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Note

Elution behaviour of typical transition metals on single and mixed ion-exchange columns

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We have previously investigated the elution behaviour of rare earth elements by using mixed ion-exchange columns of cation- and anion-exchange resins^{1,2}. In those studies, it was observed that the elution behaviour of the rare earth elements varied on changing the pH of the eluent or on changing the proportions of the cation- and anion-exchange resins; in particular, it was found that the elution time was considerably shortened, maintaining a high degree of separability.

As shown previously¹, the distribution ratio of a mixed column, K_d^M , changes greatly in accordance with the stability constants of the complexes, the pH of the solution phase and the mixing ratio of the ion-exchange resins. The effect of the mixing ratio on K_d^M is most influenced by the values K_d^+ and K_d^- , and is different from the effect of pH on K_d^M , because an increase in the pH always causes a decrease in K_d^M , whereas changes in the mixing ratio result in a different effect.

In the elution behaviour of the rare earth elements so far reported^{1,2}, we observed only a decrease or increase in the elution times, and not the reversal of the order of elution. On the other hand, in the separation of transition metals, not only a decrease in the elution time but also a reversal of the order of elution will be expected, and therefore a combination of different mixing ratios and pH values will make very difficult separations possible in practice.

In this study, we carried out the separation of typical transition metals (except lead) with lactic acid by changing the mixing ratios of the ion-exchange resins at a constant pH of the eluent.

EXPERIMENTAL

Preparation of columns

The cation- and anion-exchange resins used were strongly acidic and strongly basic (Diaion SK and SA, *ca.* 23 μ m, respectively), 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 columns were as follows: 100:0, 85:15, 65:35, 50:50, 35:65, 15:85 and 0:100.

Column operation and determination of metal ions

The total amount of the resins in the column was about 4 ml and the height of

the resins in the 5-mm I.D. column was 200 mm. A 0.5-ml volume of each of $4 \cdot 10^{-3}$ M solutions of the metal ions or mixed ions was added to the upper part of the column and then developed with the eluent, consisting of 0.5 M lactic acid and 0.06 M sodium chloride solution at pH 3.20 (except for the separations on the cation-exchange column, which were carried out at pH 3.40 and 3.60 as well as at pH 3.20), at an elution rate of 60 ml/h.

The concentration of each metal ion was continuously determined coulometrically with a Hitachi Type 030 coulometric monitor.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the results of the separations of the transition metals. Fig. 1 shows the results of the separations of six metals (copper, zinc, cobalt, cadmium, lead and manganese) on a single column of the cation-exchange resin by changing the pH of the eluent. In this case, a decrease in the elution times is observed with an increase in pH (from A to C), but no reversal of the order of elution was found.

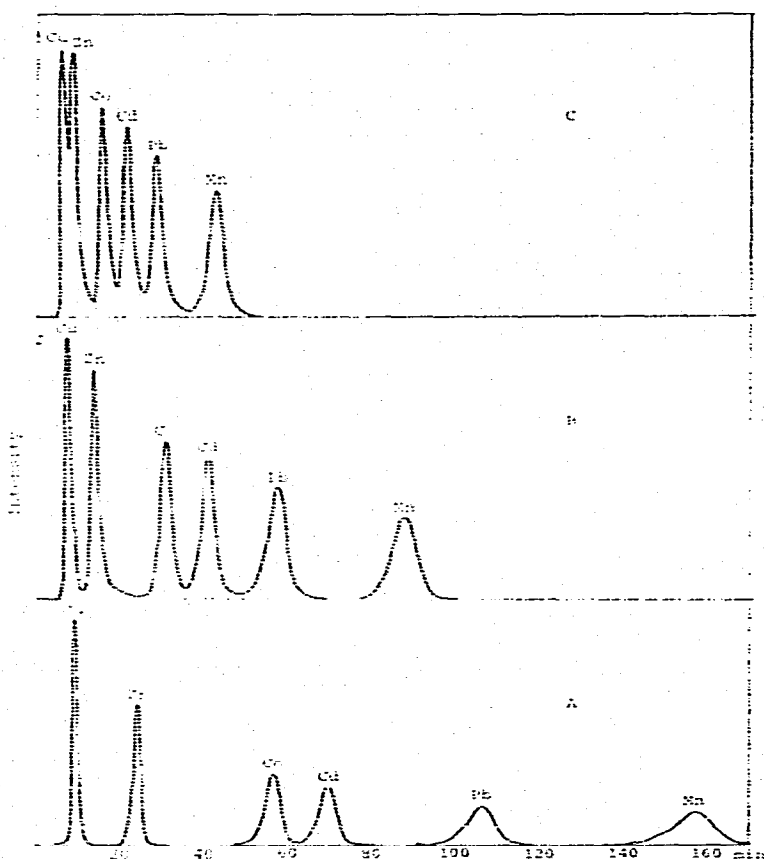


Fig. 1. Separation of transition metals with lactic acid using a cation-exchange resin. pH: A, 3.2; B, 3.4; C, 3.6.

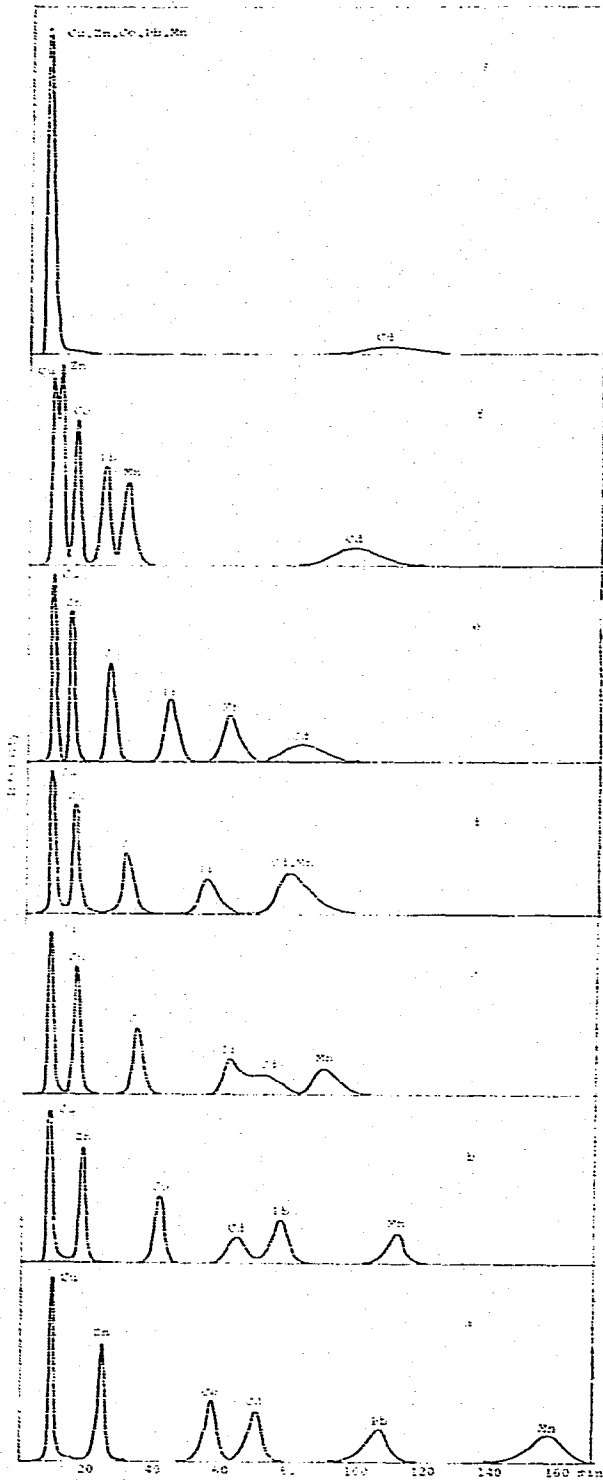


Fig. 2. Separation of transition metals with lactic acid at pH 3.2 using mixed columns. Diaion SK: Diaion SA ratio: a. 100:0; b. 85:15; c. 65:35; d. 50:50; e. 35:65; f. 15:85; g. 0:100.

Fig. 2 shows the results of the separations of the same metals by changing the mixing ratios of the ion-exchange resins at constant pH (3.20). In this case, Fig. 2a shows the same result as in Fig. 1A, but an increase in the proportion of the anion-exchange resin (from b to g) results in a decrease in the elution times and reversal of the order of elution. In comparison with Fig. 2a, Fig. 2b shows the decrease in the elution times of the six metals, in particular cobalt, lead and manganese, but there is no change in the order of elution.

As the proportion of anion-exchange resin increases (from Fig. 2c to f), in general, the elution times are shortened, but that of cadmium increases. In Fig. 2c, therefore, the order of elution of cadmium and lead reverses, and from Fig. 2d to e that of cadmium and manganese also. Thus, in Fig. 2e, complete separation can be achieved as in Fig. 2a. Comparing Fig. 2e with Fig. 2a, which is obtained on a single column of the cation-exchange resin, we can observe certain characteristics:

- (1) the elution time is shortened from 170 (Fig. 2a) to 95 min (Fig. 2e), and therefore in the latter case a more favourable separation is obtained;
- (2) changes in the order of elution are observed.

These characteristics, although they are not always observed on the mixed columns, make it possible to effect separations favourably in such instances when separation is difficult on single columns.

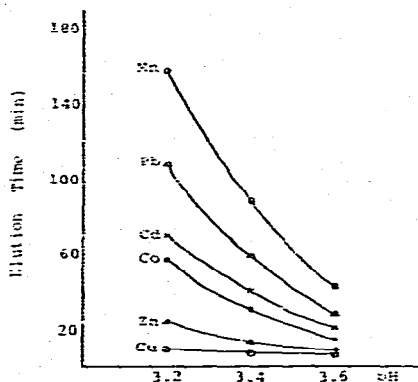


Fig. 3. Relationship between pH and elution time for transition metals.

Fig. 3 shows the relationship between the pH and the elution times in the separations of the six metals on a single column of the cation-exchange resin. It is obvious that the elution times of every metal are shortened, and the curves do not intersect each other. But, as shown in Fig. 4, which shows the relationship between the mixing ratios and the elution times of the six metals at pH 3.20, the curve of cadmium crosses those of lead and manganese with an increase in the proportion of anion-exchange resin.

Although in this study a satisfactory result is obtained with a ratio of Diaion SK:SA of 35:65, from Fig. 4 we can expect, in principle, that more favourable separation conditions exist with ratios between 65:35 and 50:50 or between 50:50 and 35:65.

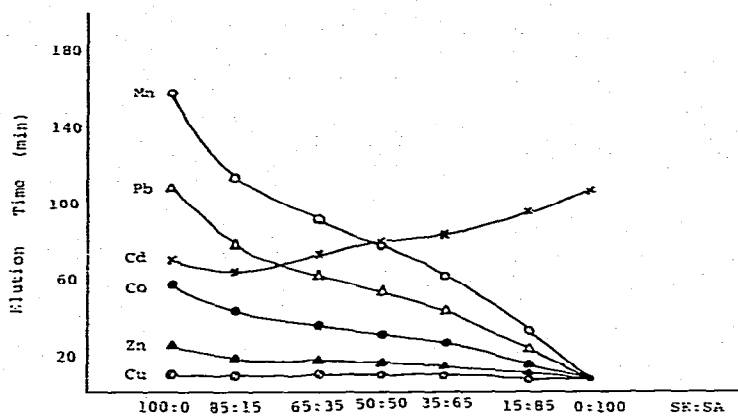


Fig. 4. Relationship between Diaion SK: Diaion SA mixing ratio and elution time for transition metals.

As the above results show, the elution behaviour of cadmium ions differs from that of other metal ions. It seems that the different behaviour of cadmium ions is due to the fact that cadmium and chloride ions form a stable anionic complex which is adsorbed on the anion-exchange resins.

Therefore, if a mixed ligand was used in the method of mixed columns, more favourable separations of metals would be expected.

REFERENCES

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- 2 T. Hayashi and T. Yamabe, *J. Chromatogr.*, 87 (1973) 227.