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## CHROMATOGRAPHIC SEPARATION OF METAL IONS ON A MACRORETICULAR CATION-EXCHANGE RESIN WITH HYDROCHLORIC ACID IN AN AQUEOUS ACETONE SOLUTION

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### SUMMARY

Forced-flow chromatography on a cation-exchange resin has been used to obtain rapid separations of metal ions, such as Cd(II), Zn(II), Fe(III), Pb(II), Cu(II), Co(II) and Mn(II). The macroreticular resin used provides rapid separations in hydrochloric acid-acetone media covering acid and acetone concentration ranges of 0.1-1.88 *M* and 70-96%, respectively. On-stream addition of a colour-forming reagent provides continuous detection and quantitation of the eluted metals.

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### INTRODUCTION

There have been many attempts to improve the cation-exchange separation of metal ions by the addition of a water-miscible organic solvent with the aim of promoting chloride complex formation selectively in the external phase. Systematic surveys of cation-exchange distribution coefficients for many elements in hydrochloric acid-organic solvent<sup>1-3</sup> (dimethylformamide<sup>4</sup>, acetone<sup>5-11</sup>, ethanol<sup>12</sup>, tetrahydrofuran<sup>13</sup> and dimethyl sulphoxide<sup>14,15</sup>)-water mixtures have been reported, and many schemes for the separation of metal ions have been suggested. Favourable distribution coefficients do not always guarantee a good separation because they cannot predict features of the column behaviour such as peak broadening. The intention of this work was to investigate these aspects in detail by preparing elution curves and carrying out column experiments with a synthetic mixture including many metal ions.

Good gravity-flow cation-exchange separations of metal ions<sup>5,6,10</sup> have been obtained in acetone-water-hydrochloric acid media. The eluted metal ions exhibited some tailing, which could be eliminated by decreasing the flow-rate of the eluent or by using a finer mesh fraction of resin beads. In addition, new macroreticular cation-exchange resins have been shown to provide rapid separations in forced-flow chromatography with solutions of acetone<sup>16</sup>, 2-propanol<sup>17</sup> and acetonitrile<sup>18</sup> in dilute hydrochloric acid as eluent. The present work has demonstrated the advantages in some instances of separations using the macroreticular cation-exchange resin Amberlyt 15 with a solution of hydrochloric acid in acetone-water as eluent. In a previous paper<sup>16</sup> we described the rapid separation of transition metal ions on a macroreticular

resin by varying the acetone concentration while keeping the hydrochloric acid concentration constant (0.64 *M*) in the eluent. This paper describes separations with hydrochloric acid and acetone concentrations in the eluent ranging from 0.1 to 1.88 *M* and from 70 to 96%, respectively, and discusses the elution conditions for the separation of metal ions.

It has been demonstrated<sup>16,18</sup> that the on-stream addition of a colour-forming reagent provides continuous detection and quantitation of eluted metal ions. The same method was applied to the chromatographic separation of metals with acetone-hydrochloric acid eluents in this work.

## EXPERIMENTAL

### *Equipment*

Metering pumps from Japan Electron Optics Lab. Co. (JEOL, Tokyo, Japan) were used for forcing the eluent through a chromatographic column and the colour-forming reagent solution through a mixing chamber.

A sample-injection valve was obtained from JEOL. A sample loop was made of 1-mm I.D. PTFE tubing, and the volume (0.2 ml) of a loop was calibrated by collecting the effluent solution from the loop filled with hydrochloric acid solution and titrating it with standard sodium hydroxide solution.

A three-way PTFE tap obtained from JEOL was used as a mixing chamber.

PTFE tubing (1.0 mm I.D.) was used for the pipeline of the chromatographic system. In order to ensure the reaction of a colour-forming reagent with a metal ion, a 150-cm PTFE tube was used between the mixing chamber and the flow-through cell.

The chromatographic column (8 mm I.D.) was equipped with an outlet plunger for decreasing the bed height.

A Hitachi Model 207 atomic-absorption spectrophotometer was used for the determination of metals in the eluted fractions. An acetylene-air flame was used for the atomization of metal ions.

A Shimadzu Model MAF flame spectrophotometer was fitted with a pre-mixed atomizer (Hitachi Model 207-0070) for the determination of aluminium in the eluted fractions. The emission of aluminium in a hydrogen-oxygen flame was measured at a wavelength of 3961.5 Å.

A Hitachi Model 034-0041 spectrophotometer with a flow-through cell was used for the continuous determination of metal ions in the eluate from the column. The light path of the cell was 4 mm long. The materials contacting the solution were made of quartz and stainless steel and the internal volume of the cell was approximately 90  $\mu$ l. Optical filters (520 and 540 nm wavelengths) and photocells were used for measurement of the absorbance.

### *Reagents*

*Resin.* The macroreticular strongly acidic cation-exchange resin Amberlyst 5 was received as beads from Rohm and Haas (Philadelphia, Pa., U.S.A.). The dried beads of the resin were ground in a mill and sieved to obtain the 100-200-mesh fraction. This was slurried repeatedly in water and the extreme fines were removed by acetone flotation.

This fraction of the resin was packed in a large chromatographic tube and

washed with *N,N*-dimethylformamide, 2-propanol, acetone, 3 *M* hydrochloric acid and deionized water. A portion of the purified resin was washed with acetone and dried and the air-dried resin was used for the measurement of the ion-exchange capacity. The dried resin had a capacity of 4.2 mequiv./g.

The stock solution and synthetic sample of metal ions were prepared according to the procedure described previously<sup>16</sup>.

**Eluents.** The eluents were solutions of hydrochloric acid in water-acetone. Each eluent was prepared so that the concentrations of acetone and hydrochloric acid were expressed as a percentage by volume and as a molarity, respectively.

**Colour-forming reagent.** A 1-g amount of 4-(2-pyridylazo)resorcinol (Dotite PAR, Dogin Pharmaceutical Lab., Kumamoto, Japan) was mixed with 40 ml of 0.6 *N* ammonia solution, crushing the lumps with a stirring rod. The solution was transferred to a 1-l beaker and diluted to volume with deionized water. After agitation for half an hour, this solution was filtered on rapid filter-paper. A colour-forming reagent solution for continuous determination of metals was prepared by mixing an aliquot of this stock solution and ammonia solution of an appropriate concentration.

The PAR stock solution showed a large decrease in its colour-forming capability after 2 weeks. A PAR stock solution in ammonia solution of concentration higher than 0.3 *N* might maintain a high sensitivity of detection for a longer period, but this alternative has not been checked.

### Procedure

The distribution coefficients were determined by the batch equilibrium method and by column chromatography. In the batch experiment, 25 ml of solution containing 0.1 mequiv. of each metal was equilibrated with 1.00 g of the air-dried resin in the hydrogen form. After equilibration for 16 h in a mechanical shaker at ambient temperature, the resin was filtered off. The metal ions in the filtrate were determined

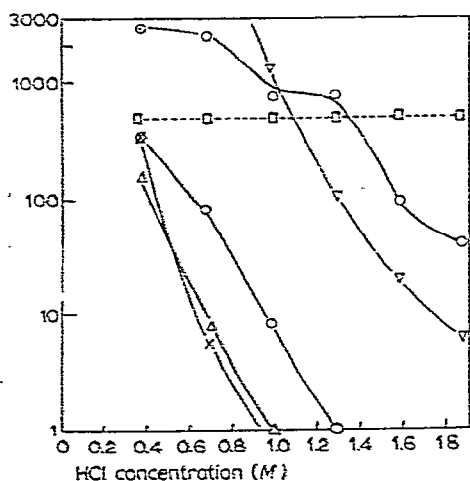


Fig. 1. Distribution coefficients as a function of hydrochloric acid concentration in 70% acetone. Resin, Amberlyst 15 (100-200 mesh); temperature, ambient. Distribution coefficients of Cd(II) and Ni(II) are less than unity in 0.38-1.88 *M* hydrochloric acid. ×, Fe(III); △, Pb(II); ○, Cu(II); ▽, Co(II); ⊙, Mn(II); □, Cr(III).

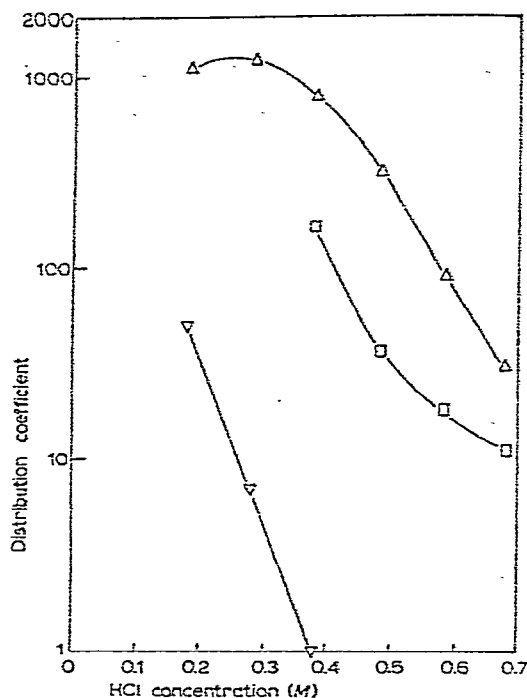
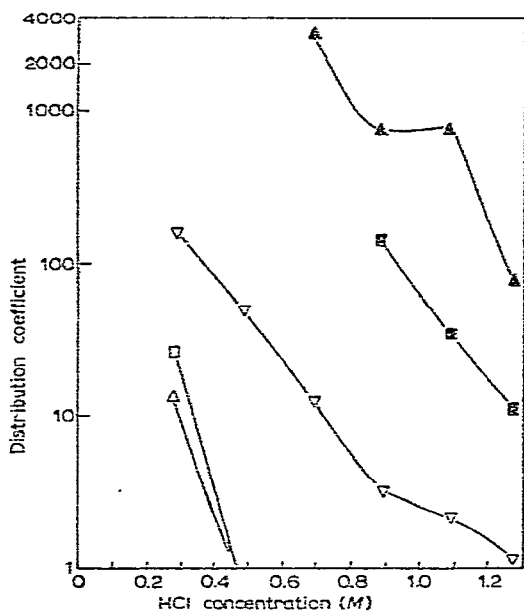


Fig. 2. Distribution coefficients as a function of hydrochloric acid concentration in 80% acetone. Temperature, ambient. Distribution coefficients of other metals in 0.28–1.28 M hydrochloric acid: Cd and Zn < unity; Ni > 100; Cr(III) > 500.  $\Delta$ , Fe(III);  $\square$ , Pb(II);  $\nabla$ , Cu(II);  $\boxtimes$ , Co(II);  $\blacktriangle$ , Mn(II).

Fig. 3. Distribution coefficients as a function of hydrochloric acid concentration in 90% acetone. Temperature, ambient. Distribution coefficients of other metals in 0.18–0.68 M hydrochloric acid: Cd, Zn, Fe and Pb < unity; Cr(III) > 500.  $\nabla$ , Cu(II);  $\square$ , Co(II);  $\Delta$ , Mn(II).

by atomic-absorption spectrophotometry or flame photometry. The concentrations of hydrochloric acid and organic solvent in the solution phase were expressed as the values before equilibrium. The uptake of solvents (acetone and water) on the resin phase were disregarded.

Some distribution coefficients were obtained by calculation from the retention volumes measured by the column method. The 8-mm I.D. chromatographic tube was filled with resin slurried in acetone. The slurried resin was aspirated by a syringe mounted at the bottom of the tube so that all of the resin settled rapidly. More than 80 ml of each eluent was passed through the column in order to equilibrate the resin with the eluent. The method of continuous detection by flow spectrophotometry was adopted in order to obtain the elution curves of metal ions. The flow-rate (0.5–1.0 ml/min) and the ammonia concentration of the colour-forming reagent solution were chosen so that the effluent stream from the flow-through cell would have a pH in the range 8.5–10.

## RESULTS AND DISCUSSION

### *Distribution coefficients and separation factors*

The distribution coefficients of the metals were first obtained by the batch

equilibrium method. They can be used to predict the elution behaviour of metals on an ion-exchange column. The effects of the hydrochloric acid concentration on the distribution coefficients in 70, 80 and 90% acetone can be seen in Figs. 1, 2 and 3, respectively. The distribution coefficients of many of the metal ions studied decreased with increasing concentration of hydrochloric acid. Ni(II), Cr(III), Al(III), Ca(II) and Mg(II) did not exhibit such a decrease, the distribution coefficients remaining high (> 100) in these media. The separation factors for the pairs Cu(II)–Co(II) and Co(II)–Mn(II) were sufficiently large in these acetone–hydrochloric acid media. However, the use of 90% acetone is recommended because it provided favourable separation conditions at a comparatively low concentration of hydrochloric acid.

The distribution coefficient of an eluted metal ion should be very low (near unity or less) so that the metal ion may be eluted with a small volume of eluting agent. Distribution coefficients ranging from 0.5 to 6 were determined by column chromatography. The effect of the hydrochloric acid concentration on the distribution coefficients in 90% acetone media can be seen in Fig. 4. The separation factor for the Fe(III)–Pb(II) pair was small in 70 and 80% acetone media, as shown in Figs. 1 and 2. However, a large separation factor was obtained in 90% acetone medium, as shown in Fig. 4. The effect of the hydrochloric acid concentration and the column temperature the distribution coefficients of Cd(II) and Zn(II) in 80% acetone media can be seen in Fig. 5. The separation factor for the Cd(II)–Zn(II) pair was very small in 70 and 90% acetone media, but a favourable separation factor was obtained in 80% acetone solution containing 0.15–0.22 M hydrochloric acid at ambient temperature.

### Chromatographic separations

The separation of Cd(II) and Zn(II) was achieved with 80% acetone–0.19 M hydrochloric acid as eluting agent at a flow-rate of 1.8 ml/min at ambient temperature.

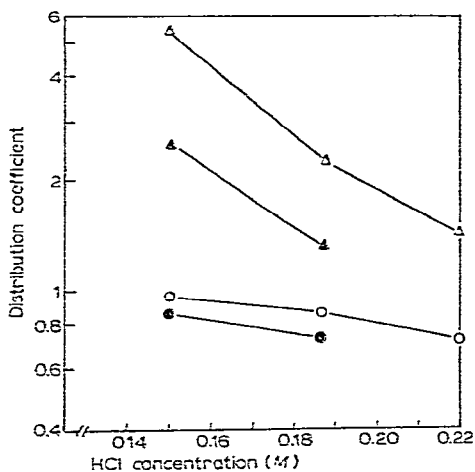
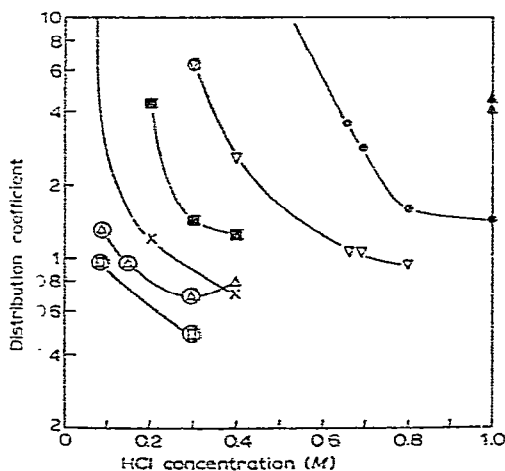


Fig. 4. Distribution coefficients as a function of hydrochloric acid concentration in 90% acetone. Column temperature, ambient. Flow-rates: single symbols, 1.8 ml/min; symbols enclosed by circles, 1. ml/min.  $\square$ , Cd(II);  $\triangle$ , Zn(II);  $\times$ , Fe(III);  $\blacksquare$ , Pb(II);  $\nabla$ , Cu(II);  $\odot$ , Co(II);  $\blacktriangle$ , Mn(II).

Fig. 5. Distribution coefficients as a function of hydrochloric acid concentration in 80% acetone. Flow-rate, 1.8 ml/min. Column temperature: open symbols, ambient (20–25°); closed symbols, 40°.  $\odot$ ,  $\circ$ , Cd(II);  $\blacktriangle$ ,  $\triangle$ , Zn(II).

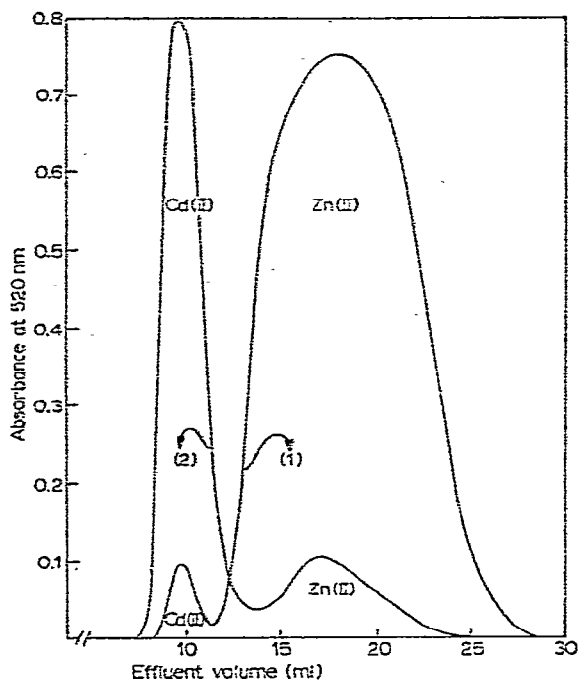


Fig. 6. Elution curves of Cd(II) and Zn(II). Column, 200 mm  $\times$  8 mm I.D.; temperature, ambient; eluent, 80% acetone-0.19 M hydrochloric acid; flow-rate, 1.8 ml/min. Amounts of metals: curve 1. Cd(II)  $4.38 \cdot 10^{-8}$  mole, Zn(II)  $4.34 \cdot 10^{-6}$  mole; curve 2, Cd(II)  $4.06 \cdot 10^{-6}$  mole, Zn(II)  $1.02 \cdot 10^{-7}$  mole.

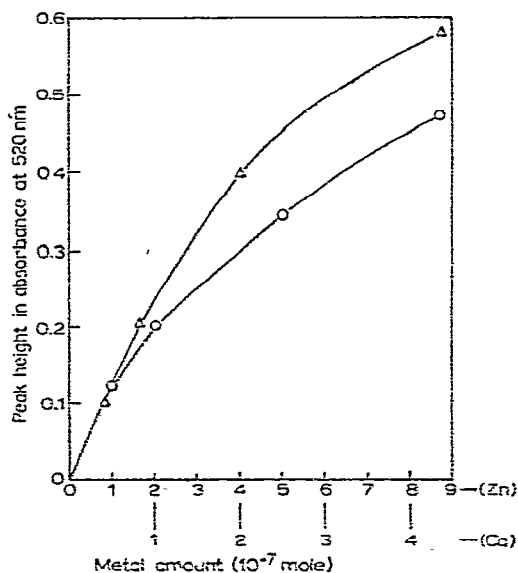


Fig. 7. Calibration graphs for Cd(II) and Zn(II). Eluent, 80% acetone-0.19 M hydrochloric acid.  $\Delta$ , Cd(II);  $\circ$ , Zn(II).

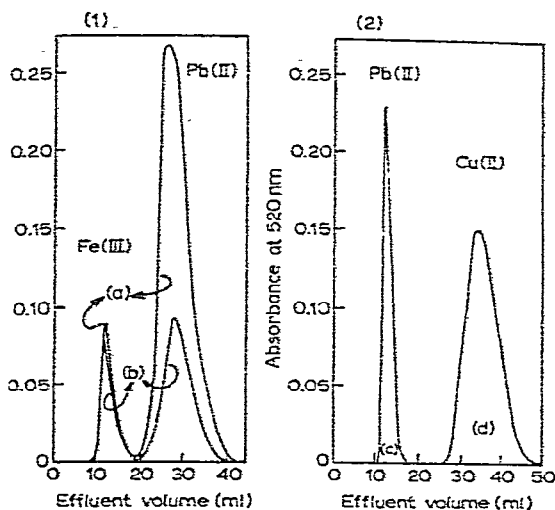


Fig. 8. Elution curves of Fe(III), Pb(II) and Cu(II). Column, 195 mm  $\times$  8 mm I.D.; temperature, ambient. Curve 1: flow-rate, 1.8 ml/min; eluent 90% acetone-0.20 *M* hydrochloric acid; amounts of metals, (a)  $3.0 \cdot 10^{-7}$  mole, (b)  $1.1 \cdot 10^{-7}$  mole. Curve 2: flow-rate, 1.4 ml/min; eluent, 90% acetone-0.30 *M* hydrochloric acid; amounts of metals, (c)  $2.0 \cdot 10^{-7}$  mole, (d)  $4.1 \cdot 10^{-7}$  mole.

Two typical elution curves are shown in Fig. 6, the ratio of the amounts of metals (Cd:Zn) being 40:1 or 1:100. Although the separation of these metals was not complete, the use of the peak heights permitted the quantitation of each metal at levels up to those covered in the calibration graphs (Fig. 7), viz., up to  $4.3 \cdot 10^{-7}$  mole for Cd(II) and up to  $8.6 \cdot 10^{-7}$  mole for Zn(II).

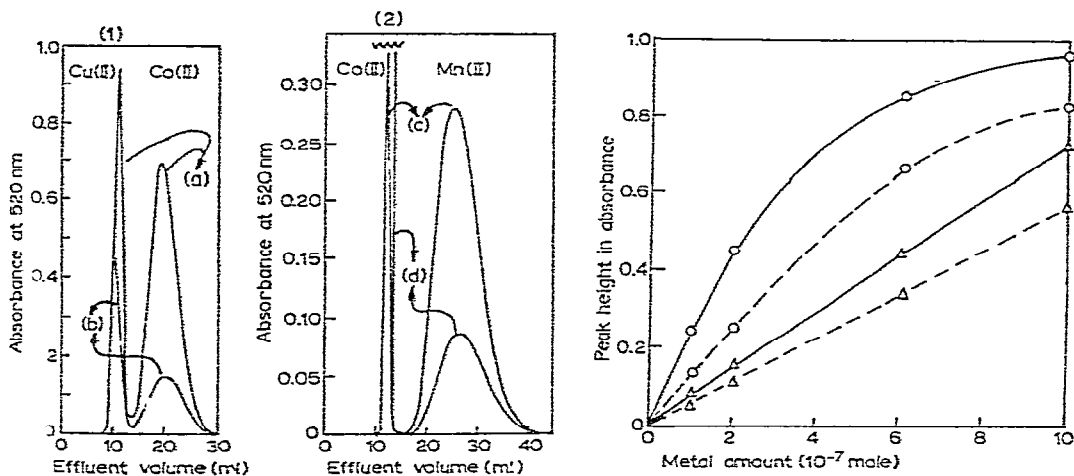


Fig. 9. Elution curves of Cu(II), Co(II) and Mn(II). Column, 195 mm  $\times$  8 mm I.D.; temperature, ambient; flow-rate, 1.8 ml/min; concentration of hydrochloric acid in 90% acetone eluent, (1) 0.1 *M*, (2) 1.0 *M*. Amounts of metals: (a) Cu(II)  $10.1 \cdot 10^{-7}$ , Co(II)  $10.1 \cdot 10^{-7}$  mole; (b) Cu(II)  $2.0 \cdot 10^{-7}$ , Co(II)  $2.0 \cdot 10^{-7}$  mole; (c) Co(II)  $1.0 \cdot 10^{-7}$ , Mn(II)  $10.9 \cdot 10^{-7}$  mole; (d) Co(II)  $10.1 \cdot 10^{-7}$ , Mn(II)  $3.3 \cdot 10^{-7}$  mole.

Fig. 10. Calibration graphs for Cu(II) and Co(II). Eluent, 90% acetone-0.69 *M* hydrochloric acid; colour-forming reagent, 0.04% PAR in 1.2 *N* ammonia solution. Wavelength: —, 520 nm; ---, 540 nm. O, Cu(II);  $\Delta$ , Co(II).

The separation of Fe(III) and Pb(II) was achieved with 90% acetone-0.20 *M* hydrochloric acid as eluting agent at a flow-rate of 1.8 ml/min. The elution curves of these metals are shown in Fig. 8 (1). Linear calibration graphs were obtained for the determination of Pb(II) up to  $3.0 \cdot 10^{-7}$  mole (absorbance, 0.27) by the use of the peak height. However, no simple relation was found between the peak height and the amount of Fe(III) in the chromatographic separation with this eluting agent.

The complete separation of Pb(II) and Cu(II) was accomplished with 90% acetone-0.30 *M* hydrochloric acid as eluent at a flow-rate of 1.4 ml/min. The elution curves of these metals are shown in Fig. 8 (2).

Cu(II) and Co(II) were separated with 90% acetone-0.69 *M* hydrochloric acid as eluent at a flow-rate of 1.8 ml/min. The elution curves of these metals are shown in Fig. 9 (1). The calibration graphs for these metals were obtained by using the peak height at 520 or 540 nm, as shown in Fig. 10. A higher sensitivity of detection was given by measuring the absorbance at 520 nm.

The separation of Co(II) and Mn(II) was achieved with 90% acetone-1.0 *M* hydrochloric acid as eluent at a flow-rate of 1.8 ml/min. The elution curves of these metals are shown in Fig. 9 (2). The calibration graphs for these elements were obtained by using the peak height or the peak area, as shown in Fig. 11. The peak area gave a better linearity with the amount of metal than did the peak height.

From the distribution coefficients and the actual separations, the following stepwise elution scheme was applied to the chromatography of metal ions. Before the elution, the resin of the column was equilibrated with 0.06 *M* hydrochloric acid while the metal ions were taken up by the resin. Successive elution conditions were chosen

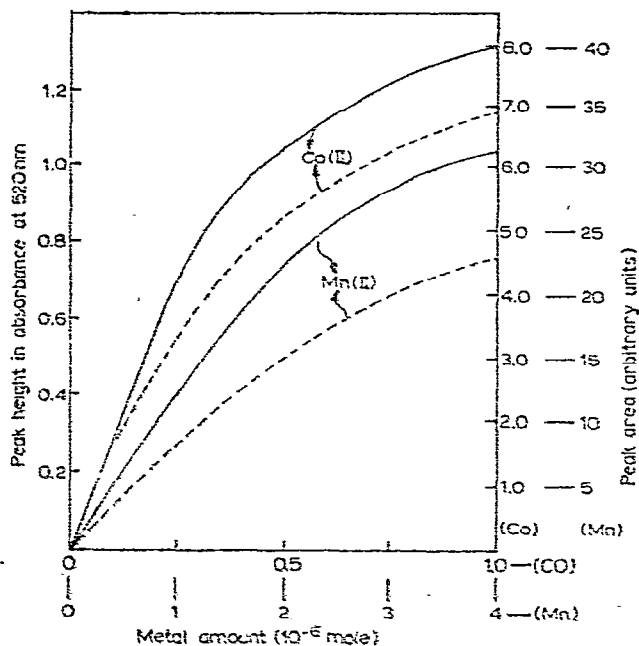


Fig. 11. Calibration graphs for Co(II) and Mn(II). —, Peak area; ---, peak height. Column, 200 mm  $\times$  8 mm I.D.; temperature, ambient; eluent, 90% acetone-1.0 *M* hydrochloric acid (flow rate 1.8 ml/min); colour-forming reagent, 0.04% PAR in 1.2 *N* ammonia solution.



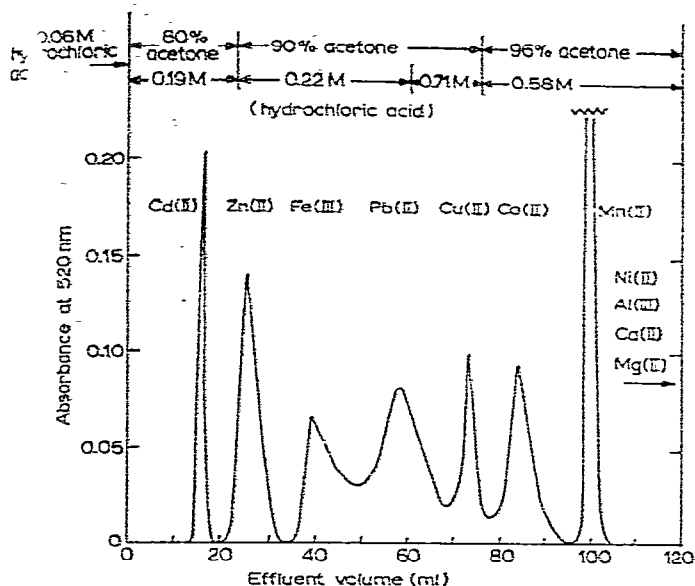


Fig. 12. Elution curve of multicomponent mixture. Column, 195 mm  $\times$  8 mm I.D.; temperature, ambient; flow-rate, 1.8 ml/min; sample, Fe  $9.8 \cdot 10^{-6}$  mole, Ca(II)  $1.9 \cdot 10^{-5}$  mole, Mg(II)  $8.9 \cdot 10^{-6}$  mole, other metals  $1.9 \cdot 10^{-7}$  mole.

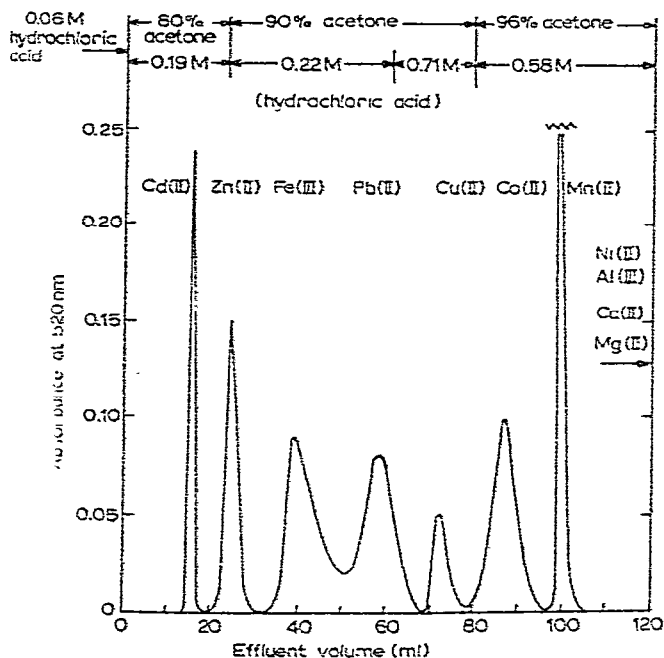


Fig. 13. Elution curve of multicomponent mixture. Column, 195 mm  $\times$  8 mm I.D.; temperature, ambient; flow-rate, 1.4 ml/min; sample, Fe  $9.8 \cdot 10^{-6}$  mole, Ca(II)  $1.9 \cdot 10^{-5}$  mole, Mg(II)  $8.9 \cdot 10^{-6}$  mole, other metals  $1.9 \cdot 10^{-7}$  mole.

so that two metal ions were eluted by each eluting agent. In this work, the concentrations of acetone and hydrochloric acid are the variables that determine the composition of the eluting agent.

Cd(II) and Zn(II) were eluted with 80% acetone-0.19 M hydrochloric acid, Fe(III) and Pb(II) with 90% acetone-0.22 M hydrochloric acid, Cu(II) and Co(II) with 90% acetone-0.71 M hydrochloric acid and Mn(II) with 96% acetone-0.58 M hydrochloric acid. Ni(II), Al(III), Ca(II) and Mg(II) were retained by the column in the above eluents, and were eluted as a group with 3 M hydrochloric acid.

Elution curves of seven metal ions are shown in Figs. 12 and 13. Amounts of each metal in the sample were as follows: Cd(II), Zn(II), Pb(II), Cu(II), Co(II), Mn(II), Al(III) and Ni(II),  $1.9 \cdot 10^{-7}$  mole each; Fe(III),  $9.8 \cdot 10^{-6}$  mole; Ca(II),  $1.9 \cdot 10^{-5}$  mole; and Mg(II),  $8.9 \cdot 10^{-6}$  mole. The mutual separation of Fe(III), Pb(II), Cu(II) and Co(II) was not complete at a flow-rate of 1.8 ml/min because of peak broadening, as shown in Fig. 12. At a flow-rate of 1.4 ml/min, seven different metal ions were separated completely from each other, except for Fe(III), which exhibited some tailing, as shown in Fig. 13. Transformation from a partially non-aqueous medium to an aqueous medium and *vice versa* did not decrease the performance of the column packed with the macroreticular resin.

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