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SEPARATION OF THE LANTHANIDES BY ION EXCHANGE WITH ALPHA-HYDROXY ISOBUTYRIC ACID

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UCRL-3265

UNIVERSITY OF CALIFORNIA

Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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January 20, 1956

Printed for the U. S. Atomic Energy Commission

SEPARATION OF THE LANTHANIDES BY ION EXCHANGE WITH ALPHA-HYDROXY ISOBUTYRIC ACID

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Separation factors have been reported recently for the tripositive trans-plutonium actinide elements on elution from a cation exchange resin column with a solution of ammonium α-hydroxy isobutyrate.[1] Table I is a summary of the separation factors, α_o, of the lanthanide elements expressed relative to gadolinium. These data were obtained from elution volumes after subtraction of the free column volume. Curium is included in order that the relative positions of the lanthanides and actinides may be compared by using the data in Ref. 1. The probable error in these separation factors is of the order of five percent.

A Dowex-50 X-12 (400 + mesh) resin bed 5 cm x 0.2 cm was used in a column of the type previously described.[2] The elution was performed at 87° C at a flow rate of 1.0 ml/cm^2/min although preliminary experiments indicate that elution at 25° C does not decrease the separation factors more than 10 percent. The large separation factors made it necessary to perform a number of elutions using various combinations of three to five adjacent lanthanides. The eluting solutions ranged from 0.2 M in α-hydroxy isobutyric acid pH 4.0 for lutetium-ytterbium-thulium separations to 0.4 M pH 4.6 for neodymium-praseodymium-cerium-lanthanum. The pH necessary to elute an ion in a desired volume was determined for a 0.4 M solution of isobutyrate from a pH vs. drop number curve (Ref. 1, Fig. 2) by using the separation factor relative to curium. In order to minimize pH sensitivity, it was desirable to use solutions in a pH range of 4.2 to 4.8. If for a particular separation the curve indicated the choice of a 0.4 M solution of pH lower than 4.2, concentrations of 0.3 M or 0.2 M were used instead. Since the concentration of free isobutyrate ion determines the elution volume, the acid constant expression was used to calculate the pH necessary to give the same isobutyrate ion concentration as the 0.4 M - pH combination obtained from the curve. The value for the K_a at 25° C ($10^{-3.96}$) could be used in this calculation with satisfactory results.

Table II is a comparison of the separation factors relative to samarium for several rare earths with ethylenediamine tetracetic acid (EDTA), citric acid, and lactic acid solutions as reported by Mayer and Freiling.[3] The data for α-hydroxy isobutyric acid has been entered in the last column. While the separation factors for the α-hydroxy isobutyric acid are comparable to those for EDTA the flow rate with the former is five times greater. This was the flow rate which gave a 10 percent value for the full width at half maximum for the elution peaks. The data are for the band elution method rather than the band displacement method usually used with EDTA.[4] The solubility of the lanthanum salt of α-hydroxy isobutyric acid was determined to be 70 g/l (0.5 N) at 19° C and pH 5.8 which is greater than the reported solubility of the lanthanum salt of EDTA.[5] These considerations suggest that α-hydroxy isobutyric acid may be superior to EDTA even for the band displacement method.

Since the presence of the dimer in lactic acid will lower the actual concentration of free acid, the column calibration data may vary from batch to batch of C.P. lactic acid. The presence of the dimer in lactic acid can be demonstrated by a simple test for esters.[6] By saponifying a portion of the lactic acid with sodium hydroxide, then removing the Na^+ with a H^+ form Dowex-50 column, lactic acid which gave a negative dimer test was obtained. The same separation factors were obtained with this acid, but the elution volume was one-fourth that required by solutions of the same concentration (as determined by alkali titration) and pH of the untreated acid. It could be calculated that approximately 30 percent of the lactic acid was dimerized. This might be due to a distillation step in the final purification industrially. Neither glycolic nor α-hydroxy isobutyric acid showed a positive dimer test. Being crystalline they probably were purified by recrystallization which avoids the conditions (very hot, concentrated solutions) necessary for dimer formation.

The assistance of Roberta Garrett in this work and the helpful suggestions of B. G. Harvey, R. M. McCready and S. G. Thompson are gratefully acknowledged.

TABLE I

Element	α_o	Element	α_o
La	34.10	Tb	0.49
Ce	16.70	Dy	0.26
Pr	10.45	Ho	0.16
Nd	6.60	Er	0.13
Pm	4.10	Tm	0.10
Sm	2.25	Yb	0.075
Eu	1.40	Lu	0.055
Gd	1.00	Y	0.25
		Cm	3.45

TABLE II

R.E.	.026M EDTA 0.4ml/cm^2/min	.5M Citrate 0.4ml/cm^2/min	.24 M Lactate 3.5ml/cm^2/min	.3M Isobutyrate 2.0ml/cm^2/min
Sm	1.00	1.00	1.00	1.00
Eu	1.57	1.20	1.28	1.60
Tb	5.18	1.87	2.22	4.60
Y		2.56	4.08	9.00

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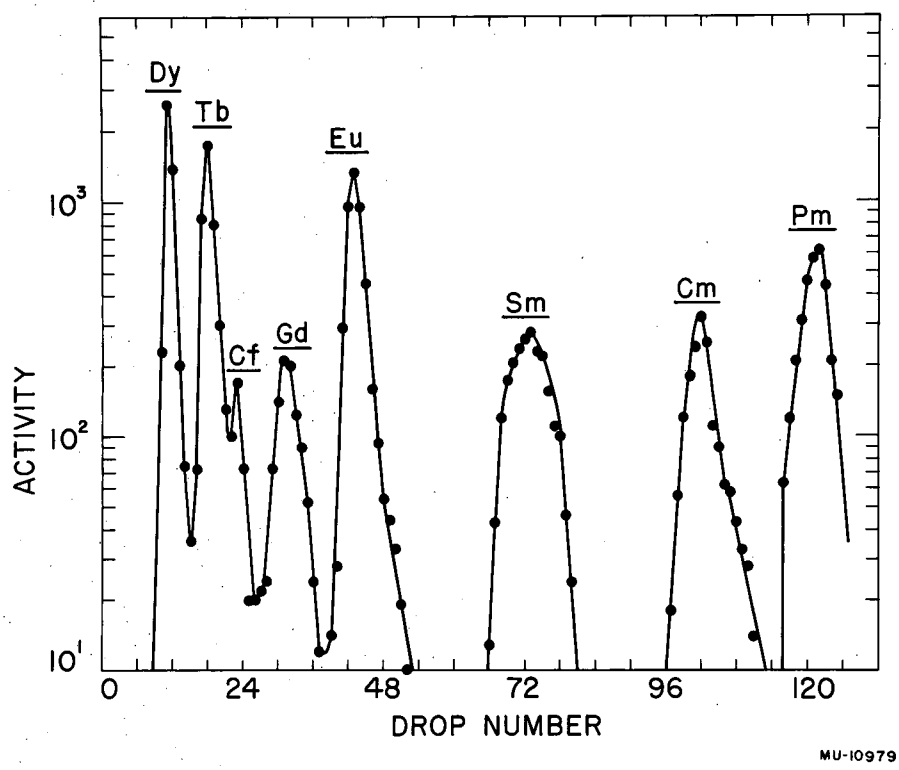

Fig. 1. Elution with 0.4 M ammonium α-hydroxy isobutyrate at pH 3.9. The large half width of the samarium peak is attributable to a macro weight of the element.