

Separation of Zinc from Mixtures by Extraction Chromatography with Tributyl Phosphate

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A novel method was developed for extraction chromatographic separation of zinc with tributyl phosphate as the stationary phase. Zinc was extracted from 1 M ammonium thiocyanate and was stripped with 0.25 M ammonium chloride. In addition, all mineral acids of appropriate strength and ammonium acetate (2 M) were also effective as stripping agents. Zinc was separated from a variety of elements in binary and multicomponent mixtures by exploiting the difference in their extractability or stripping characteristics by different media. The method was extended for the analysis of zinc in soil and effluent samples.

TRIOCTYLAMINE was used for the extraction chromatographic¹, separation of zinc. Tributyl phosphate² was used in extraction chromatographic separation of zinc from hydrochloric acid. It was separated from indium³ with tributyl phosphate. The separation of zinc from beryllium and manganese was carried out from thiocyanate media⁴. Although tributyl phosphate was used for the solvent extraction of zinc⁵ from ammonium thiocyanate (0.01–1 M), no systematic efforts were made on the extraction chromatographic separation of zinc with tributyl phosphate, therefore, such studies are reported in this paper.

Experimental

A ECIL GS 866 C spectrophotometer and a ECIL 822 digital pH meter were used. Silica gel (100–200 mesh) was made hydrophobic and coated with tributyl phosphate as usual⁶.

A stock solution of zinc was prepared by dissolving zinc sulphate heptahydrate (2.20 g) in deionised water (100 ml) containing 2% concentrated H₂SO₄. It was standardised complexometrically, when it was found to contain 4.5 mg ml⁻¹ of zinc. The diluted solution containing 5 μg ml⁻¹ zinc was prepared by appropriate dilution.

General procedure: An aliquot of solution containing zinc (5 μg) was made up to 1 M in ammonium thiocyanate in total volume of 5 ml. The solution was passed through the column at the flow rate of 1 ml min⁻¹. Zinc was extracted on the column by tributylphosphate. It was stripped with various mineral acids and salts. Fifteen fractions each of 2 ml were collected and zinc from each fraction was determined fluorimetrically with Rhodamine B⁷.

Results and Discussion

Effect of thiocyanate concentration: The extraction chromatographic studies of zinc from 0.5 to 8 M ammonium thiocyanate showed that it was quantitatively extracted from 1 to 8 M ammonium thiocyanate. Hence 1 M ammonium thiocyanate was used for extraction.

TABLE 1—EFFECT OF VARIOUS STRIPPING AGENTS

Stripping agent M	Peak elution volume (V _{max}) ml	Total volume of eluant (V _t) ml	Total recovery %
HCl	0.10–0.25	8	30
	0.5	6	30
	1.0	6	30
	2–3	4	10
H ₂ SO ₄	0.12	6	20
			96.3
HNO ₃	0.10	8	30
	0.25	6	30
	0.50	6	30
	1–2	4	10
NH ₄ Cl	0.1–2	4	10
			100.1
CH ₃ COONH ₄	0.05	10	20
	0.10	10	20
	0.25–2	4	12
			75.5
			90.0
			100.0

Effect of stripping agent: The study of stripping of zinc from column with acids and salts showed that it was completely stripped with concentration greater

TABLE 2—SEPARATION OF ZINC FROM MULTICOMPONENT MIXTURES

Sl. no.	Element	Amount taken μg	Amount found μg	Recovery %	Stripping agent M	Volume ml
1.	Pb	500	499.0	98.8	2 M NH_4SCN	15
	Zn	5	5.1	102.0	0.25 M NH_4Cl	10
	Bi	250	245.0	98.0	4 M HCl	15
2.	Cr ⁺⁺⁺	250	245.0	98.6	1.5 M NH_4SCN	15
	Mn	250	250.0	100.6	1.0 M NH_4SCN + 0.5 M HCl	15
	Zn	5	4.9	98.0	3 M HCl	10
	Fe	100	96.5	96.5	0.1 M HCl	50
3.	Sn/Pb	100	95.0	95.0	1 M NH_4SCN	15
	Sb	100	101.0	101.0	1 M NH_4SCN + 0.5 M HCl	20
	Zn	5	5.1	101.0	3 M HCl	15
	Cu	50	45.0	90.0	0.1 M HCl	30
4.	Cr ⁺⁺⁺ /Ni	250	250.0	100.0	2 M NH_4SCN	15
	Cd	100	95.0	95.0	1 M NH_4SCN + 0.5 M HCl	15
	Zn	5	5.0	100.0	3 M HCl	12
	V	100	98.0	98.0	1 M HCl	12
	Fe	100	95.0	95.0	0.1 M HCl	50

than 2 M hydrochloric acid, 1 M nitric acid or 0.25 M ammonium acetate, or 0.1 M ammonium chloride. Therefore, a 0.25 M ammonium chloride solution was preferred as the stripping agent (Table 1).

Separation of zinc from binary mixtures : It was possible to separate zinc from binary mixtures by taking the advantage of difference in extractability of various ions. When Zn was passed through the column along with alkali metals, Cr⁺⁺⁺, Pb, Mo^{VII}, Ni and Sn from 1 M ammonium thiocyanate, all except Zn passed through the column and were thus separated from Zn.

Separation of zinc from multicomponent mixtures : It was possible to exploit the difference in stripping characteristics of some stripping agents, e.g. when mixture of Zn with Al, Sb, Be, Cd, Co and Mn was passed through column all elements were extracted. While stripping, these ions were first stripped by 0.5 M hydrochloric acid containing 1 M ammonium thiocyanate. Zn was stripped latter. When binary mixture of Zn with Cu or Fe was passed through the column from 1 M ammonium thiocyanate all were extracted. However, Zn was first stripped with 3 M hydrochloric acid followed by Fe or Cu with 0.1 M hydrochloric acid. Bi, Cu, Fe and V were also extracted with Zn. However, Zn was first stripped with 3 M hydrochloric acid while all these ions were stripped with diluted hydrochloric acid (Table 2) and thus separated. In all these separations these elements were determined from eluted solution by spectrophotometer with suitable chromogenic ligands⁷.

Sequential separation of Zn, Cd and Hg : When the mixture of Zn, Cd and Hg was passed through the column from 0.5 M hydrochloric acid containing 2 M ammonium thiocyanate, Cd was not extracted while Hg and Zn were extracted. Zn was stripped with 0.25 M ammonium chloride while Hg was stripped with 0.01 M sodium citrate at pH 5. Thus it was possible to separate these elements from one another in different proportions.

Analysis of Zn from soil or effluent samples : A known amount of soil or effluent sample was first treated with perchloric acid or nitric acid mixture and it was evaporated to dryness to destroy the organic matter. Then residue was dissolved in hydrochloric acid and it was made upto known volume with distilled water. A known aliquot was passed through the column from 1 M ammonium thiocyanate, when lead was not extracted. Al or Mn were stripped with 0.5 M hydrochloric acid containing 1 M ammonium thiocyanate. Zn was stripped with 3 M hydrochloric acid and finally Cu or Fe were stripped with 0.1 M hydrochloric acid. The results of three analysis showed that the zinc content in soil sample being 91 ppm against the reported value of 92 ppm. Similarly, amount of zinc in effluent from electroplating industry was found to be 6.8 ppm against the reported value of 6.7 ppm. In both the cases the reported values were determined by atomic absorption spectrometry.

As Zn, Cd and Hg belong to the same group, their separation has great significance. The separation of Zn from Cu, Pb, Fe⁺⁺⁺ and Sb⁺⁺⁺ is important as they are associated in alloys. The total

time required for separation and analysis is 3 h.
The method is accurate to $\pm 1.5\%$.

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