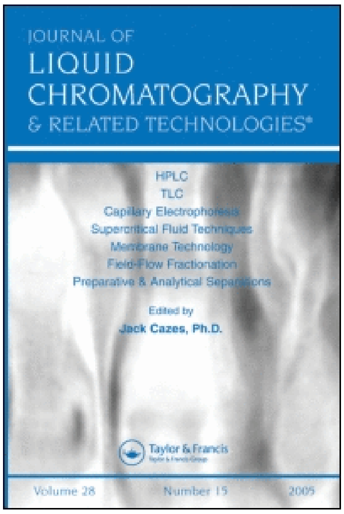

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation of Zirconium by Extraction Chromatography with Amberlite LA-1 from Malonic Acid

Prakash Narayanan[a]; S. M. Khopkar[a]
[a] Department of Chemistry, Indian Institute of Technology, Bombay, India

To cite this Article Narayanan, Prakash and Khopkar, S. M.(1985) 'Separation of Zirconium by Extraction Chromatography with Amberlite LA-1 from Malonic Acid', Journal of Liquid Chromatography & Related Technologies, 8: 4, 765 — 776

To link to this Article: DOI: 10.1080/01483918508067117

URL: http://dx.doi.org/10.1080/01483918508067117

JOURNAL OF LIQUID CHROMATOGRAPHY, 8(4), 765-776 (1985)

SEPARATION OF ZIRCONIUM BY EXTRACTION CHROMATOGRAPHY WITH AMBERLITE LA-1 FROM MALONIC ACID

Prakash Narayanan and S. M. Khopkar
Department of Chemistry
Indian Institute of Technology
Bombay-400 076, India

Abstract

Zirconium was separated by extraction chromatography with Amberlite LA-1 as an extractant from 1 x 10^{-3} M to 2.5 to 10^{-1} M of malonic acid at pH 2.0 to 6.0. It was stripped with various mineral acids and determined spectrophotometrically with arsenazo-III at 665 nm. Zirconium was separated from alkali, alkaline earths, yttrium, lanthanum, chromium(III), manganese, cobalt, nickel, copper, zinc, cadmium and aluminium by process of selective extraction. It was also separated from scandium, titanium, thorium, uranium and bismuth by process of selective stripping with various mineral acids. The method was extended for the analysis of zirconium in zircon.

0148-3919/85/0804-0765$3.50/0

Solvent extraction separation of methods for zirconium are summarised in a monograph (1). The extraction of zirconium with high molecular weight amines from organic acids (2,3) were reported earlier. The extraction chromatographic methods for the separation of zirconium with high molecular weight amines are few in number. Trioctyl amine (4,5) or its isomeric derivative (6) was explored as an extractant on cellulose and corvic support. Aliquat 336 (7) impregnated on kel-F support was used for the separation of zirconium from thorium and uranium. Amberlite LA-2 (8,9) permitted the separation of zirconium from uranium, thorium and scandium in sulphate media. However so far no endeavour was made to utilise dicarboxylic acids like, malonic acid as the media for separation of zirconium from associated elements.

Experimental

Apparatus and reagents

ECIL spectrophotometer provided with matched 10 mm corex glass cuvetts; Cambridge pH meter with combined glass electrode; chromatographic column (7 mm x 200 mm); Amberlite LA-1 [N-dodecyl (trialkyl methyl) amine] (Rohm and Hass Co., Philadelphia, USA.)

A stock solution of zirconium was prepared by dissolving 1 gm of zirconium nitrate pentahydrate in 25 ml of nitric acid and then diluting it to 250 ml with distilled water. The solution on standardisation, complexometrically with EDTA (10) contained 1 mg/ml of zirconium. A diluted solution containing 50 μg/ml of zirconium was prepared by twenty fold dilution. Silica gel (100-200 mesh) was made hydrophobic and coated with Amberlite LA-1 as per procedure described earlier (11). It was then packed in a column with bed dimensions of 7 mm x 100 mm.

General Procedure

An aliquot of solution containing 50 μg of zirconium was taken and mixed with 5 ml of 0.01 M malonic acid. Then the pH of the solution was adjusted to 5.0 with either 0.01 M malonic acid or sodium hydroxide. It was then passed on the column at the flow rate of 1 ml/min. Zirconium which was extracted on the column was stripped with various mineral acids. Eight fractions each of 5 ml were collected and from each fraction, zirconium was determined spectrophotometrically with arsenazo-III at 665 nm (12).

Results and Discussions

Zirconium in batch extraction (3) was extracted with 4% Amberlite LA-1, LA-2 in xylene at pH 2.5 to 6.0 in presence of 0.01 M malonic acid. It was stripped with > 1 M of mineral acids. This extraction characteristics was confirmed on the column by carrying out systematic investigations between pH 1.0 to 7.0 (Fig. 1) in the presence of 0.01 M malonic acid. The same extraction behaviour was confirmed on the column as zirconium was quantitatively extracted from pH 2.5 to 6.0.

The effect of malonic acid concentration on extraction of zirconium was studied by varying the concentration of malonic acid from 10^{-4} M to 5×10^{-1} M (Fig. 2). Zirconium was quantitatively extracted with 10^{-3} M to 2.5×10^{-1} M of malonic acid. At higher concentrations of malonic acid it showed a decrease in extraction possibly due to setting up of competitive equilibria between anionic malonato complex of zirconium and the malonato anion for the extractant.

Various mineral acids were tested as the stripping agent in the concentration range of 0.5 to 3.0 M (Table 1). Zirconium

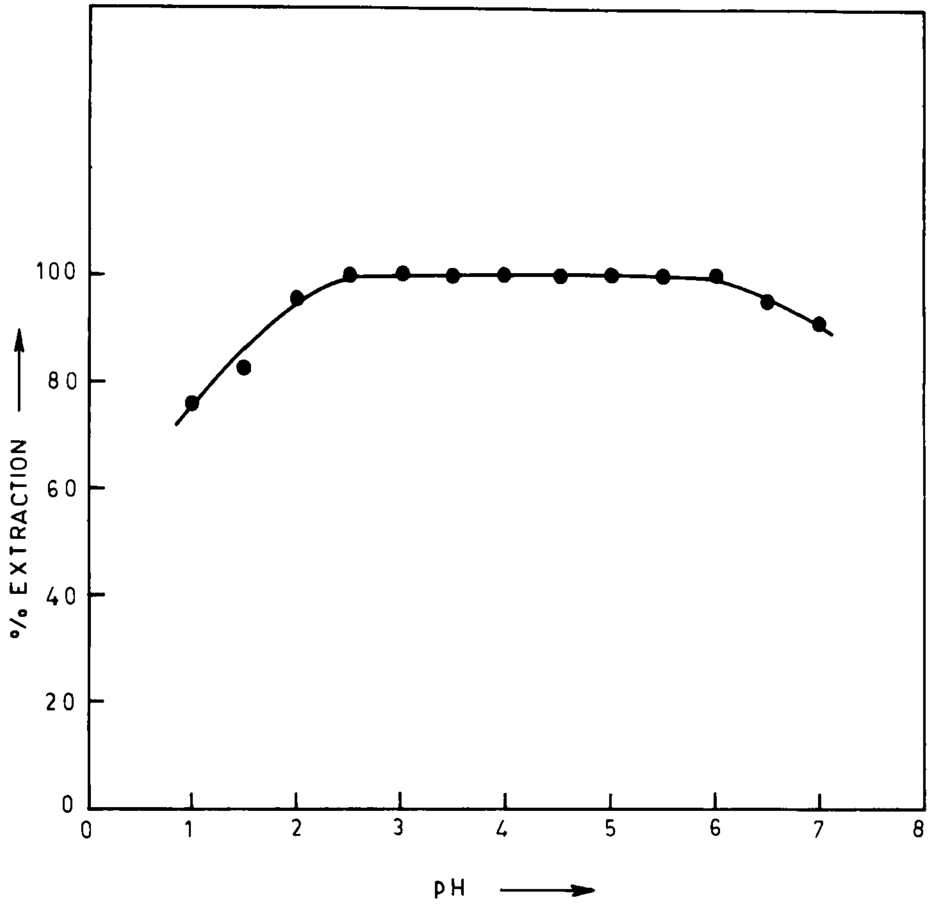

FIGURE 1. Effect of pH on Extraction of Zirconium.

was stripped quantitatively with greater than 2 M hydrochloric or 1 M sulphuric or 3 M of nitric acid. Below 1.5 M hydrochloric or 0.75 M sulphuric or 2.0 M nitric acid stripping was incomplete. 2 M hydrochloric acid was however preferred as the stripping agent.

Table - 1

Elution Behaviour of Zirconium

Eluant (M)		Peak elution volume, ml	Volume for total recovery ml	% Recovery
HCl	0.5	15	40	13.0
	1.0	15	35	34.7
	1.5	15	35	64.5
	2.0	10	30	100.2
	3.0	10	25	100.1
H_2SO_4	0.5	15	40	48.2
	0.75	15	35	78.1
	1.0	10	30	100.6
	2.0	10	25	102.1
	3.0	10	25	100.2
HNO_3	1.0	20	40	13.0
	2.0	15	40	65.2
	3.0	15	35	100.8

Separation of Zirconium from Binary Mixtures

Zirconium was separated from several elements in binary mixtures by taking the advantage of the difference in pH at which various elements formed anionic malonato complexes e.g., at pH 5.0, alkali, alkaline earths, yttrium, lanthanum, chromium(III), manganese (II), cobalt, nickel, copper, zinc, cadmium, aluminium were incapable of forming anionic complex, while zirconium formed extractable anionic malonato complex. Hence when a mixture was passed on the column zirconium was extracted and subsequently

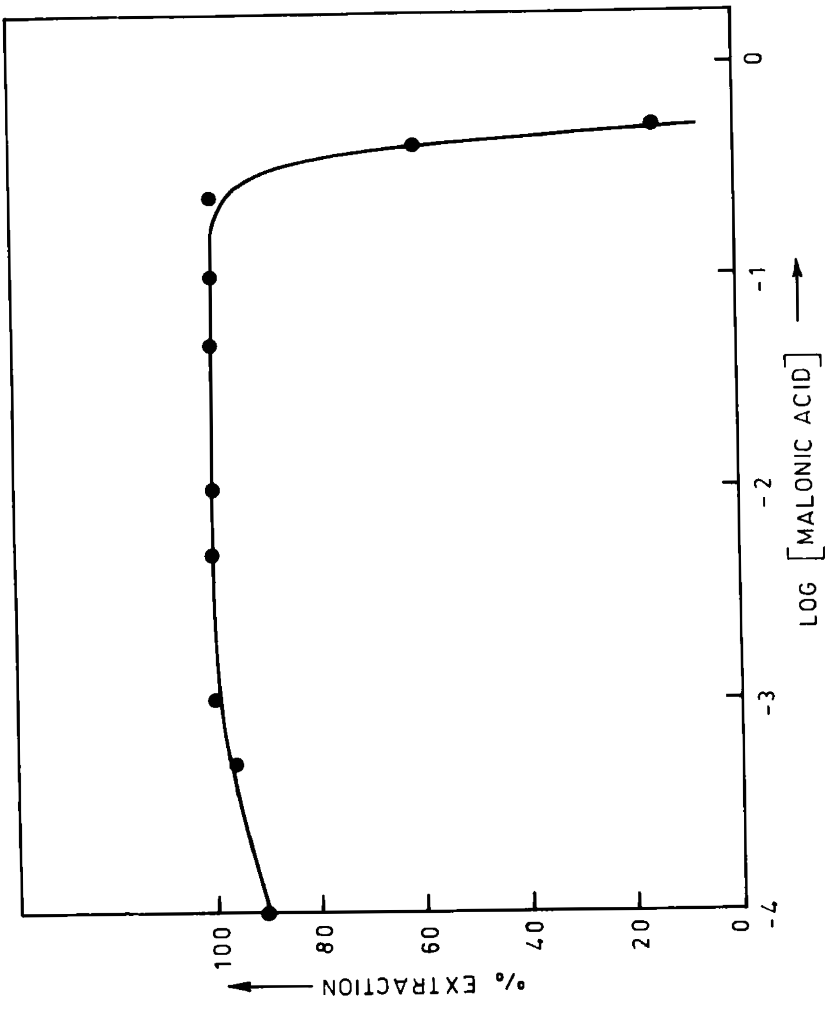

FIGURE 2. Effect of Malonic Acid Concentration on Extraction of Zirconium.

stripped with 2 M hydrochloric acid, while all other elements passed through during the extraction stage. Zirconium was thus separated from these elements in the ratio 1:40.

It was also possible to separate some elements from zirconium with various stripping agents. Since scandium, titanium, vanadium, bismuth and thorium formed malonato complex they were extracted along with zirconium but were first stripped with 0.04 M sulphuric acid (thorium with 0.25 M sulphuric acid). Zirconium was reextracted as its anionic sulphato complex on the column and was later stripped with 2 M hydrochloric acid. Zirconium was separated from iron (III), thallium(III) and uranium(VI) after co-extraction with zirconium in binary mixtures. Since zirconium could not form chloro complex while other elements were reextracted on the column as their chlorocomplexes, zirconium was washed out first followed by these elements with suitable mineral acids.

Separation of Zirconium from Multicomponent Mixtures

Some elements like chromium(III), nickel, yttrium, cadmium, lanthanum were incapable of forming malonato complexes and therefore could be stripped with water. The difference in the concentration of sulphuric acid at which various metals formed sulphato complexes was also utilised to develop separations eg. vanadium, scandium, bismuth, titanium, thorium were incapable of forming anionic sulphato complexes at 0.25 M sulphuric acid, in contrast zirconium formed stable anionic sulphato complex and was therefore retained on the column. It was subsequently stripped with 2 M hydrochloric acid. Few separations based upon these principles are described.

The mixture of chromium(III), zirconium and iron(III) was passed on the column when chromium passed through the column as

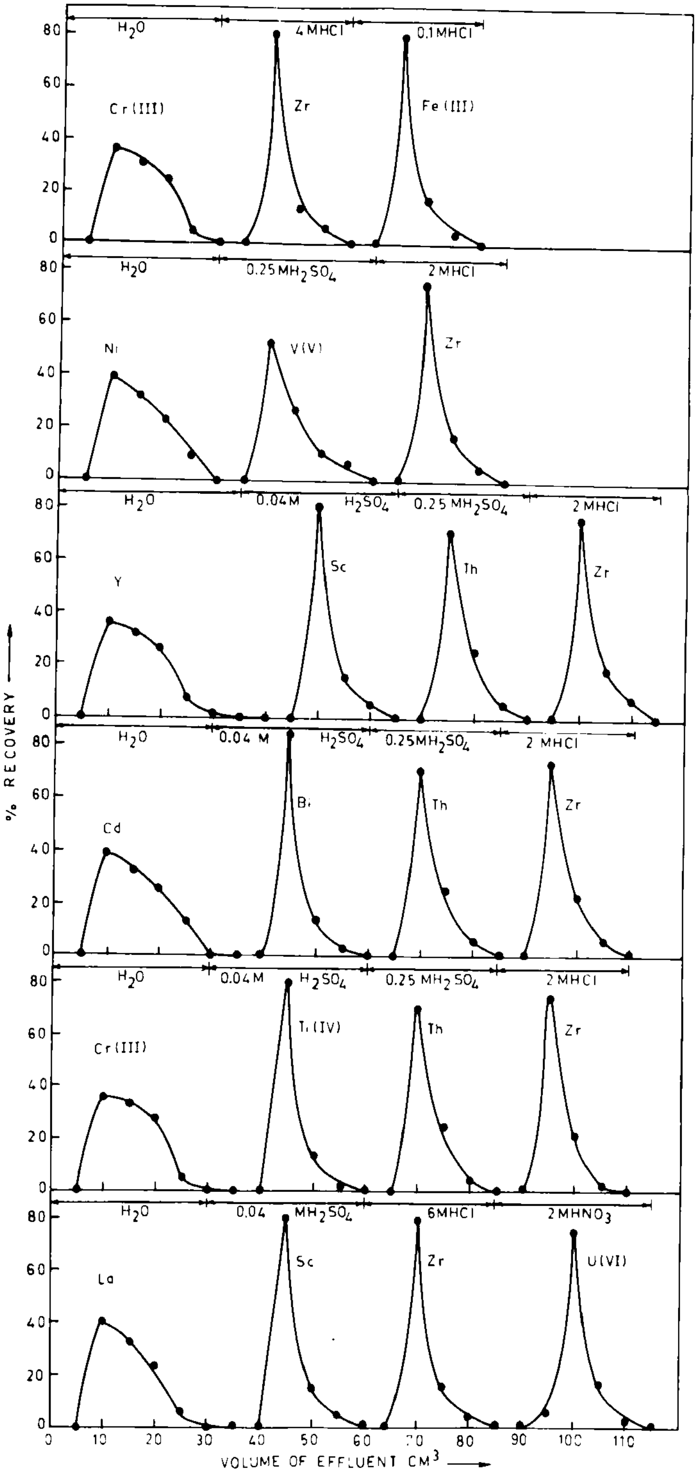

FIGURE 3. Separation of Zirconium from Multicomponent Mixtures.

it could not form malonato complex. The extracted zirconium was stripped with 4 M hydrochloric acid when iron was reextracted as its chloro complex. This in turn was stripped with 0.1 M hydrochloric acid.

The mixture containing nickel, vanadium(V) and zirconium was passed on the column when nickel was not extracted and it passed through the column but vanadium and zirconium were coextracted. Then vanadium was stripped with 0.25 M sulphuric acid while zirconium was stripped with 2.0 M hydrochloric acid.

Yttrium, scandium, thorium and zirconium were separated by process of selective extraction. On passing the mixture through the column yttrium could not be extracted hence passed through. The extracted scandium was stripped with 0.04 M sulphuric acid, thorium with 0.25 M sulphuric acid and finally zirconium with 2.0 M hydrochloric acid.

Cadmium, bismuth, thorium and zirconium were separated from each other by passing the mixture on the column when cadmium was not extracted and was washed with water while other metals were extracted. Bismuth was stripped with 0.04 M sulphuric acid thorium with 0.25 M sulphuric acid and zirconium with 2 M hydrochloric acid.

Chromium(III), titanium(IV), thorium and zirconium were separated by washing chromium with water followed by stripping of titanium with 0.04 M sulphuric acid, thorium with 0.25 M sulphuric acid and zirconium with 2 M hydrochloric acid.

Lanthanum, scandium, zirconium and uranium(VI) were separated by stripping lanthanum with water, scandium with

Table - 2

Separation of Zirconium from Multicomponent Mixtures

S.N.	Elements	Taken (µg)	Found (µg)	Recovery %	Eluant used (M)
1	Cr(III)	300	301	100.3	H_2O
	Zr	50	49	98.6	4 HCl
	Fe(III)	100	99.6	99.6	0.1 HCl
2	Ni	300	302	100.6	H_2O
	V(V)	96.7	97.8	101.2	0.25 H_2SO_4
	Zr	50	50.1	100.2	2 HCl
3	Y	300	301.5	100.4	H_2O
	Sc	100	99.8	99.8	0.04 H_2SO_4
	Th	98.5	98.5	100.0	0.25 H_2SO_4
	Zr	50	49.3	98.6	2 HCl
4	Cd	300	300.5	100.2	H_2O
	Bi	100	98.5	98.5	0.04 H_2SO_4
	Th	98.5	96.8	98.3	0.25 H_2SO_4
	Zr	50	49.5	99.0	2 HCl
5	Cr(III)	300	301	100.3	H_2O
	Ti	94.6	93.1	98.4	0.04 H_2SO_4
	Th	98.5	96.5	98	0.25 H_2SO_4
	Zr	50	50.5	101.0	2 HCl
6	La	300	302	100.6	H_2O
	Sc	100	99.5	99.5	0.04 H_2SO_4
	Zr	50	49	98	6 HCl
	U(VI)	100	101.5	101.5	2 HNO_3

0.04 M sulphuric acid, zirconium with 6.0 M hydrochloric acid and finally uranium with 2 M nitric acid (Table 2, Fig. 3).

The mixtures in all separations were first adjusted to pH 5.0 in presence of 0.01 M malonic acid to form extractable anionic complex. They were then passed through the column at a flow rate of 1 ml/min. After stripping out all these elements, they were determined spectrophotometrically by complexing with appropriate chromogenic ligands (13).

The proposed method was extended for the analysis of zirconium in zircon.

Separation of Zirconium from Zircon

About 2 gm of zircon was fused with same amount of borax in a platinum crucible. After cooling the mass, it was laxivated with 2 M hydrochloric acid. An aliquot of solution was taken and proceded as per general procedure and was passed on the column when lanthanides, aluminium,iron(II) were not extracted and were washed with water. Titanium and iron(III) stripped with 0.1 M sulphuric acid zirconium was stripped with 6.0 M hydrochloric acid and finally uranium was stripped with 2.0 M nitric acid. The amount of ZrO_2 determined as per procedure was 64.5% as against standard value of 64.15%.

Acknowledgement

We are thankful to Council of Scientific and Industrial Research, India, for awarding senior research fellowship to one of us (P.N.).

References

1. A.K. De, S.M. Khopkar and R.A. Chalmers, 'Solvent Extraction of Metals', Van Nostrand Reinhold, London (1970).
2. C.P. Vibhute and S.M. Khopkar, Anal. Letters, 16, 1037 (1983).
3. M.A. Sawant and S.M. Khopkar, Talanta, 27, 209 (1980).
4. E. Cerrai and C. Testa, J. Chromatog., 6, 443 (1961).
5. I.M. Gibalo and N.A. Mymrik, Zh. Anal. Khim., 25, 1744 (1970).
6. T.B. Pierce and W.M. Henry, J. Chromatog., 23, 457 (1966).
7. M.N. Sastri, A.P. Rao and A.R.K. Sarma, Ind. J. Chem., 4, 287 (1966).
8. T. Shimizu, J. Chromatog., 85, 123 (1973).
9. T. Shimizu, J. Chromatog., 96, 262 (1974).
10. F.J. Welcher, 'Analytical Uses of Ethylene diamine Tetraacetic Acid', p 185, D. Van Nostrand Co. Inc. USA (1958).
11. S.N. Bhosale and S.M. Khopkar, Talanta, 26, 889 (1979).
12. H. Onishi, Japan Analyst, 12, 1153 (1963).
13. F.D. Snell, 'Photometric and Fluorometric Methods of Analysis', Wiley and Sons, New York (1978).