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COMPARISON OF EFFICIENCY OF CATION-EXCHANGE RESINS IN THE CHROMATOGRAPHIC SEPARATION OF METAL IONS WITH AQUEOUS ACETONE-HYDROCHLORIC ACID SOLUTION

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SUMMARY

The efficiencies of macroreticular and microreticular cation-exchange resins in the column chromatography of metal ions with aqueous acetone-hydrochloric acid solutions were compared. The macroreticular resin Amberlite 200 was superior in the chromatographic separation of Cd(II), Zn(II), Fe(III), Pb(II), Cu(II), U(VI), Co(II), Fe(II), Mn(II), V(IV) and Ni(II). Trace amounts (10^{-8} – 10^{-7} mole) of metal ions concentrated on the column resin from a large volume of very dilute concentration were separated from each other by stepwise elution chromatography and detected automatically by flow spectrophotometry in 35 min.

INTRODUCTION

There have been many attempts¹⁻⁴ to improve the cation- and anion-exchange separations of metal ions by adding a water-miscible organic solvent in order to increase the adsorption selectivity. Hydrochloric and hydrobromic acids have been used as such solutes in the eluent because of their capability of undergoing complex formation with many metal ions. The use of hydrochloric acid is to be preferred as it is more stable chemically than hydrobromic acid.

There have been many studies on the separability of metal ions on anion-exchange resins in aqueous organic solvent-hydrochloric acid media. Some separations of metal ions, such as Fe(III)-Pb(II) and Ni(II)-Al(III), have been found to be difficult in this system. Further, the chloride (or bromide) complexes of some metal ions, such as Bi(III), Hg(II) and Sn(IV), are so stable that their rapid elution from the column is difficult.

Acetone⁵⁻⁷ promotes the formation of chloride complexes considerably more strongly than other water-miscible organic solvents such as methanol, ethanol, isopropanol and dimethyl sulphoxide, and provides favourable conditions for separations at low concentrations of the organic solvent and hydrochloric acid. In addition, the low viscosity of acetone is advantageous for the column procedure. Acetonitrile seems to be a comparable solvent to acetone as regards low viscosity and high complex-formation capability.

An effective scheme for the chromatographic separation of a mixture of many metal ions (especially transition metal ions) can be predicted from systematic surveys⁵⁻¹¹ of cation-exchange distribution coefficients in aqueous acetone-hydrochloric acid solutions. The adsorption selectivity has been improved so much that one metal ion may be eluted with a small volume of the eluent while another metal ion may be strongly retained by the column resin. Therefore, the composition of the eluent has to be changed in order to elute a series of metal ions consecutively from the column in a short time.

In general, the ion-exchange resin shrinks or swells on changing the eluent, and the change in the dimensions of the resin disturbs the uniform packing of the column and might be detrimental to the separation. In addition, the low degree of swelling of the resin in partially non-aqueous solution results in a slow ion-exchange reaction rate, which is undesirable in the column chromatography. On the other hand, a macroreticular resin has a permanent macroscopic structure regardless of the ionic form and the solvent used^{12,13}. Macroreticular cation-exchange resins have been used for rapid separations in forced-flow chromatography with solutions of 2-propanol^{14,15}, acetone^{14,16}, dimethylformamide¹⁷ and acetonitrile¹⁸ in dilute hydrochloric acid because of their durability and minimal shrinking or swelling on changing the eluent.

A sharp separation can be achieved with a column with a small height equivalent to a theoretical plate (HETP) in addition to a large separation factor. Although a small HETP can often be obtained by the use of fine particles of packing resin with a narrow size range, a significant pressure drop occurs on increasing the flow-rate of the eluent, which may be limited by the pressure capability of the chromatographic system used. If the HETP is a function of the capacity factor (important contributions to band broadening from stationary-phase mass transfer or from stagnant mobile-phase diffusion), the optimal value of the capacity factor occurs between 1.5 and 4 (ref. 19), which leads to a large number of the effective theoretical plates per second. Such a low capacity factor is convenient for the rapid elution of each component, and it is therefore desirable that a small HETP should be obtained, especially with a small range of the capacity factor.

In this study, the efficiencies of the macro- and microreticular resins were compared by investigating the dependence of the HETP on the capacity factor and on the particle size of the packing resin. Some advantages were found in the stepwise elution chromatography of many metal ions on macroreticular resins with partially non-aqueous eluents containing hydrochloric acid. It was also demonstrated that cation-exchange chromatography may be useful for the determination of metal ions at concentrations below the detection limit of the usual spectrophotometric and electrochemical methods by adopting the pre-concentration procedure. This paper describes a method that combines rapid separation and spectrophotometric detection for trace amounts (10^{-8} - 10^{-7} mole) of eleven metal ions.

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. These pumps can deliver liquid

at an outlet pressure of up to 30 atm. A reciprocating mini-pump of the single-piston type (Milton-Roy, St. Petersburg, Fla., U.S.A.) was used at pressures up to 50 atm for dynamic packing of a chromatographic column.

A sample-injection valve was obtained from Kyowa Seimitsu Co. (Mitaka, Tokyo, Japan) and fitted with calibrated sample loops made of 1-mm I.D. PTFE tubing. The volume (0.2 ml) of a loop was calibrated according to the procedure described previously¹⁶.

A chromatographic glass tube of 8 mm I.D. obtained from JEOL was equipped with a movable outlet plunger for decreasing the bed height of the resin. A chromatographic glass tube of 5 mm I.D., obtained from Kyowa Seimitsu Co., was used with fixed outlet plungers. A three-way polytrifluoroethylene (PTFCE) tap obtained from Kyowa Seimitsu Co. 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 long PTFE tube was used between the mixing chamber and the flow-through cell.

A Hitachi Model 124 spectrophotometer was used for the continuous detection of metal ions in the eluate from the column. The sample compartment of the spectrophotometer was altered so as to accommodate a flow-through cell (Hitachi Model 034-0249). The light path of the cell was 4 mm long and the internal volume was approximately 90 μ l. The materials contacting the solution were made of quartz and stainless steel.

Reagents

Resins. Several strongly acidic cation-exchange resins were used. The microreticular resin Hitachi Custom ion exchanger No. 2611 (cross-linking 10%), manufactured by Mitsubishi Chem. Ind. (Yokohama, Japan), was obtained as spherical beads in the sodium form of diameter 13–17 μ m. The porous resin DIAION PK 228 was received as spherical beads in the sodium form of diameter 30–50 μ m from the Commodity Research Institute of Mitsubishi Chem. Ind. The macroporous resin AG MP 50 was obtained as granular beads in the hydrogen form of diameter 40–80 μ m from Bio-Rad Labs. (Richmond, Calif., U.S.A.); the surface area of this resin is 35 cm²/g. The macroreticular (macroporous) resin Amberlite 200 was received as large beads in the sodium form from Rohm and Haas (Philadelphia, Pa., U.S.A.). The dried beads were ground in a mill and sieved to obtain the 250–325-mesh fraction. The diameter of the swollen particles of this fraction was calculated to be 60–80 μ m from the fact that the volume of the resin swollen in liquid was approximately twice as great as that of the air-dried resin. Another fraction of graded particles (diameter 25–30 μ m) of Amberlite 200 was obtained by the continuous elutriation method described previously¹⁷.

Each fraction of the resin was purified¹⁷ by the procedure described previously¹⁷. The capacity of each resin was 4.2 mequiv./g (dried).

The stock solutions and synthetic samples of metal ions were prepared according to the procedure described previously^{16,17}. The stock solution of U(VI) was prepared by dissolving uranyl acetate dihydrate in dilute nitric acid.

Eluents. The eluents were solutions of aqueous acetone or acetone–dimethylformamide in dilute hydrochloric acid. Each eluent was prepared so that the concen-

trations of hydrochloric acid and organic solvent were expressed as a molarity and a percentage by volume, respectively.

Colour-forming reagent. 4-(2-Pyridylazo)resorcinol(PAR) solution was prepared according to the procedure described previously¹⁶.

Procedure

A chromatographic tube was filled with a thick slurry of each resin fraction in acetone. The method of dynamic packing was carried out as described previously¹⁷. More than 80 ml of each eluent was passed through the column in order to equilibrate the resin with the eluent. The distribution coefficients were obtained by calculation from the retention volumes measured by the column method.

The method of continuous detection by flow spectrophotometry was adopted in order to obtain the elution curves of the metal ions. The colour-forming reagent reacted with a number of metal ions in ammonium chloride solutions of aqueous acetone or acetone-dimethylformamide to produce the chelate complexes, which had their absorption maxima at wavelengths from 500 to 550 nm. The flow-rate and the ammonia concentration of the colour-forming reagent solution were set so that the effluent stream from the flow-through cell would have a pH in the range 8-10.

RESULTS AND DISCUSSION

Use of a microreticular resin

The chromatographic separation of metal ions was examined by using aqueous acetone-hydrochloric acid eluents on a column of the microreticular resin Hitachi Custom No. 2611 (13-17 μm). The effect of the acetone concentration on the distribution coefficients in 0.1 and 0.64 *M* hydrochloric acid media can be seen in Figs. 1 and 2, respectively. The distribution coefficient decreased with increase in the acetone concentration. The separation factor for the Cd(II)-Zn(II) pair was greater than 2 in the 0.1 and 0.64 *M* hydrochloric acid solutions with acetone concentrations of less than 83% and 54%, respectively. The separation factor for the Fe(III)-Pb(II) pair was greater than 3 in the 0.1 and 0.64 *M* hydrochloric acid solutions with acetone concentrations of less than 87% and 66%, respectively. Favourable separation factors for other metal ions were obtained by choosing the appropriate concentrations of acetone in the eluents.

The height equivalent to an effective plate (H_{eff}) decreased with increase in the distribution coefficient in the aqueous acetone-0.1 and 0.64 *M* hydrochloric acid solutions, as shown in Figs. 3 and 4, respectively. Although the H_{eff} values of several metal ions were still small even with the small range of the distribution coefficient, the H_{eff} value of U(VI) was consistently large in the range of the distribution coefficient examined.

The peak heights in the absorbance graphs of the eluted metal ions decreased with increase in the distribution coefficient. In the elution of Fe(III), a larger peak height and lower H_{eff} were obtained by the use of the aqueous acetone in 0.64 *M* hydrochloric acid than in 0.1 *M* hydrochloric acid as the eluent. The peak width of each metal ion changed little in the range of the distribution coefficient as H_{eff} decreased with increase in the distribution coefficient.

The following elution scheme was applied for the separation of Cd(II), Zn(II),

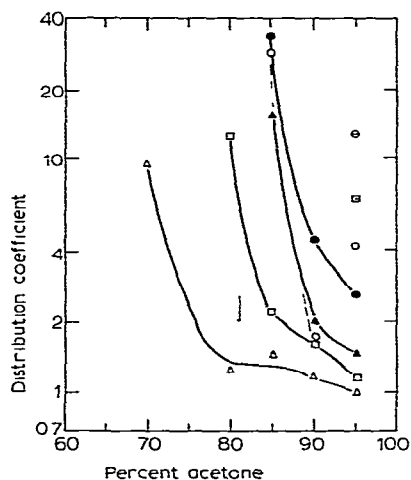


Fig. 1. Distribution coefficients as a function of acetone concentration in 0.1 *M* hydrochloric acid. Column, 90 × 5 mm I.D.; resin, Hitachi Custom ion exchanger No. 2611 (13–17 μm); flow-rate, 9 cm/min. Δ, Cd(II); □, Zn(II); ▲, Fe(III); ○, Ga(III); ●, Pb(II); ○, Cu(II); □, U(VI); ⊖, Co(II).

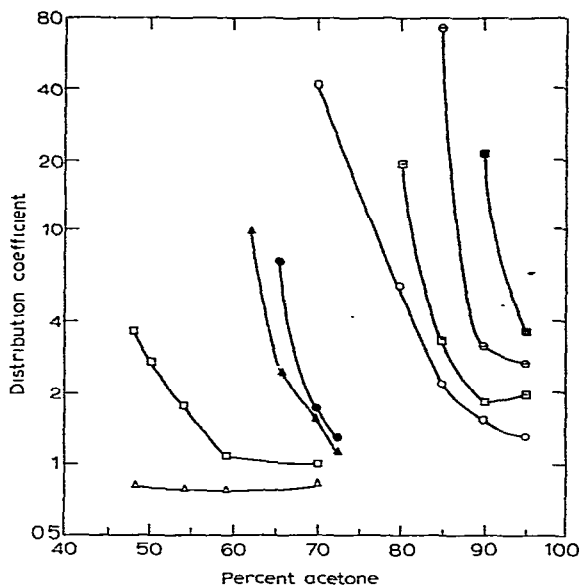


Fig. 2. Distribution coefficients as a function of acetone concentration in 0.64 *M* hydrochloric acid. Column, 90 × 5 mm I.D.; resin, Hitachi Custom ion exchanger No. 2611 (13–17 μm); flow-rate, 9 cm/min (48–70% acetone eluent) or 19 cm/min (80–85% acetone eluent). ■, Mn(II); symbols for other metal ions as in Fig. 1.

Fe(III) and Pb(II): Cd(II) and Zn(II) were separated with 54% acetone–0.64 *M* hydrochloric acid; and Fe(III) and Pb(II) with 66% acetone–0.64 *M* hydrochloric acid, as shown in Fig. 5. The peak of Fe(III) was sharp as the overall result of the fact that the metal ion was eluted with an initial portion of the eluent (the distribution coefficient was 2) and a small HETP (0.5 mm) was obtained. In contrast, the peak of Pb(II) was broad because the metal ion was eluted with a subsequent portion of the eluent (the distribution coefficient was 7) and a large HETP (3.5 mm) was obtained. The separation of Cu(II) and U(VI) was difficult as the peak of U(VI) was broad and tended to exhibit tailing, in addition to the small separation factor obtained for this pair of metal ions. Further, the peak height of U(VI) was particularly small. Co(II) and Mn(II) were eluted stepwise with small volumes of 90% and 95% acetone solutions in 0.64 *M* hydrochloric acid.

The effect of the column diameter on the peak heights of Cd(II) and Zn(II) was examined. A larger (approximately double) peak height was obtained by the use of a 5 mm I.D. column rather than an 8 mm I.D. column under the same elution conditions (column bed volume, linear flow-rate of the eluent and column temperature).

Use of a porous resin

The chromatographic separation of metal ions with aqueous acetone–hydrochloric acid solution on a column of the porous (not highly porous) resin DIAION

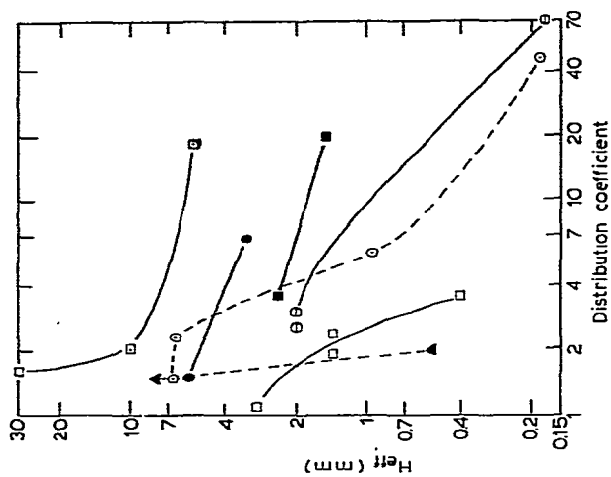
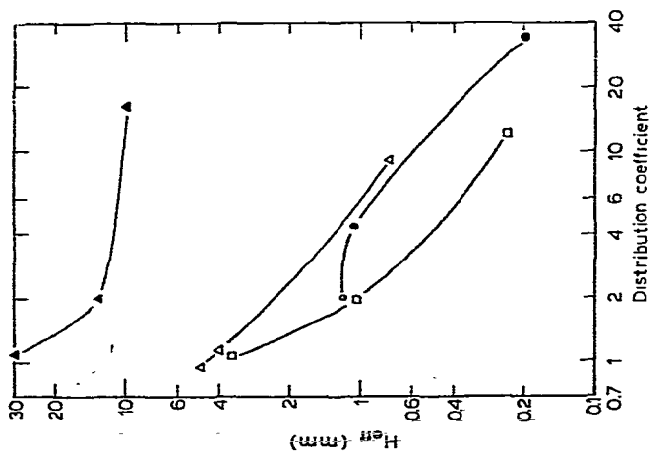


Fig. 3. H_{err} as a function of distribution coefficient in aqueous acetone-0.1 M hydrochloric acid solution. Column, 90 x 5 mm I.D.; resin, Hitachi Custom ion exchanger No. 2611 (13-17 μ m); flow-rate, 8 cm/min. Symbols of metal ions as in Fig. 1.

Fig. 4. H_{err} as a function of distribution coefficient in aqueous acetone-0.64 M hydrochloric acid solution. Column, 90 x 5 mm I.D.; resin, Hitachi Custom ion exchanger No. 2611 (13-17 μ m); flow-rate, 8 cm/min (Zn) or 19 cm/min (other metal ions). Symbols of metal ions as in Figs. 1 and 2.

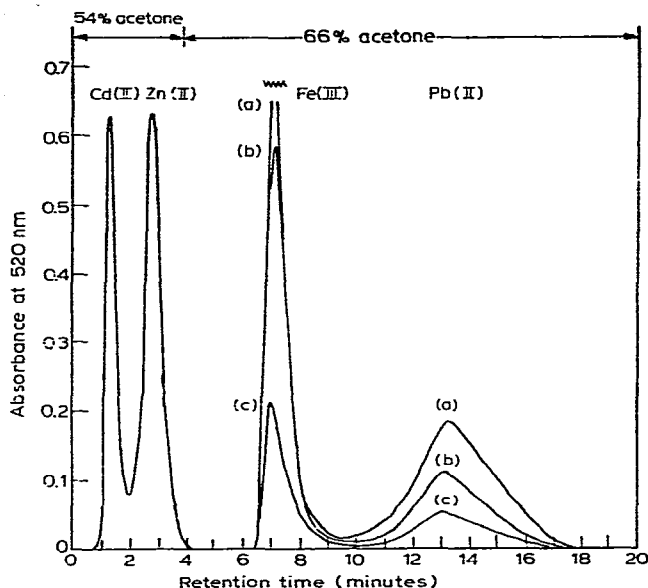


Fig. 5. Separation of Cd(II), Zn(II), Fe(III) and Pb(II) on Hitachi Custom ion exchanger No. 2611 (13–17 μm). Eluent, 0.64 M hydrochloric acid; column, 80 \times 8 mm I.D.; flow-rate, 8 cm/min; column inlet pressure, 15–18 atm.; amount of metal ($\times 10^{-7}$ mole): Cd and Zn, 5; Fe and Pb, (a) 10, (b) 5, (c) 2; sample volume, 0.2 ml.

PK 228 (30–50 μm) was examined. The effect of the hydrochloric acid concentration in 90% acetone solution on the distribution coefficient can be seen in Fig. 6. The separation factor of the Cd(II)–Zn(II) pair was too small for these ions to be separated. Favourable separation factors of the Fe(III)–Pb(II) and Pb(II)–Cu(II) pairs were

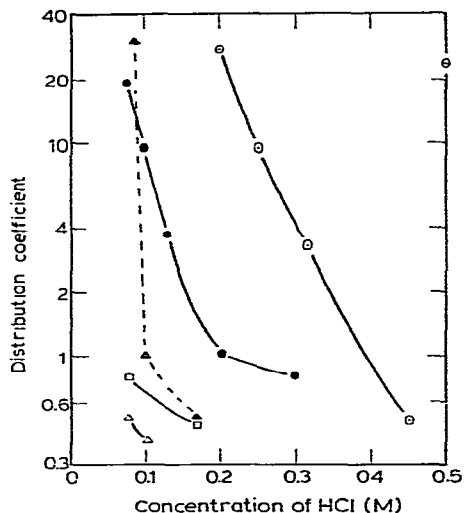


Fig. 6. Distribution coefficients as a function of hydrochloric acid concentration in 90% acetone solution on DIAION PK 228 (30–50 μm). Column, 180 \times 80 mm I.D.; flow-rate, 8 cm/min; symbols of metal ions as in Fig. 1.

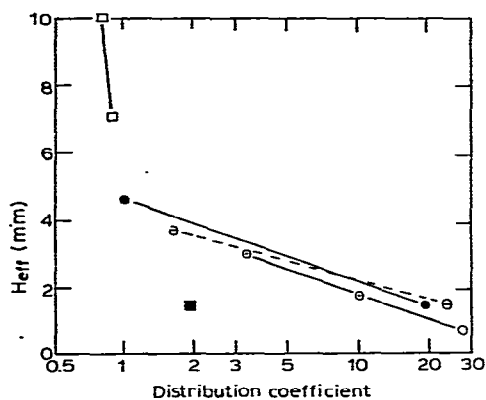


Fig. 7. H_{eff} as a function of distribution coefficient in 90% acetone-hydrochloric acid. Resin, DIAION PK 228 (30–50 μ m); column, 180 \times 8 mm I.D.; flow-rate, 8 cm/min.

obtained by the use of 90% acetone solutions in 0.13 and 0.3 *M* hydrochloric acid, respectively.

The effect of the distribution coefficient on H_{eff} in aqueous 90% acetone-hydrochloric acid solutions can be seen in Fig. 7. The peak width changed little over the range of the distribution coefficient as H_{eff} increased with a decrease in the distribution coefficient.

The effect of the acetone concentration on the distribution coefficient in 0.1 and 0.64 *M* hydrochloric acid solution can be seen in Figs. 8 and 9, respectively. Favourable separation factors for some pairs of metal ions were obtained by choosing

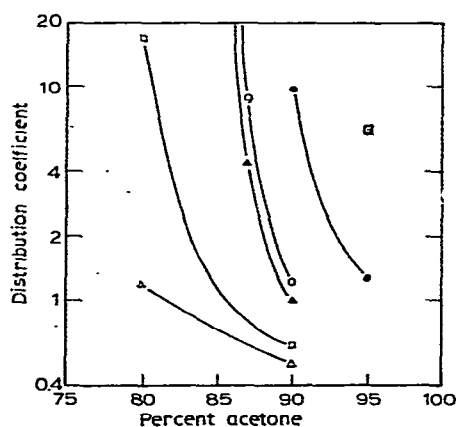


Fig. 8. Distribution coefficient as a function of acetone concentration in 0.1 *M* hydrochloric acid solution on DIAION PK 228 (30–50 μ m). Column, 180 \times 5 mm I.D.; flow-rate, 21 cm/min.

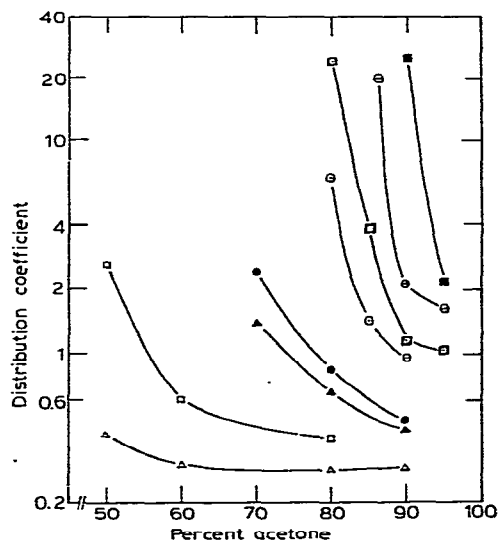


Fig. 9. Distribution coefficient as a function of acetone concentration in 0.64 *M* hydrochloric acid solution on DIAION PK 228 (30–50 μ m). Column, 180 \times 5 mm I.D.; flow-rate, 19 cm/min.

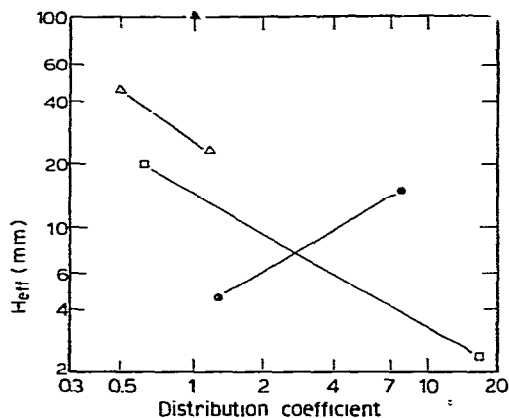


Fig. 10. H_{eff} as a function of distribution coefficient in aqueous acetone-0.1 M hydrochloric acid solution. Conditions as in Fig. 8.

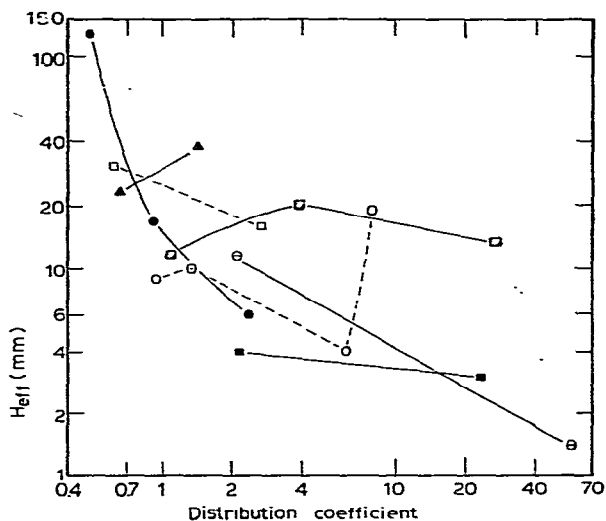


Fig. 11. H_{eff} as a function of distribution coefficient in aqueous acetone-0.64 M hydrochloric acid solution. Conditions as in Fig. 9.

a suitable concentration of acetone in these solutions. A larger separation factor for the Fe(III)-Pb(II) pair was obtained by the use of 0.1 M instead of 0.64 M hydrochloric acid solution. Cu(II), U(VI), Co(II) and Mn(II) were separated stepwise with 0.64 M hydrochloric acid solutions in 85% and 93% acetone.

The effect of the distribution coefficient on H_{eff} in aqueous acetone-0.1 and 0.64 M hydrochloric acid solutions can be seen in Figs. 10 and 11, respectively. It is unfavourable for the separation of the component with a small distribution coefficient that the H_{eff} value of most metal ions remained large (more than 5 mm) over such a small range of the distribution coefficient. The peak height for the metal ion decreased rapidly with increase in the distribution coefficient (over 1.5). In the detection of Fe(III), a larger peak height was obtained by the use of an aqueous acetone solution in 0.64 M than in 0.1 M hydrochloric acid.

Use of the macroporous resin MP 50

The macroporous resin MP 50 (40-80 μm) was used for the chromatographic separation of metal ions with aqueous acetone-hydrochloric acid solutions. The effect of the acetone concentration on the distribution coefficients in 0.1 and 0.64 M hydrochloric acid media can be seen in Figs. 12 and 13, respectively. The distribution coefficient decreased with increase in the acetone concentration. Favourable separation factors (greater than 3) were obtained by choosing the appropriate acetone concentration. As it was difficult to separate Fe(III) and Ga(III) from each other, they could only be eluted together. Aqueous acetone-0.64 M hydrochloric acid solution was a better eluent than aqueous acetone-0.1 M hydrochloric acid solution for these metal ions because less tailing occurred.

The effects of the distribution coefficient on H_{eff} in 0.1 and 0.64 M hydrochloric

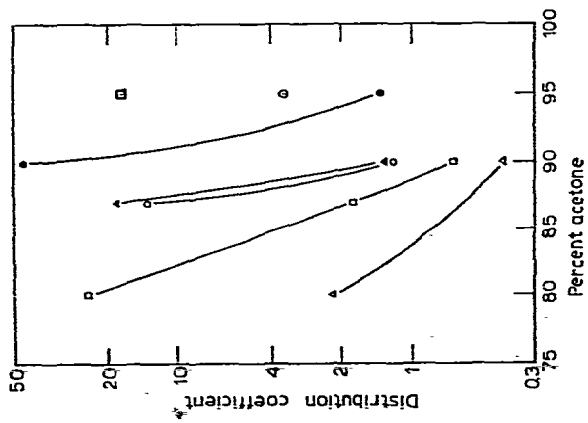


Fig. 12. Distribution coefficient as a function of acetone concentration in aqueous acetone-0.1 *M* hydrochloric acid solution on MP 50 (40-80 μm). Column, 180 \times 5 mm I.D.; flow-rate, 20 cm/min.

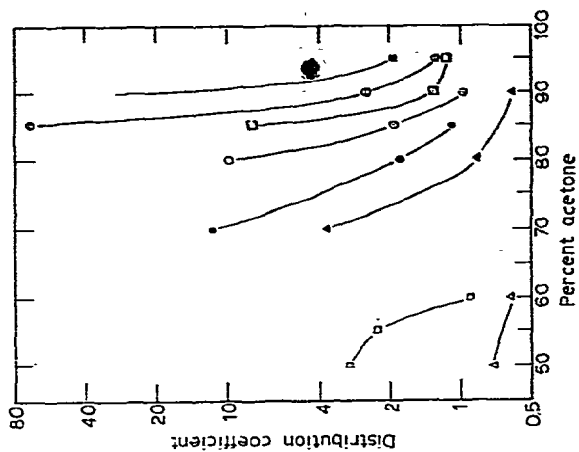


Fig. 13. Distribution coefficient as a function of acetone concentration in aqueous acetone-0.64 *M* hydrochloric acid solution on MP 50 (40-80 μm). Column, 180 \times 5 mm I.D.; flow-rate, 20 cm/min.

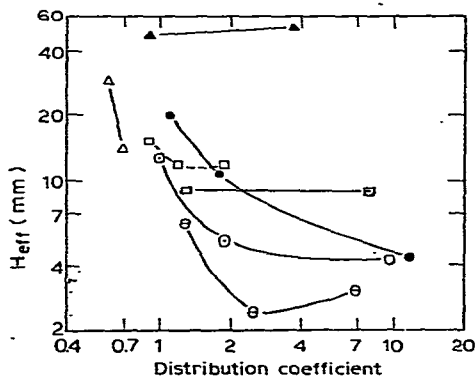
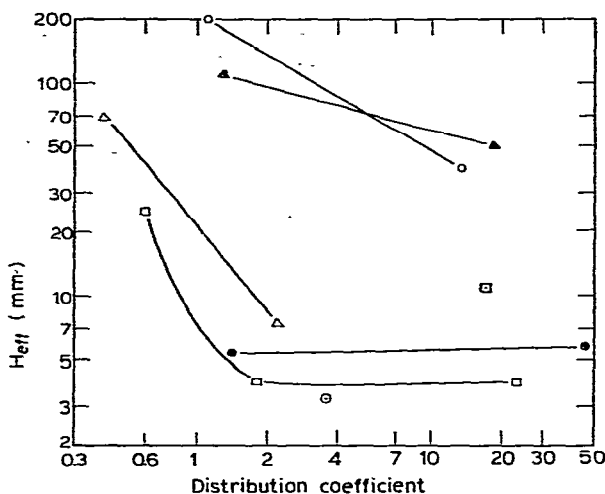


Fig. 14. H_{eff} as a function of distribution coefficient in aqueous acetone-0.1 M hydrochloric acid solution on MP 50 (40-80 μm). Column, 180 \times 5 mm I.D.; flow-rate, 20 cm/min.

Fig. 15. H_{eff} as a function of distribution coefficient in aqueous acetone-0.64 M hydrochloric acid solution on MP 50 (40-80 μm). Column, 180 \times 5 mm I.D.; flow-rate, 20 cm/min.

acid-aqueous acetone eluents are shown in Figs. 14 and 15, respectively. For most metal ions, H_{eff} increased slightly with increase in the distribution coefficient at values greater than 3. Sharp peaks (small peak width and large peak height) were obtained when the metal ion was eluted with a small volume of the eluent (*i.e.*, with distribution coefficients less than 2). Hence stepwise elution chromatography is recommended for the separation of metal ions from each other in a short time with a high detection sensitivity.

An example of the chromatographic separation of Cd(II) and Zn(II) can be

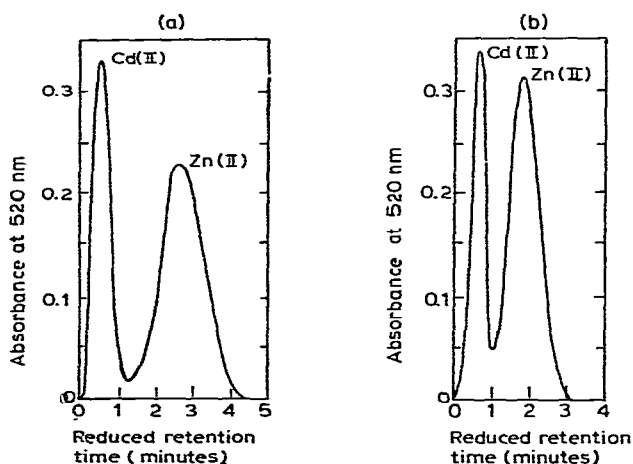


Fig. 16. Separation of Cd(II) and Zn(II) on MP 50 (40-80 μm). Column, 250 \times 5 mm I.D.; Eluent: (a) 55% acetone-0.64 M hydrochloric acid; (b) 59% acetone-0.64 M hydrochloric acid. Flow-rate, 21 cm/min; amount of metal, $8 \cdot 10^{-8}$ mole; sample volume, 0.2 ml; column inlet pressure, 5 atm.

seen in Fig. 16. This chromatogram can be compared with that in Fig. 19, which shows the chromatographic separation on a column of the macroreticular resin Amberlite 200 (60–80 μm) under similar conditions (flow-rate, sample size, column dimensions and eluting agent). In the elution of Zn(II), a larger number of effective theoretical plates per second (0.2) was obtained by the use of Amberlite 200 (60–80 μm) than that (0.1) obtained by the use of MP 50 (40–80 μm). A large H_{eff} value (90–100 mm) was obtained in the separation of Cd(II). Such a large value may be common for a metal ion that is hardly adsorbed by the column under certain conditions of sample injection (distribution coefficient less than 0.5).

Use of the macroreticular resin Amberlite 200

The macroreticular resin Amberlite 200 was used for the chromatographic

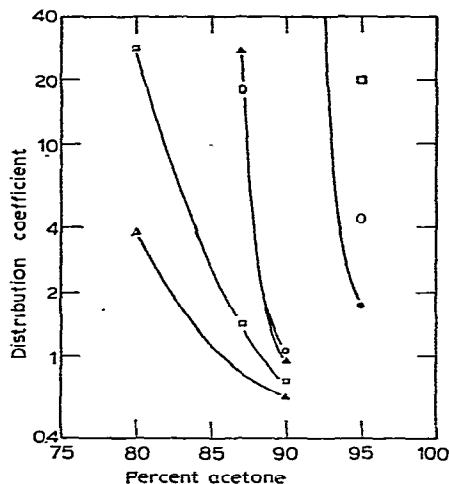


Fig. 17. Distribution coefficients as a function of acetone concentration in 0.1 M hydrochloric acid solution on Amberlite 200. Flow-rate, 22 cm/min; temperature, 25°.

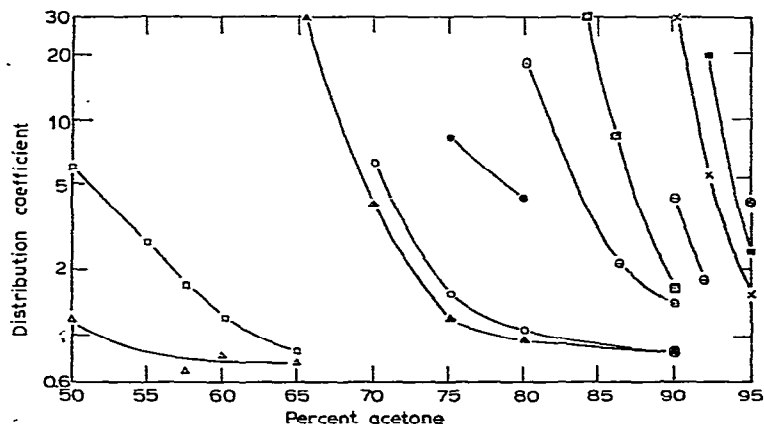


Fig. 18. Distribution coefficients as a function of acetone concentration in 0.64 M hydrochloric acid solution on Amberlite 200. The distribution coefficient of V(IV) was greater than 30 in 92–95% acetone–0.64 M hydrochloric acid solution. \otimes , V(V) (0.1% hydrogen peroxide added); temperature, 40°.

separation of metal ions with aqueous acetone-hydrochloric acid solutions. The distribution coefficients were obtained by the calculation from retention volumes measured by the column method. The effect of the acetone concentration in 0.1 and 0.64 *M* hydrochloric acid solutions on the distribution coefficients can be seen in Figs. 17 and 18, respectively. The distribution coefficients of most metal ions decreased rapidly with increase in the acetone concentration. However, the distribution coefficients of V(IV) and Ni(II) remained high (greater than 30) even at high acetone concentrations. The eluent 0.1% hydrogen peroxide-95% acetone-0.64 *M* hydrochloric acid was used for the rapid elution of V(V) (the distribution coefficient was 4). V(IV) adsorbed on the column was also eluted with this solution but tailing occurred because of the slow oxidation reaction that occurred during the elution. The rapid separation of V(IV) and Ni(II) with aqueous acetone-dimethylformamide-hydrochloric acid solution has been reported previously¹⁷.

Favourable separation factors were obtained by choosing suitable concentrations of acetone for the separation of many metal ions from each other, except Fe(III) and Ga(III), which were eluted together. Less tailing and much larger peak heights were obtained by the use of the aqueous acetone-0.64 *M* hydrochloric acid than by the use of aqueous acetone-0.1 *M* hydrochloric acid as the eluent.

The effect of the particle size of the resin on the column efficiency was examined. Fig. 19 shows a comparison of separations performed on columns of resin of particle size 60-80 and 25-30 μm under the same conditions (flow-rate, sample size, column dimensions and eluent). The finer resin provided the better resolving power and larger peak heights, as expected. The effect of the particle size on the column inlet pressure, H_{eff} and the number of effective plates per second for the elution of Zn(II) can be seen in Table I.

From the distribution coefficients and the actual separations, the following stepwise elution scheme was applied to the chromatography of metal ions. A 60-ml volume of the aqueous sample solution in 0.06 *M* hydrochloric acid was passed through the column, and the metal ions in the sample were adsorbed on the column.

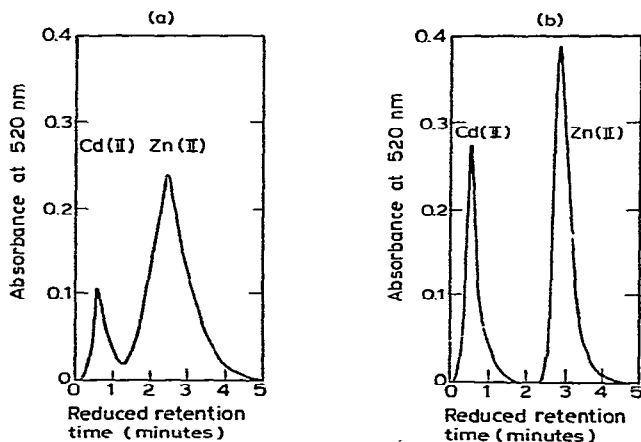


Fig. 19. Separation of Cd(II) and Zn(II) on columns of Amberlite 200 of particle size (a) 50-80 μm and (b) 25-30 μm . Column, 230 \times 5 mm I.D.; eluent, 58% acetone-0.64 *M* hydrochloric acid; flow-rate, 22 cm/min; temperature, 25°; amount of metal, $8 \cdot 10^{-8}$ mole; sample volume, 0.2 ml.

TABLE I

EFFECT OF RESIN PARTICLE SIZE ON THE SEPARATION OF Zn(II)

Operating conditions as in Fig. 19.

Diameter of particle (μm)	Column inlet pressure (atm)	H_{eff}^* (mm)	N_{eff}^{**}/t (sec^{-1})
60-80	4	8.0	0.2
25-30	22	1.3	0.9

* H_{eff} = height equivalent to an effective theoretical plate.** N_{eff} = number of effective theoretical plates.

Then successive elution conditions were chosen such that each eluting agent eluted one or two metal ion(s) stepwise, as shown in Figs. 20, 21 and 22. In the separation of Cd(II), Zn(II), Fe(III), Ga(III), Pb(II), Cu(II), U(VI), Co(II), Fe(II) and Mn(II), the percentage of acetone in the eluent was changed while the concentration of hydrochloric acid was kept constant at 0.64 M. Although Cd(II) was separated from Zn(II) with 50-55% acetone-0.64 M hydrochloric acid, the Cd(II) peak was overlapped by the blank noise and therefore 40% acetone was used in order to delay the elution of Cd(II). V(IV) and Ni(II) were eluted together with aqueous 93% dimethylformamide-1.07 M hydrochloric acid solution. The separation of these metal ions from each other was achieved by using aqueous acetone-dimethylformamide-hydrochloric acid, as reported previously¹⁷.

The stepwise elution chromatography of eight metal ions can be seen in Fig. 20. Several separations were not possible with this scheme: the pairs Fe(III)-Ga(III), Cu(II)-U(VI), Fe(II)-Mn(II) and V(IV)-Ni(II) were separated only as groups.

Eleven metal ions were separated from each other by stepwise elution chromatography as shown in Fig. 21. The elution scheme was as follows: Cd(II) was eluted with 40% acetone, Zn(II) with 60% acetone, Fe(III)-Ga(III) and Pb(II) with

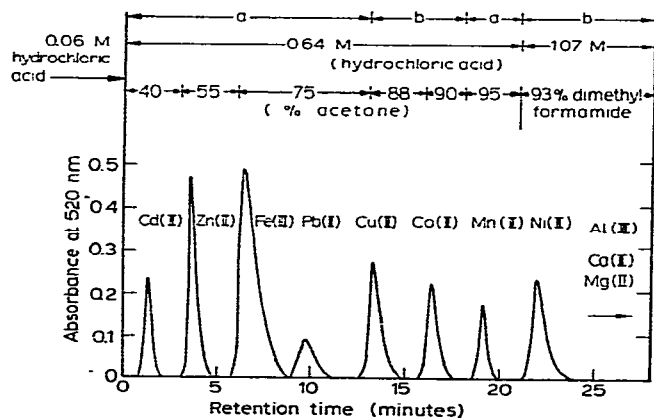


Fig. 20. Separation of metal ions on Amberlite 200 (25-30 μm). Column, 120 \times 5 mm I.D.; flow-rate, 22 cm/min; temperature, 40°; column inlet pressure, 16-25 atm; colour-forming reagent solution, 0.02% PAR in ammonia, concentration (a) 0.7 M and (b) 1.2 M. Amount of metal (mole): Ca(II), $5 \cdot 10^{-5}$; Mg(II), $2.5 \cdot 10^{-5}$; Fe(III), $5 \cdot 10^{-6}$; others, $5 \cdot 10^{-8}$. Sample volume, 60 ml.

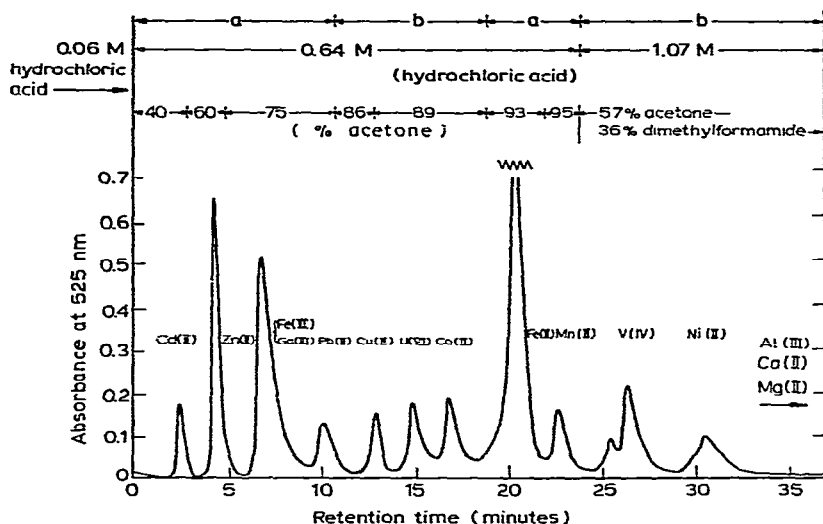


Fig. 21. Separation of metal ions on Amberlite 200 (25–30 μm). Column operating conditions as in Fig. 20. Amount of metal ($\times 10^{-8}$ mole): Cd(II), 2.4; Zn(II), 1.2; Fe(III), 6.0; Ga(III), 1.1; Pb(II), 3.0; Cu(II), 1.2; U(VI), 6.0; Co(II), 1.8; Fe(II), 32; Mn(II), 3.0; V(IV), 14; Ni(II), 3.0; Al(III), 2.4; Ca(II), 300; Mg(II), 150. Sample volume, 60 ml.

75% acetone, Cu(II) with 86% acetone, U(VI) and Co(II) with 89% acetone, Fe(II) with 93% acetone and Mn(II) with 95% acetone in 0.64 M hydrochloric acid. V(IV) and Ni(II) were separated with 36% dimethylformamide–57% acetone–1.07 M hydrochloric acid solution, while Al(III), Ca(II) and Mg(II) remained on the column. These

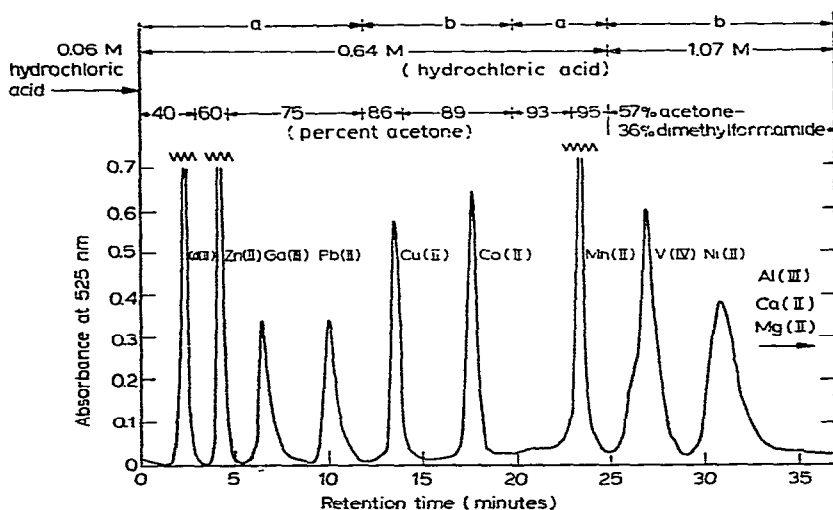


Fig. 22. Separation of metal ions on Amberlite 200 (25–30 μm). Column operating conditions as in Fig. 20. Amount of metal ($\times 10^{-8}$ mole): Cd(II), 9.6; Zn(II), 4.8; Ga(III), 4.5; Pb(II), 12; Cu(II), 4.8; Co(II), 7.2; Mn(II), 12; V(IV), 57; Ni(II), 12; Al(III), 9.6; Ca(II), $1.2 \cdot 10^3$; Mg(II), $6 \cdot 10^2$. Sample volume, 60 ml.

metal ions were eluted with aqueous 3 *M* hydrochloric acid solution so that the column resin was regenerated for the next operation.

Fig. 22 shows the chromatographic separation of nine metal ions [Cd(II), Zn(II), Ga(III), Pb(II), Cu(II), Co(II), Mn(II), V(IV) and Ni(II)] under the same elution conditions as in Fig. 21. Comparison of these chromatograms shows that the good resolving power of the column was maintained even if the sample contained a high ratio of one constituent to another, provided that the column was not overloaded. The retention volume of each metal ion was reproducible with respect to the types of eluents, their order of application to the column, the flow-rate of the eluent and the column temperature.

The proposed chromatographic separation method can be applied to the automated determination of trace amounts of diverse metal ions, even in large volumes of a sample at very dilute concentrations. However, the ion-exchange behaviour and the incidental detection of metal ions not mentioned above must be examined further in order to use the proposed method effectively as a systematic scheme for the analysis of samples that contain metallic elements of different types.

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