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# ELUTION BEHAVIOUR OF THE RARE EARTH ELEMENTS ON SINGLE AND MIXED ION-EXCHANGE COLUMNS

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## SUMMARY

The separation of the rare earth elements with lactic acid at different pH values was carried out by using mixed ion-exchange columns. The elution behaviour of the rare earth elements in single and mixed columns is discussed.

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## INTRODUCTION

In a previous paper[1], the separation of rare earth elements by using mixed ion-exchange columns was discussed. The results showed that, compared with the use of single columns for the separation of rare earth elements, mixed columns were more successful, for instance, in terms of the resolution or the elution time. The distribution ratio for a mixed ion-exchange column, $K_d^M$, depends on the stability constant of the complex, and also on the pH of the solution phase and the mixing ratio of the ion-exchange resins.

In the previous paper[1], we changed only the pH of the solution phase at a constant mixing ratio of the ion-exchange resins. In the present work, we have shown that the separation efficiency is also considerably influenced when the mixing ratio of the ion-exchange resins is changed.

## EXPERIMENTAL

### *Preparation of columns*

The cation- and anion-exchange resins used were strongly acidic and strongly basic (Diaion SK and SA, respectively, *ca.* 23 μm) and were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. The mixing ratios of the resins (Diaion SK:Diaion SA) in the column were as follows: 100:0, 85:15, 65:35, 50:50, 35:65, 15:85 and 0:100.

### *Column operation*

The method of column operation was described in the previous paper[1]. The separation of rare earth elements was carried out with an eluent consisting of 0.5 *M* lactic acid and 0.06 *M* sodium chloride at an elution rate of 60 ml/h. The concentration of the rare earth elements was determined coulometrically with a Hitachi Coulometric Monitor, Type 030.

## RESULTS AND DISCUSSION

Under static conditions, rare earth elements form complex ions of different compositions with the complexing reagent in the solution phase and with different stability constants and these different complexes are present together. When the separation of metal ions is carried out under dynamic conditions, for instance by chromatography, a large excess of the complexing reagent is always present in comparison with the absolute amounts of the metal ions. Therefore, the chemical equilibrium shifts in the direction of the formation of the most stable complex ions.

The rate of the transfer of elements through the layer of sorbent in the column is determined by the proportion of the elements present as complexes, which cannot be adsorbed. The rate of transfer through cation-exchange resins is determined by the neutral or negative elements present and through anion-exchange resins by the neutral or positive elements present. In general, in chromatographic separations with cation- or anion-exchange resins, when calculating the distribution coefficient or the separation factor, we take into consideration the formation of only the most stable complex ion[2]. However, complex ions of different compositions and different stabilities are actually present together in the solution phase and the absolute amounts of these complex ions are determined by the chemical equilibrium. Each complex ion behaves differently relative to the cation- and anion-exchange resins. Therefore, if a separation is carried out on a mixed ion-exchange column, then, compared with the separation on a single column, we will observe a large difference in the distribution equilibrium. The equation for this behaviour of elements in the layer of mixed ion-exchange resins[1] is:

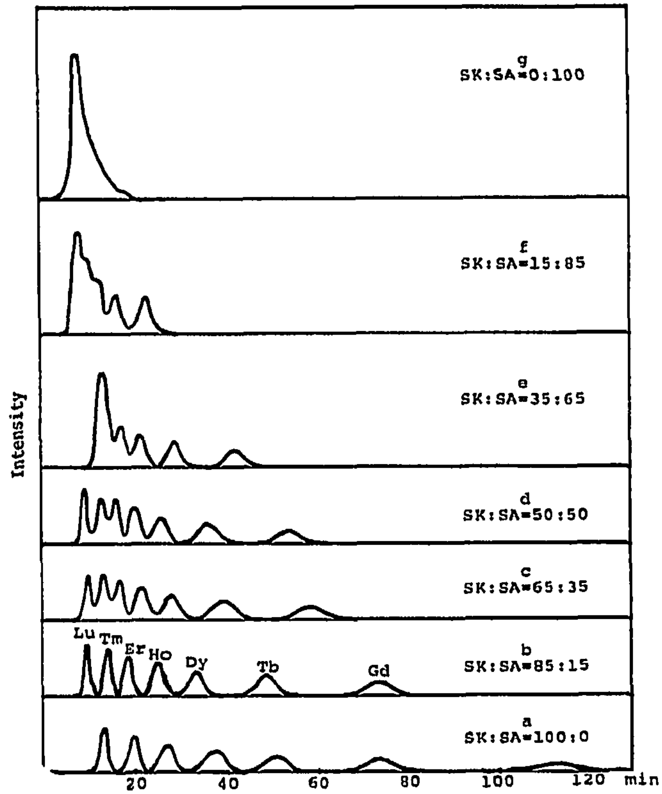
$$
\begin{aligned}
K_d^M = \frac{1}{V_R}\Bigg\{ & \frac{V_R^+(1+k_1[\mathrm{Y}^-]+k_1k_2[\mathrm{Y}^-]^2)K_d^{0+}(\mathrm{Ln}^{3+},\ \mathrm{LnY}^{2+},\ \mathrm{LnY}_2^+)}{1+k_1[\mathrm{Y}^-]+k_1k_2[\mathrm{Y}^-]^2+k_1k_2k_3[\mathrm{Y}^-]^3} \\
& \frac{+V_R^-(k_1k_2k_3k_4[\mathrm{Y}^-]^4+k_1k_2k_3k_4k_5[\mathrm{Y}^-]^5+k_1k_2k_3k_4k_5k_6[\mathrm{Y}^-]^6)K_d^{0-}(\mathrm{LnY}_4^-,}{+k_1k_2k_3k_4[\mathrm{Y}^-]^4+k_1k_2k_3k_4k_5[\mathrm{Y}^-]^5} \\
& \frac{\mathrm{LnY}_5^{2-},\ \mathrm{LnY}_6^{3-})}{+k_1k_2k_3k_4k_5k_6[\mathrm{Y}^-]^6}\Bigg\} \qquad (1)
\end{aligned}
$$

where $V_R{}^+$, $V_R{}^-$ = the volumes of the cation- and anion-exchange resins; $V_R$ = total volume of the resins;

$$[\mathrm{Y}^-] = C_\mathrm{Y}\frac{K_a}{K_a+[\mathrm{H}^+]},$$

where $K_a$ = dissociation constant and $C_\mathrm{Y}$ = total concentration; $k_1, k_2, \ldots k_6$ = successive formation constants; $K_d^{0+}$, $K_d^{0-}$ = distribution coefficients for the cations and anions.

Fig. 1a–g shows the separation of lutetium, thulium, erbium, holmium, dysprosium, terbium and gadolinium on seven mixed ion-exchange columns with 0.5 *M* lactic acid at pH 2.8, and Fig. 2a,b shows the separation of these elements at pH 3.0 and 3.2. Fig. 1a shows the separation of these rare earth elements on a single column of Diaion SK. As Table I shows, the separation is good and the elution time is 120 min. In this case, the elution times can be shortened considerably by changing the pH from 2.8 to 3.0 or 3.2, but the separation becomes less satisfactory (see Fig. 2a, b). If such an operation is carried out with column b (SK:SA=85:15), the separation is complete (Table I) and the elution time is shortened from 120 to 80 min.



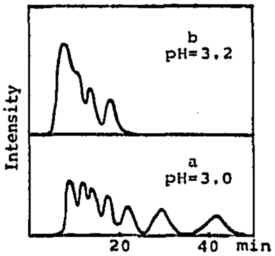


Fig. 1. Separation of rare earth elements with lactic acid at pH 2.8 using mixed columns a–g with Diaion SK: Diaion SA ratios from 100:0 to 0:100.

Fig. 2. Separation of rare earth elements with lactic acid at (a) pH 3.0 and (b) pH 3.2 using a cation-exchange resin.

It seems that $K_d^M$, under the experimental conditions used, depends mainly on the first term in the numerator in eqn. 1. Therefore, when the cation-exchange resin volume, $V_R^+$, decreases, $K_d^M$ also decreases. After this, with a further increase in the volume of the anion-exchange resin, the separation becomes worse (Fig. 1c–g). When the volume ratio of the cation-exchange and anion-exchange resins is 0:100, metal ions will flow through the column virtually unadsorbed, and small differences in the elution times for each metal ion are observed. However, if we compare columns a (SK:SA=100:0) and b (SK:SA=85:15) in terms of the ratio of the decrease in the elution times, then for a decrease in the stability constants from lutetium to gadolinium, the ratio increases, with the exception of thulium, as follows: 23.1, 27.5, 25.4, 31.6, 33.3, 33.8, 34.5%. These results show that not only cations (metal ions) and cation complexes, but also anion complexes are present in the solution phase and that a competitive reaction proceeds between the interaction of the cation-exchange resin with cations (metal ions) or cation complexes and the anion-exchange resin with anion complexes.

TABLE I

RESOLUTION OF RARE EARTH ELEMENTS AT pH 2.8 WITH DIFFERENT MIXING RATIOS OF THE ION-EXCHANGE RESINS

| *Elements separated* | *Resolution (R)* | |
|---|---|---|
| | *SK:SA = 100:0* | *SK:SA = 85:15* |
| Lu-Tm | 1.56 | 1.43 |
| Tm-Er | 1.17 | 1.00 |
| Er-Ho | 1.25 | 1.56 |
| Ho-Dy | 1.47 | 1.33 |
| Dy-Tb | 1.92 | 1.88 |
| Tb-Gd | 2.69 | 2.38 |

TABLE II

RESOLUTION OF RARE EARTH ELEMENTS AT pH 3.1 WITH DIFFERENT MIXING RATIOS OF THE ION-EXCHANGE RESINS

| *Elements separated* | *Resolution (R)* | |
|---|---|---|
| | *SK:SA = 100:0* | *SK:SA = 35:65* |
| Sm-Nd | 2.42 | 1.33 |
| Nd-Pr | 1.75 | 1.00 |
| Pr-Ce | 3.56 | 1.71 |
| Ce-La | 7.20 | 3.31 |

Fig. 3a-g and Table II show some results obtained in the separation of samarium, neodymium, praseodymium, cerium and lanthanum at pH 3.1 by using these seven columns. In this case, the separation obtained by using the cation-exchange column, as shown in Table II and Fig. 3, is satisfactory, but the elution times were too long and should be shortened. This problem can be resolved by changing the pH or the mixing ratio of the resins. The latter procedure is more satisfactory than the former, because, by changing the ratio of the resins from SK:SA = 100:0 to SK:SA = 35:65, the elution times shorten from 250 to 110 min while the separation factor remains almost constant. If we calculate the ratio of the decrease in the elution times, then for a decrease in the stability constants from samarium to lanthanum, the ratio increases in the reverse order. This result proves that anion complexes, when present together with other metal ions or cation complexes, interact chemically with the anion-exchange resin. It is therefore obvious that the anion-exchange resin in the mixed column does not act as a diluent, but, as with the cation-exchange resin, it interacts chemically with complex ions in the solution phase.

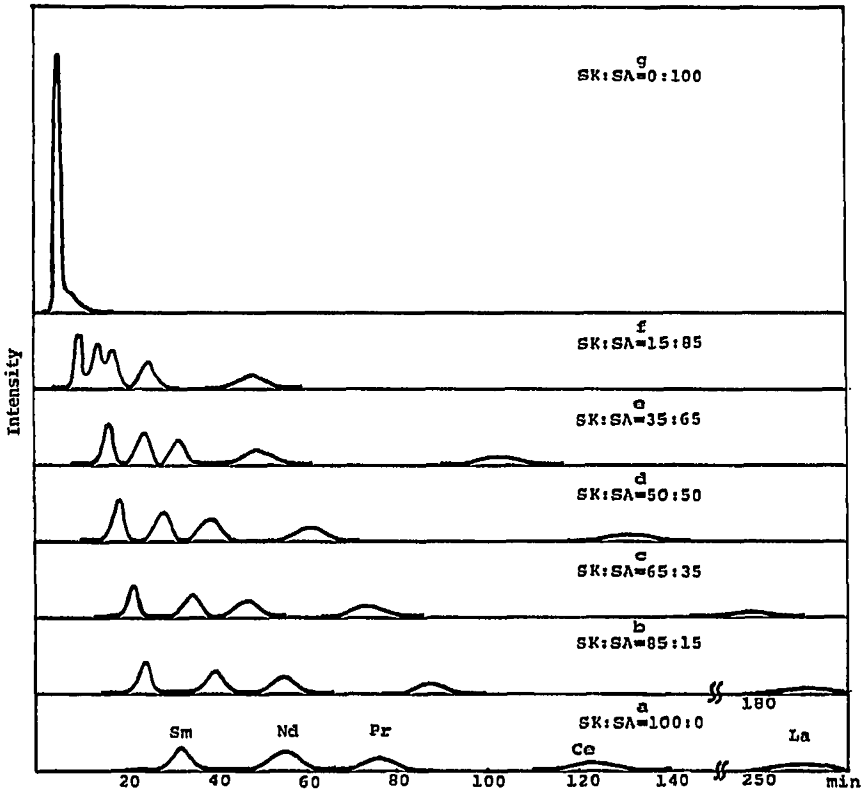


Fig. 3. Separation of rare earth elements with lactic acid at pH 3.1 using mixed columns a–g as in Fig. 1.

## REFERENCES

1 T. Yamabe and T. Hayashi, *J. Chromatogr.*, 76 (1973) 213.
2 *Theory of Ion Exchange and Chromatography*, (in Russian), Nauka, Moscow, 1968, pp. 170 and 185.