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RAPID LANTHANIDE AND ACTINIDE SEPARATIONS WITH PRESSURIZED ION EXCHANGE CHROMATOGRAPHY*

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The first major triumph for inorganic ion exchange chromatography was the separation of rare earths in the World War II Manhattan Project[1]. Both elution development[2,3] and displacement development[4] chromatography were described in a series of papers published in 1947. Since then, a number of different complexing agents have been studied; and although various ones may be advantageous for the separation of particular combinations of elements, α -hydroxyisobutyrate[5] has proved to be perhaps the most effective for general application to separations of any combination of lanthanide or actinide elements by elution development.

Although the ion exchange method is tremendously more rapid than previous rare earth separation methods, the small-scale separation of two elements generally has required several hours, and larger-scale production separations required several days. Attempts to accelerate these separations met with only limited success, especially when macro quantities were processed.

During the past few years, the successful development of the pressurized ion exchange (PIX) technique has permitted such separations to be carried out more rapidly. The PIX technique was developed at Oak Ridge National Laboratory for the separation of organic compounds of biological interest, and maximum resolution was the goal[6]. The original high-pressure systems were modified for the present application, in which separations are less difficult, by sacrificing resolution in favor of more rapid separation.

PIX involves the use of very finely divided resin, which permits greatly increased mass transfer rates and, hence, higher flow rates. Higher flow rates, in turn, can be achieved only by use of a high pressure drop along the length of the ion exchange column. The recent commercial availability of reliable high-pressure

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metering pumps and components has permitted the construction of simple and dependable high-pressure chromatographic systems which can be applied to both small- and large-scale separations.

Campbell and Buxton[7] first demonstrated rapid lanthanide separations by means of PIX with the quantitative separation of tens of milligrams of adjacent lanthanides in less than 30 min. Tracer separations were shown to be possible in a very few minutes [8].

The ultimate goal of this PIX development was to separate and purify the extremely radioactive transcurium elements produced at Oak Ridge National Laboratory, and rare earths were also studied as stand-ins for actinides. It was critical that the separation time be minimized so that radiation damage to the ion exchange system would be tolerable. Separations of the elements Am, Cm, Bk, Cf, Es, and Fm were achieved with the PIX system in times of about 1 hr[9].

The PIX systems are now used routinely; and quantities approaching 100 mg of Cf, along with comparable amounts of other actinides, have been successfully processed. At Savannah River the PIX concept was also applied to displacement development separations of hundreds of grams of actinide and lanthanide elements[10]. Thus, all substantial production of heavy actinides in the United States depends on PIX, and it is the only method having a demonstrated capability for accomplishing the necessary separations.

The initial application of PIX to these problems was so successful that little optimization of the technique has been done. The first installations were geometrically similar to conventional actinide ion exchange systems. The differences were that finely divided resin (-400 mesh) and greatly increased flow rates (10 to 20 ml cm⁻² min⁻¹) were used, and that pressures around 1000 psi were necessary. There were indications that these systems were not optimum; for example, one would logically expect that shorter columns should be advantageous with the smaller-sized resin.

The application of PIX has reduced the time required for the separation of mass quantities of all the rare earths from about 48 hours to less than 5 hr[11]. Most other rapid separations reported have been made at the tracer level.

EXPERIMENTAL

The purpose of the present work was to examine the effects of some of the experimental variables so that more nearly optimum conditions could be defined. Two sets of experiments were conducted. In one a gradient elution was used to separate all the rare earths, with the goal being separation of macro amounts of all 15 elements in about 1 hr. In the second the separation of the 7 rare earths from Tb to Pr was studied with a constant eluent concentration so variables other than gradient could be optimized.

The ion exchange system has been described before[7]. Most experiments were done with a 9-mm-diam glass column. A 33-cm-long resin bed (22 ml) was used for the gradient elutions, and a 9.1-cm-long (6 ml) resin bed was used for the constant eluent elutions.

In addition, with the glass column approximately 1 ml of 20- to 40- μ -glass beads was placed both above and below the resin bed.

Gradient elutions were also done with two stainless steel columns, one 132-cm-long made from 1/4-in. tubing, and the other 11.7-cm-long by 1.5-cm-diam with tapered sections in each end to reduce the diameter to 8 mm to fit existing hardware. The glass columns may be used at pressures up to 800 psi; the pump is satisfactory to 1500 psi, and other components to much higher pressure.

The ion exchange resin was Dowex 50W-X8, hydraulically graded to a 25- to 60- μ -particle size range. The same resin was used in all experiments, being transferred from one column to the next.

In all except two experiments the feed was 5 mg of each rare earth except Pm; 5 mg of Y was also added in a few cases. The total quantity of rare earth was 70 or 75 mg for the gradient elutions, which would load about 3% of the resin, and 30 mg for the constant eluent tests, which would load about 5% of the resin. Two gradient experiments were made with 20 mg of each rare earth, which would load 12% of the resin. A portion of each rare earth was irradiated in the Oak Ridge Research Reactor to provide tracers for all 15 elements, including Pm but not Y.

After loading, the column was washed with 0.2 M NH_4NO_3 solution to displace any hydrogen ion, and finally with water. Eluent solutions were prepared by dilution of 1 M α -hydroxyisobutyric acid that had been neutralized to pH 4.4 with ammonium hydroxide.

Elate fractions were collected with a drop counter if the flow rate was low enough, or by manually timed samples otherwise, and counted with a 2 x 2 in. NaI(Tl) crystal with a 512-channel pulse height analyzer. Each rare earth was determined by integrating the central part of its gamma peak most free of interferences from other gamma rays, and subtracting a baseline correction.

RESULTS AND DISCUSSION

Gradient Elutions. A typical elution of all the rare earths is shown in Fig. 1. The flow rate, 10 ml/min, was limited by pump capacity, and the pressure drop was only about 500 psi. The entire run required less than 2 hr, and the elution less than 1-1/2 hr. Each element was obtained in greater than 99% yield at a purity of 99.9% or greater with respect to other rare earths. The first pair, Lu-Yb, showed the worst band overlap, but a slightly lower initial concentration of eluent would improve this.

The concentration of the eluent was increased from 0.115 M to 0.5 M, as indicated in the lower part of Fig. 1. The gradient was established and adjusted between runs on an intuitive basis.

Comparable results were obtained in two similar experiments which were made at a lower flow rate, 4 ml/min. Since the lower flow rate, per se, did not clearly have a significant effect on resolution, a flow rate even higher than 10 ml/min might give a separation nearly as good as that shown in Fig. 1, but in less time.

Two experiments were performed using a larger rare earth loading, 20 mg of each or a total of 280 mg, which loads about 12%

of the resin. It was recognized that less satisfactory separations are generally obtained at loadings approaching 10%. Although a longer and less steep eluent gradient was used, the separations were poorer than one would expect, based only on the wider loaded band (see Table 1). Band overlap occurred for the difficult separations, as expected; however, in both runs the worst overlap occurred for Dy and Tb, a pair which is usually less troublesome than some of the others.

It appears that some different factor limits these separations at high loading. Possibilities include precipitation or mutual interferences during the early part of the run, which could cause some characteristics of displacement development. Separations in the latter half of the run are much better.

The effect of column length was investigated by using the same resin (and, of course, the same volume) in columns of various diameters. With the 132-cm-long column, the pressure drop was so high that the flow rate had to be reduced (1200 psi at 4 ml/min). The elution curve was similar to that shown in Fig. 1, so the longer column provided no clear improvement in separation.

Two experiments were made with the 11.7-cm-long column, but at room temperature. Elution at 10 ml/min gave a much poorer separation than shown in Fig. 1 (see Table 1). A similar run at 5 ml/min, however, showed better resolution; band overlap occurred at about a five fold lower concentration, and was <1% in all cases.

This short and noncylindrical column, then, is near the border line for separations that are satisfactory. A factor of 2 decrease in flow rate markedly improved resolution. Since plate height[12] should increase nearly linearly with flow rate, this twofold decrease in flow rate should nearly double the number of theoretical plates. This is reasonably consistent with the observed improvement in the separations.

Chromatographic separations may be compared empirically in terms of resolution for successive pairs of bands. Resolution, R , [13] is defined in this discussion as

$$R = (V_2 - V_1)/2(\sigma_2 + \sigma_1),$$

where V is the eluate volume to the band maximum, 2σ is the band width at a height $e^{-1/2}$ times the peak height, and the subscripts refer to successive bands. Although the bands obtained in the work reported here were not generally Gaussian, this expression is probably reasonably appropriate. However, it should be mentioned that at very low concentrations, $<10^{-3}$ times the peak height, these bands display tailing to the right.

Table 1 lists resolution values for each pair of adjacent rare earths for the experiment shown in Fig. 1, and also for a run with the 280 mg loading and for a run with the 11.7-cm-long column, all at 10 ml/min flow rate. For the smaller resin loading (column 2), each band was rather well resolved. At the higher loading (column 3), the difficult separations early in the elution and the Gd-Eu pair were poorly resolved. The Dy-Tb resolution was surprisingly small in all these runs.

Table 1. Resolution of Eluted Lanthanide Bands

Element Pair	In Fig. 1	High Loading, 280 mg	Short Column, 11.7-cm-long
Lu-Yb	1.45	0.77	0.83
Yb-Tm	1.67	1.10	1.24
Tm-Er	1.80	0.79	1.19
Er-Ho	1.48	1.28	1.42
Ho-Dy	1.61	2.38	0.87
Dy-Tb	1.26	0.50	1.07
Tb-Gd	2.44	1.84	1.98
Gd-Eu	1.30	0.90	1.09
Eu-Sm	1.72	1.54	1.37
Sm-Pm	1.79	2.13	1.28
Pm-Nd	2.60	2.38	1.48
Nd-Pr	1.54	1.52	1.23
Pr-Ce	2.23	1.85	1.59
Ce-La	2.2	2.88	1.60

With the short column (column 4), band resolution was poorer, particularly for the Ho-Dy and Dy-Tb pairs. At the lower flow rate of 5 ml/min the resolution was much improved, the lowest values being about 1.4 for the Ho-Dy, Dy-Tb, and Gd-Eu pairs. This decreased band width at lower flow rate resulted primarily from a steeper right side, or trailing edge.

In terms of production, the purification of all 15 rare earths in slightly more than 1 hr on a scale of 70 mg with a 22-ml resin volume corresponds to about 75 g per day per liter of resin. The processing rate could be increased substantially by using smaller resin and a more favorable geometry. Displacement chromatography is ordinarily favored for production separations because of the higher initial loading that is possible. However, the rate limiting step may be slower with displacement development so that elution development may still be competitive.

The theory of ion exchange cannot be readily applied to these results because of the use of an eluent gradient. In general, the first one or two bands were eluted before the eluent concentration was increased, and the width of these bands corresponded to plate heights of around 1 mm. The following series of experiments was carried out to provide more information about the mechanism of the elution.

Constant Elution. In these tests a constant eluent composition, 0.15 M, pH 4.4, was used to elute the 7 elements Tb through Pr at 25°C. Flow rates of 1.5, 4.0, and 10.0 ml/min were used. A typical elution curve is presented for 1.5 ml/min, with both a log and linear concentration scale (Fig. 2).

Qualitatively, the separation is quite good. The Gd-Eu bands, which have the lowest separation factor, overlap at a concentration about 1% of the peak, and all other bands overlap at concentrations

(Figure 2 has not been completed. It will be a combination of these two drawings.)

less than 0.1% of the peak. At 10 ml/min, band overlap occurred at concentrations some tenfold higher.

Typical resolution values for the three flow rates are shown in Table 2. The Gd-Eu resolution is poorest, as expected, since the separation factor is smallest. The separation factors, α , reported by Choppin[5] for tracer concentrations are given in the last column.

Table 2. Resolution Values for Bands

Elements	Flow rate (ml/min)			α
	1.5	4.0	10.0	
Tb-Gd	1.50	1.55	1.23	2.0
Gd-Eu	1.02	1.10	0.91	1.4
Eu-Sm	1.89	1.80	1.47	1.6
Sm-Pm	3.73	3.01	2.58	1.8
Pm-Nd	1.81	1.58	1.57	1.6
Nd-Pr	2.19	-	1.69	1.6

The first few bands eluted, which have smaller distribution coefficients, also show lower resolution than the later bands. As expected, resolution decreases with increasing flow rate.

The most striking feature of the elution curve is the change in shape of the bands as elution proceeds. The early bands have a less steep leading edge and a very sharp trailing edge, while the Nd and Pr bands show the reverse shape. The shape of the earlier bands has generally been observed in actinide and lanthanide elutions with appreciable (nontracer) concentration and with reasonable distribution coefficients (generally from 5 to 50).

Although not obvious, the relative positions of the Nd and Pr bands, which show the reversed shape, are not in accord with reported separation factors; they eluted sooner than expected. The first five bands gave separation factors in agreement with the values of Choppin.

It is well known that nonlinear absorption isotherms may cause unsymmetrical bands and changes in distribution coefficient at macro concentrations. The rare earth concentration in these experiments was appreciable, except for tracer Pm; at the peak of each band at the column exit it ranged from 0.0024 M for Tb down to 0.00033 M for Pr. This is adequate to complex from 1 to 7% of the α -hydroxyisobutyrate ion. There was direct evidence for complexing of the eluent ion at high rare earth concentrations, since the measured electrical conductivity of the eluate decreased in the vicinity of band peaks.

The concentration of rare earth in the resin phase, estimated from the observed aqueous phase concentration and the distribution coefficient, increased from 0.04 M for Tb to about 0.10 M for Sm, Nd, and Pr. This would occupy 5 to 15% of the resin capacity.

The calculated peak rare earth concentrations in the resin phase at column exit compare well with the known initial condition of the loaded resin band. Six rare earths were present, each at one-sixth

of resin capacity, or about 0.1 M. The later band peaks were near this value, and the earlier peaks were progressively lower.

Another factor contributing to a nonlinear absorption isotherm is the change in competing ion in the resin as the bands move down the column. At the top, when elution starts, the resin is loaded with rare earths, and the ammonium ion concentration is small. However, after the rare earth bands separate, the resin is largely in the ammonium form.

If the distribution coefficient is dependent on concentration, the central part of each band (except Pm) should move at a velocity different from that of the edges, which are at low concentration. The shape of the early bands is consistent with the velocity of the peak being less than that of the edges. Thus, the leading edge is broad and the trailing edge is sharp.

One can estimate the effective number of theoretical plates by applying the equations derived for Gaussian bands[12]; admittedly, the results are of questionable value since the bands in this work are not ideal. Table 3 presents the number of plates, N, for each band for the three flow rates. The value of N is the average of the values based on band width (w) at e^{-1} and at $e^{-1/2}$ of the peak concentration (which are $8(V/w_1)^2$ and $4(V/w_2)^2$, respectively, where V is the eluate volume to the band peak).

Table 3. Apparent Number of Plates

Metal	Flow rate (ml/min)		
	1.5	4.0	10.0
Tb	60	61	55
Gd	125	136	96
Eu	200	190	160
Sm	355	315	200
Pm	720	380	290
Nd	410	360	290
Pr	310	-	220

For the first five bands, N increased approximately in proportion to the distribution coefficient, which is consistent with the hypothesis that particle diffusion is limiting. However, flow rate dependence is quite small, rather than linear. The number of plates decreased for the last two bands, which also showed the reversed shape. The diffusion terms do not appear capable of explaining a decrease in N for very large distribution coefficients; as for Nd and, especially, Pr.

The fact that these estimates of N cannot be adequately correlated indicates that the band shapes are controlled by interference factors which are not considered in the usual idealized treatment. The separations are consistent with effective plate heights in the range of 0.3 to 1.5 mm, with the higher value occurring for the first band eluted in all cases. For Nd and Pr, with distribution coefficients around 200, the controlling factors appear to be different from those for the heavier rare earths with smaller

distribution coefficients.

In spite of these deviations from theory, which appear in band shape, band width, and band peak position, and which may preclude reasonable correlation of the data, it is still entirely practical to obtain good separations of these elements. Rare earth separations require a few hundred theoretical plates at most. Under the conditions of these experiments quantitative separations are provided with column lengths of 30 cm in times approaching 1 hr.

The results indicate that the use of smaller-sized resin, about 10 μ , should yield good separations with columns only about 10 cm long and with length to diameter ratios as low as 10. Pressure drops would be reasonable with flow rates of 10 to 20 ml cm⁻² min⁻¹. Production rates should exceed 100 g of rare earth per day per liter of resin.

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