Journal of Chromatography, 108 (1975) 323–328
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CHROM. 8162

APPLICATION OF MIXED LIGANDS TO SEPARATIONS OF METALS ON MIXED ION-EXCHANGE COLUMNS

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(Received December 31st, 1974)

SUMMARY

Mixed ligands were applied to the separations of transition metals on mixed ion-exchange columns. The influence of the mixed ligands on the elution behaviour of the transition metals is discussed.

INTRODUCTION

In the preceding paper[1], the elution behaviour of typical transition metals when using mixed ion-exchange columns was discussed. In the separation of transition metals, we observed not only a decrease in the elution time but also a reversal of the elution order, which makes the separation more favourable in practice.

The elution behaviour of cadmium ions[1] differs from that of other metal ions, and it is thought that this different behaviour is due to the fact that cadmium and chloride ions form stable complexes that are adsorbed on the anion-exchange resins.

This fact suggests that by controlling the concentration of complexing agents, the separation of metals could be greatly enhanced. Consequently, this effect is interesting from the standpoint of the application of a mixed eluent that contains two complexing agents, for example, lactic and chloride ions in this instance, to the separation of metals.

In this work, we first studied the elution behaviour of transition metals (manganese, cobalt, copper, zinc and cadmium) and lead with a mixed eluent of lactic acid and sodium chloride by changing the chloride ion concentration in the eluent on mixed ion-exchange columns at a constant pH of the eluent. Next we carried out the separation of iron, nickel, copper and zinc with a mixed eluent of lactic acid and sodium acetate. In this instance, sodium acetate was utilized by considering the stability constants of the acetate complexes of the four metals.

EXPERIMENTAL

Preparation of single and mixed ion-exchange columns

The cation- and anion-exchange resins used were strongly acidic and strongly basic (Diaion SK and SA, *ca.* 23 μm, respectively), and were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. After conditioning, appropriate amounts of the ion-exchange resins were mixed in a concentrated electrolyte solution, such as 20% sodium chloride solution, so as to avoid the violent aggregation that occurs in pure water. The total amount of the resins in each column was about 4 ml and the height of the ion-exchange resins in the 5-mm I.D. column was 200 mm.

The mixing ratios of the ion-exchange resins (SK:SA) in the columns were 100:0, 85:15, 65:35, 50:50, 35:65, 15:85 and 0:100.

Preparation of eluents, column operation and determination of metal ions

In the separation of six metals (manganese, cobalt, copper, zinc, cadmium and lead), the eluent consisted of 0.5 *M* lactic acid plus 0.03–0.5 *M* sodium chloride solution and the pH was carefully adjusted to 3.2 with sodium hydroxide. Subsequent experiments of the separation of four metals (iron, nickel, copper and zinc) were carried out with 0.5 *M* lactic acid plus 0.1 *M* sodium acetate solution at pH 3.5 as eluent. In each sample the metal ions were used as the nitrates.

A 0.5-ml volume of each of 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 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

Separation of manganese, cobalt, copper, zinc, cadmium and lead

First, we examined the influence of the concentration of chloride ion in the eluent on the elution times of the six metals. Elution was carried out with 0.5 *M* lactic acid at pH 3.2 by changing the concentration of chloride ion in the eluent from 0.03 to 0.5 *M*. Fig. 1 shows the relationship between the elution times and the concentrations of chloride ion using the cation-exchange resin (column SK:SA = 100:0).

In this instance, a specific influence of the concentration of chloride ion on the elution time of cadmium was observed, as the elution order of cadmium and cobalt reversed at a chloride ion concentration of *ca.* 0.07 *M*. This specific influence of chloride ion on cadmium was observed not only on the cation-exchange column, but also on the mixed ion-exchange columns. In the former instance, as shown in Fig. 1, with an increase in the concentration of chloride ion, the elution order of cadmium becomes earlier relative to the other metals, and in the latter instance it becomes later, in particular with an increase in the proportion of the anion-exchange resin in the mixed columns.

Fig. 2 shows the results of the separations of the six metals with 0.5 *M* lactic acid plus 0.1 *M* sodium chloride at pH 3.2 using the single and mixed ion-exchange resins. On the column of the cation-exchange resin (SK:SA = 100:0), cadmium is eluted third, after copper and zinc. As the proportion of the anion-exchange resin increases, in general, the elution times of metals become shorter, but that of cadmium increases[1]. Therefore, the elution order of cadmium and cobalt changed on the mixed ion-exchange column with SK:SA = 85:15, and then for SK:SA = 65:35 the elution order of cadmium, lead and manganese also changed.

Fig. 3 shows the results of the separations of the six metals with 0.5 *M* lactic

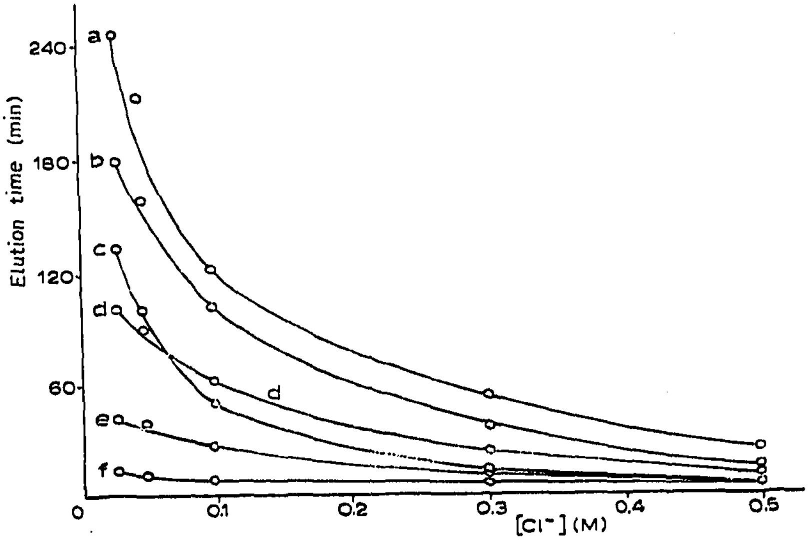


Fig. 1. Relationship between elution time and chloride ion concentration in 0.5 *M* lactic acid as eluent at pH 3.2 using a cation-exchange resin. a, Mn; b, Pb; c, Cd; d, Co; e, Zn; f, Cu.

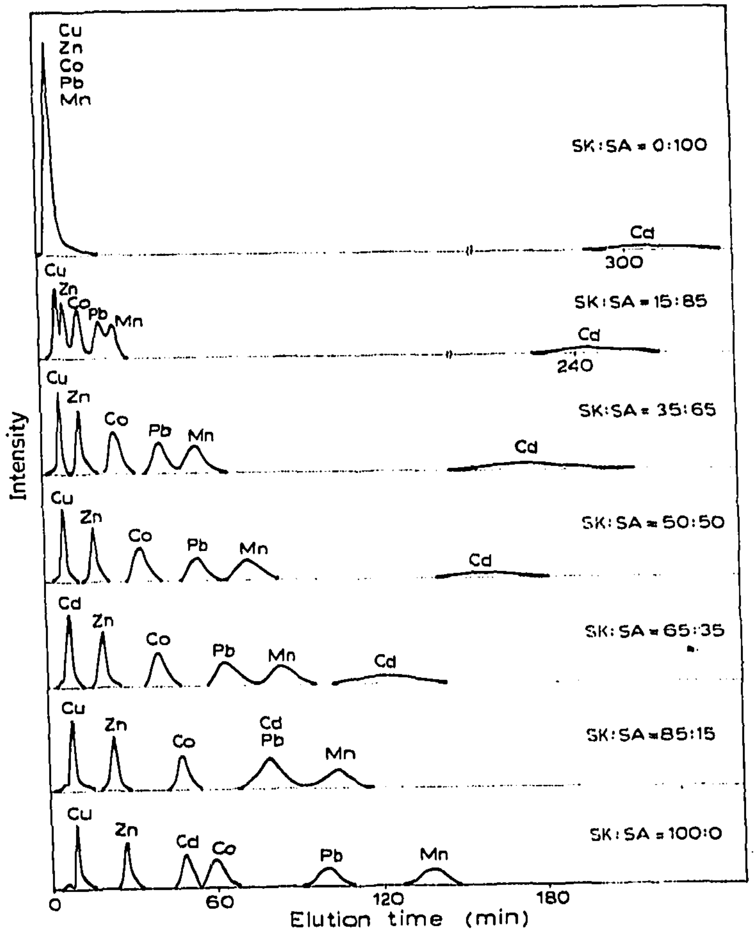


Fig. 2. Separation of transition metals with 0.5 *M* lactic acid plus 0.1 *M* sodium chloride solution a pH 3.2 using mixed columns.

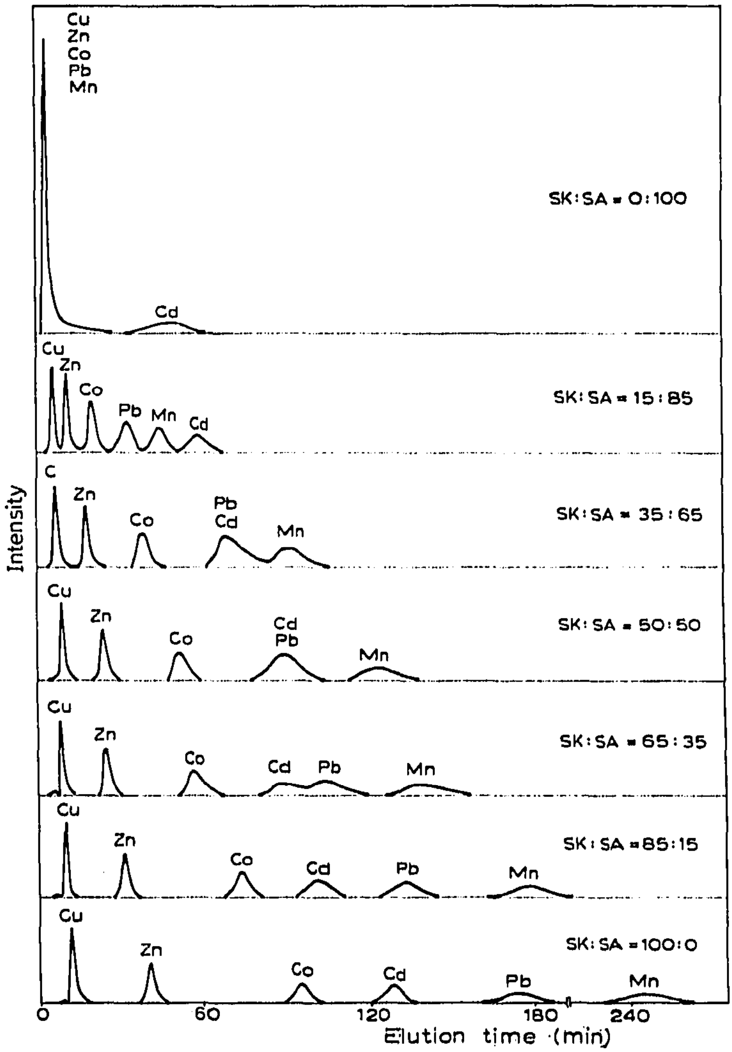


Fig. 3. Separation of transition metals with 0.5 *M* lactic acid plus 0.03 *M* sodium chloride solution at pH 3.2 using mixed columns.

acid plus 0.03 *M* sodium chloride at pH 3.2 using the single and mixed ion-exchange resins. In this instance, on the column of the cation-exchange resin, cadmium is eluted fourth, after copper, zinc and cobalt, because the chloride ion concentration in the eluent is less than 0.07 *M*.

In contrast with the previous effect, in this instance, as the proportion of anion-exchange resin increases, not only the elution times of copper, zinc, cobalt, lead and manganese but also those of cadmium are shortened. However, as the elution times of cadmium are shortened less than those of lead and manganese, the elution order of cadmium and that of the latter metals reverse when SK:SA changes from 85:15 to 15:85. Thus, the six metals are completely separated in 70 min under the conditions when cadmium is eluted last at SK:SA = 15:85.

Separation of iron, nickel, copper and zinc

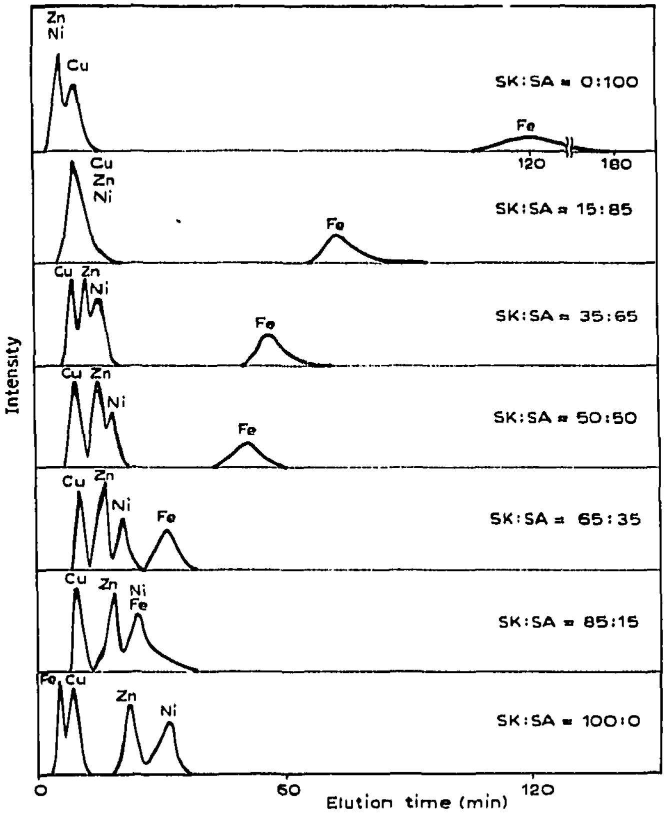
Next we examined the separation of the four metals with a mixed eluent of an organic plus an organic compound, *i.e.*, lactic acid plus sodium acetate.

The stability constants (log K) of lactate complexes of the four metals are *ca.* 3 and those of acetate complexes of nickel, zinc and copper are *ca.* 1.25–3, while that of iron is *ca.* 9.

As expected, iron, copper, zinc and nickel are eluted in that order on the column of the cation-exchange resin and in this instance the separation of iron and copper is incomplete. However, with an increase in the proportion of anion-exchange resin, the adsorption of iron is enhanced, and consequently the distribution ratio[2] of iron in the mixed column (K_d^M) increases, contrary to that of the other metals, and the elution order of the metals reverses, as shown in Fig. 4.

Thus, good separations of the four metals are achieved in 40 min on the mixed column with SK:SA = 65:35.

The advantage of the mixed eluent is obvious when Fig. 5, which was obtained in the absence of sodium acetate, is examined. In this instance also, more effective



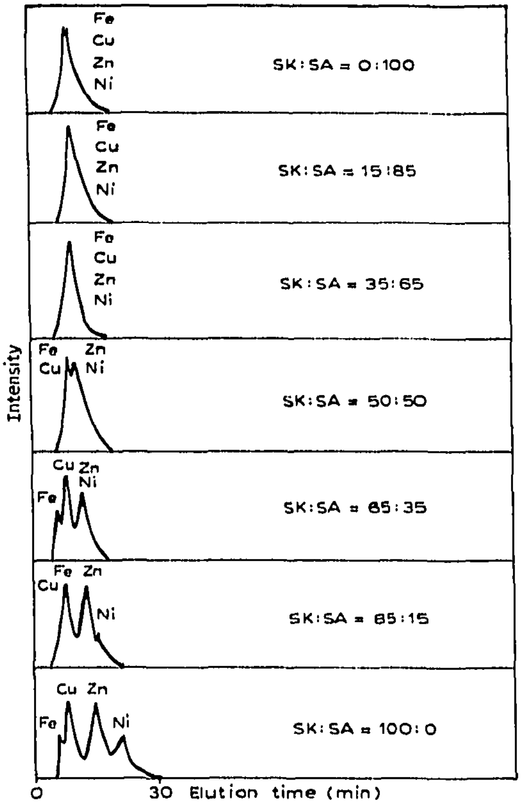


Fig. 4. Separation of transition metals with 0.5 M lactic acid plus 0.1 M sodium acetate solution at pH 3.5 using mixed columns.

Fig. 5. Separation of transition metals with 0.5 M lactic acid at pH 3.5 using mixed columns.

separations of the metals could be achieved by choosing more suitable combinations of the mixing ratio of cation- to anion-exchange resins, pH and concentrations of ligands in the mixed eluent.

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