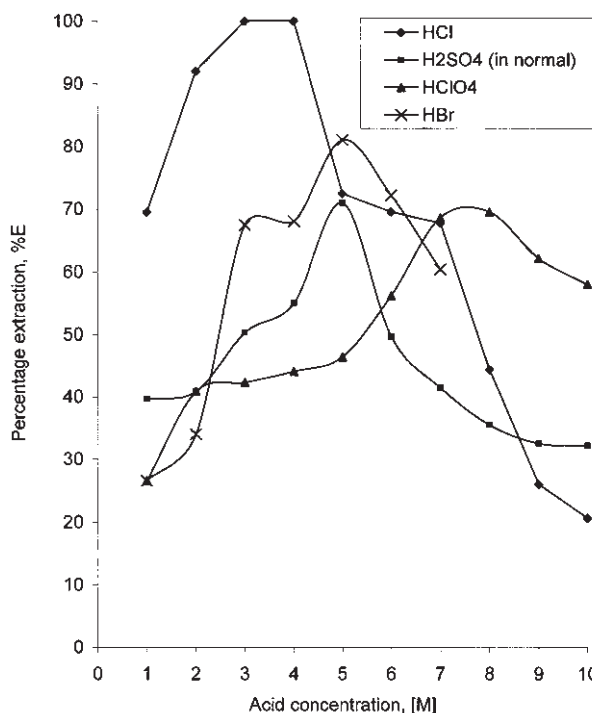


Fig. 1. Extraction of Sb(III) with 4% *N-n*-octylaniline in xylene as a function of acid concentration, Sb(III) = 300 μ g.

the percentage extraction of antimony was found to decrease (Fig. 1). Moreover, the extraction from sulfuric acid (71.00 %), perchloric acid (69.52 %), hydrobromic acid (81.06 %) were incomplete and from nitric acid medium emulsion formation was observed.

Extraction as a function of N-n-octylaniline concentration

Antimony(III) was extracted over the acidity range 0.5–10 M hydrochloric acid with various concentrations of *N-n*-octylaniline. The reagent concentration was varied from 0.1 to 4 % (Table I). It was found that 4 % *N-n*-octylaniline in xylene was needed for quantitative extraction of metal ion from 2.5 M hydrochloric acid.

Time of equilibration

Variation of the shaking period from 5 s to 20 min showed that an equilibration time of 15 s was adequate for quantitative extraction of antimony(III) from hydrochloric acid media. It was found that the time required for extraction and back extraction of antimony(III) is not specific. In the general procedure, a 1 min equilibration time was recommended in order to ensure complete extraction of the metal ions from hydrochloric acid medium. However, prolonged shaking upto 20 min had no adverse effect on the extraction.

Effect of stripping agent

Various stripping agents, such as ammonia, sodium hydroxide, potassium hydroxide, acetate buffer solution (pH 5.0), ammonia buffer solution (pH 10.0) perchloric acid and water, were used for the recovery of antimony(III) from the organic extract. It was found that, of all the solutions examined, only ammonia (0.3 to 1.0 M), sodium hydroxide (0.5 to 2.0 M) and potassium hydroxide (0.5 to 2.0 M) were effective in stripping antimony(III) from the organic layer. However, ammonia (0.5 M) is recommended as the stripping agent for antimony(III) because removal of ammonia by evaporation is easier than the removal of the other stripping agents before estimation by the iodide method.

TABLE I. Extraction behaviour of antimony(III) as a function of *N-n*-octylaniline concentration. Antimony(III) = 300 μ g; aqueous phase = 3.0 M HCl; Aq : Org = 25:10; strippant = 0.5 M NH₃; equilibration period = 1 min

[HCl]/M	<i>N-n</i> -octylaniline/%(v/v)	Percentage extraction/% <i>E</i>	Distribution ratio <i>D</i>
1	0.1	0.90	0.02
	0.3	0.31	0.033
	0.5	5.01	0.13
	0.7	13.03	0.37
	1.0	24.85	0.83
	2.0	42.30	1.83
	3.0	61.83	4.05
	4.0	69.52	5.70
2	0.1	2.66	0.07
	0.3	6.21	0.17
	0.5	14.20	0.41
	0.7	23.57	0.77
	1.0	37.84	1.52
	2.0	72.48	6.58
	3.0	92.01	28.79
	4.0	96.08	61.27
3	0.1	3.84	0.10
	0.3	8.57	0.23
	0.5	15.38	0.45
	0.7	21.00	0.66
	1.0	52.95	2.81
	2.0	76.03	7.93
	3.0	100.00	∞
	4.0	100.00	∞

TABLE I. Continued

[HCl]/M	<i>N-n</i> -octylaniline/%(v/v)	Percentage extraction/% <i>E</i>	Distribution ratio <i>D</i>
4	0.1	6.50	0.17
	0.3	9.76	0.27
	0.5	13.60	0.39
	0.7	19.82	0.62
	1.0	25.44	0.73
	2.0	43.78	1.95
	3.0	84.31	13.43
	4.0	100.00	∞
5	0.1	3.39	0.09
	0.3	4.28	0.11
	0.5	10.77	0.30
	0.7	17.95	0.54
	1.0	29.58	1.05
	2.0	62.14	4.10
	3.0	72.61	6.63
	4.0	87.50	17.50
6	0.1	10.94	0.31
	0.3	12.31	0.35
	0.5	34.31	1.31
	0.7	40.82	1.72
	1.0	46.74	2.19
	2.0	50.88	2.59
	3.0	55.02	3.06
	4.0	69.80	5.78

Extraction with various diluents

The suitability of several diluents, such as benzene, xylene, toluene, amyl alcohol, *n*-butanol, chloroform, carbon tetrachloride, amyl acetate, MIBK and ethylene chloride, for the extraction of antimony(III) from chloride medium using the proposed method was investigated. It was found that a 4 % (v/v) solution of *N-n*-octylaniline in benzene, xylene, toluene, carbon tetrachloride, MIBK, amyl acetate and ethylene chloride provides quantitative extraction of antimony(III), while the extraction of antimony(III) was incomplete in chloroform (69.5 %), amyl alcohol (71.6 %), *n*-butanol (63.0 %). The inert solvent xylene is preferred as the diluent, as it provides better phase separation and is less toxic than the other possible extractants.

TABLE II. Effect of foreign ions on the extractive determinatio of antimony(III). Sb(III) = 300 µg; aqueous phase = 3.0 M HCl; Aq : Org = 25 : 10; *N-n*-octylaniline = 4 % in xylene; equilibrium period = 1 min; strippant = 0.5 M NH₃

Tolerance limit/mg	Foreign ion added
500	Citrate; tartarate; malonate; acetate
400	Fluoride; thiosulphate
300	Oxalate; thiourea; nitrate
200	EDTA; ascirbate
100	Succinate; iodide
10	Cd(II); Mn(II); Bi(III); Mo(VI); Hg(II)
7	Pb(II); Sr(II); Al(III); Fe(III); Pd(II)
5	Zn(II); Hg(II); Ni(II); Sn(II); In(III); Tl(I); ^a Te(IV); ^a Se(IV); Be(II); Ge(IV) ^c ; Sn(IV) ^d
3	Cu(II); Mg(II); Ga(III); Au(III) ^b
1	Mn(VII); Fe(III)

^a Masked with 400 mg fluoride; ^b Masked with 400 mg thiocyanate; ^c Masked with 300 mg ascorbic acid; ^d Masked with 200 mg EDTA

Effect of aqueous to organic volume ratio on the extraction

Antimony(III) was extracted from 10 to 250 mL of aqueous 3 M hydrochloric acid medium with 10 mL of 4 % *N-n*-octylaniline in xylene. The antimony(III) was stripped with 0.5 M ammonia and estimated by the recommended procedure. It was found that the extraction of antimony(III) was quantitative when the aqueous to organic volume ratio was 1:1 to 10:1, while it decreased when the ratio was changed from 10:1 to 25:1. Hence, an aqueous to organic volume ratio of is 2.5:1 is recommended.

Loading capacity of N-n-octylaniline

The concentration of antimony(III) was varied to determine the loading capacity of *N-n*-octylaniline. The loading capacity of 10 mL of 4 % *N-n*-octylaniline was found to be 3.5 mg of antimony(III).

Nature of extracted species

The nature of extracted species was ascertained by plotting a graph of log $D_{[Sb(III)]}$ against log $c_{[N-n-octylaniline]}$ for 2.0 and 5.0 M hydrochloric acid media. The obtained slopes of 1.15 and 1.07, respectively, indicate that the metal to amine ratio in the extracted species is 1:1 (Fig. 2). A possible extraction mechanism appears to be protonation of *N-n*-octylaniline, whereby cationic species such as $[RR'NH_2^+]$ are formed while the chloride ions combine with antimony(III) to form

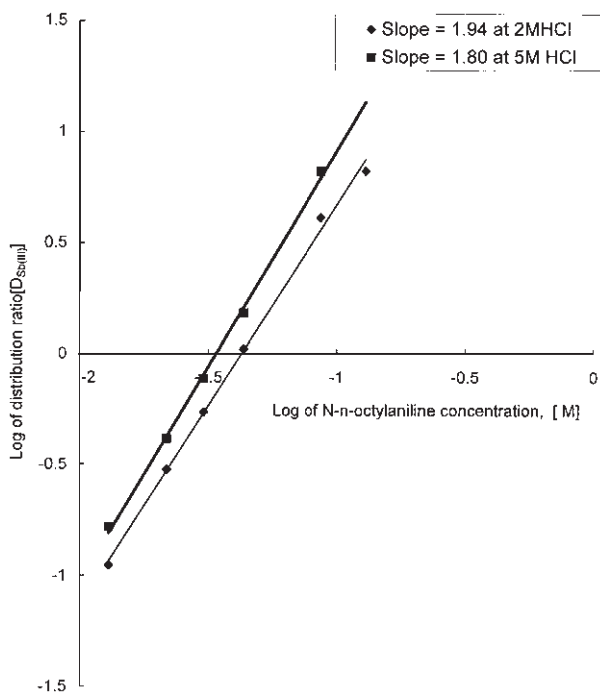


Fig. 2. Log-log plot of distribution ratio $[D_{\text{Sb(III)}}]$ as a function of *N-n*-octylaniline concentration using 2 M and 5 M HCl.

anionic species such as $[\text{SbCl}_4^-]$.²⁵ The probable extracted species is $[(\text{RR}'\text{NH}_2^+) \text{SbCl}_4^-]_{(\text{org})}$. The extraction mechanism can be explained as follows:



where, $\text{R} = -\text{C}_6\text{H}_5$ and $\text{R}' = -\text{CH}_2(\text{CH}_2)_6\text{CH}_3$.

Effect of foreign ions

The effect of various foreign ions commonly associated with antimony(III) on the recommended extraction procedure was studied. The criterion for interference was an error of $\pm 2\%$. The tolerance limits for the tested ions are given in Table II. Of the various cations examined, only Se(IV) and Te(IV) interfered, the interference was eliminated by masking with 400 mg fluoride.

APPLICATIONS

Binary separation of antimony(III) from Te(IV), Se(IV), Pb(II), Bi(III), Sn(IV), Ge(IV), Cu(II), Au(III), Fe(III) and Zn(II)

This method permits the separation of antimony(III) from commonly associated metal ions by taking advantage of the difference in the extraction conditions of the other metal ions and by employing masking agents.

Antimony(III) was separated from Pb(II), Zn(II), Bi(II), Cu(II), and Fe(III) by its extraction with 10 mL of 4 % *N-n*-octylaniline in xylene from 3.0 M hydrochloric acid medium. Under these conditions Pb(II), Bi(III), Cu(II), Fe(III) and Zn(II) remained quantitatively in the aqueous phase, where they were determined spectrophotometrically with PAR,²⁴ 4'-bromo PTPT²⁶ 4'-chloro PTPT²⁷ thiocyanate,²⁸ respectively. Antimony(III) from the loaded organic phase was stripped with two 10 mL portions of 0.5 M ammonia and estimated as per the recommended procedure.

TABLE III. Binary separation of antimony(III)

	Metal ion	Amount taken/ μg	Average/ μg	Recovery/%	RSD/%
1.	Sb(III)	300	299.10	99.70	0.30
	Te(IV) ^a	100	99.75	99.75	0.25
2.	Sb(III)	300	298.15	99.65	0.35
	Se(IV) ^a	400	398.28	99.57	0.43
3.	Sb(III)	300	299.40	99.80	0.20
	Pb(II)	35	34.63	98.95	1.057
4.	Sb(III)	300	299.10	99.70	0.30
	Bi(III)	300	298.68	99.56	0.44
5.	Sb(III)	300	298.74	99.58	0.42
	Sn(IV) ^b	50	49.73	99.47	0.54
6.	Sb(III)	300	299.10	99.70	0.30
	Ge(IV) ^c	20	19.88	99.41	0.60
7.	Sb(III)	300	299.25	99.75	0.25
	Cu(II)	300	298.62	99.54	0.46
8.	Sb(III)	300	299.10	99.70	0.30
	Au(III) ^d	200	199.16	99.58	0.42
9.	Sb(III)	300	299.10	99.70	0.30
	Fe(III)	300	298.77	99.59	0.41
10.	Sb(III)	300	299.10	99.70	0.30
	Zn(II)	20	19.87	99.39	0.65

^a Masked with 400 mg fluoride; ^b Masked with 200 mg EDTA; ^c Masked with 300 mg ascorbate;

^d Masked with 400 mg thiocyanate

Antimony(III) was separated from Te(IV) and Se(IV) by extraction with 10 mL of 4 % *N-n*-octylaniline in xylene from 3 M hydrochloric acid medium in the

presence of 400 mg of fluoride as masking agent. Here antimony(III) is quantitatively extracted into the organic phase, while Te(IV) and Se(IV) remain in the aqueous phase. Antimony(III) from the organic phase was stripped with two 10 mL portions of 0.5 M ammonia and was estimated by the recommended procedure. The aqueous phase containing Te(IV) and Se(IV) was demasked with 2 mL of concentrated hydrochloric acid and the solution was evaporated to moist dryness, Te(IV) and Se(IV) were determined by 4'-bromo PTPT.^{29,30} Similarly, antimony(III) was separated from Sn(IV), Ge(IV) and Au(III) by extraction with 10 mL of 4% *N-n*-octylaniline in xylene from 3 M hydrochloric acid medium in the presence of 200 mg EDTA, 300 mg ascorbic acid and 400 mg thiocyanate as masking agents, respectively. Here antimony is quantitatively extracted into the organic phase, while Sn(IV), Ge(IV) and Au(III) remain in the aqueous phase. Antimony(III) from the organic phase was stripped with 0.5 M ammonia and was estimated by the recommended procedure. The aqueous phases of Sn(IV), Ge(IV) and Au(III) was demasked with 2 mL concentrated hydrochloric acid and solution was evaporated to moist dryness. The moist residue was extracted into dilute hydrochloric acid. Sn(IV), Ge(IV) and Au(III) were determined by the pyrocatechol violet,²⁴ phenylfluorone²⁴ and stannous chloride³¹ method, respectively.

The recovery of antimony(III) and that of the added ions was > 99.5. The results are given in Table III.

Separation of antimony from multicomponent mixtures

Antimony(III) was separated from Te(IV) and Bi(III) by its extraction with 10 mL of 4% *N-n*-octylaniline in xylene from 3 M hydrochloric acid medium in the presence of 400 mg fluoride. Under these conditions, Te(IV) and Bi(III) remain quantitatively in the aqueous phase. Antimony(III) from the organic phase was stripped with two 10 mL portions of 0.5 M ammonia and estimated by the recommended procedure. Tellurium(IV) and Bi(III) in the aqueous phase were demasked with 2 mL of concentrated hydrochloric acid and the solution was evaporated to moist dryness. The aqueous phase was maintained in 7 M hydrochloric acid and then equilibrated with 4% *N-n*-octylaniline in xylene. Tellurium(IV) was extracted into the organic phase, while Bi(III) remained in the aqueous phase. The Te(IV) from the organic phase was stripped with 1:1 ammonia and estimate by 4'-bromo PTPT.²⁹ The Bi(III) from the aqueous phase was estimated by 4'-bromo PTPT.²⁶

Antimony(III) was separated from Se(IV) and Te(IV) by its extraction with 4% *N-n*-octylaniline in xylene from 3 M hydrochloric acid medium in the presence of 400 mg fluoride. Under these conditions, antimony(III) is extracted into the organic phase, whereas Se(IV) and Te(IV) remain quantitatively in the aqueous phase. Antimony(III) from the organic phase was stripped with two 10 mL portions of 0.5 M ammonia and estimated as per the recommended procedure. Se(IV) and Te(IV) in the aqueous phase were demasked with 2 mL concentrated hydro-

chloric acid and solution was evaporated to moist dryness. The aqueous phase was maintained in 0.5 M hydrochloric acid and then equilibrated with 4 % *N-n*-octylaniline in xylene. Selenium(IV) is extracted into the organic phase, while Te(IV) remains in the aqueous phase. The selenium from the organic phase was stripped with 1:1 ammonia and estimated by 4'-bromo PTPT.³⁰ Tellurium(IV) from the aqueous phase was estimated by 4'-bromo PTPT.²⁹

Antimony(III) was separated from Se(IV) and Cu(II) by its extraction with 4 % *N-n*-octylaniline in xylene from 3 M hydrochloric acid medium in the presence of 400 mg fluoride. Under these conditions antimony(III) is extracted into the organic phase, whereas Se(IV) and Cu(II) remain quantitatively in the aqueous phase. Antimony(III) from the organic phase was stripped with two 10 mL portion of 0.5 M ammonia and estimated as per the recommended procedure. Se(IV) and Cu(II) in the aqueous phase were demasked with 2 mL concentrated hydrochloric acid and solution was evaporated to moist dryness. The aqueous phase was maintained in 0.5 M hydrochloric acid and then equilibrated with 4 % *N-n*-octylaniline in xylene. Selenium(IV) was extracted into the organic phase, while Cu(II) remained in the aqueous phase. Selenium(IV) from the organic phase was stripped with 1:1 ammonia and estimated by 4'-bromo PTPT.³⁰ Copper(II) from aqueous phase was estimated by 4'-chloro PTPT.²⁷

TABLE IV. Separation of antimony(III) from multicomponent mixtures

	Metal ion	Amount taken/ μg	Average/ μg	Recovery/%	RSD/%
1.	Sb(III)	300	299.40	99.80	0.20
	Te(IV) ^a	100	99.51	99.51	0.49
	Bi(III)	300	297.36	99.12	0.88
2.	Sb(III)	300	300.00	100.00	0.00
	Se(IV) ^a	400	398.28	99.57	0.43
	Te(IV) ^a	100	99.75	99.75	0.25
3.	Sb(III)	300	299.07	99.69	0.31
	Se(IV) ^a	400	398.28	99.57	0.43
	Cu(II)	400	400.00	100.00	0.00
4.	Sb(III)	300	299.10	99.70	0.30
	Te(IV) ^a	100	99.51	99.51	0.49
	Pb(II)	70	69.62	99.47	0.54

^a Masked with 400 mg fluoride

Antimony(III) was separated from Te(IV) and Pb(II) by its extraction with 10 mL of 4 % *N-n*-octylaniline in xylene from 3 M hydrochloric acid in presence of 400 mg fluoride. Under these conditions, Te(IV) and Pb(II) remain quantitatively in the aqueous phase. Antimony(III) from the organic phase was stripped with two

10 mL portions of 0.5 M ammonia and estimated as per the recommended procedure. Tellurium(IV) and Pb(II) in the aqueous phase were demasked with 2 mL of concentrated hydrochloric acid and the solution was evaporated to moist dryness. The aqueous phase was maintained in 7 M hydrochloric acid and then equilibrated with 4 % *N-n*-octylaniline in xylene. Tellurium(IV) is extracted into the organic phase, while Pb(II) remains in the aqueous phase. Tellurium(IV) from organic phase was stripped with 1:1 ammonia and estimated by 4'-bromo PTPT.²⁹ Lead(II) from the aqueous phase was estimated by PAR method,²⁴ (Table IV).

Analysis of synthetic mixtures

The proposed method was applied to the extraction and determination of antimony(III) from 3 M hydrochloric acid media from various synthetic mixtures. The results are given in Table V.

TABLE V. Analysis of synthetic mixture

Amount of metal ion present/ μg	Amount found/ μg	Average/ μg	Recovery/%	RSD/ %
Sb 300, Bi 500, Te ^a 500 Se ^a 500, Pd 500	299.8	299.6	99.81	0.13
	299.6			
	299.7			
	299.5			
	299.6			
Sb 300, Cu 500, Pd 500 Te ^a 500, Se ^a 500, Al 500	299.8	299.7	99.9	0.10
	300.0			
	299.5			
	299.7			
	299.6			
Sb 300, Au ^b 500 Ag 500, Cd 200, Fe 200	299.6	299.7	99.9	0.10
	299.7			
	300.00			
	299.7			
	299.8			
Sb 300, Pd 500, Cu 500 Bi 500, Mo 500, Te 500	299.5	299.7	99.9	0.10
	299.7			
	299.6			
	299.8			
	299.7			
	299.8			

^a Masked with 400 mg fluoride; ^b Masked with 400 mg thiocyanate.

Analysis of real samples

The procedure was used for the determination of antimony(III) in synthetic mixtures corresponding to allays, such as the mineral cylindrite and recording material. The results of the analyses are reported in Table VI.

TABLE VI. Synthetic mixtures corresponding to alloys

Alloy sample	Composition/%	Amount taken/ μg	Recovery/%	RSD/%
1. Mineral cylindrite	Sn (21–26) Sb (7–13) Pb (34–39) Ag (70.6) S (24); Fe (3) In (0.054) Si (in traces)	300	99.8	0.2
2. Recording material	Sb (47) Ag (9.2) In (44)	300	99.4	0.6

Similarly, the method permits the separation and determination of antimony(III) in gun metal and a tin-based white metal alloys, (Table VII). The results obtained by the present method are in good agreement with the certified values. The method is selective and permits rapid separation of antimony(III).

TABLE VII. Analysis of real sample of alloy.

Alloy sample	Composition/%	Antimony taken/ μg	Recovery/%	RSD/%
1. Gun metal alloy	Cu, 84.95; Sn, 4.89; Sb, 31; Pb, 2.31	300	99.80	0.20
2. 434/1 Tin-Based white metal	Sn, 82.2; Sb, 9.45; Cu, 4.58; Pb, 3.18; As, 1.15; Bi, 0.10; Cd, 0.14; Fe, 0.024; Ni, 0.17; Zn, 0.4	300	99.60	0.40

*Procedure for the dissolution of gun metal and the tin-based white metal alloy.*²⁶ A known weight (1 g) of alloy was dissolved in a mixture of 9 mL of concentrated sulfuric acid and 50 mL of water. After the initial reaction was finished, the solution was heated with a 5 mL portion of nitric acid until white fumes were observed, boiled to dissolve the soluble matter and finally, filtered to remove manganic acid. The filtrate was diluted to an appropriate volume. An aliquot of this solution was analysed by the recommended procedure.

Analysis of antimony(III) in semiconductor film. The proposed method was also applied for the determination of antimony(III) in a semiconductor film [CdSb₂SeO₄]. The amount of antimony(III) found in the sample by the proposed

method is in good agreement with the certified values (Table VIII).

TABLE VIII. Analysis of a semiconductor film

Sample	Composition	Amount of Sb(III) certified/%	Amount found by the proposed method/%	RSD/%
Semiconducting material*	CdSb ₂ SeO ₄	36.25	36.12	0.36

* Manufacturer: Material Research Lab. Department of Chemistry, Shivaji University, Kolhapur, 416004 (India).

*Procedure for the determination of antimony(III) in semiconductor film.*³² The support with the film was placed in a 50 ml beaker; 5 mL nitric acid (2:1) was added and the film dissolved with moderate heating. When the dissolution of the film was complete, the support was removed and rinsed with doubly-distilled water. The mass of the film was obtained from the difference in the weight of the support before and after dissolution. Quartz glass, insoluble in nitric acid, was used as the support. The obtained solution was treated with 3 mL sulfuric acid (1:1) and evaporated until the appearance of white fumes. The residue is dissolved in 0.1 M sulfuric acid, transferred to a 25 mL volumetric flask and brought to the mark with doubly distilled water. An appropriate aliquot of this solution was transferred to a 25 mL volumetric flask and the analysis continued as in the determination of antimony(III) by the recommended procedure.

CONCLUSION

The important features of the method described here are that,

1. It permits the selective separation of antimony(III) from other associated metals.
2. It is free from interference from a large number of foreign ions which are often associated with naturally occurring antimony(III).
3. A low reagent concentration is required for the quantitative recovery of antimony(III).
4. The time required for equilibration is very short.
5. The method is applicable to the analysis of real samples, alloys and semiconductor thin films.
6. The determination of antimony in the aqueous medium after back extraction leads to a much simpler procedure.
7. It is very simple, selective, reproducible and rapid, requiring only 25 min for separation and determination.

Acknowledgement: The authors express their gratitude to Professor M. B. Chavan for his valuable discussion and kind encouragement.

NOMENCLATURE

[] – Concentration
 D – Distribution ratio
 % E – Percentage extraction
 % R – Percentage recovery
 aq – Aqueous phase
 org. – Organic phase.

ИЗВОД

СЕЛЕКТИВНА ТЕЧНО-ТЕЧНО ЕКСТРАКЦИЈА АНТИМОНА(III) ИЗ
 ХЛОРОВОДНИЧНО КИСЕЛИХ МЕДИЈА *N-n*-ОКТИЛАНИЛИНОМ У
 КСИЛЕНУ

B. M. SARGAR, M. M. RAJMANE и M. A. ANUSE

Analytical Chemistry Laboratory, Department of Chemistry Shivaji University, Kolhapur-416 004, India (e-mail: maanuse@rediffmail.com)

За екстракциону сепарацију антимоно(III) из хлороводнично киселе средине коришћен је *N-n*-октиланилин у ксилену. Антимон(III) екстрахован је квантитативно са 10 mL 4 % *N-n*-октиланилина у ксилену. Из органске фазе повраћен је са 0,5 M амонијум-хидроксидом и одређен фотометријски јодидном методом. Испитан је утицај концентрација металног јона, киселине и реагенса као и различитих других страних јона. Метода пружа могућност двојних и тројних сепарација антимоно(III) од телура(V), селена(IV), олова(II), бизмута(III), калаја(IV), бабра(II), злата(III), гвожђа(III) и цинка(II). Метода је погодна за анализу синтетичких смеша, легура и полупроводничких танких филмова. Метода је брза, репродуктивна и прецизна.

(Примљено 2. јуна 2003)

REFERENCES

1. C. Juan, N. Cristina, *Afinidad* **39** (377) (1982) 51
2. A. Alian, W. Sanad, *Talanta* **14** (1967) 659
3. S. Toshio, O. Hiroyuki, S. Kiyoshi, *Anal. Sci.* **2** (1986) 25
4. Y. Koichi, S. Takayuki, *Anal. Sci.* **16** (2000) 641
5. P. Navarro, J. Simpson, F. J. Alguacil, *Hydrometallurgy* **53** (1999) 121
6. A. D. Barve, G. S. Desai, V. M. Shinde, *Bull. Chem. Soc. Jpn.* **66** (1993) 1079
7. D. B. Dreisinger, B. J. Y. Leong, B. R. Saito, P. G. West-Shells, *Hydrometall. Proc. Milton E. Wadsworth Int. Symp.* **4** (1993) 801
8. D. B. Dreisinger, B. J. Y. Leong, I. Grewal, Impurity Control Disposal *Hydrometall. Processes, Annu. Hydrometall 24th Meeting*, (1994) 71
9. S. Facon, G. Cote, D. Bauer, *Solvent Extr. Ion Exch.* **9** (1991) 717
10. S. G. Sarkar, P. M. Dhadke, *Sep. Purif. Technol.* **15** (1999) 131
11. Szymanowski, Jan, *Miner. Process. Extr. Metall. Rev.* **18** (1998) 389
12. S. V. Bandekar, P. M. Dhadke, *Solvent Extraction for the 21st Century, Proceedings of ISEC 99 Barcelona, Spain*, July 11–16 (1999) 71
13. S. V. Bandekar, P. M. Dhadke, *Indian J. Chem.* **39 A** (2000) 548
14. K. A. Ali, A. K. Vanjara, *Indian J. Chem. Tech.* **8** (2001) 239
15. A. P. Mehrotra, M. Rajan, V. M. Shinde, *Indian J. Chem.* **35A** (1996) 530
16. G. K. Schweitzer, L. E. Storms, *Anal. Chim. Acta.* **19** (1958) 154
17. S. S. M. A. Khorasani, M. H. Khundkar, *Anal. Chim. Acta.* **21** (1959) 24

18. T. N. Lokhande, M. A. Anuse, M. B. Chavan, *Talanta* **46** (1998) 163
19. T. N. Lokhande, M. A. Anuse, M. B. Chavan, *Talanta* **47** (1998) 823
20. T. N. Lokhande, G. B. Kolekar, M. A. Anuse, M. B. Chavan, *Sep. Sci. Technol.* **35** (2000) 153
21. T. N. Lokhande, M. A. Anuse, *J. Saudi Chem. Soc.* **4** (2000) 1
22. J. Bassett, R. C. Denny, G. H. Jeffery, J. Mendham, *Vogel's Text Book of Quantitative Inorganic Analysis*, 4th ed., Longman, London, 1979
23. Z. G. Gardlund, R. J. Curtis, G. W. Smith, *Liq. Cryst. Ord. Fluids* **2** (1973) 541
24. Z. Marczenko, *Spectrophotometric Determination of Elements*, Wiley, New York, 1976, p.p. 125, 326, 605, 549, 275
25. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, 1988
26. G. B. Kolekar, T. N. Lokhande, P. N. Bhosale, M. A. Anuse, *Anal. Lett.* **31** (1998) 2241
27. M. A. Anuse, S. R. Kuchekar, M. B. Chavan, *Indian J. Chem.* **25A** (1986) 1041
28. A. I. Vogel, *Textbook of Quantitative Chemical Analysis*, 5th ed., Longman, London, 1997 p. 690
29. G. B. Kolekar, M. A. Anuse, *Bull. Chem. Soc. Jpn.* **71** (1998) 859
30. G. B. Kolekar, B. M. Sargar, M. A. Anuse, *Chem. Environ. Res.* **9** (2000) 37
31. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience, New York, 1965, p. 503
32. P. P. Kish, I. S. Baloq, V. A. Andruk, M. G. Golomb, *Zh. Anal. Khim.* **45** (1990) 915.