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HIGH-SPEED SEPARATION OF THE RARE EARTHS BY ION EXCHANGE
PART II*,**

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SUMMARY

Using the techniques of high-pressure liquid chromatography, it has been possible to separate mass quantities of all fourteen rare earths in less than 5 h. The importance of solvent gradient, particle size and resin cross-linkage were examined.

INTRODUCTION

Ion exchange has been successfully applied to the separation of the rare earths for many years and the literature on this subject is quite extensive. In the last few years, the development of high-pressure liquid chromatography and the commercial production of the required high-pressure, accurate flow-rate pumping equipment has made the high-speed separation of the rare earths a possibility.

CAMPBELL and other workers have shown that the high-speed separation of adjacent rare earths is practical¹⁻³ and additional work on the actinide elements has been reported^{4,5}. While good separations can be obtained at the tracer level, the rapid, quantitative separation of substantial amounts of these elements was not demonstrated prior to the development of pressurized ion exchange. The complete high-speed separation of mass quantities of all of the rare earths presents rather unique difficulties which have not been addressed previously.

In ion-exchange chromatography, for a given column geometry, the volume of eluant required to elute a given species is constant regardless of flow-rate, assuming equilibrium is maintained. In order to maintain equilibrium, the particle diameter must be decreased as the flow-rate is increased.

In addition to particle size, the selection of eluant can dramatically affect the speed and quality of separation. Most eluants are aqueous solutions of strongly complexing organic acids. One of the most common eluants for the rare earths is α -hydroxyisobutyric acid (α -but)⁶.

The distribution coefficients of the heaviest and lightest rare earths differ by

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factors of more than 100 in this system, although adjacent elements may differ by factors of only 1.3. As a result, an eluant which will adequately resolve the heavy rare earths (which elute first) will not elute the light ones until a very large volume of eluant has passed through the column. This effect may be compensated for by increasing the concentration of eluant (the α -hydroxyisobutyrate ion) as the distribution coefficients of the elements being eluted successively increase. The use of such a gradient elution substantially decreases the time required for the separation of several elements. The gradient may be a concentration gradient at constant pH, as used in our work, or a pH gradient at constant concentration.

The selection of the gradient is possibly the most important part of the separation technique and, as we will show, can actually predominate over other parameters usually associated with high-pressure liquid chromatography, *e.g.*, flow-rate, particle size and temperature.

Using large-diameter resin beads (100–300 μ), low-pressure columns used at our laboratories have required from 42 to 48 h for a complete rare-earth separation, Lu through La. We will show that high-pressure liquid chromatographic techniques greatly reduce the time required to obtain the same separations.

EXPERIMENTAL

Equipment

A Nester/Faust, Model 1200, liquid chromatograph equipped with two high-pressure stainless-steel digital pumps, gradient modification, oven, electrical conductivity detector and fraction collector was used. Chromatronix, Inc., glass columns were used with 10- μ bed supports. AG 50W ion-exchange resin was hydraulically graded to obtain particles having the desired range of diameters⁷ (Table I). "Con-O" brand α -hydroxyisobutyric acid was diluted with distilled water and neutralized with carbonate-free ammonium hydroxide solution. Stainless-steel or Teflon tubing was used for all plumbing. Sample injection was accomplished using a Chromatronix, Inc., sample injection valve and 5-ml loop. The *differential* electrical conductivity detector was supplied by Wescan Instrument Co.

Technique

The resin column was prepared by adding a slurry of acid-form resin and then pumping about ten column volumes of water at a flow-rate* of 10–12 ml/cm²/min. More resin was added and the process repeated to obtain the desired resin bed length. The column was washed with six to seven column volumes of 1 M α -but solution at pH 5.0–5.1 (producing 2–4 % shrinkage), followed by five to ten column volumes of water.

A 0.63 \times 24-cm column filled with 25 \pm 7- μ particles having 12 % divinylbenzene cross-linkage contained *ca.* 7.5 ml of resin bed having a capacity of *ca.* 17 milliequivalents.

Samples consisted of 5 mg each of lutetium, ytterbium, thulium, terbium, gadolinium, europium, neodymium, cerium and lanthanum plus 5 mg of yttrium**.

* The flow-rate is defined as the volume of solution pumped per unit time divided by the cross-sectional area of the resin bed.

** Tracer quantities of several of the remaining rare earths were present in many runs (see Fig. 1).

TABLE I
PARTICLE SIZE DISTRIBUTIONS^a

Resin	Fraction	Relative distribution (%)				
		Particle size (μ)				
		10-20	20-30	30-40	40-50	>50
X4	25	24.6	56.5	15.4	3.1	0.5
X12	25	14.1	73.2	7.7	1.2	0.4
X12	33	~5	~37	~52	~5	>1

^a Size distribution determined using a HIAC particle analyzer.

Pure solutions of these elements were mixed, then precipitated as the hydroxides with an excess of ammonium hydroxide solution. The precipitate was washed free of excess reagents and dissolved in 1 ml of 1 M hydrochloric acid, giving a final solution of pH 2.0-2.5. This solution was loaded directly on to the resin bed using the sample injection valve, then washed with 0.2 M ammonium chloride solution at pH 5.0-5.1 to remove the excess acid.

The column was eluted using 0.05 M and 0.42 M α -but solutions at pH 5.2-5.3, using several different gradients. The flow-rate was varied from 5 to 13.5 ml/cm²/min. All elutions were performed at 23°.

Additional columns were prepared using AG 50W-X4, 25 \pm 7 μ particles, to measure the effect of cross-linkage, and AG 50W-X12, 33 \pm 8 μ particles, to measure the effect of particle size.

The procedure was then: (1) eluate collected at 2-min intervals and mass rare earth detected by precipitation using 8-hydroxyquinoline and ammonium hydroxide solution; (2) the ionic species was detected using a flow-through electrical conductivity detector; or (3) tracer radioactivity was added to the mass samples and subsequently detected using a flow-through, end-window anthracene β -detector. Approximately 1 ml of the flowing eluate was in the β -detector at any time. (We have confirmed that the visual detection of mass rare earth precipitate coincides with the detection of trace rare earth and that studies made without tracer can be equated to our later tracer studies.)

RESULTS

The results of a typical separation are shown in Fig. 1. Because the anthracene detector is quite specific for β -radiation and the tracers did not have the same β -specific activity, the plot does not reflect the total mass present for each element. A plot of solution conductivity (Figs. 2 and 3) gives the expected plot for equal loadings of each element.

The resolutions*, as determined by any of the three detection techniques, are comparable (Table II). Using a "standard" 0.63 \times 24-cm column filled with X12 resin, complete baseline separation of mass quantities (5 mg) of all 14 rare earths plus yttrium can be obtained in less than 5 h.

* Resolution is defined as the distance between peak maxima divided by the average peak widths at the baseline.

Solvent gradient

Throughout the work, the solvent gradient proved to be the primary experimental parameter.

We examined a number of different gradients, three of which are shown in Fig. 4. In order to separate the Lu-Yb pair properly, the gradient must be minimized or even delayed until the heavy elements are eluted (Fig. 4A). Once the heavy elements have been obtained, the gradient must be increased rapidly in order to realize the maximum speed of this technique. We have found that a simple exponential

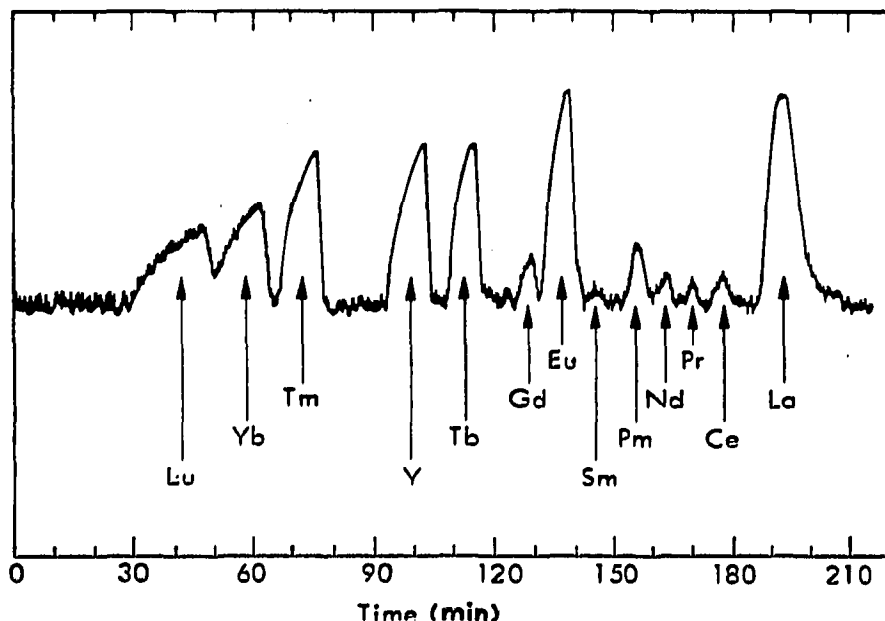


Fig. 1. Elution of 12 rare earths and Y using a full α -but gradient and an anthracene β -detector (log count rate vs. time).

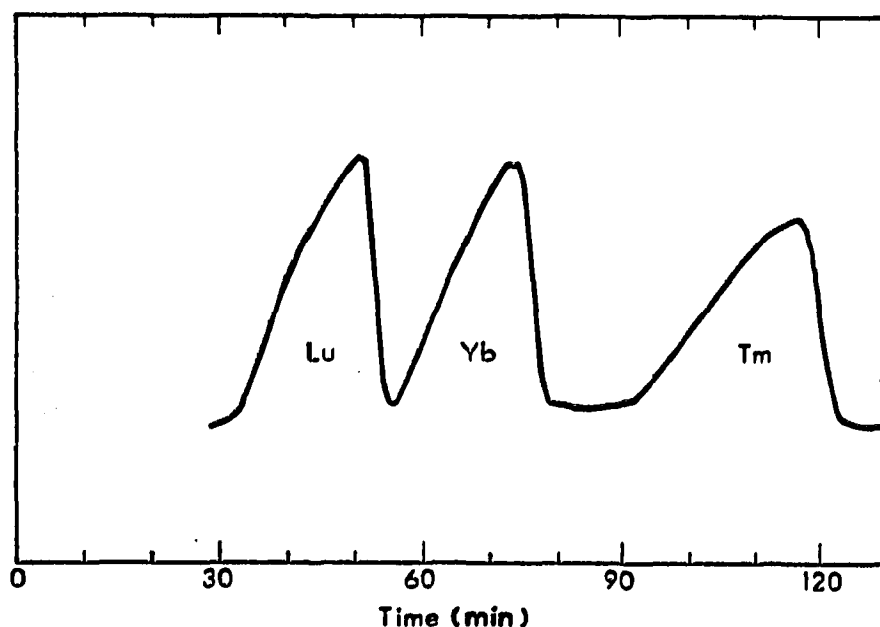


Fig. 2. Elution of Lu, Yb and Tm using 0.05M α -but with anthracene β -detector (log count rate vs. time).

gradient (Fig. 4C) gives the fastest separation without significantly affecting resolution, and is quite simple to generate⁸. Slight adjustments in the gradient to obtain the optimum separation of any selected pair of elements would not significantly change the total time for the elution.

While it was generally possible to adjust the gradient to overcome most other experimental parameters, we did attempt to isolate the effects of resin cross-linkage and resin particle size.

Resin cross-linkage

Our standard column filled with X₁₂ resin contained *ca.* 7.5 ml of resin bed with a capacity of *ca.* 17 milliequivalents. This same column filled with X₄ resin had a capacity of *ca.* 9 milliequivalents. Quite obviously, the number of available sites for adsorption was significantly less for the X₄ resin than for the X₁₂ resin.

When the two columns were run using identical operating conditions, the X₁₂ resin did show a slightly better overall separation, but it was not as obviously superior as we had anticipated (Table III).

It should be noted that the operating conditions selected had been optimized for the X₁₂ resin and readjustment of the gradient could easily alter the performance.

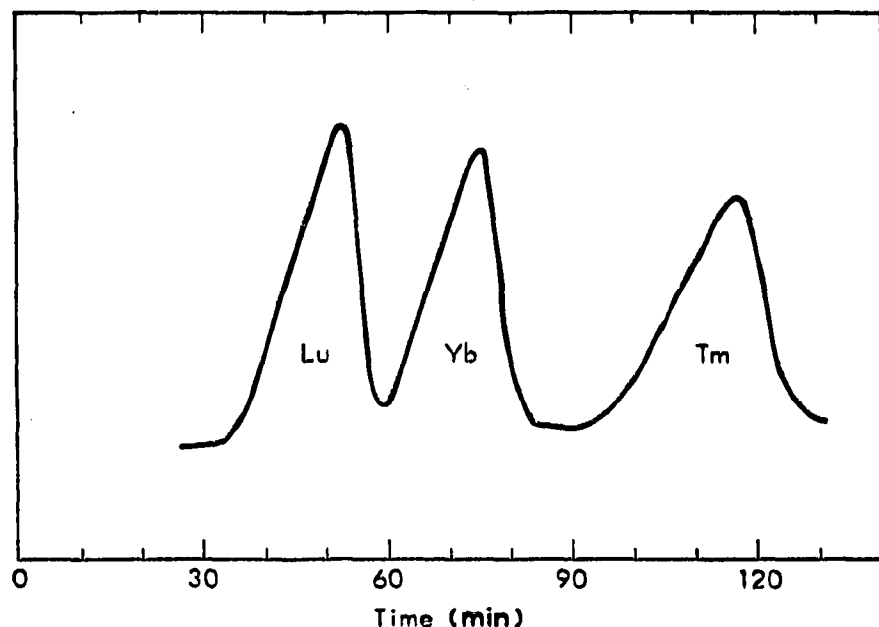


Fig. 3. Elution of Lu, Yb and Tm using 0.05 M α -but with differential electrical conductivity detector (conductance *vs.* time).

TABLE II

RESOLUTION AS A FUNCTION OF DETECTION TECHNIQUE

Detector	Without gradient		With gradient	
	Lu-Yb	Yb-Tm	Lu-Yb	Yb-Tm
Gravimetric	—	—	1.05 \pm 0.06	1.67 \pm 0.10
β -Activity	1.03	1.49	0.93 \pm 0.06	1.53 \pm 0.08
Conductivity	0.99 \pm 0.04	1.60 \pm 0.09	—	—

Particle size

Because the separation process involves contact of the ionic species with the active sites, an increase in exposure of the active sites to the mobile phase will produce better separations per unit quantity of resin. Two techniques have been used to obtain this increased contact: small-diameter beads to increase the surface area per particle, and coated beads to give large surface areas and to minimize internal diffusion within the active substrate.

While coated beads appear to offer the best conditions, they have significantly

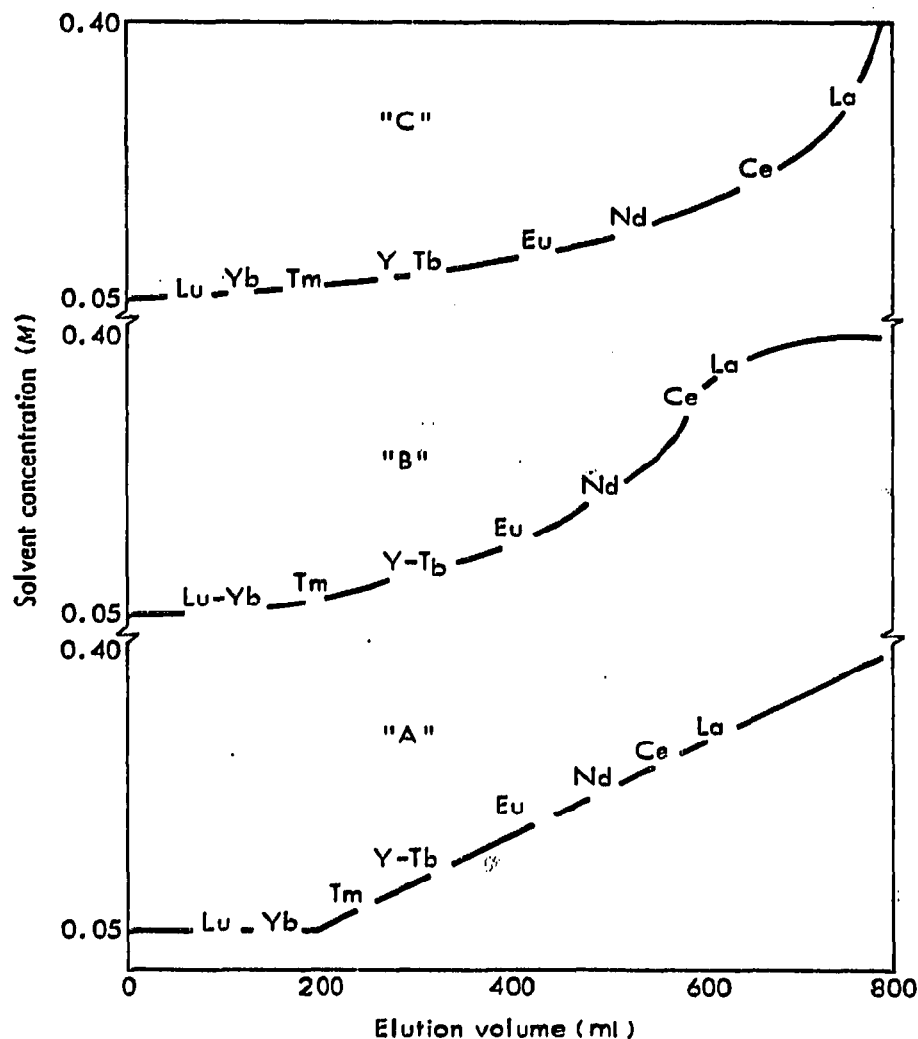


Fig. 4. Selected solvent gradients with approximate positions of the eluted rare earth elements.

TABLE III

RESOLUTION AS A FUNCTION OF RESIN CROSS-LINKAGE ($25 \pm 5 \mu$)

Resin	Lu-Yb	Yb-Tm	Tm-Y	Y-Tb	Tb-Gd	Gd-Eu	Nd-Ce	Ce-La
X ₄	1.0	1.5	3.8	1.8	2.2	1.0	1.8	1.8
X ₁₂	1.0	1.8	3.7	2.1	2.4	1.0	2.7	2.3

TABLE IV

RESOLUTION AS A FUNCTION OF RESIN PARTICLE SIZE (X12 RESIN)

Particle size (μ)	Lu-Yb	Yb-Tm	Tm-Y	Y-Tb	Tb-Gd	Gd-Eu	Nd-Ce	Ce-La
25 \pm 5	1.0	1.9	3.9	2.3	2.3	1.0	2.4	2.2
33 \pm 8	1.0	1.6	3.2	1.7	2.0	1.0	2.1	1.9

less capacity per volume of resin bed and are exceedingly expensive for large-scale preparative operations.

We examined two different fractions of X12 resin: 25 \pm 7- μ beads and 33 \pm 8- μ beads. The total volumes of resin bed and total bed capacities were identical for the two columns. Because X12 resin was used in both columns, the resolutions obtained were independent of solvent gradient.

As expected, the smaller beads did give better overall resolution (Table IV). The range in bead size is probably as important as the average bead size, but we have not quantitatively determined how large a range can be tolerated without degrading the separation. While the fractionation or sieving of the resin to obtain fine particles is obviously necessary for the success of the technique, the larger diameter beads gave a completely acceptable separation.

Final conditions

Using X12 resin, bead diameters of 25 \pm 7 μ and a flow-rate of 10.3-13.5 ml/cm²/min, the mean resolution for the complete separation was 1.28. Baseline resolution was obtained for all components except the Lu-Yb pair. For this pair, $R = 0.96$, indicating a small cross-contamination. It is possible to obtain a baseline Lu-Yb separation if the α -but concentration is maintained at 0.05 M until after the lutetium has eluted. The gradient can then be started with no loss in resolution for the remaining components. This delay in starting the solvent gradient does increase the total time for the complete elution by *ca.* 15 %.

There have been essentially no "scale-up" difficulties in adapting our existing gravity operation to high-pressure chromatographic operation. Once the resin was obtained, it was only necessary to optimize the solvent gradient for the resin cross-linkage and particle size, and acceptable separations were obtained.

ACKNOWLEDGEMENTS

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