

CHROM. 8529

Note

Elution behaviour of transition metals with eluents containing ethanol on mixed ion-exchange columns

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(Received June 18th, 1975)

We have previously investigated the separation of manganese, cobalt, copper, zinc, cadmium and lead on columns of mixed cation- and anion-exchange resins^{1,2}. The distribution ratio of a mixed column³, K_d^M , changes in accordance with the proportions of the ion-exchange resins, the stability constants of the complexes and the pH of the solution phase. The effects of these three factors on K_d^M are different, and appropriate combination of the factors can make difficult separations possible in practice.

Many investigations of the ion-exchange of metals have been made in non-aqueous systems⁴⁻¹⁰, and it has been found that the addition of non-electrolytes to the system generally causes a shift in the ion-exchange equilibrium. This effect is of interest from the standpoint of using ethanol in the separation of metals on mixed ion-exchange columns.

In this paper, we describe the elution behaviour of six metals with a mixed eluent of lactic acid, sodium chloride and ethanol on mixed ion-exchange columns.

EXPERIMENTAL

Preparation of single and mixed ion-exchange columns

The cation- and anion-exchange resins used were strongly acidic and strongly basic types (Diaion SK and SA, size *ca.* 23 μm ; Diaion CK and CA, size *ca.* 12 μm , respectively), and were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. After conditioning, appropriate amounts of the resins were mixed in a concentrated electrolyte solution, such as 20% sodium chloride solution, so as to prevent the severe aggregation that occurs in pure water. The total volume of resin in each column was about 1.5 ml and the height of the resin in a 5-mm i.d. column was 70 mm.

The ratios (SK:SA) in which the resins were mixed in the columns were 100:0, 85:15, 65:35, 50:50, 35:65, 15:85 and 0:100. The other resins (CK and CA) have finer particles and were used only in the ratio (CK:CA) 35:65.

Preparation of eluents, column operation and determination of metal ions

The eluent consisted of 0.5-0.625 *M* lactic acid plus 0.03-0.09 *M* sodium

chloride; the pH was carefully adjusted to 2.9–3.3 with sodium hydroxide, then 95% ethanol was added to give concentrations of 5–90% of ethanol.

A 0.5-ml portion of a 10^{-3} M solution of each metal, or of the mixed metal ions (as nitrates), was added to the upper part of the column, and development was carried out at 1 ml per min with the eluent. The concentration of each metal ion in the eluate was continuously determined coulometrically with a Hitachi Type 034 coulometric monitor.

RESULTS AND DISCUSSION

Determination of useful concentration range of ethanol in the eluent

We first examined the influence of the proportion of ethanol in the eluent on the elution behaviour of the six metals. Elution was carried out with 0.625 M lactic acid plus 0.0725 M sodium chloride at pH 3.0. the ethanol content of the eluent ranging from 10 to 90%. Fig. 1 shows the relationship between the elution time and the ethanol content of the eluent for the column in which SK:SA was 100:0.

In this instance, as the ethanol content increased, the elution times of copper, zinc, cobalt and manganese generally shortened, as did that of lead (except at ethanol contents of 80 and 90%). However, the elution behaviour of cadmium was different: for ethanol contents from 10 to 40%, its elution time was shortened, whereas for ethanol contents from 40 to 90%, the elution time increased. Fig. 1 shows that the useful content of ethanol for the separation of the six metals is less than 50%; at higher concentrations, the separation of copper from zinc (or that of cadmium, lead and manganese) from one another is difficult.

Characteristics of the elution behaviour of the metals on mixed columns

We next examined in detail the elution behaviour of the six metals on single and mixed ion-exchange columns. Elution was carried out with 0.5 M lactic acid plus 0.03 M sodium chloride at pH 3.15, changing the ethanol content of the eluent from 0 to 50% by volume.

Fig. 2 shows the relationship between the elution time and the mixing ratio of the resins for this range of ethanol contents. Comparing the six graphs, in general, we can observe the following characteristics:

(1) As the proportion of anion-exchange resin increases (from SK:SA = 100:0 to 0:100), the elution times of all the metals except cadmium are shortened.

(2) Also, with increase in the ethanol content, the elution times of all the metals except cadmium are shortened.

(3) For cadmium, as the proportion of anion-exchange resin increases, its elution time either decreases (at ethanol contents less than 20%) or increases (at ethanol contents much above 20%), with a few exceptional points.

(4) The relationship between the elution time of cadmium and the ethanol content of the eluent is remarkably dependent on the mixing ratios of the ion-exchange resins (see Fig. 3).

Consequently, by controlling not only the concentration of chloride ion², but also the ethanol content of the eluent, the elution times of the metals and their elution order (in particular, for cadmium) can be changed.

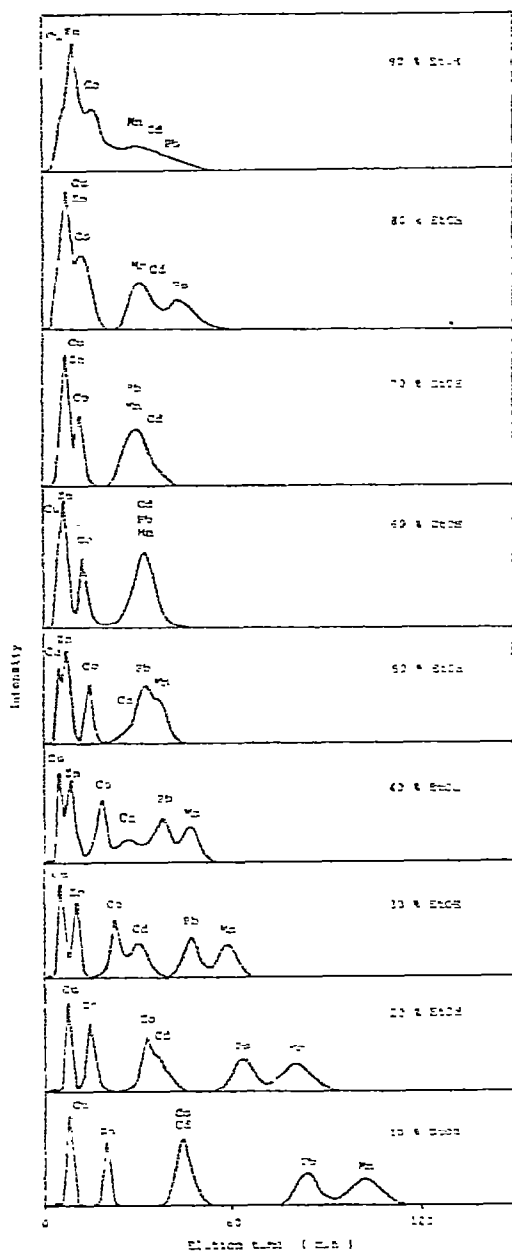


Fig. 1. Relationship between elution times and ethanol (EtOH) contents in 0.625 *M* lactic acid plus 0.0725 *M* sodium chloride at pH 3.0 using a cation-exchange resin.

Separation by addition of ethanol

On the basis of the findings described above, we attempted separation of the metals on the finer resins (CK and CA) in order to achieve more favourable separation. The difference between these resins and the SK and SA resins is only in

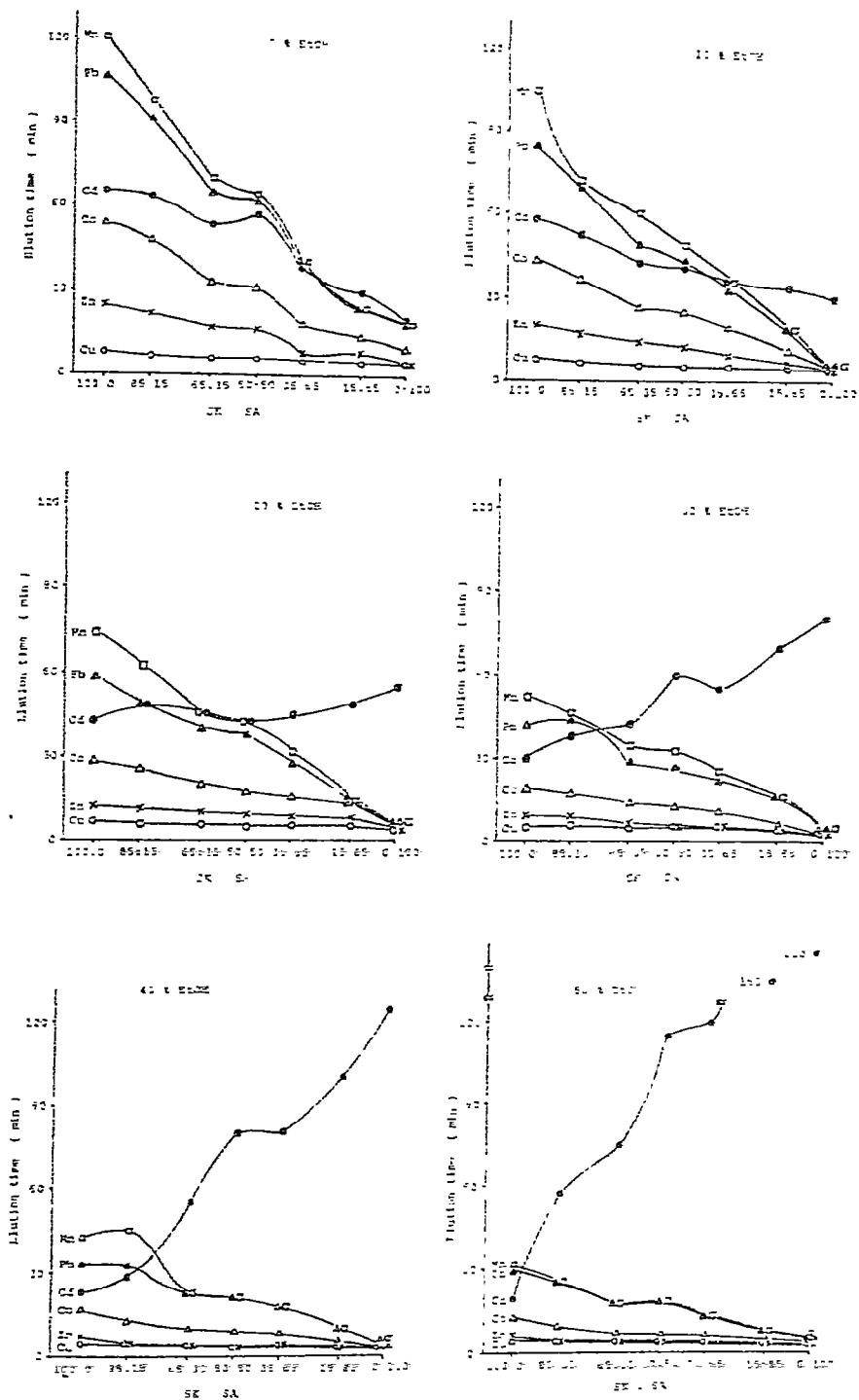


Fig. 2. Relationship between elution times and mixing ratios of the ion-exchange resins with 0.5 M lactic acid plus 0.03 M sodium chloride at pH 3.15 for various contents of ethanol (EtOH).

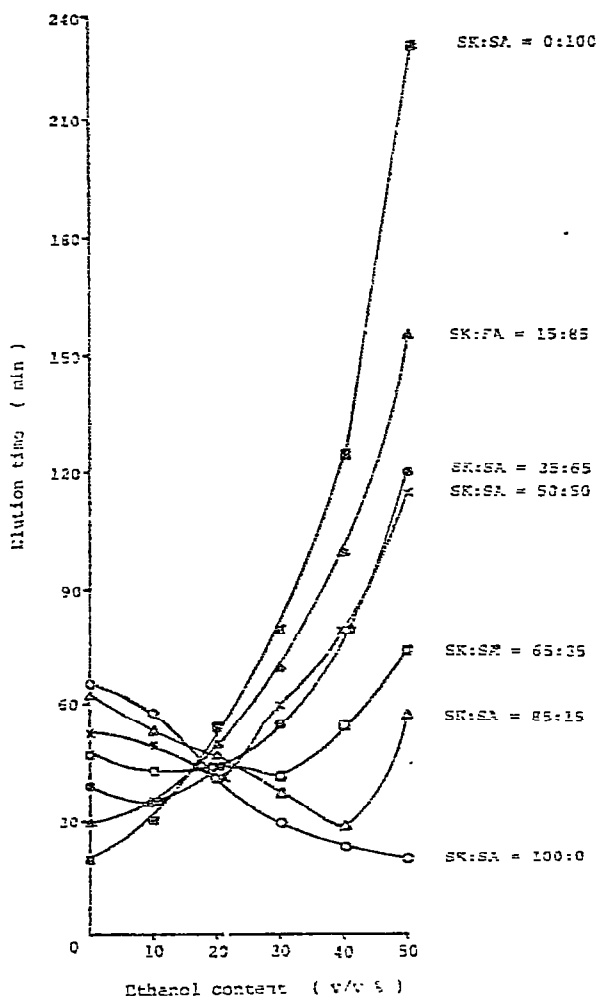


Fig. 3. Relationships between elution times, mixing ratios of the ion-exchange resins and ethanol contents.

particle size, and their relative behaviour in our operating conditions was almost the same.

Elution was carried out with 0.5 *M* lactic acid plus 0.06 *M* sodium chloride changing in pH from 3.1 to 3.3 on the mixed column (CK:CA = 35:65). As shown in Fig. 4, at pH 3.15 and 3.2, copper, zinc, cobalt and lead were completely separated, whereas cadmium and manganese overlapped. On the other hand, at pH 3.25, the elution times of all the metals were shortened, and the elution order of cadmium became later relative to manganese. However, the separation of manganese from cadmium was not complete and that of copper from zinc became unsatisfactory.

Next, elution was carried out on the same column with 0.5 *M* lactic acid at pH 3.2, but with the concentration of sodium chloride changing from 0.04 to 0.08 *M*. As shown in Fig. 5, at a sodium chloride concentration of 0.05 *M*, cadmium and

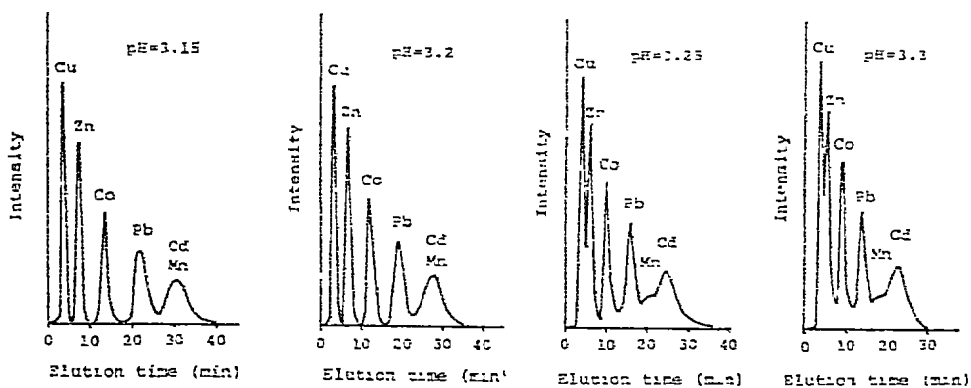


Fig. 4. Separation of the six metals with 0.5 M lactic acid plus 0.06 M sodium chloride on a mixed column (CK:CA = 35:65) by changing the pH.

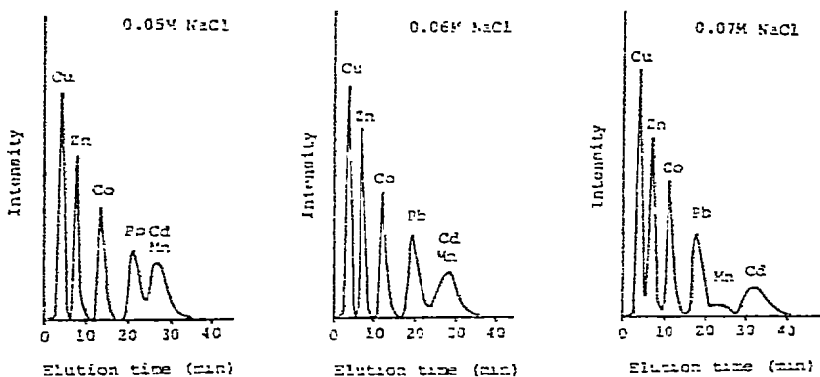


Fig. 5. Separation of the six metals with 0.5 M lactic acid at pH 3.2 on a mixed column (CK:CA = 35:65) by changing the concentration of sodium chloride.

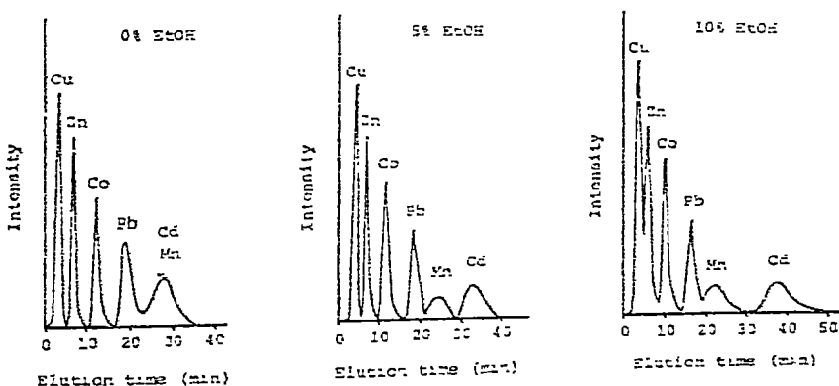


Fig. 6. Separation of the six metals with 0.5 M lactic acid plus 0.06 M sodium chloride at pH 3.2 on a mixed column (CK:CA = 35:65) by changing the ethanol content.

manganese overlapped each other and separation between lead, cadmium and manganese was not complete. Similarly, at sodium chloride concentration of 0.06 M, manganese and cadmium overlapped. On the other hand, when the concentration of sodium chloride was 0.07 M, manganese and cadmium were completely separated, but separation of lead from manganese was unsatisfactory. With increase in the concentration of sodium chloride above 0.07 M, separation of copper from zinc became unsatisfactory and the elution time of cadmium increased.

Elution was then carried out on the same column with 0.5 M lactic acid plus 0.06 M sodium chloride at pH 3.2, but with an ethanol content changing from 0 to 20%. As shown in Fig. 6, with the eluent containing 5% of ethanol, all six metals were completely separated within 40 min, accompanied by a decrease in the elution times of lead and manganese and an increase in that of cadmium.

Thus, by suitable combination of the mixing ratio of the ion-exchange resins, the pH of the eluent, the concentration of sodium chloride and the ethanol content, the separation of the six metals was greatly enhanced.

These results suggest that it might be interesting to study the effects of some non-electrolytes with different dielectric constants on the separation of metals on mixed columns.

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