

Extraction Chromatographic Studies of Aluminium(III) with Versatic Acid and Its Analytical Applications

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Manuscript received 27 June 1997, revised 18 February 1998, accepted 10 March 1998

A selective method has been developed for reversed phase extraction chromatographic studies of Al^{III} with Versatic-10 as a stationary phase on a column of silica gel. Quantitative extraction of Al^{III} has been achieved from 0.02 M acetate buffer solution in the pH range 4.75–5.5. The extracted Al^{III} has been stripped with 2.5 M nitric acid and estimated spectrophotometrically. The effects of pH, stripping agent, flow rate on extraction and elution behaviour have been examined. Exchange capacity and breakthrough capacity of the exchanger have been determined. Al^{III} has been separated from several synthetic multicomponent mixtures. The method has also been applied for the analysis of various ores and alloy samples.

A large number of papers have been published on the extraction of metal ions by carboxylic acids¹. There are reports on investigation of metals with C₇-C₉ acids² and with commercially available naphthenic and versatic acids³. In our laboratory, Versatic-10 has been used for the extraction of several metal ions^{4,5}. These results have encouraged us to undertake systematic investigation for the extraction chromatographic studies of microgram amount of Al^{III} with high molecular mass carboxylic acid.

Results and Discussion

The systematic studies on extraction chromatographic behaviour of Al^{III} with Versatic-10 at pH 2.5–5.5 from acetate buffer showed that Al^{III} is quantitatively extracted at pH 4.75–5.5. The optimum flow rates during extraction was kept at 2.5 ml min⁻¹ for complete retention of Al^{III} in the column. After extraction Al^{III} was stripped with various mineral acids, salts and deionised water. The results are given in Table 1.

Breakthrough capacity, i.e. the number of milliequivalent of ions which can be retained without any leakage being observed with respect to Al^{III} in versatic acid coated on silica gel, was determined at pHs 4.75 and 5.5. An exchanger bed was prepared from 1.0 g exchanger. The pH of the exchanger bed and aluminium solution (2.90 mg ml⁻¹) was adjusted to the desired value with the acetate buffer and then the solution was passed through the column. It was found that the leakage of Al^{III} started at pHs 4.75 and 5.5 after passing 23.5 and 34.75 ml of the effluent respectively. Hence the uptake of Al^{III} increases with the increase in pH. The maximum amount of Al^{III} loaded quantitatively by Versatic-10 impregnated on silica gel at pHs 4.75 and 5.5 are 47.75 and 61.23 mg respectively.

Separation of Al^{III} from binary mixtures : It was possible to separate Al^{III} from elements in binary mixture by exploiting the differences in pH for extraction and strip-

TABLE 1—EFFECT OF STRIPPING AGENT FOR REMOVING Al^{III}
Al^{III} taken = 50 µg, Column : 0.8×6.5 cm, Flow rate = 1 ml min⁻¹

Stripping agent	Concn. M	Peak elution volume (V _{max}) ml	Volume for total recovery (V _t) ml	Recovery %
HCl	1	30	50	12.1
	2	25	35	32.4
	3	20	30	94.0
	4	10	20	100.7
H ₂ SO ₄	1	25	50	10.2
	2	25	30	46.1
	3	15	25	79.9
	3.5	10	20	100.2
HNO ₃	0.5	20	40	6.8
	1	15	40	37.0
	2	12.5	30	89.6
	2.5	10	20	100.4
Mixed acid	1	20	45	17.3
	2	15	40	51.0
	2.5	12.5	25	87.9
	3	10	20	100
NaNO ₃	4	—	—	—
NaCl	4	—	—	—
H ₂ O (Deionised water)	—	—	—	—
pH value	5.0			

ping behaviour. At pH 5.0, Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II} and Cd^{II} were not extracted along with Al^{III}, i.e. they passed through the column and aluminium was retained. Later aluminium was stripped from the column with 2.5 M HNO₃. The separation of Al^{III} from binary mixtures containing U^{VI}, Th^{IV}, Y^{III}, La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Dy^{III}, Tl^{III}, In^{III}, Ga^{III}, Pb^{II}, Cu^I, Zr^{IV}, Pd^{II} and Hg^{II} was achieved by passing the mixtures at pH 5.0. U^{VI}, Y^{III}, La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III} and Dy^{III} were eluted first with 0.025 M HNO₃, Th^{III} and In^{III} eluted with 0.025 M HNO₃, and Pb^{II} and Ga^{III} eluted with 0.5 M HNO₃. Tl^{III} was eluted with 0.1 M HCl and Hg^{II} with 1 M NH₄NO₃. Finally, Al^{III} was eluted

with 2.5 M HNO₃. In case of binary mixture containing Al^{III} and Ce^{IV}, the latter was eluted with 1 M H₂SO₄ followed by Al^{III} with 2.5 M HNO₃. In case of binary mixture containing Al^{III} and Zr^{IV}, aluminium(III) was eluted first with 2.5 M HNO₃ followed by Zr^{IV} with 4 M HNO₃. Fe^{III} and Al^{III} were separated from each other by passing the mixture through the column at pH 3. Al^{III} passed through the column with the mobile phase while extracted iron was eluted with 0.1 M HCl. After separation, Al^{III} was determined spectrophotometrically⁶ while the foreign ions were estimated complexometrically⁷. The result of binary separation are given in Table 2.

TABLE 2—SEPARATION OF Al^{III} FROM BINARY MIXTURE*

Al^{III} taken = 50 µg, Column : 0.8×6.7 cm, Flow rate = 1 ml min⁻¹

Metal ion	Wt. added mg	Wt. recovered mg	Recovery of Al ^{III} µg	Eluent used
Mg ^{II}	4.65	4.63	51	—
Mn ^{II}	4.20	4.22	49	—
Fe ^{IIIa}	3.54	3.51	52	0.1 M HCl
Co ^{II}	5.52	5.50	50	—
Ni ^{II}	6.12	6.13	50	—
Cu ^{II}	6.38	6.35	51	—
Zn ^{II}	5.96	5.95	53	—
Cd ^{II}	4.04	4.02	49	—
Hg ^{II}	4.77	4.75	50	1.0 M NH ₄ NO ₃
In ^{III}	4.92	4.94	52	0.25 M HNO ₃
Tl ^{III}	5.05	5.00	51	0.1 M HCl
Ce ^{IV}	2.13	2.12	48	1.0 M H ₂ SO ₄
Zr ^{IV}	3.11	3.13	48	4.0 M HNO ₃
La ^{III}	2.87	2.85	53	0.02 M HNO ₃
Pr ^{III}	4.55	4.57	48	0.025 M HNO ₃
Sm ^{III}	6.07	5.99	52	0.025 M HNO ₃
Y ^{III}	4.88	4.89	50	0.025 M HNO ₃
Nd ^{III}	4.53	4.53	50	0.025 M HNO ₃
Gd ^{III}	5.57	5.56	51	0.025 M HNO ₃
Dy ^{III}	5.50	5.50	50	0.025 M HNO ₃
Th ^{IV}	5.02	5.00	49	0.025 M HNO ₃
U ^{VI}	5.12	5.11	50	0.025 M HNO ₃
Pb ^{II}	4.78	4.77	51	0.1 M HNO ₃

*Average values of three determinations. pH values = 5.5,^apH = 3.0.

Separation of Al^{III} from synthetic multicomponent mixtures : In order to assess the possible analytical applications, the proposed method was applied to separate Al^{III} from several synthetic mixtures and the results are given in Table 3.

Separation of Al^{III} from ore and alloy : The proposed method was applied for the extraction of Al^{III} from bauxite

TABLE 3—SEPARATION OF Al^{III} FROM SYNTHETIC MIXTURE

Column : 0.8×6.5 cm, Flow rate = 1 ml min⁻¹

Sl. no.	Metal	Weight added µg	Weight recovered µg	Eluent used	Recovery %	Eluent volume
1.	Mn ^{II}	2110	2109	—	99	25
	Fe ^{IIIa}	1725	1727	0.1 M HCl	100.1	25
	Al ^{III}	50	50.2	2.5 M HNO ₃	100.4	20
2.	U ^{VI}	2506	2503	0.025 M HNO ₃	99.88	25
	Th ^{IV}	2501	2503	0.25 M HNO ₃	100.07	20
	Al ^{III}	50	50.49	2.5 M HNO ₃	100.98	20
3.	Zn ^{II}	2884	2884	—	100	25
	Hg ^{II}	2335	2336	1.0 M NH ₄ NO ₃	100.04	25
	Al ^{III}	50	50.49	2.5 M HNO ₃	100.98	20
4.	Tl ^{III}	2501	2503	0.1 M HCl	100.07	25
	In ^{III}	2451	2450	0.25 M HNO ₃	99.95	25
	Al ^{III}	50	50.48	2.5 M HNO ₃	100.96	20
	Zr ^{IV}	1506	1504	4.0 M HNO ₃	99.86	20
5.	U ^{VI}	2501	2498	0.025 M HNO ₃	99.88	25
	Fe ^{IIIa}	1725	1727	0.2 M HCl	100.11	25
	Th ^{IV}	2506	2504	0.25 M HNO ₃	99.99	25
	Al ^{III}	50	50	2.5 M HNO ₃	100	20
6.	La ^{III}	2870	2873	0.025 M HNO ₃	100.10	25
	Th ^{IV}	2501	2498	0.25 M HNO ₃	99.88	25
	Ce ^{IV}	2130	2128	1.0 M H ₂ SO ₄	99.90	20
	Al ^{III}	50	50.56	2.5 M HNO ₃	101.12	20

*Average values of three determinations. pH = 5;^apH = 3.0.

and brass samples. In both the cases, the results agree well with the certified values.

Experimental

An Elico LI-120 pH meter provided with glass and saturated calomel electrodes, Beckman DU-6 and ECIL GS 5700A spectrophotometers were used. Versatic-10 (Shell Chemicals), a mixture of high molecular weight C₁₀ isomeric tertiary monocarboxylic acids, was used as the liquid cation exchanger. A standard stock solution of Al^{III} was prepared by dissolving Al(NO₃)₃ (A.R.) in HNO₃ and a solution containing 50 µg ml⁻¹ of Al^{III} was prepared through appropriate dilution. Buffer solutions of different pH were prepared from acetic acid (0.1 M) and ammonium acetate (0.1 M).

Ion exchange material : Silica gel (30–120 mesh) was rendered hydrophobic by exposing it to vapour of dimethyldichlorosilane (DMDCS) in N₂-atmosphere. The gel was then washed with anhydrous methanol and dried at 100°. For 10 g of silica gel, 1 ml DMDCS was adequate. The siland silica gel was impregnated with Versatic-10, diluted in benzene dried to uniform coating. About 1 g of hydrophobic silica gel can take up about 0.2 ml of Versatic-10. Excess benzene was removed by washing the exchanger with 2 M HCl. The impregnated silica gel (2–3 g) was slur-

ried with distilled water and poured into the column. Each column could be used for at least 30 cycles without loss of exchange capacity. The exchange capacity of the exchanger was found to be 2.92 meq of H^+ /g at 25°.

Extraction procedure : Versatic-10 impregnated on silica gel was loaded in the chromatographic column and pH of the exchanger bed was adjusted to the desired value with the buffer solution. An aliquot containing 50 μg of Al^{III} was mixed acetic acid-ammonium acetate buffer and its pH adjusted to 5.5. It was passed through the pre-treated column at a flow rate of 1 ml min^{-1} . After extraction Al^{III} was stripped with HNO_3 . A number of fractions were collected and the amount of Al^{III} from each fraction was determined spectrophotometrically using sodium alizerin sulfonate at 485 nm⁶.

Acknowledgement

One of the authors (O.D.) gratefully acknowledges the

facilities provided by the Department of Chemistry, Visva-Bharati, and wishes to thank U.G.C., New Delhi, for financial assistance.

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