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CHROMATOGRAPHIC SEPARATION OF METAL IONS ON A MACRORETICULAR CATION-EXCHANGE RESIN WITH HYDROCHLORIC ACID IN MIXED SOLVENTS

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SUMMARY

Forced-flow chromatography on a cation-exchange resin has been used to obtain separations of metal ions, such as Cu(II), Co(II), Mn(II), V(IV) and Ni(II). The macroreticular resin used provides rapid separations in hydrochloric acid containing organic solvents (tetrahydrofuran, 2-propanol–tetrahydrofuran, dimethyl sulphoxide, dimethylformamide or acetone–dimethylformamide).

INTRODUCTION

Macroreticular cation-exchange resins have been shown to provide rapid separations of metal ions in forced-flow chromatography with solutions of acetone[1,2], 2-propanol[3] and acetonitrile[4] in dilute hydrochloric acid as eluents. This work also demonstrated the advantages in some instances of separations using the macroreticular cation-exchange resins Amberlyst 15 and Amberlite 200 with non-aqueous or partially non-aqueous solutions containing hydrochloric acid.

Few studies have been carried out on the cation-exchange separation of Ni(II) from other elements, such as Cu(II), Co(II), Mn(II), V(IV), Al(III), Ca(II) and Mg(II). This paper describes separations with hydrochloric acid containing organic solvents (tetrahydrofuran, 2-propanol–tetrahydrofuran, dimethyl sulphoxide, dimethylformamide or acetone–dimethylformamide), and the elution conditions for the separation of Ni(II) and other metal ions are discussed.

The chromatographic separation of Ni(II) and other metal ions with hydrochloric acid in 2-propanol has been reported in a previous paper[3]. In the present work, a solution of 2-propanol plus tetranydrofuran in hydrochloric acid was used to separate Ni(II) from other metal ions.

Janauer *et al.*[5] reported cation-exchange distribution coefficients of metal ions including Co(II), Ni(II) and Al(III) in an aqueous dimethyl sulphoxide solution of hydrochloric acid. Birze *et al.*[6] studied the cation-exchange behaviour of Bi(III), Cd(II), Zn(II), Sn(IV), Pb(II) and Cu(II) in an aqueous dimethyl sulphoxide solution of hydrochloric acid and confirmed the separations of some of these metal ions experimentally. The chromatographic separation of Cu(II), Co(II), Mn(II) and Ni(II)

was examined by using 90% dimethyl sulphoxide–hydrochloric acid as eluent in the present work.

Cummings and Korkisch[7] reported cation-exchange distribution coefficients of metal ions including Cu(II), Mn(II), Ni(II), Zr(IV), Ca(II), Mg(II) and Al(III) in 0.6 M hydrochloric acid–90% dimethylformamide solution. However, the practical scheme for the chromatographic separation of these metal ions was not given. This paper describes the complete separation of Cu(II), Co(II), Mn(II) and Ni(II) on a column using selective aqueous dimethylformamide–hydrochloric acid solutions. Ni(II) was accompanied by V(IV) in the separations effected with these eluents, and the rapid separation of these metal ions was performed with mixtures of acetone and dimethylformamide in dilute hydrochloric acid.

It has been demonstrated[1,2,4] that the on-stream addition of a colour-forming reagent provides continuous detection and quantitation of the eluted metal ions. The same method was applied to the chromatography of V(IV) and Ni(II), which were eluted with solutions of dimethylformamide or acetone–dimethylformamide in dilute hydrochloric acid 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. These pumps can deliver mobile phase at an outlet pressure below 30 kg/cm². A reciprocating mini-pump of the single-piston type (Milton-Roy, St. Petersburg, Fla., U.S.A.) was used at pressures up to 45 kg/cm² for dynamic packing of the chromatographic column.

A sample injection valve was obtained from JEOL and fitted with calibrated sample loops made of 1-mm I.D. PTFE tubing. The volumes (1.0 and 0.2 ml) of the loops were calibrated according to the procedure described previously[2].

A chromatographic glass tube (8 mm I.D.) was equipped with a movable outlet plunger for decreasing the bed height of the resin. A glass chromatographic tube (5 mm I.D.) packed with Amberlite 200 resin (24–30 μm in diameter) was equipped with fixed outlet plungers.

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 long PTFE tube was used between the mixing chamber and the flow-through cell.

A Hitachi Model 207 atomic-absorption spectrophotometer was used for the determination of metals in the eluted fractions. An acethylene–air flame was used for the atomization of metal ions. A Shimazu Model MAF flame spectrophotometer fitted with a pre-mix atomizer (Hitachi Model 207-0070) was used for the determination of aluminium in the eluted fractions. The emission of aluminium in an acetylene–oxygen flame was measured at a wavelength of 396.15 nm.

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 to accomodate 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 μl. Materials that came into contact with the solution were made of quartz and stainless steel.

Reagents

Resins. The macroreticular strongly acidic cation-exchange resins Amberlyst 15 and Amberlite 200 were received as beads in the sodium form from Rohm and Haas (Philadelphia, Pa., U.S.A.). Amberlyst 15 was ground in a mill and sieved so as to obtain the 100–200-mesh fraction. The following method of continuous elutriation was used in order to separate the particles of Amberlite 200 resin into the fraction of 24–30 μm in diameter. A large amount of the resin beads was fragmented in a ball mill, the pulverized resin was suspended in water and colloidal material was removed according to the procedure reported by Hamilton[8]. The apparatus used for the elutriation with water was similar to that reported by Scott[9]. A 20-l container equipped with a device for overflowing provided a continuous supply of tap water at a constant flow-rate adjusted by means of an adequate virtual head at ambient temperature.

Each fraction of the graded resin was suspended in acetone and the extreme fines were removed by repeated decantation. These fractions were slurried in acetone, packed in a column and washed with dimethylformamide, 2-propanol, acetone, 3 M hydrochloric acid and deionized water. A portion of the purified resin was washed with acetone and dried. The capacity of the air-dried resin was 4.2 mequiv./g.

A stock solution and synthetic sample of metal ions were prepared according to the procedure described previously[1]. A stock solution of V(IV) was prepared by dissolving vanadyl sulphate hydrate (VOSO$_4 \cdot$2H$_2$O) in 0.5 M sulphuric acid.

Eluents. The eluents were aqueous solutions of hydrochloric acid in organic solvents. Each eluent was prepared so that the concentrations of solvents and hydrochloric acid were expressed as a percentage by volume and as a molarity, respectively. 2-Propanol containing a high concentration of hydrogen chloride was prepared by bubbling the hydrogen chloride gas into 2-propanol which was kept cool in order to increase the solubility of the hydrogen chloride.

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

Procedure

The distribution coefficients were determined by the previously reported batch equilibrium method[2] and by column chromatography.

Some distribution coefficients were obtained by calculation from the retention volumes measured by the column method. A chromatographic tube was filled with a thick slurry of Amberlyst 15 resin (100–200 mesh) in acetone. The slurried resin was aspirated with a syringe mounted at the bottom of the tube so that all of the resin settled rapidly. When a chromatographic tube was packed with Amberlite 200 (24–30 μm), dynamic packing via slurry displacement was accomplished by connecting a chamber to the chromatographic tube, filling the chamber with a thick slurry of the resin in acetone and then displacing the slurry into the tube with acetone that was pumped into the slurry chamber at a flow-rate of approximately 9 ml/min. 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 Ni(II) and V(IV). The colour-forming reagent (PAR) reacted with Ni(II) and V(IV) ions in an ammonium chloride solution of aqueous dimethylformamide or dimethylformamide–acetone to produce the chelate complexes which had their absorption maxima at wavelengths of 500 and 550 nm, respectively. The flow-rate 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 8–10.

RESULTS AND DISCUSSION

Separations in hydrochloric acid media containing tetrahydrofuran and 2-propanol–tetrahydrofuran

Solutions of 90% tetrahydrofuran in hydrochloric acid of concentration ranging from 0.3 to 1.0 M were used in order to examine the chromatography of metal ions on the Amberlyst 15 column. As the separation of Cd(II), Zn(II), Fe(III), Pb(II) and Cu(II) with these eluents was difficult, these metal ions were eluted as a group with 90% tetrahydrofuran–0.5 M hydrochloric acid. The eluent was then changed to 90% tetrahydrofuran–1.0 M hydrochloric acid in order to elute Co(II) and Mn(II), while Ni(II), Al(III), Ca(II) and Mg(II) were strongly retained by the column. The result of the chromatographic separation is shown in Fig. 1 (1).

Solutions of 75% tetrahydrofuran–25% 2-propanol in hydrochloric acid of concentration ranging from 0.5 to 1.5 M were used to examine the distribution behaviour of many elements by the batch equilibrium method. The distribution coefficients of Cd(II), Zn(II), Fe(III), Pb(II) and Cu(II) were less than unity and those of Ca(II), Mg(II) and Al(III) were more than 50. The effect of the hydrochloric acid
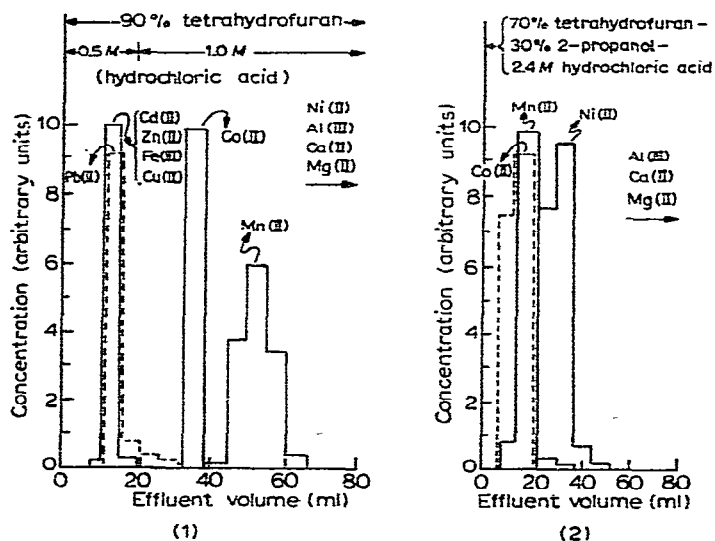

Fig. 1. Elution histograms for metal ions. Column, 200 × 8 mm I.D.; resin, Amberlyst 15 (100–200 mesh); temperature, 40°. Sample: Ca(II), 10 mg/ml; Mg(II), 5 mg/ml; other metals, 0.1 mg/ml. Flow-rate: (1) 1.2 ml/min; (2) 0.9 ml/min.

concentration on the distribution coefficients of Co(II), Mn(II) and Ni(II) is shown in Fig. 2. The distribution coefficients of these metal ions decreased with increase in the hydrochloric acid concentration. The distribution coefficient of Ni(II), even in 1.5 M hydrochloric acid containing 75% tetrahydrofufan–25% 2-propanol was not so small as Ni(II) would be eluted with a small volume of the eluent. The rapid separation of Ni(II) from Co(II) and Mn(II) was performed by using a solution of 70% tetrahydrofuran–30% 2-propanol in 2.4 M hydrochloric acid as the eluent on the Amberlyst 15 column, while Al(III), Ca(II) and Mg(II) were strongly retained by the column. The result of the chromatographic separation is shown in Fig. 1 (2).
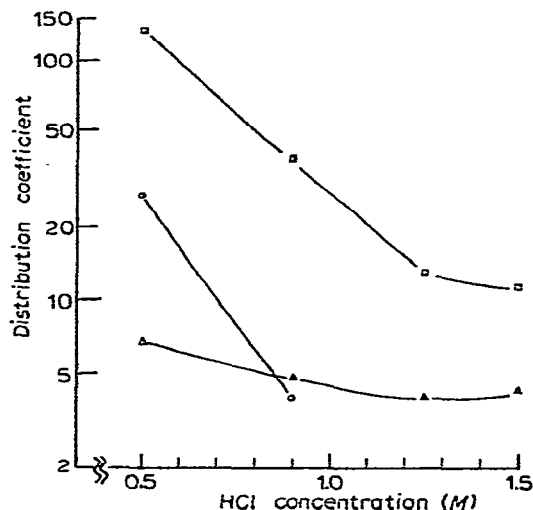

Fig. 2. Distribution coefficients as a function of hydrochloric acid concentration in 75% tetrahydro-furan–25% 2-propanol. Resin, Amberlyst 15 (100–200 mesh); temperature, ambient. △, Co(II); ○, Mn(II); □, Ni(II).

Separation in hydrochloric acid–dimethyl sulphoxide media

Solutions of 90% dimethyl sulphoxide in hydrochloric acid were used as eluents in order to examine the chromatographic separations of Cu(II), Co(II) and Mn(II) on the Amberlyst 15 column. As it was difficult to separate Cu(II) and Co(II) from each other with 90% dimethyl sulphoxide solutions in hydrochloric acid of various concentrations, 90% dimethyl sulphoxide–0.5 M hydrochloric acid was first used to elute these metal ions as a group and then the eluent was changed to 90% dimethyl sulphoxide–1.2 M hydrochloric acid in order to separate Mn(II) from Ni(II), Al(III), Ca(II) and Mg(II), which were strongly retained by the column. The result of the chromatographic separation is shown in Fig. 3.

Separations in hydrochloric acid media containing dimethylformamide and dimethyl-formamide–acetone

Chromatographic separations of metal ions with 90% dimethylformamide–hydrochloric acid solutions on the Amberlyst 15 column were studied. As it was difficult to separate Hg(II), Cd(II), Zn(II), Fe(III) and Pb(II) with 90% dimethyl-
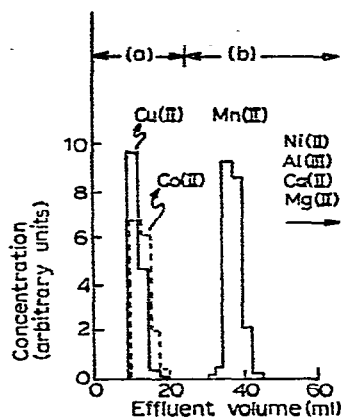
Fig. 3. Elution histogram for metal ions. Column, 200 × 8 mm I.D.; resin, Amberlyst 15 (100–200 mesh); temperature, 40°. Concentration of hydrochloric acid in 90% dimethyl sulphoxide eluent: (a) 0.5 M; (b) 1.2 M. Flow-rate: 1.0 ml/min. Sample: Ca(II), 10 mg/ml; Mg(II), 5 mg/ml; other metals, 0.1 mg/ml.

formamide–hydrochloric acid media covering the acid concentration range 0.05–1.0 M, these metal ions were separated with 90% 2-propanol solutions in 0.24–0.98 M hydrochloric acid as eluents according to the conditions reported previously[3]. Then the eluent was changed to the following eluents at a flow-rate of 1.4 ml/min in order to separate Cu(II), Co(II), Mn(II) and Ni(II), as shown in Fig. 4: Cu(II) was eluted with 0.17 M hydrochloric acid, Co(II) with 0.51 M hydrochloric acid, Mn(II) with 0.70 M hydrochloric acid and Ni(II) with 1.0 M hydrochloric acid in 90% dimethyl-formamide as eluent, respectively. Al(III), Ca(II) and Mg(II) were eluted as a group
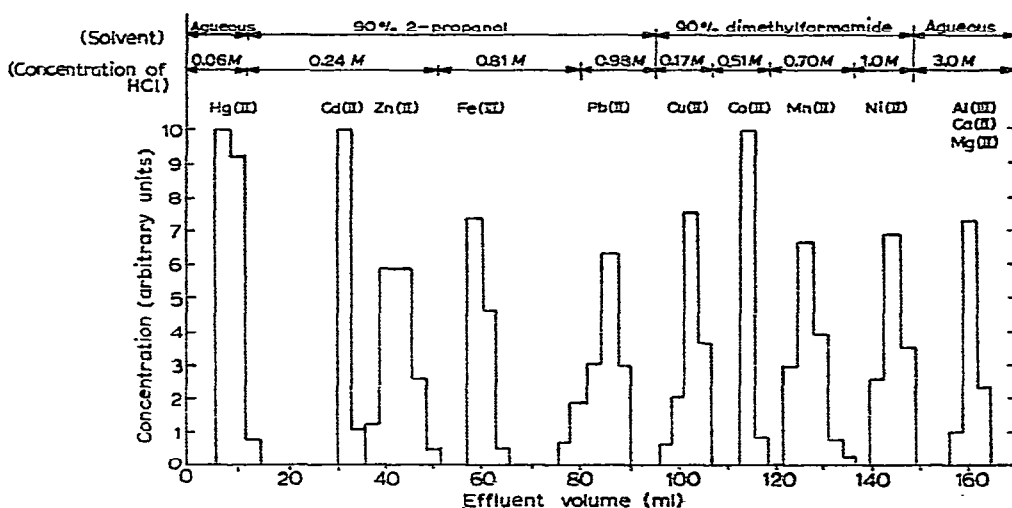

Fig. 4. Elution histogram for metal ions. Column, 200 × 8 mm I.D.; resin, Amberlyst 15 (100–200 mesh); temperature, 40°. Flow-rate: 1.4 ml/min. Sample: Ca(II), 10 mg/ml; Mg(II), 5 mg/ml; other metals, 0.1 mg/ml.

with aqueous 3 *M* hydrochloric acid. The amount of each metal in the sample (1.0 ml) was as follows: Ca(II), 10 mg; Mg(II), 5 mg; other metals, 0.1 mg. An increase in the flow-rate of the eluents to 1.8 ml/min resulted in slight broadening of the each peak and partial overlapping of the Co(II) peak with the neighbouring Cu(II) and Mn(II) peaks.

Ni(II) was eluted with 90% dimethylformamide–1.3 *M* hydrochloric acid solution as well as with 90% dimethylformamide–1.0 *M* hydrochloric acid solution. More rapid elution was achieved by using 93% dimethylformamide–1.07 *M* hydrochloric acid or 94% dimethylformamide–0.84 *M* hydrochloric acid as the eluent. In addition, the use of resin beads of finer mesh resulted in a reduction in the analysis time and an increase in the peak height. The method of flow spectrophotometric detection was applied to the rapid separation on the column packed with Amberlite 200 (24–30 μm). Ni(II) was always accompanied by V(IV) in the chromatography in aqueous dimethylformamide–hydrochloric acid media mentioned above. Fig. 5 shows an example of the elution of V(IV) and Ni(II), which were eluted almost simultaneously with 93% dimethylformamide–1.07 *M* hydrochloric acid at a flow-rate of 1.8 ml/min in 8 min. The cation-exchange behaviour of these metal ions in 93% organic (acetone and dimethylformamide)–7% aqueous solutions containing 1.07 *M* hydrochloric acid was investigated in order to find the optimal conditions for the separation of these metal ions. The distribution coefficients were obtained by calculation from the retention volumes measured by the column method. Fig. 6 shows the effect of the concentration of the organic solvents on the distribution coefficients, which decreased with increase in the dimethylformamide concentration (*i.e.*, decrease in the acetone concentration). The favourable separation factor (above 2) was obtained by using 1.07 *M* hydrochloric acid solution at a dimethylformamide
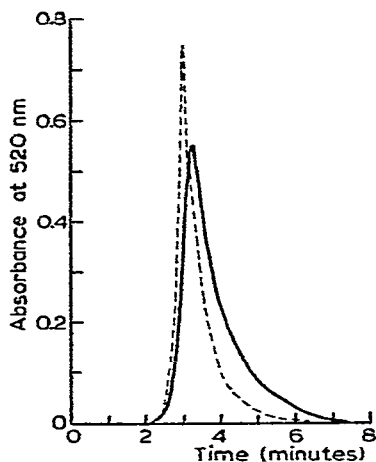

Fig. 5. Elution curves for V(IV) and Ni(II). Column. 120 × 5 mm I.D.; resin, Amberlite 200 (24–30 μm); eluent, 93% dimethylformamide–1.07 *M* hydrochloric acid; flow-rate, 1.8 ml/min; column inlet pressure, 16 kg/cm²; temperature, 40°. Sample: V(IV) 20 μg and Ni(II) 9.4 μg in 0.2 ml. Solid line, Ni(II); broken line, V(IV).
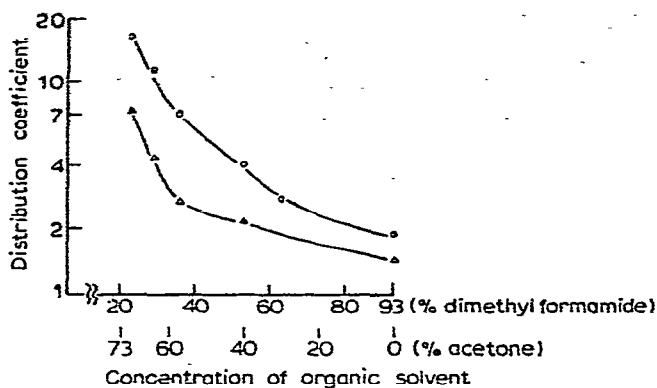
Fig. 6. Distribution coefficients as a function of the concentration of organic solvents in 1.07 M hydrochloric acid solution. Column, 120 × 5 mm I.D.; resin, Amberlite 200 (24–30 μm); column temperature, 40°; flow-rate, 1.8 ml/min. O, Ni(II); △, V(IV).

concentration of less than 50% (*i.e.*, at an acetone concentration of more than 43%). The eluent 29% dimethylformamide–64% acetone in 1.07 M hydrochloric acid separated V(IV) and Ni(II) completely in 12 min with a resolution of 1.7. However, the eluent 36% dimethylformamide–57% acetone in 1.07 M hydrochloric acid was more useful for the rapid separation, which was achieved in 10 min with a resolution of 1.3, as shown in Fig. 7.
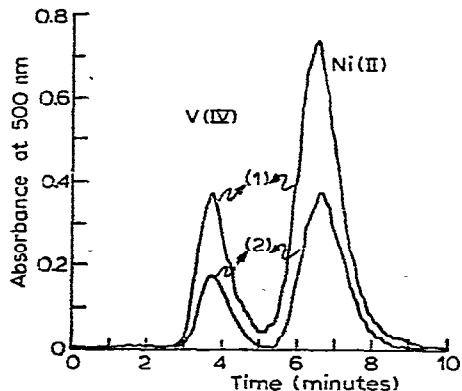

Fig. 7. Elution curve for V(IV) and Ni(II). Column, 120 × 5 mm I.D.; resin, Amberlite 200 (24–30 μm); eluent, 57% acetone–36% dimethylformamide–1.07 M hydrochloric acid; flow-rate, 1.8 ml/min; column inlet pressure, 14 kg/cm²; temperature, 40°. Sample: (1) V(IV) 20 μg and Ni(II) 9.4 μg in 0.2 ml; (2) V(IV) 10 μg and Ni(II) 4.7 μg in 0.2 ml.

V(IV) and Ni(II) adsorbed by the column resin were rapidly separated by stepwise elution chromatography using mixed solvents–hydrochloric acid solutions as eluents. Before the elution, the Amberlite 200 resin of the column was equilibrated with 0.06 M hydrochloric acid solution while the metal ions were taken up by the resin. The eluent was changed to 64% acetone–29% dimethylformamide–1.07 M hydrochloric acid (eluent A) and then 93% dimethylformamide–1.07 M hydrochloric
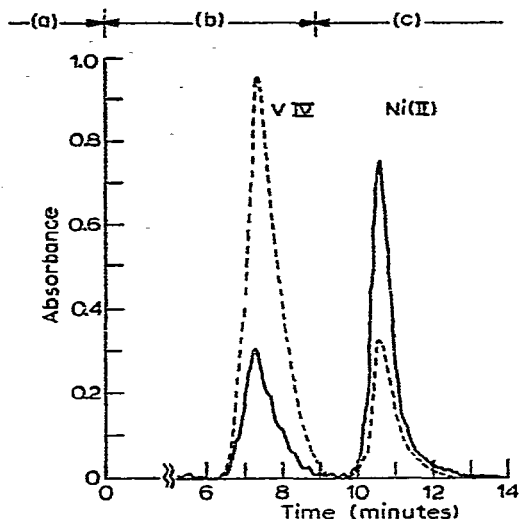
Fig. 8. Stepwise elution of V(IV) and Ni(II). Column, 120 × 5 mm I.D.; resin, Amberlite 200 (24–30 μm). Eluent: (a) 0.06 M hydrochloric acid; (b) 64% acetone–29% dimethylformamide–1 07 M hydrochloric acid; (c) 93% dimethylformamide–1.07 M hydrochloric acid. Flow-rate, 1.8 ml/min; column inlet pressure, 12–16 kg/cm^2; temperature, 40°. Sample: V(IV) 20 μg and Ni(II) 9.4 μg in 0.2 ml. Wavelength: solid line, 500 nm; broken line, 550 nm.

acid (eluent B) for the elution of V(IV) and Ni(II), respectively. The result of the chromatographic separation is shown in Fig. 8, where the concentrations of V(IV) and Ni(II) in the eluate are shown at absorbances at 550 and 500 nm, respectively, for the sensitive detection of these metal ions. Although eluent A can be used for the elution of Ni(II), eluent B was specially chosen in order to increase the peak height and reduce the analysis time of Ni(II).

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