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Extraction and Separation Studies of Tin(IV) with Tri-*n*-octylamine

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NOTE

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Abstract

A selective method is developed for the separation of tin(IV) from copper, manganese, zinc, cadmium, mercury, nickel, lead, aluminum, bismuth, and molybdenum with tri-*n*-octylamine either from hydrochloric or acetic acid media. The metal ion from the organic phase is stripped with nitric acid solution and determined photometrically in the aqueous phase. The method is shown to be applicable to synthetic mixtures.

Tri-*n*-octylamine (TOA) has been used as an extractant in this laboratory for the selective separations of copper (*1*) and mercury (*2*). This paper describes systematic studies on its use for separation of quadrivalent tin from associated elements. A 5% solution of TOA in benzene extracts tin(IV) quantitatively from 0.5 *M* HCl or acetic acid solution. The metal ion from the organic phase is back-stripped with nitric acid solution and subsequently determined photometrically with pyrocatechol violet (*3*).

Solvent extraction methods for tin have been reviewed by De et al. (*4*) and Korkisch (*5*) in their monographs. TBP (*6*) and MIBK (*7, 8*) are used for the extraction of tin from HCl or HBr solutions; ether (*9*) extracts tin(IV) from thiocyanate solution, whereas *N*-benzoyl phenyl hydroxylamine (*10*) has been used for extraction of tin(IV) from acetic acid solution. Liquid-ion exchangers such as Alamine 336 (*11*) and Amberlite

LA-2 (*12*) have also been used for the extraction of tin(IV) and tin(II), respectively.

In none of these methods were attempts made to separate tin from co-extracted elements. The proposed method provides for the separation of μg amounts of tin(IV) from metal ions such as copper, nickel, zinc, cadmium, mercury, lead, manganese, aluminum, and bismuth. The separation is quantitative and rapid.

EXPERIMENTAL

Apparatus and Reagents

Absorbance measurements were taken on a Zeiss Spectrophotometer (German) using 1-cm quartz cells. pH was measured on a Radiometer pH meter (Philips).

A stock solution of tin(IV) was prepared by dissolving 2.9 g of AR stannic chloride in 100 ml of 2 *M* HCl solution. The solution was standardized (*17*) and then diluted as required for working solution. All other chemicals used were of GR grade.

A 5% w/v solution of TOA (Kochlight, England) in benzene was equilibrated for 10 min with equal volumes of 4 *M* HCl or 1 *M* CH_3COOH before use.

General Procedure

A solution containing 10 to 50 μg of tin(IV) was mixed with enough hydrochloric acid or acetic acid to give a final acid concentration of 0.5 *M* in a total volume of 10 ml. The solution was then equilibrated for 5 min with 5 ml of 5% TOA dissolved in benzene. The organic phase was separated and extracted (1 min each) with nitric acid (3 × 5 ml of 0.5 *M* HNO_3) solution to strip tin into the aqueous phase. The combined aqueous phase was again extracted with 5 ml of pure benzene to remove traces of amine, and finally tin in the aqueous phase was determined photometrically with pyrocatechol (*3*) by measuring at 555 nm.

RESULTS AND DISCUSSION

The extraction behavior of tin with varying acid concentration and TOA concentration is shown in Table 1. Five percent TOA dissolved in benzene extracts tin quantitatively from 0.5 *M* hydrochloric or acetic

TABLE 1

Distribution Ratio of Tin(IV) as a Function of Acid Concentration and TOA Concentration[a]

Initial acid concentration	1% TOA (0.028 *M*)		2% TOA (0.055 *M*)		3% TOA (0.083 *M*)		4% TOA (0.11 *M*)		5% TOA (0.14 *M*)	
	%*E*	*D*	%*E*	*D*	%*E*	*D*	%*E*	*D*	%*E*	*D*
HCl										
0.1 *M*	40.00	1.33	65.63	3.81	79.69	7.84	82.80	9.63	95.32	40.74
0.25 *M*	43.33	1.53	71.88	5.11	81.28	8.68	89.06	16.19	98.45	127.00
0.5 *M*	43.33	1.53	70.33	4.74	81.28	8.68	89.06	16.19	99.40	331.20
CH_3COOH										
0.1 *M*	31.60	0.92	35.00	1.07	36.67	1.15	40.00	1.33	43.33	1.53
0.5 *M*	28.33	0.79	36.67	1.15	43.33	1.53	68.34	4.27	99.40	331.20
1.0 *M*	21.67	0.55	31.60	0.92	40.00	1.33	51.66	2.14	65.00	3.71
3.0 *M*	20.00	0.50	28.33	0.79	33.34	1.00	46.67	4.25	61.67	3.22
5.0 *M*	18.33	0.44	23.33	0.60	31.60	0.92	40.00	1.33	43.33	1.53

[a]Tin(IV) = 20 μg, extracting solution = 5 ml of 5% TOA.

acid solution. The log-log plot of distribution ratio vs $[TOA]_{org}$ at fixed HCl (0.5 *M*) and acetic acid (1.0 *M*) concentrations gave slopes of 1.84 and 2.05, respectively, indicating that the metal-to-amine ratio in the extractable species is 1 : 2. The extracted species is thus $(R_3NH^+)_2SnX_6^{2-}$. Tin extracts also from H_2SO_4 and HBr solution, but back-extraction is not feasible with any agent. Extraction is incomplete from HNO_3 (0.1 to 6 *M*) solution.

Interferences

A number of ions were tested for their interference in the extraction and determination of tin. The tolerance limit was set at the amount required to cause $\pm 2\%$ error in the recovery of tin. About 400 μg of cobalt; 250 μg each of nickel, cadmium, mercury, thorium, selenium, tellurium, platinum, citrate, tartrate, thiourea, thiosulfate, phosphate, and nitrate; and 125 μg each of chromium, indium, manganese, lead, zinc, oxalate, ascorbate, fluoride, and sulfate do not interfere, but ions such as iron, antimony, vanadium, and EDTA interfere strongly. Ions such as copper, zinc, cadmium, mercury, manganese, and bismuth co-extract.

Separation of Tin(IV) from Copper, Manganese, Zinc, Cadmium, Mercury, Nickel, Lead, Aluminum, and Bismuth from Acetic Acid Solution

The percentage extractions of Sn, Cu, Mn, Zn, Cd, Hg, Ni, Pb, Al, and Bi, shown in Table 2, indicate the possibility of separation of tin(IV). When extracted with 5% TOA from 0.5 *M* acetic acid solution, tin (20 μg) extracts quantitatively into the organic phase whereas lead, aluminum, and nickel (1 mg each) are retained in the aqueous phase and are estimated titrimetrically (*15*, *16*). Co-extracted bismuth and mercury (2 mg each) are retained in the aqueous phase by selective masking with thiourea and ascorbic acid, respectively. Bismuth in the aqueous phase is estimated titrimetrically (*15*); however, the aqueous solution has to be treated with a few drops of nitric acid and then with 2 ml of hydrogen peroxide before mercury is determined titrimetrically (*15*). Copper, zinc, cadmium, and manganese (1 mg each) show co-extraction with tin but are back-washed from the organic phase with water (2 × 10 ml) and determined in the aqueous phase by standard procedures (*15*, *16*); finally, tin is stripped and determined as described in the working procedure. The results of various synthetic mixtures are shown in Table 3. The average recovery

TABLE 2

Percentage Extraction of Tin(IV) and Other Metal Ions into 5% TOA

	HCl			CH_3COOH		
Metal ions	0.5 *M*	1–4 *M*	5–6 *M*	0.5 *M*	1–3 *M*	5 *M*
Tin(IV)	99.4	89.4	87.8	99.4	61–65	43.3
Copper	0.0	10–86.8	100.0	2.5	10–24	33.0
Nickel	0.0	0.0	0.0	0.0	0.0	0.0
Zinc[a]	98.5	—	—	0.0	—	—
Cadmium[a]	100.0	—	—	1.0	—	—
Mercury	86.0	80.0	68.0	100.0	—	—
Manganese	—	—	—	4.20	4.2–10.5	12.7
Lead	23.8	47.6	34.6	0.0	—	—
Bismuth[a]	—	—	—	1.0	—	—
Aluminum	—	—	—	1.0	—	—
Molybdenum	1.0	10–86.9	99.0	—	—	—

[a]Zn, Cd, and Bi co-extract with Sn(IV), Bi with thiourea, and Hg with ascorbic acid are masked.

TABLE 3

Analysis of Synthetic Mixtures

Composition of synthetic mixture	Percentage recovery of tin (triplicate analysis)	Relative error (%)	Percentage recovery of added ions	Relative error (%)
Sn, 0.02 mg; Cu, 1 mg	99.4	0.6	99.5	0.5
Sn, 0.02 mg; Mn, 1 mg	99.2	0.8	99.5	0.5
Sn, 0.02 mg; Zn, 1 mg	98.9	1.1	99.0	1.0
Sn, 0.02 mg; Cd, 1 mg	99.3	0.7	98.8	1.2
Sn, 0.02 mg; Hg, 1 mg	98.9	1.1	99.0	1.0
Sn, 0.02 mg; Ni, 1 mg	99.4	0.6	99.8	0.2
Sn, 0.02 mg; Pb, 1 mg	99.2	0.8	99.5	0.5
Sn, 0.02 mg; Al^{3+}, 1 mg	99.0	1.0	99.0	1.0
Sn, 0.02 mg; Bi^{3+}, 1 mg	99.0	1.0	99.5	0.5
Sn, 0.02 mg; Mo^{6+}, 0.04 mg[a]	99.4	0.6	99.0	1.0
Sn, 0.02 mg; Cu, 0.1 mg[a]	99.5	0.5	99.4	0.6
Sn, 1 mg; Cu, 1 mg; Ni, 1 mg; Zn, 1 mg; Pb, 1 mg	99.0	1.0	—	—
Sn, 0.02 mg; Cu, 1 mg; Ni, 1 mg; Zn, 1 mg; Pb, 1 mg; Mn, 1 mg; Al, 1 mg	98.8	1.2	—	—

[a]Separation done from HCl solution.

of tin is 99.2 ± 0.4%. The average recoveries of Pb, Al, Ni, Bi, Hg, Cu, Zn, Cd, and Mn from binary mixtures are 99.5, 99.0, 99.8, 99.5, 99.0, 99.5, 99.0, 99.8, and 99.5%, respectively.

Separation of Tin(IV) from Copper and Molybdenum from Hydrochloric Acid Solution

The results in Table 2 also indicate the possibility of separation of tin from copper and molybdenum from hydrochloric acid solution. A sample solution (0.5 *M* in HCl) containing 20 μg of tin(IV), 100 μg of copper, and 40 μg of molybdenum is extracted with 5% TOA solution as described in the general procedure. Tin is removed in the organic phase, while copper and molybdenum are retained in the aqueous phase. Tin is stripped from the organic phase with nitric acid (0.5 *M*) solution and determined photometrically, whereas copper (*13*) and molybdenum (*14*) are determined in the aqueous phase by standard procedures. The results are reported in Table 3.

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