ELUTION BEHAVIOUR OF THE RARE EARTH ELEMENTS ON A MIXED ION-EXCHANGE COLUMN

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SUMMARY

The separation of all fourteen rare earth elements was achieved in 4 h by using mixed ion-exchange columns. The elution behaviour of the rare earth elements in single and mixed columns is discussed.

INTRODUCTION

The ion-exchange separation of rare earth elements is based upon the steady decrease in size and consequent decrease in basicity and increase in the binding energy of ligands with increasing atomic number.

The hydrated radii of the trivalent rare earth ions were found to increase with increase in atomic number. As the binding energy of a cation to the anionic sites of ion-exchange resins involves electrostatic attraction of the hydrated cation by the negatively charged site, it was found that the larger the hydrated radius of the ion, the less strongly it was bound. This character alone therefore tends to cause separation of the trivalent rare earths on a cation-exchange resin. The affinities of the rare earth ions for cation exchangers are, however, quite similar to each other.

These difficulties can be overcome by utilizing organic complexing agents with different pH values or, better, by using gradient elution techniques. Attempts to achieve the separation of rare earth elements in this way met with only limited success.

We used mixed columns for the group separation of amino acids[1] and later for the separation of metal ions[2,3]. We have not found any investigations in the literature on the application of mixed columns for the ion-exchange separation of rare earth elements. In this paper, we describe the use of a mixed ion-exchange column for this separation.

EXPERIMENTAL

Preparation of mixed column

The cation- and anion-exchange resins used were strongly acidic and strongly basic (Diaion SK and SA, 25 μm), respectively, and were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. After conditioning, ap-

propriate amounts of the resins were mixed in a concentrated electrolyte solution, such as 20 % sodium chloride solution, so as to avoid violent aggregation in pure water.

Column operation and determination of metal ions

The total amount of the resins in the column was 4.02 ml and the height of the resin in the column was 205 mm. A 0.5 ml volume of each of 10^{-3} M solutions of the metal ions and of a 10^{-3} M solution of mixed ions was added to the upper part of the column, and then developed with an eluent consisting of 0.5 M lactic acid and 0.06 M NaCl at pH 2.8 at an elution rate of 60 ml/h (except for the separation of the mixed ion solution of Lu, Yb and Tm, which was carried out at pH 2.63 and a flow-rate of eluent of 30 ml/h, and for the mixed ion solution of Eu, Sm and Nd, at pH 2.8, 2.9 and 3.0, respectively, and at a flow-rate of 60 ml/h).

The concentration of each metal ion was determined coulometrically with a Hitachi Coulometric Monitor, Type 030.

RESULTS AND DISCUSSION

Figs. 1–4 show typical elution curves of the rare earth elements in single and mixed columns.
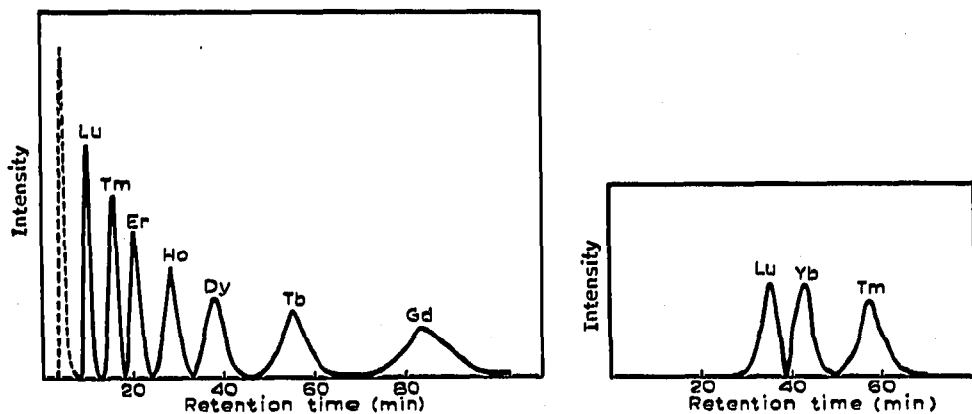

Fig. 1. Separation of rare earth elements with lactic acid at pH 2.8. Broken line, single column (anion-exchange resin); full line, mixed column (SA:SK = 2:1).

Fig. 2. Separation of rare earth elements with lactic acid at pH 2.63 using a mixed column (SA:SK = 2:1).

The existence of equilibrium between the resin phase (r) which contains ion-exchange resins and the aqueous phase (aq) containing lanthanide ions, as described in the following reaction, was taken into consideration:

$$Ln^{3+}{}_{(1)}(aq) + 3XR(r) \rightleftharpoons Ln_{(1)}(R)_3(r) + 3X^-(aq)$$

The distribution coefficient of a lanthanide ion at this stage is given by

$$K_{d1}^0 = C_{Ln^{3+}{}_{(1)(r)}}/C_{Ln_3{}^+{}_{(1)(aq)}} \qquad (1)$$
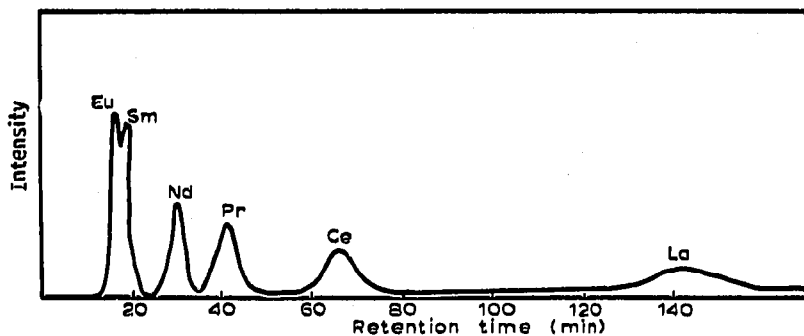
where C is concentration.

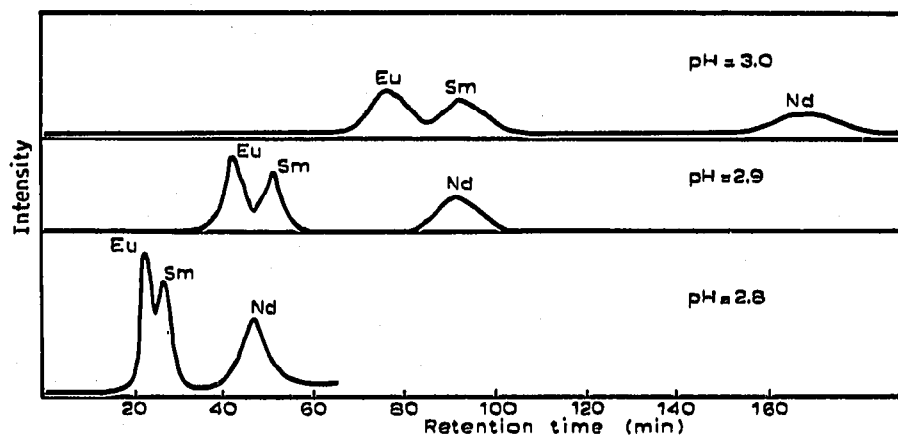Fig. 3. Separation of rare earth elements with lactic acid at pH 3.1 using a mixed column (SA:SK = 2:1).

Fig. 4. Separation of rare earth elements with lactic acid at different pH values using a mixed column (SA:SK = 2:1).

The distribution coefficient, K_d^0, in this equation is the value when chelating agent does not exist in the column.

The equation for the second lanthanide ion, $Ln^{3+}_{(2)}$, is

$$K_{d2}^0 = C_{Ln^{3+}_{(2)}(r)}/C_{Ln^{3+}_{(2)}(aq)} \tag{2}$$

Therefore, the separation factor, S, is given by

$$S = K_{d2}^0/K_{d1}^0 = C_{Ln^{3+}_{(2)}(r)} \cdot C_{Ln^{3+}_{(1)}(aq)}/C_{Ln^{3+}_{(1)}(r)} \cdot C_{Ln^{3+}_{(2)}(aq)} \tag{3}$$

In most instances S does not have values far from unity for the separation of lanthanides when no chelating agent is present.

When a chelating agent is added, the equilibria in the solution become as follows:

$$Ln^{3+}_{(1)} + 6Y^- \rightleftharpoons Ln_{(1)}Y_6^{3-} \tag{4}$$

$$Ln^{3+}_{(2)} + 6Y^- \rightleftharpoons Ln_{(2)}Y_6^{3-} \tag{5}$$

Therefore,

$$K_{d1} = C_{Ln^{3+}_{(1)(r)}}/[C_{Ln^{3+}_{(1)(aq)}} + C_{Ln_{(1)}Y_{6(aq)}}] \tag{6}$$

Also, if the stability constant of the complex for the case in eqn. 4 is taken as K_c, this equation will become

$$K_c^1 = C_{Ln_{(1)}Y^{3-}_{6(aq)}}/C_{Ln^{3+}_{(1)(aq)}} \cdot C^6_{Y^-(aq)} \tag{7}$$

From eqns. 6, 7 and 1, the following equation is obtained:

$$K_{d1} = K^0_{d1}/(1 + K^1_c \cdot C^6_{Y^-(aq)}) \tag{8}$$

and for the second lanthanide ion $Ln^{3+}_{(2)}$:

$$K_{d2} = K^0_{d2}/(1 + K^2_c \cdot C^6_{Y^-(aq)}) \tag{9}$$

Therefore, if the separation factor when the chelating agent is present is taken as S', the equation will become

$$S' = K^0_{d2} \cdot K^2_c/K^0_{d1} \cdot K^1_c \tag{10}$$

Thus, if two or more lanthanide ions form complexes with different stability constants with one type of chelating agent, the separation factors will be altered considerably.

In general, when a chelating agent is weakly acidic, the distribution coefficient changes owing to the dissociation constant and the pH of the solution, as the result of which S' is changed also.

The purpose of our experiment was to separate lanthanide ions by the mixed column method, with lactic acid as the eluent. We studied the distribution ratio K_d^M by the mixed column method in relation to the stability constant of the complex, the dissociation constant and the pH, and also the effect of the mixing ratio of cation- and anion-exchange resins.
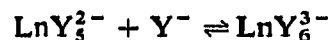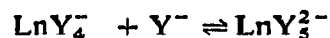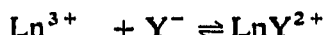
Lactic acid dissociates as follows:

$$HY \rightleftharpoons H^+ + Y^-$$

and the dissociation constant, Ka, is:

$$Ka = \frac{[H^+][Y^-]}{[HY]} \tag{11}$$

The equilibria in the process of forming a complex between a lanthanide ion Ln^{3+} and Y^- are:

$$Ln^{3+} \quad + Y^- \rightleftharpoons LnY^{2+}$$
$$LnY^{2+} + Y^- \rightleftharpoons LnY_2^+$$
$$LnY_2^+ + Y^- \rightleftharpoons LnY_3$$
$$LnY_3 \quad + Y^- \rightleftharpoons LnY_4^-$$
$$LnY_4^- \quad + Y^- \rightleftharpoons LnY_5^{2-}$$
$$LnY_5^{2-} + Y^- \rightleftharpoons LnY_6^{3-}$$

If the successive formation constants are k_1, k_2, ... k_6, and the total formation constant (stability constant) is K_c, the following equations are obtained:

$$k_1 = \frac{[LnY^{2+}]}{[Ln^{3+}]\cdot[Y^-]}$$

$$k_2 = \frac{[LnY_2^+]}{[LnY^{2+}]\cdot[Y^-]}$$

$$k_3 = \frac{[LnY_3]}{[LnY_2^+]\cdot[Y^-]}$$

$$k_4 = \frac{[LnY_4^-]}{[LnY_3]\cdot[Y^-]}$$

$$k_5 = \frac{[LnY_5^{2-}]}{[LnY_4^-]\cdot[Y^-]}$$

$$k_6 = \frac{[LnY_6^{3-}]}{[LnY_5^{2-}]\cdot[Y^-]}$$

$$K_c = k_1 k_2 k_3 k_4 k_5 k_6 = \frac{[LnY_6^{3-}]}{[Ln^{3+}]\cdot[Y^-]^6} \tag{12}$$

If the total concentrations of lactic acid and lanthanide ion are C_Y and C_{Ln}, respectively, then

$$C_Y = [Y^-] + [HY] \tag{13}$$

$$C_{Ln} = [Ln^{3+}] + [LnY^{2+}] + [LnY_2^+] + [LnY_3] + [LnY_4^-] + [LnY_5^{2-}] + \\ + [LnY_6^{3-}] \tag{14}$$

If K_{d1}^0, K_{d2}^0 and K_d^M are the distribution coefficients for the cations and the total species, respectively, the equations will be:

$$K_d^+(Ln^{3+}, LnY^{2+}, LnY_2^+)$$
$$= \frac{[Ln^{3+}] + [LnY^{2+}] + [LnY_2^+]}{C_{Ln}} K_d^{0+}(Ln^{3+}, LnY^{2+}, LnY_2^+) \tag{15}$$

$$K_d^-(LnY_4^-, LnY_5^{2-}, LnY_6^{3-})$$
$$= \frac{[LnY_4^-] + [LnY_5^{2-}] + [LnY_6^{3-}]}{C_{Ln}} K_d^{0-}(LnY_4^-, LnY_5^{2-}, LnY_6^{3-}) \tag{16}$$

If eqns. 15 and 16 are substituted by eqn. 14 and the successive formation constants $k_1 ... k_6$ are taken into consideration and are rearranged, the equations will be as follows:

$$K_d^+(Ln^{3+}, LnY^{2+}, LnY_2^+)$$

$$= \frac{(1 + k_1[Y^-] + k_1k_2[Y^-]^2)K_d^0(Ln^{3+}, LnY^{2+}, LnY_2^+)}{1 + k_1[Y^-] + k_1k_2[Y^-]^2 + k_1k_2k_3[Y^-]^3 + \dots + k_1k_2k_3k_4k_5k_6[Y^-]^6} \quad (17)$$

$$K_d^-(LnY_4^-, LnY_5^{2-}, LnY_6^{3-})$$

$$= \frac{(k_1k_2k_3k_4[Y^-]^4 + \dots + k_1k_2k_3k_4k_5k_6[Y^-]^6)K_d^0(LnY_4^-, LnY_5^{2-}, LnY_6^{3-})}{1 + k_1[Y^-] + k_1k_2[Y^-]^2 + k_1k_2k_3[Y^-]^3 + \dots + k_1k_2k_3k_4k_5k_6[Y^-]^6} \quad (18)$$

Combining eqs. 11–13,

$$[Y^-] = C_Y \frac{Ka}{Ka + [H^+]}$$

The distribution ratio, K_d^M, in the mixed column method can be described as follows:

$$K_d^M = \frac{1}{V_R} \left\{ \frac{V_R^+(1 + k_1[Y^-] + k_1k_2[Y^-]^2)K_d^{0+}(Ln^{3+}, LnY^{2+}, LnY_2^+)}{1 + k_1[Y^-] + k_1k_2[Y^-]^2 + k_1k_2k_3[Y^-]^3} \right.$$

$$+ \frac{V_R^-(k_1k_2k_3k_4[Y^-]^4 + k_1k_2k_3k_4k_5[Y^-]^5 + k_1k_2k_3k_4k_5k_6[Y^-]^6)K_d^{0-}(LnY_4^-,}{+ k_1k_2k_3k_4[Y^-]^4 + k_1k_2k_3k_4k_5[Y^-]^5}$$

$$\left. \frac{LnY_5^{2-}, LnY_6^{3-})}{+ k_1k_2k_3k_4k_5k_6[Y^-]^6} \right\} \quad (19)$$

where the volumes of the cation- and anion-exchange resins are V_R^+ and V_R^-, respectively, and the total volume of the resins is V_R.

As shown in eqn. 19, the distribution ratio, K_M^d, changes greatly in accordance with the stability constant of the complexes, the pH of the solution phase and the mixing ratio of the ion-exchange resins.

On the other hand, the following equation is obtained in ion-exchange chromatography:

$$V_m = V_s + \overline{K_d} \cdot V_R \quad (20)$$

where V_m is the peak volume (ml), V_s the volume (ml) of interstitial water, V_R the resin volume (ml) and $\overline{K_d}$ the distribution coefficient during column operation, which is almost equal to the distribution coefficient, K_d, at equilibrium.

If the peak volumes of two types of lanthanide ions, $Ln^{3+}{}_{(1)}$ and $Ln^{3+}{}_{(2)}$, are $V_m(Ln^{3+}{}_{(1)})$ and $V_m(Ln^{3+}{}_{(2)})$, respectively, and their peak base widths are $W(Ln^{3+}{}_{(1)})$ and $W(Ln^{3+}{}_{(2)})$, respectively, the resolution, R, is given by

$$R = \frac{2[V_m(Ln^{3+}{}_{(2)}) - V_m(Ln^{3+}{}_{(1)})]}{W(Ln^{3+}{}_{(1)}) + W(Ln^{3+}{}_{(2)})} \quad (21)$$

As $V_m(Ln^{3+}{}_{(1)}) \gg V_m(Ln^{3+}{}_{(2)})$, separation is complete when $R \geq 1$ and separation is incomplete when $0 < R < 1$.

Table I shows R values obtained in the separation of Lu to Gd (excluding Yb) at pH 2.8 and SA:SK = 2:1, and R values obtained in the separation of Lu, Yb and Tm at pH = 2.63 and SA:SK = 2:1.

Table II shows R values obtained in the separation of Eu to La at pH = 3.1 and SA:SK = 2.1, and in the separation of Eu, Sm and Nd at pH = 2.8, 2.9 and 3.0, respectively, and SA:SK = 2:1.

TABLE I

RESOLUTION OF RARE EARTH ELEMENTS AT DIFFERENT pH VALUES AND SA:SK = 2:1

Eluent, 0.5 M lactic acid.

Elements separated	Resolution, R	
	pH 2.8	pH 2.65
Tm/Lu	1.50	—
Er/Tm	1.10	—
Ho/Er	1.23	—
Dy/Ho	1.00	—
Tb/Dy	1.57	—
Gd/Tb	1.71	—
Yb/Lu	—	1.00
Tm/Yb	—	1.50

Types of elution behaviour in single and mixed columns

The elution behaviour of solutions of metal ions was studied in single and mixed columns. The following three types of elution behaviour were observed.

(a) In separations on cation-exchange resins, the distribution coefficient was very large when the pH was fixed at 2.8 and the elution of the metal ion was not observed for 2–3 h. This happened even for Lu, which has the greatest stability constant (experiment was carried out for Lu to Gd), and therefore all of the metal ions must have been cations or cation complexes.

(b) Conversely, when the distribution coefficient was very small, under the same conditions metal ions flow out without being adsorbed (see Fig. 1).

(c) In a mixed column, where the ratio of the volumes of the cation-exchange resin and the anion-exchange resin was 1:2, the distribution coefficient has intermediate values that correspond to the ratio of the volumes of the resins, different from the cases under (a) and (b). This shortened the elution times of metal ions to a certain extent, and at the same time their resolution improved also (see Fig. 1). As shown in Fig. 1, when their resolution was greater than 1, separation was good.

The separation of the mixed samples of Lu, Yb and Tm was not successful when the ratio of the volumes of the cation- and anion-exchange resins was 1:2 at pH 2.8, but separation was successful at pH 2.63 under the same conditions. In the separation of Eu, Sm and Nd, favourable resolutions were obtained at pH 2.8, 2.9 and 3.0, respectively (see Table II).

TABLE II

RESOLUTION OF RARE EARTH ELEMENTS AT DIFFERENT pH VALUES AND SA:SK = 2:1

Eluent, 0.5 M lactic acid.

Elements separated	Resolution, R			
	pH 3.1	pH 3.0	pH 2.9	pH 2.8
Sm/Eu	—	0.55	0.86	0.79
Nd/Sm	1.85	—	—	—
Pr/Nd	1.16	—	—	—
Ce/Pr	1.92	—	—	—
La/Ce	3.38	—	—	—

CONCLUSION

When the concentration of the eluent was fixed, the most favourable conditions for separation were obtained by changing the mixing ratio of the cation- and anion-exchange resins or by changing the pH of the eluent.

When the concentration of the eluent (lactic acid) was 0.5 M at pH 2.8, and the mixing ratio of the cation- and anion-exchange resins was 1:2, a mixed sample of Lu, Tm, Er, Ho, Dy, Tb and Gd was completely separated within 90 min

Lu and Yb were completely separated within 50 min when the pH was 2.63 and the eluent flow-rate was 30 ml/h, under the above conditions.

When concentration of the eluent (lactic acid) was 0.5 M at pH = 3.1, and the mixing ratio of the cation- and anion-exchange resins was 1:2, a mixed sample of Eu, Sm, Nd, Pr, Ce and La was separated within 140 min, except for Eu and Sm (see Fig. 3).

Eu and Sm were separated at pH 2.9 and R = 0.86 under the above conditions when the pH was changed to 2.8, 2.9 and then to 3.0 (see Fig. 4).

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