CHAPTER VII

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY

RESUME

The solvent extraction and spectrophotometric determination of antimony(III) in the sub-ppm quantities with N-p-tolyl-α-phenyl-p-methoxy-cinnamohydroxamic acid (PTPMCHA) is described. The antimony forms a colourless complex with PTPMCHA at 1.0 M HCl extractable into chloroform. Phenyl fluorone is added into the Sb-PTPMCHA extract which forms a reddish yellow coloured mixed-ligand complex having a maximum absorbance at 505 nm and molar absorptivity 1.0×10^4 l $mol^{-1} cm^{-1}$. The photometric sensitivity of the colour reaction is 0.0122 µg of antimony per cm^2. The effect of diverse ions and several experimental parameters have been studied. The composition of the antimony : PTPMCHA : phenylfluorone is 1:1:2. The antimony is also estimated by atomic absorption spectrophotometry.

INTRODUCTION

Antimony is used in lead alloys, storage battery, grids, rubber, matches, ceramics, paints and textile industries. It is well recognised that the toxicity and physiological behaviour of antimony depends on its oxidation state. The toxicology of antimony has been comprehensively reviewed by Fairhall and Hyslop (1). As antimony occurs in the environment at very low concentration therefore a selective and sensitivity method for its determination has received a considerable attention.

A large number of extraction and photometric methods have been developed for the separation and determination of antimony with the several organic reagents viz. bromopyrogallol red (2), brilliant green (3), rhodamine B (4) and its derivatives (5), bis (aroylhydrazones) of 2,6-diacetyl pyridine (6), salicylfluorone (7) etc. Although these methods are sensitive, however, they are not specific and reproducible. Much less attention has been devoted to the possible use of hydroxamic acids as an extracting reagent. The hydroxamic acids are widely used as potential analytical reagents for the separation, detection and determination of number of metal ions (8-17). Only a few data are available with the N-phenylbenzohydroxamic acid (PBHA) (18).

In present investigation the solvent extraction and spectrophotometric determination of antimony(III) with PTPMCHA and phenylfluorone is described.

EXPERIMENTAL

CHEMICALS AND REAGENTS

All the chemicals used were of AnalaR and G.R. grades of B.D.H. or E. Merck, respectively, unless otherwise specified.

Hydroxamic acids

These are synthesised as described in Chapter II. 0.25% reagent solutions of hydroxamic acids were prepared in chloroform.

The standard antimony solution was prepared by dissolving requisite amount of potassium antimony tartarate ($K(SbO)C_4H_4O_6$) in double distilled water along with 3 ml of 10 M HCl to prevent the hydrolysis. Its final concentration was determined spectrophotometrically (19).

Phenylfluorone

A 0.01% (w/v) solution was prepared in pure methanol.

APPARATUS

The spectral measurements were made on Shimadzu UV-VIS 240 spectrophotometer.

A GBC 901 atomic absorption spectrophotometer equipped with a GBC HG 900 Vapour Generation Assembly and antimony hollow cathode lamp was used. The 217.6 nm, antimony line and air acetylene flame were used for direct AAS measurements.

EXTRACTION PROCEDURE

An aliquot of the solution containing 4.87 ppm (2.0 ml of 5.0×10^{-4} M) of Sb(III) was transferred to a 60-ml separatory funnel. Added a sufficient quantity of distilled water and 10 M HCl to maintain the molarity 1.0 to a total volume of aqueous phase 20 ml. 10 ml of 0.25% PTPMCHA solution in chloroform was added and the mixture was shaken vigorously for 20 min. The phases were allowed to separate and the colourless chloroform layer was collected in 25 ml volumetric flask after drying over anhydrous sodium sulphate. Further, 10 ml of 0.01% solution of phenylfluorone was added in the chloroform extract of Sb-PTPMCHA and the contents were diluted to 25 ml with chloroform ($CHCl_3$:MeOH:: 3:2). The absorbance was measured at 505 nm against a reagent blank.

Atomic absorption measurements

The chloroform extract was directly aspirated into the flame for AAS measurements. However, for the lower concentration of antimony (0.005-0.03 ppm) the antimony was determined by the hydride method using GBC HG 900 Vapour Generation Assembly. The following parameters were set for Sb:wavelength 217.6 nm, lamp current 10 mA, band pass 0.2 nm, working range 0.005-0.03 ppm of Sb, sample volume 20 ml, fuel air acetylene (flow rate 2-3 mm high) inert gas nitrogen at 20 psi.

The chloroform extract of antimony-hydroxamic acid complex was back-extracted with 10 ml 0.1 M NH_4OH solution. Then 10 ml concentrated HCl was added and the acidic solution was used for determination of antimony. The concentration of antimony was computed from the calibration curve which was prepared in the range of 0.005-0.03 ppm using above method.

RESULTS AND DISCUSSION

The spectral characteristics of antimony complexes with hydroxamic acids and phenylfluorone are summarised in Table 1. From the preliminary studies, it is observed that N-p-tolyl-α-phenyl-p-methoxycinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the hydroxamic acids studied here. Hence the optimum conditions for the extraction of antimony with PTPMCHA have been further investigated.

Effect of acidity

The extraction of antimony was studied in different hydrochloric acid molarities. The results show that the extraction of the metal is very poor at more than 4 M hydrochloric acid concentration but becomes quantitative at less than 4 M HCl. The complete extraction is quantitative at 0.5-1 M HCl. Hence all the extractions were carried out at 0.5-1 M.HCl (Table 2).

Effect of reagent concentration

The extraction was carried out with various amounts of PTPMCHA in chloroform. It was observed that 10 ml of 0.25% PTPMCHA in chloroform gives the complete extraction of antimony (Table 3).

TABLE 1

Spectral characteristic of antimony substituted cinnamohydroxamic acids with phenylfluorone

Sb(III) : 4.87 ppm

Hydroxamic acids : 0.25%, 10 ml in $CHCl_3$

Phenylfluorone : 0.01%, 10 ml in MeOH

Shaking time : 20 min

Molarity : 1 M HCl

Solvent : $CHCl_3$ + MeOH (3:2)

Colour of complex : Reddish yellow

Compd No.	Cinnamohydroxamic acid	λmax nm	Molar absorptivity $l\ mol^{-1} cm^{-1}$	Sandell's Sensitivity $\mu g\ cm^{-2}$
I	N-Phenyl-α-phenyl-p-methoxy-	505	9.5×10^3	0.0128
II	N-p-Tolyl-α-phenyl-p-methoxy-	505	1.0×10^4	0.0122
III	N-m-Tolyl-α-phenyl-p-methoxy-	505	9.8×10^3	0.0124
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	505	9.0×10^3	0.0135
V	N-Phenyl-α-phenyl-	505	9.3×10^3	0.0131
VI	N-p-Tolyl-α-phenyl-	505	9.5×10^3	0.0128
VII	N-m-Tolyl-α-phenyl-	505	9.3×10^3	0.0131
VIII	N-p-Chlorophenyl-α-phenyl-	505	8.8×10^3	0.0138
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy-	505	9.3×10^3	0.0131

TABLE 2

Effect of acidity on the extraction of antimony(III)

Sb(III) : 4.87 ppm

PTPMCHA : 0.25%, 10 ml in $CHCl_3$

Phenylfluorone : 0.01%, 10 ml in MeOH

Shaking time : 20 min

Solvent : $CHCl_3$ + Methanol (3:2)

λ_{max} : 505 nm

Colour of complex : Reddish yellow

Molarity	Absorbance	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$	% E
0.5	0.40	1.0×10^4	100
1.0	0.40	1.0×10^4	100
1.5	0.36	9.0×10^3	90
2.0	0.28	7.0×10^3	70
3.0	0.20	5.0×10^3	50
4.0	0.10	2.5×10^4	25

TABLE 3

Effect of reagent concentration

Sb(III) : 4.87 ppm

Phenylfluorone : 0.01%, 10 ml in MeOH

Shaking time : 20 min

Molarity : 1 M HCl

Solvent : $CHCl_3$+MeOH (3:2)

λ_{max} : 505 nm

Colour of complex : Reddish yellow

PTPMCHA (0.25%) ml	Molar concentration of PTPMCHA (M)	Absorbance	Molar absorptivity $l\ mol^{-1} cm^{-1}$	%E
3.0	0.2087	0.24	6.0×10^3	60.0
5.0	0.3478	0.28	7.0×10^3	70.0
6.0	0.4173	0.31	7.8×10^3	77.5
8.0	0.5564	0.36	9.0×10^3	90.0
10.0	0.6955	0.40	1.0×10^4	100.0
15.0	1.0433	0.40	1.0×10^4	100.0

Effect of Phenylfluorone concentration

Different amounts of phenylfluorone solution in methanol were added in the antimony hydroxamate. It was observed that 10.0 ml of 0.01% solution of phenylfluorone in methanol was adequate for the complete colour development (Table 4). A further excess of phenylfluorone forms turbidity.

Effect of shaking time

Extraction of antimony complex is rapid under recommended condition. Shaking for 20 min is enough for the complete complexation.

Beer's Law

The coloured system obeys Beer's law in the range 0.49-14.61 ppm of antimony(III). The molar absorptivity is 1.0×10^4 l $mol^{-1} ml^{-1}$ with a photometric Sandell"s sensitivity 0.0122 µg cm^{-2}.

Effect of diverse ions

Different amounts of diverse ions were added to a fixed amount of antimony and antimony was extracted according to the procedure. Most of the metal ions associated with antimony do not interfere. Although phenylfluorone gives colour reaction with Sn^{4+}, Ta^{5+}, Nb^{5+}, Zr^{4+}, Hf^{4+}, Mo^{6+}, W^{6+}, Fe^{3+} and Ge^{3+} in the acidic medium (1), these do not interfere

TABLE 4

Effect of phenylfluorone concentration

Sb(III)	: 4.87 ppm	Molarity	: 1 M HCl
PTPMCHA	: 0.1%, 10 ml in $CHCl_3$	Solvent	: $CHCl_3$: MeOH (3 : 2)
Phenylfluorone	: 0.01%, in MeOH	λmax	: 505 nm
Shaking time	: 20 min	Colour of complex	: Reddish yellow

Concentration of Phenylfluorone in ml	Absorbance	Molar absorptivity $l\ mol^{-1}cm^{-1}$	% E
2.0	0.23	5.8×10^3	59
4.0	0.28	7.0×10^3	70
6.0	0.31	7.8×10^3	78
8.0	0.36	9.0×10^3	90
10.0	0.40	1.0×10^4	100
11.0	0.40	1.0×10^4	100*

* Turbidity

TABLE 5

Effect of cations and anions on the extraction of antimony(III)

Sb(III) : 4.87 ppm

PTPMCHA : 0.25%, 10 ml in $CHCl_3$

Phenylfluorone : 0.01%, 10 ml in MeOH

Shaking time : 20 min

Molarity : 1 M HCl

Solvent : $CHCl_3$+MeOH (3:2)

λmax : 505 nm

Colour of complex : Reddish yellow

Ions	Added as	Amount added (mg)	Absorbance
Ag^+	$AgNO_3$	15	0.40
As^{3+}	As_2O_3	15	0.41
Al^{3+}	$AlCl_3$	20	0.40
Bi^{3+}	$Bi(NO_3)_3$	15	0.39
Cu^{2+}	$CuSO_4$	30	0.40
Pb^{2+}	$Pb(NO_3)_2$	30	0.40
Ni^{2+}	$NiCl_2$	30	0.40
Co^{2+}	$Co(NO_3)_2$	25	0.40
Cd^{2+}	$CdSO_4$	20	0.40
Mg^{2+}	$MgSO_4$	20	0.40
Fe^{3+}	$FeCl_3$	15	0.39
Sn^{4+}	$SnCl_4$	20	0.40
Hg^{2+}	$HgCl_2$	25	0.40
Ti^{4+}	TiO_2	20	0.40
Ti^{3+}	$TiBr_3$	20	0.40
Zr^{4+}	$ZrOCl_2$	15	0.40
Hf^{4+}	$HfOCl_2$	15	0.40
Nb^{5+}	Nb_2O_5	25	0.40
Ta^{5+}	Ta_2O_5	25	0.40
* V^{5+}	NH_4VO_3	20	0.40
Zn^{2+}	$ZnCl_2$	25	0.39
Cl^-	NH_4Cl	15	0.40
F^-	NaF	10	0.40
SO_4^-	Na_2SO_4	15	0.40

* Masked with EDTA

in the present method for the determination of antimony since the antimony is first extracted with PTPMCHA and then the phenylfluorone is added. However, V^{5+} interfere in the determination of antimony. Its interference was removed by masking with EDTA (Table 5).

Composition of the complex

The stoichiometric composition of the Sb:PTPMCHA: phenylfluorone complex was determined by slope ratio method (20). The stoichiometry of the Sb:PTMMCHA complex was determined by taking fixed amount of antimony and phenylfluorone and gradually increasing the amount of PTPMCHA (L_1) keeping the volume of the PTPMCHA solution in chloroform constant. The slope of the plot of log D_M Vs - log (L_1) was found to be 1.0; confirms the metal to ligand (L_1) ratio 1:1.

The stoichiometry of the Sb-phenylfluorone complex was determined by taking fixed amount of metal solution and PTPMCHA in chloroform and gradually increasing the amount of phenylfluorone (L_2). The slope of the plot of log D vs - log (L_2) was found to be 2.0; confirms the metal to ligand (L_2) ratio 1:2.

Thus the overall composition of the Sb::PTPMCHA:Phenylfluorone complex found to be 1::1:2.

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