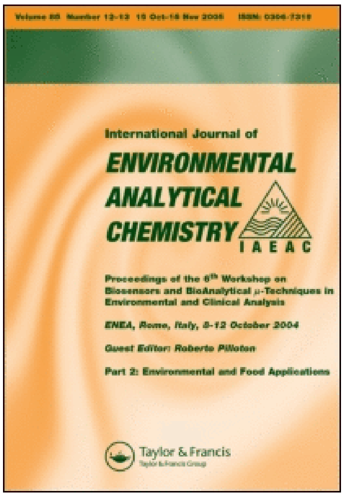

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Extraction and Spectrophotometric Determination of Antimony in the Environment:

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A new sensitive method for the extraction and spectrophotometric determination of antimony in the environment is described. The antimony forms a greenish yellow coloured complex with *N*-phenylbenzohydroxamic acid (PBHA) at 4 M HCl which is extracted from chloroform.

The Sb-PBHA complex is back extracted in 0.01 M NH_4OH and then antimony is estimated with rhodamine B in 6 M HCl media. This bluish violet coloured complex is extractable in benzene. The maximum absorbance of the antimony rhodamine B complex is observed at 565 nm. The effects of acidity, reagent concentration and diverse ions are discussed. The method is applied to the trace determination of antimony in industrial effluents and natural resources.

KEY WORDS: Antimony, hydroxamic acid, spectrophotometry, environment.

INTRODUCTION

The antimony is used in lead alloys, storage battery, grids, rubber, matches, ceramics, enamels, paints and textile industries. Acid treatment of metals containing antimony release colourless stibine (SbH_3). Trivalent antimony compounds are much more toxic than pentavalent.[1] The maximum allowable concentration (m.a.c.) in the air for antimony and stibine is 0.5 mg/m^3, and 0.1 ppm respectively.[2] The average body burden in man is about 90 mg[3]. Antimony is strongly irritating to mucous membrane, hemolysis and the central nervous system.[4] Various reagents were used for extraction and spectrophotometric determination of antimony.[5–9] In one method[5] Hg^{2+}, Ag^+, Bi^{3+}, Cd^{2+} and Ni^{2+} are interfering. Diethyldithiophosphoric acid,[6] methyl violet and 1-pyridylazo-

2-naphthol reagents were used for extraction of antimony but interference of common metal ions are observed.[7] Antimony compounds are extracted with rhodamine B[8] in benzene. But Au^{3+}, Tl^{3+}, W^{6+}, Fe^{3+}, Hg^{2+} and Ga^{3+} are interfering. The hydroxamic acids are the potential analytical reagents and used for the spectrophotometric determination of several metal ions.[9] *N*-phenylbenzohydroxamic acid (PBHA) has been used for the gravimetric determination and isotopic extraction of antimony.[10,11] In the present investigation *N*-phenylbenzohydroxamic acid (PBHA) is used for extraction and spectrophotometric determination of antimony.

EXPERIMENTAL

Apparatus

The spectral measurements were made on a Spekol (Carl Zeiss Jena).

Reagent and Chemicals

All the chemicals used were of G.R. grades of E. Merck unless otherwise specified.

The *N*-phenylbenzohydroxamic acid (PBHA) was synthesized as described elsewhere,[12] (mp 120°C). Its purity was checked by TLC, IR and UV spectra. Its 0.05 M solution was prepared in chloroform.

A 0.4 M solution of rhodamine B was prepared by dissolving 10 mg of rhodamine B in 100 ml of water.

A standard antimony solution was prepared by dissolving known amounts of potassium antimony tartrate in distilled water and its final concentration was determined volumetrically.[13]

Procedure

Transfer 2 ml of antimony stock solution (1.3×10^{-4} M) into a 125-ml separatory funnel, add 5 ml ammonium persulphate solution (0.3 M) and adjust molarity of aqueous phase to 4 M with conc HCl and water to a total volume 25 ml. Then add 10 ml of reagent solution (PBHA). Shake for five minutes, allow the phases to separate, dry over anhydrous sodium sulphate and transfer to a 25-ml volumetric flask. To ensure the complete recovery of antimony extract the aqueous layer with 5×2 ml reagent solution and finally dilute the extract with chloroform to 25 ml. Measure the absorbance of the greenish yellow coloured complex at 385 nm then reextract the organic phase with 10 ml 0.01 M NH_4OH, neutralise it with 0.01 M HCl solution, adjust the molarity of the aqueous phase to 6 M of HCl with conc HCl and water to a total volume of 25 ml and add 1 ml of rhodamine B (0.4 M). Extract bluish violet coloured complex with pure benzene (10 ml), separate the benzene layer, dry over anhydrous sodium sulphate and wash it twice with 2 ml of benzene. To ensure the complete recovery repeat the extraction with 5 ml of benzene and finally dilute the extract to 25 ml with benzene. Measure the absorbance against reagent as blank.

Calibration Curve

The standard curve[5] is established by taking antimony conc 0.1–6 ppm adding 10 ml of water and 1 ml 0.3 M solution of ammonium persulphate, adjust the molarity 4 M HCl of aqueous solution. The antimony forms a complex with rhodamine B (0.4 M) and is extracted with benzene.

Determination of Antimony in Industrial Effluents

100 ml of industrial effluent was transferred into 250-ml separatory funnel. To this add 5 ml 0.3 M solution of ammonium persulphate and 5 ml 0.1 M E.D.T.A. solution. The molarity of the aqueous solution was adjusted to 4 M with the conc hydrochloric acid and the antimony is estimated as described in procedure. The concentration of antimony was calculated from calibration curve.

Determination of Antimony from Plant and Soil Samples

Depending upon the concentration of antimony in plants or soils, about 1 to 10 g of samples were digested with excess of hydrochloric acid and 10 ml perchloric acid. The filtrate was evaporated and diluted to 100 ml with 0.01 M HCl. To this 5 ml of 0.3 M ammonium persulphate and 5 ml 0.1 M E.D.T.A. were added. The antimony was determined by adjusting the molarity of HCl to 4 M with conc HCl as in the above procedure and its concentration was calculated from calibration curve.

RESULTS AND DISCUSSION

The greenish yellow coloured complex of Sb-PBHA gives a general absorption, but measurements are reproducible at 385 nm. Hence all the measurements were made at this wavelength. The reagent has no absorption at this wavelength. The molar absorptivity of Sb-PBHA complex is $5.7 \times 10^2 \, l \, mol^{-1} \, cm^{-1}$ at 385 nm. Beers law is obeyed within the range of 6–40 ppm.

The bluish violet coloured antimony rhodamine B complex estimated by back extraction of antimony PBHA complex has a maximum absorbance at 565 nm.

Validity of Beer's Law

Beer's law is obeyed within the range of 6–40 ppm for Sb-PBHA complex. Antimony is estimated by the rhodamine B method and the concentration is calculated from the calibration curve.

Beer's law is obeyed for the antimony rhodamine B complex system estimated after back extraction of Sb-PBHA complex within the range of 0.31–3.16 ppm.

Effect of Acidity

There was no noticeable colour in the benzene extract from a lower acid concentration (0.5 to 3 M HCl) but the bluish violet colour is developed at higher acidities. Maximum colour intensity was observed at 4 M HCl.

Effect of Reagent Concentration

Antimony was extracted at 4 M HCl with varying volume and concentration of reagent. Results indicate that single extraction with 10 ml of 0.05 M reagent was adequate for the quantitative extraction of antimony, while extraction was incomplete with 0.005, 0.001, 0.03 M reagent solution. Excess of reagent could be used without any difficulty.

Effect of Solvents

Antimony is extracted with chloroform, benzene, carbon tetrachloride, isobutylmethylketone etc, chloroform was found the most suitable solvent.

Effect of Diverse Ions

The 5 ppm of antimony is extracted in the presence of various amounts of different ions (20–100 ppm) Ba^{2+}, Sr^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Be^{2+}, Mg^{2+}, Cu^{2+}, As^{3+}, Bi^{3+}, T^{4+}, Zr^{4+}, Hf^{4+}, Hg^{2+}, Nb^{5+}, Ta^{5+}, Mo^{6+} and $W^{6+}SO_4^{2-}$, F^- and Cl^- are not interfering with the determination of antimony. However, V^{5+} is interfering and is masked with E.D.T.A. The data are given in Table I.

Determination of Antimony in Standard Samples and in the Environment

The data on the determination of the concentration of antimony in standard samples, plants and industrial effluents are given in Tables II and III.

TABLE I
Effect of Cation and Anion on the Extraction and Spectrophotometric Determination of Antimony

Antimony = 5 ppm　　Medium = 4 M HCl
λ max = 565 nm　　Absorbance 0.130

(Antimony is first extracted at 4 M HCl in presence diverse ions then back extracted with 0.01 M NH_4OH and finally determined as rhodamine B complex at 6 M HCl)

Ions	Added as	(mg)	Absorbance
Ba^{2+}	$BaCl_2$	(40)	0.130
Sr^{2+}	$SrCl_2$	(50)	0.130
Ca^{2+}	$CaCl_2$	(40)	0.129
Pb^{2+}	$Pb(C_2H_3O_2)_2$	(50)	0.129
Cd^{2+}	$CdSO_4$	(40)	0.130
Be^{2+}	$BeSO_4$	(50)	0.130
Mg^{2+}	$MgSO_4$	(50)	0.130
Cu^{2+}	$CuSO_4$	(50)	0.130
Ni^{2+}	$NiCl_2$	(50)	0.130
Co^{2+}	$CoCl_2$	(50)	0.131
As^{3+}	As_2O_3	(40)	0.131
Ti^{4+}	$TiCl_4$	(50)	0.131
Hf^{4+}	HfO_2	(25)	0.130
Zr^{4+}	$Zr(NO_3)_45H_2O$	(30)	0.131
Nb^{5+}	Nb_2O_5	(60)	0.130
Ta^{5+}	Ta_2O_5	(60)	0.131
Mo^{6+}	$(NH_4)_6Mo_7O_{24}$	(30)	0.129
W^{6+}	H_2WO_4	(40)	0.130
V^{5+}	NH_4VO_3	(40)	0.130
Hg^{2+}	$HgCl_2$	(50)	0.130
SO_4^{2-}	Na_2SO_4	(80)	0.130
Cl^-	NaCl	(80)	0.130
F^-	NaF	(80)	0.130

TABLE II
Analytical Data on the Extraction of Antimony in Standard Samples

		Antimony found %		
Sample	Certified values %	Present method	Standard deviation	AAS†
NBS 1124 B (Steel)	0.20	0.21	±0.01	0.19
NBS 53 (Steel)	10.09	10.08	±0.02	10.10
ISU 3 (Steel)	4.00	4.01	±0.01	4.00
NBS 63	0.49	0.48	±0.02	0.47
NBS 124 (Ounce metal)	0.23	0.25	±0.02	0.22
NBS 62 b (manganese bronze)	0.005	0.007	±0.002	0.008

†By atomic absorption spectrophotometer, wavelength 2598 A.

TABLE III
Concentration of Antimony in Industrial Effluents, Plants and Soils

	Antimony found (ppm)	
Sample	Present method	AAS†
Soil Sample	0.5–15	0.8–13
Plant Sample	0.5–10	0.5–10
Orchid leaves	3.2–5	3.0–5.5
Rock sample (Garnitic)	0.5–2	0.45–3.0
Hair	0.6–1.3	0.62–1.3
Industrial effluent		
i) Textile industries	0.8–5.6	1.0–5.5
ii) Paint industries	2–15	2–15
iii) Enamels coated container	5–10	5–10

†Average of 10 determinations.

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