Rapid Extraction of Antimony with Tributyl Phosphate. Direct Photometric Determination with Brilliant Green

A. A. YADAV and S. M. KHOPKAR

Department of Chemistry, Indian Institute of Technology, Bombay-76, India

(Received April 17, 1970)

A new method is developed for the rapid extraction and direct photometric determination of antimony. With 20% TBP-toluene 3 to 15 μg of antimony is extracted from 2M hydrochloric acid containing 1M magnesium chloride. From the organic phase, antimony is directly determined photometrically at 640 nm as its complex with brilliant green. Antimony can be selectively extracted in the presence of a large number of cations and anions. The total operation requires only 20 min.

The methods for the solvent extraction of antimony are best summarised by De, Khopkar[1] in their recent monograph. Tri-dodecylamine,[2] diethyl ether,[3] diisopropyl ether,[4] ethyl acetate,[5] isoamyl acetate,[6] and diisobutyl carbinol[7] were used for the solvent extraction of antimony from mineral acids. The iodocomplex of antimony[8–11] was extracted in benzene from 3—5M sulphuric acid. The complexes of antimony with dyes such as rhodamine B,[12–13] crystal violet;[12–15] methyl violet,[16] pyridylazo compounds[17] malachite green[18] and brilliant green [19–20] were extracted with organic solvents. Bis(2-ethylhexyl) phosphoric acid[21] in heptane was similarly used. However, these methods have certain limitations. They are time consuming, tedious and are neither selective nor applicable at microgram concentrations of antimony.

The method proposed in this paper is rapid, simple and permits clean-cut separation of antimony. 20% TBP-toluene quantitatively extracts antimony from 2M hydrochloric acid with 1M magnesium chloride as the salting-out agent. Antimony from the organic phase is then directly determined photometrically as its complex with brilliant green at 640 nm.

Experimental

Apparatus and Reagents. Type φ3KH-57 photoelectric photometer; Type C φ8-recording spectrophotometer with matched 10 mm glass cuvettes; Wrist action flask shaker: Cambridge pH indicator.

A stock solution of antimony was prepared by dissolving about 0.27 g of potassium antimonyl tartrate hemihydrate in 10 ml of 6N hydrochloric acid.[22] The solution was then made to one liter with water. On standardisation volumetrically with[23] Chloramine-T, it was found to contain 100 μg/ml of antimony. The dilute solution was prepared by ten-fold dilution. Tributyl phosphate (B.D.H), bp 143°C.

Brilliant green (B.D.H. Anal R): 0.05% aqueous solution.

General Procedure. An aliquot of solution containing about 10 μg of antimony was taken. In a total volume of 10 ml, hydrochloric acid and magnesium chloride were added so that each had a concentration of 2 and 1M respectively. The solution was then transferred to a separatory funnel. Ten milliliters of 20% TBP in toluene (0.73M) was then added. The mixture was vigorously shaken for about three minutes. The two phases were allowed to settle and separate. After withdrawing the aqueous phase, the organic phase was once

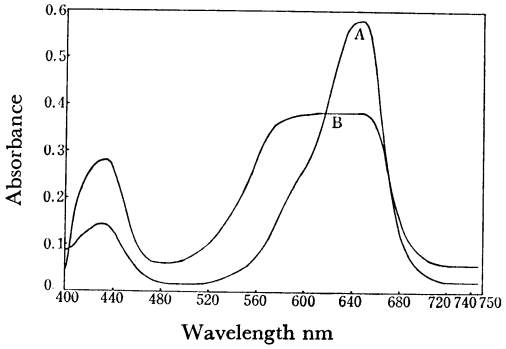

Fig. 1. Absorption spectrum of Sb (III)-brilliant green in 20% TBP toluene.

A = Absorption spectrum of Sb (III)-BG complex in 20% TBP-toluene *VS.* BG 20% TBP-toluene (Sb (III) = 8.22×10^{-6}M)

B = Absorption spectrum of brilliant Green vs 20% TBP-toluene mixture (Brilliant green = 1.19×10^{-4}M)

1) A. K. De, S. M. Khopkar, and R. A. Chalmers, "Solvent Extraction of Metals," Van Nostrand-Reinhold Co., London (1970).
2) A. Alian and W. Sanad, *Talanta*, **14**, 659 (1967).
3) G. K. Schweitzer and L. E. Storm, *Anal. Chim. Acta*, **19**, 154 (1958).
4) J. Bassett and J. C. H. Jones, *Analyst*, **91**, 176 (1966).
5) C. E. White and H. J. Rose, *Anal. Chem.*, **25**, 351 (1953).
6) N. Kosaric and C. Leliaert, *Mikrochim. Acta*, **1961**, 806.
7) R. W. Lowe, S. H. Prestwood, R. R. Rickard, and E. I. Wyatt, *Anal. Chem.*, **33**, 874 (1961).
8) R. W. Ramette, *ibid.*, **30**, 1158 (1958).
9) P. W. West and W. C. Hamilton, *ibid.*, **24**, 1025 (1952).
10) K. Tanaka, *Bunseki Kagaku*, **10**, 1087 (1961).
11) A. P. Grimanis and I. Hadzistelios, *Anal. Chim. Acta*, **41**, 15 (1968).
12) H. Onishi and E. B. Sandell, *ibid.*, **11**, 444 (1954).
13) H. Imai, *Bunseki Kagaku*, **11**, 806 (1962).
14) T. V. Lyashenko, Metallurgi. Khimi Prom. Kazakhstana Nauch Tekhn Sb. 67 (1962); *Anal. Abstr.*, **11**, 942 (1964).
15) K. Studlar and I. Janousek, *Collect. Czech. Chem. Commun.*, **25**, 1965 (1960).
16) M. Cyrankowska and J. Downarowicz, *Chemia Analit*, **12**, 137 (1967).
17) S. I. Gusev, L. V. Poplevina, and A. S. Pesis, *Zh. Anal. Khim.*, **22**, 731 (1967).
18) L. R. Narushkyavichyus, R. M. Kazlauskas and I. B. Marmakaite, *Zavod. Lab.*, **32**, 926 (1966).
19) R. W. Burke and O. Menis, *Anal. Chem.*, **38**, 1719 (1966).
20) L. N. Lapin and V. O. Gein, *Trudy Komissii Anal. Khim Akad. Nauk SSSR. Inst. Geokhim. Anal. Khim.*, **7**, 217 (1956).
21) I. S. Levin, A. A. Shatalova, and I. A. Vorsina, *Izv. Sib. Oldel. Akad. Nauk. SSSR*, 89, (1967); *Anal. Abstr.* **17**, 818 (1969).
22) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience 3rd Ed. (1959), p. 262.
23) A. I. Vogel, "Text Book of Quantitative Inorganic Analysis," Longmans Green 3rd Ed. (1961), p. 392.

again shaken with 2 ml of 0.05% solution of brilliant green for about three minutes. After separating the two phases, the green colored complex[20] of antimony in the organic phase was measured photometrically against a reagent blank at 640 nm.

Results and Discussion

Absorption Spectra. The absorption spectrum of the solution of antimony(III)-brilliant green complex in tributyl phosphate-toluene ($Sb=8.22\times10^{-6}$M) is shown in Fig. 1. The colored complex shows strong absorbance at 640 nm. The reagent blank at this wavelength also shows some absorbance. The difference in absorbance of reagent blank and complex is maximum at 640 nm; hence all absorbance measurements were carried out at this wavelength. The molecular extinction coefficient at 640 nm is 7.3×10^4.

Effect of Acidity and TBP Concentration. The hydrochloric acid concentration was varied from 0.5—5M in the presence of 1M magnesium chloride. The concentration of TBP was varied from 10—100% (0.37—3.66M) with toluene as a diluent. It was observed (Table 1) that quantitative extraction of antimony is possible from 2M hydrochloric acid with 20% TBP-toluene in the presence of 1M magnesium chloride as a salting-out agent. The distribution ratios (D) were

TABLE 1. DISTRIBUTION RATIO AS THE FUNCTION OF ACIDITY
Sb(III)=10 μg; 1M $MgCl_2$ as the salting out agent

TBP, concn. (M)	HCl, M (initial)	Extraction % E	Distribution ratio, D
10% (0.37)	0.5	35.3	0.55
	1.0	47.6	0.91
	1.5	58.8	1.40
	2.0	70.6	2.40
20% (0.73)	0.5	58.8	1.40
	1.0	76.5	3.26
	1.5	94.1	15.95
	2.0—5.0	100	∞
20% (0.73)	0.5	29.4	0.42
(in absence of	1.0	41.2	0.70
1M $MgCl_2$)	1.5	52.9	1.13
	2.0	64.7	1.83
	2.5	85.3	5.86
	3.0—5.0	100	∞
40% (1.46)	0.5	70.6	2.40
	1.0	82.4	4.68
	1.5	94.1	15.95
	2.0—5.0	100	∞
60% (2.19)	0.5	71.8	2.55
	1.0	83.5	5.00
	1.5	95.3	20.28
	2.0—5.0	100	∞
75% (2.74)	0.5	73.5	2.78
	1.0	85.3	5.80
	1.5	97.1	33.48
	2.0—5.0	100	∞
100% (3.66)	0.5	76.5	3.26
	1.0	88.2	7.47
	1.5	97.1	33.48
	2.0—5.0	100	∞

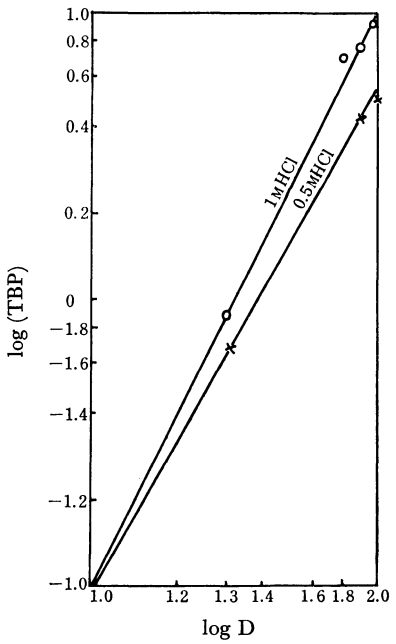

Fig. 2. Extraction as a Function of TBP-Concentration.

calculated as described earlier.[24] An attempt was made to ascertain the probable composition of the extractable species from the plot of log D *vs.* log (TBP) concentration. The slope at 1M hydrochloric acid concentration is 2.14 (Fig. 2). This shows that the probable composition of the extractable species is H [$SbCl_3$ $(TBP)_2$].

TABLE 2. EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON ABSORBANCE
Sb(III)=10 μg; 20% TBP-toluene; in absence of salting out agent.

HCl, M (initial)	Absorbance at 640 nm	Extraction % E	Distribution ratio, D
0.5	0.175	29.4	0.42
1.0	0.245	41.2	0.70
1.5	0.315	62.9	1.13
2.0	0.385	64.7	1.83
2.5	0.510	85.3	5.86
3.0—5.0	0.600	100.0	∞

Effect of Hydrochloric Acid Concentration on Absorbance. Extraction of antimony was carried out with 20% TBP-toluene with varying hydrochloric acid concentration. The results show (Table 2) that the absorbance increases as the acidity is increased. It becomes constant

TABLE 3. BEER'S LAW

Amount of antimony, μg	Absorbance at 640 nm
2.5	0.150
5.0	0.310
7.5	0.450
10.0	0.600
12.5	0.750
15.0	0.880

24) A. V. Rangnekar and S. M. Khopkar, This Bulletin, **41**, 600 (1968).

at 3M hydrochloric acid concentration. With further increase in acidity there is no change in the absorbance. Since these extractions were carried out in the absence of salting-out agent the extraction was quantitative at 3M hydrochloric acid. However, if 1M magnesium chloride is used as the salting-out agent the extraction is complete even at 2M hydrochloric acid.

Beer's Law. Different amounts of antimony were extracted at 2M hydrochloric acid in the presence of 1M magnesium chloride with 20% TBP-toluene (Table 3). They were measured at 640 nm as their complexes with brilliant green. The system conforms to Beer's law over the concentration range of 0.15—15 μg/m*l* of antimony at 640 nm. Sandell's sensitivity was found to be 0.0017 μg/cm^2 of antimony.

Table 4. Effect of salting-out agent
Sb(III)=10 μg; 20% TBP-toluene

Salting-out agent, M		HCl, M (initial)	Extraction % *E*	Distribution ratio, *D*
NH_4Cl	1.0	0.5	35.3	0.55
		1.0	47.6	0.91
		1.5	58.8	1.40
		2.0	70.6	2.40
	2.0	0.5	58.8	1.40
		1.0	70.6	2.40
		1.5	76.5	3.26
		2.0	82.4	4.69
LiCl	0.5	0.5	41.2	0.70
		1.0	52.9	1.13
		1.5	64.7	1.83
		2.0	76.5	3.26
	1.0	0.5	70.6	2.40
		1.0	82.4	4.68
		1.5	91.3	10.58
		2.0	100.0	∞
$MgCl_2$	0.5	0.5	47.6	0.91
		1.0	58.8	1.40
		1.5	70.6	2.40
		2.0	82.4	4.69
	1.0	0.5	36.4	1.40
		1.0	76.5	3.26
		1.5	94.1	15.95
		2.0	100.0	∞
$AlCl_3$	0.5	0.5	52.9	1.13
		1.0	64.7	1.83
		1.5	76.5	3.26
		2.0	88.2	7.48
	1.0	0.5	58.8	1.40
		1.0	70.8	2.40
		1.5	88.2	7.48
		2.0	100.0	∞

Effect of Salting-out Agent. Ammonium, lithium, magnesium, and aluminium chlorides (0.5—2M) were used as the salting-out agents when hydrochloric acid concentration used was 0.5—2M. The results show (Table 4) that ammonium chloride is not a good salting-out agent. 1M lithium, magnesium, or aluminium chloride are effective salting-out agents, at 2M hydrochloric acid concentration. On account of the ease of availability of 1M magnesium chloride, it was preferred as the salting-out agent.

Table 5. Effect of brilliant green concentration
Sb(III)=10 μg; 20% TBP toluene; 2M HCl+1M $MgCl_2$

Reagent concn.	Volume in m*l*	Absorbance at 640 nm
0.001	2	0.010
0.005	2	0.100
0.010	2	0.300
0.02	2	0.450
0.04	2	0.600
0.05	2	0.600
0.05	4	0.600
0.05	5	0.600

Effect of Brilliant Green Concentration. With all other factors kept constant the concentration of brilliant green was varied from 0.001 to 0.05 per cent (Table 5) in the aqueous solution. It was observed that 2 m*l* of 0.05 per cent aqueous solution of brilliant green was quite adequate for color development in 20% TBP toluene media.

Period of Shaking. The period of equilibration during extraction with TBP and during color development with brilliant green was varied from 30 sec to 20 min. In both cases the optimum period of extraction is three minutes.

Table 6. Stability of color of the complex

Time, hr	Absorbance at 640 nm
0.5	0.600
1	0.600
2	0.600
4	0.600
8	0.600
12	0.600
18	0.600
24	0.560
48	0.480

Stability of the Color. The absorbance of the colored complex was measured at lapsed intervals of time (Table 6). The complex decomposes after 18 hr. Therefore, it is recommended to measure the absorbance within the first 12 hr after extraction.

Effect of Diverse Ions. Various ions were studied to observe their effect on the process of extraction (Table 7). The tolerance limit was calculated as the amount to cause $\pm$2% error in antimony recovery. Lead, copper, zinc, cobalt, nickel, zirconium, beryllium, alkali and alkaline earths, thorium, cerium, uranium, selenite, tellurite, phosphate, acetate, and fluoride are tolerated in larger ratios (>1 : 500). Ions like silver, cadmium, bismuth, iron, organic complexing acids, thiocyanate, thiosulphate are tolerated in the ratio of 1 : 100. However, platinum metals, mercury, tin, titanium are tolerated in smaller amounts. Thallium, gold, chromate, bromide, and chlorate interfere. Some interferences can be eliminated by masking ions with EDTA, pyrophosphate, tartaric acid, and sodium fluoride (Table 7).

TABLE 7. EFFECT OF DIVERSE IONS
Sb(III) = 10 μg; 2M HCl + 1M $MgCl_2$; 20% TBP + Toluene

Foreign ion	Added as	Tolerance limit, μg	Foreign ion	Added as	Tolerance limit, μg
Pb^{2+}	$Pb(NO_3)_2$	5000	Sr^{2+}	$SrCl_2 \cdot 6H_2O$	5000
Hg^{2+}	$Hg(NO_3)_2$	500[a]	Ba^{2+}	$BaCl_2 \cdot 2H_2O$	5000
Ag^{+}	$AgNO_3$	1000[a]	Rb^{+}	RbCl	5000
Tl^{+}	$TlNO_3$	None	Cs^{+}	CsCl	5000
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	5000	Ti^{4+}	$TiCl_4 \cdot 4H_2O$	500
Cd^{2+}	$CdCl_2 \cdot 5H_2O$	2500	AsO_4^{3-}	Na_3AsO_4	5000
Sn^{2+}	$SnCl_2 \cdot 2H_2O$	500	Br^{-}	NaBr	None
Bi^{3+}	$Bi(NO_3)_3$	2500	CrO_4^{2-}	K_2CrO_4	None
Ru^{3+}	$RuCl_3 \cdot 3H_2O$	500	ClO_3^{-}	$KClO_3$	None
Rh^{3+}	$RhCl_3 \cdot 3H_2O$	500[c]	F^{-}	NaF	5000
Pd^{2+}	$PdCl_2 \cdot 2H_2O$	500[b]	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	200
Pt^{4+}	$H_2PtCl_6 \cdot 6H_2O$	500[a]	SeO_3^{2-}	Na_2SeO_3	5000
Au^{3+}	$HAuCl_4 \cdot H_2O$	None	SCN^{-}	NH_4SCN	1000
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	1000[d]	$S_2O_3^{-2}$	$Na_2S_2O_3$	1000
Al^{3+}	$Al(NO_3)_3$	30000	SO_4^{2-}	Na_2SO_4	10000
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	5000	TeO_3^{2-}	Na_2TeO_3	5000
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	500	VO_3^{-}	NH_4VO_3	1000
Co^{2+}	$CoCl_2 \cdot 6H_2O$	10000	PO_4^{3-}	Na_3PO_4	5000
Ni^{2+}	$NiCl_2 \cdot 6H_2O$	5000	$P_2O_7^{2-}$	$(NH_4)_2P_2O_7$	5000
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	10000	EDTA (disodium salt)		2500
Zr^{4+}	$Zr(NO_3)_4$	5000	Ascorbic acid		2500
Ce^{4+}	$Ce(SO_4)_2$	5000	Citric acid		2500
U^{6+}	$UO_2(NO_3)_2 \cdot 6H_2O$	5000	Malonic acid		1000
Be^{2+}	$Be(NO_3)_2 \cdot 4H_2O$	5000	Oxalic acid		2500
Ca^{2+}	$CaCl_2 \cdot 2H_2O$	5000	Tartaric acid		2500

a) 2500 μg of EDTA was used for masking.
b) 5000 μg of alkali pyrophosphate was used for masking.
c) 2500 μg of Tartaric acid was used for masking.
d) 5000 μg of sodium fluoride was used for masking.

From ten runs with 10 μg of antimony using the general procedure the average recovery is 99.2±0.8%, the relative standard deviation being 1.3%. Each determination took a total of 20 min.