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RAPID AND CONTINUOUS DETERMINATION OF METAL IONS BY CATION-EXCHANGE CHROMATOGRAPHY

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SUMMARY

Metal ions can be rapidly separated from each other using forced-flow cation-exchange chromatography with solutions of hydrochloric acid in 2-propanol–water or acetone–water as the eluent. The eluted peaks are detected and recorded after adding a color-forming reagent and mixing it with the effluent stream. A mixture containing seven different metal ions was separated in approximately 25 min.

INTRODUCTION

Virtually all chemical and electrochemical methods for determining small amounts of a metal ion are at times subject to interferences that necessitate a chemical separation. Ion-exchange methods for separating metal ions from one another are quantitative and selective, but most of the published methods are slow and often require 15 min or more to elute each element from the column. This paper describes a method that combines separation and spectrophotometric detection using a liquid chromatograph. Application to the rapid continuous determination of transition metal ions is described.

Many transition metal ions have been separated from one another with acetone–hydrochloric acid by stepwise elution from a cation-exchange column[1,2]. The eluted metal ions exhibited some tailing which could be eliminated by decreasing the flow-rate of the eluent. New macroreticular ion-exchange resins are available which provide rapid exchange rates in organic solvents[3,4]. In addition, rapid separations may be obtained with fine mesh beads of resin with a narrow range of particle sizes. Macroreticular cation-exchange resins, Amberlite-200 and Amberlyst 15 (250–325 mesh) are used in the present studies. Excellent separations of two-component mixtures are obtained very quickly using a forced-flow chromatograph. The eluted metal ions are detected automatically after formation of a colored complex with a chromogenic

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reagent which is mixed with the column stream. Measurement of peak height is used to quantitate the separation.

EXPERIMENTAL

Instruments

A schematic diagram of the liquid chromatograph is shown in Fig. 1.

The Cheminert metering pump of Chromatronix Inc. (CMP-2) was used for forcing the eluent through an analytical column at a flow-rate of 0.4, 1.0 or 2.0 ml/min. The flow-rate of 2.0 ml/min was used in most of the separation studies.

A SV-8031 sample-injection valve was obtained from Chromatronix, Inc. The sample loops of small size (38.0 and 56.3 μl) were made and calibrated using a standard curve plot of absorbance *vs.* microliter pipet volume of an indicator diluted to 50 ml.

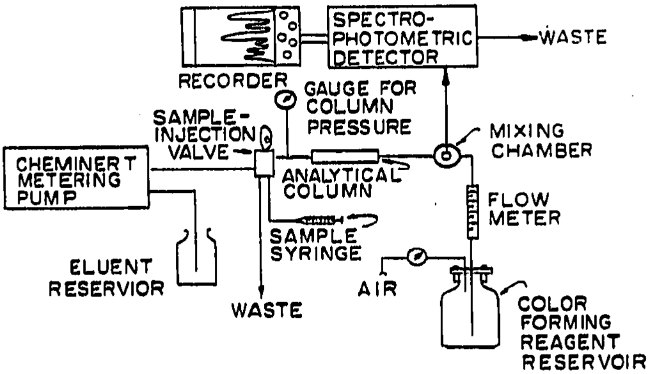


Fig. 1. Schematic diagram of liquid chromatograph.

The volume of a large sample loop (5 ml) was calibrated by collecting the effluent solution from a loop filled with primary hydrochloric acid solution and titrating it with standard sodium hydroxide solution.

The 0.031-in. I.D. Teflon tube of Chromatronix Inc. was used for the pipe line of the chromatograph. To ensure the reaction of color-forming reagent with a metal ion, a 200-cm long tube was used between the mixing chamber and flow-through cell.

A Chromatronix Model LC-6M-13 analytical column, 6.3 mm I.D., was mounted with two outlet plungers for decreasing bed height. A Robertshaw Acragage was used for monitoring the pressure of the analytical column.

Air pressure (less than 6 p.s.i.) was applied to the reservoir of color-forming reagent solution to flow through the mixing chamber. A Johnson Service Co., R-130 pressure regulator was used for the control of air supply.

A Roger Gilmont Instruments Inc., Catalog No. F-1100, size No. 1, flow-meter was used for monitoring the flow-rate of color-forming reagent solution.

A Beckman Model B spectrophotometer was fitted with a flow-through cell. The light-path is 10 mm. A blue sensitive (400–625 nm) phototube was used.

A. E. H. Sargent and Co. recorder, Catalog No. S-72150 has linear output for the measurement of transmittance.

Reagents

Resin. The macroreticular strong-acid cation-exchange resins, Amberlite 200 and Amberlyst 15 were received as beads from Rohm and Haas Co. Each resin was ground in a Model 4-E Quaker City mill and sieved dry to obtain the 250–325 mesh fraction. This was slurried repeatedly in water, and the extreme fines were decanted. This fraction of resin was packed in a large column 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. This air-dried resin was used for the measurement of the ion-exchange capacity. Each resin has the capacity of 4.2 mequiv./g dried resin.

Stock solution. The reagent grade chloride of metal ion was used and diluted to a final hydrochloric acid concentration of 0.01 *N* aqueous solution.

Sample preparation. Synthetic sample mixtures for the column separation studies were prepared by mixing given volumes of metal ion solution and deionized water.

Eluents. The eluent used for the column separation was the mixture of hydrochloric acid and organic solvent. 2-Propanol and acetone were used as organic solvents The eluent was prepared so that the amount of organic solvent is expressed as per cent by volume and the hydrochloric acid concentration as molarity.

Color forming reagent. A 1-g sample of Eastman No. 7714, 4-(2-pyridylazo)-resorcinol (PAR) was mixed with 50 ml of 6 *N* ammonium hydroxide solution crushing lumps with a stirring rod. This was transferred to a 1-l volume beaker and diluted to volume with deionized water. After agitation for 0.5 h, this solution was filtered on rapid filter-paper. A PAR solution for the continuous determination was prepared by mixing a given volume of this stock solution and ammonium hydroxide aqueous solution of proper concentration.

A 2-g sample of Baker Analyzed Reagent, No. 5891, 1-(2-pyridylazo)-2-naphthol (PAN) was mixed with 400 ml of 2-propanol, crushing lumps with a stirring rod. This solution was agitated for 0.5 h and filtered to eliminate insoluble particles. Then 600 ml of deionized water was added to this solution. A PAN solution for the continuous determination was prepared by mixing a given volume of this stock solution and a mixture of water–2-propanol (3:2) containing ammonia.

Procedure. The 6.3 mm I.D. analytical column was filled with 250–325 mesh cation-exchange resin slurred in water. The slurried resin was sucked by a syringe mounted at the bottom of the column, so that the whole amount of resin was allowed to settle down rapidly. More than 80 ml of each eluent was passed through the column at a flow-rate of 2 ml/min to equilibrate resin with the eluent. The detector was set at the wavelengths shown in Table I. The compositions of the eluent and color-forming reagent are shown in Table I.

RESULTS AND DISCUSSION

Cadmium and zinc

Cadmium(II) and zinc(II) are separated rapidly with 90% 2-propanol containing 0.25–0.35 *M* hydrochloric acid on the column of Amberlyst 15. The effect of the hydrochloric acid concentration upon the distribution coefficient may be seen in Fig. 2. The eluent containing 0.25 *M* hydrochloric acid separates cadmium(II) and

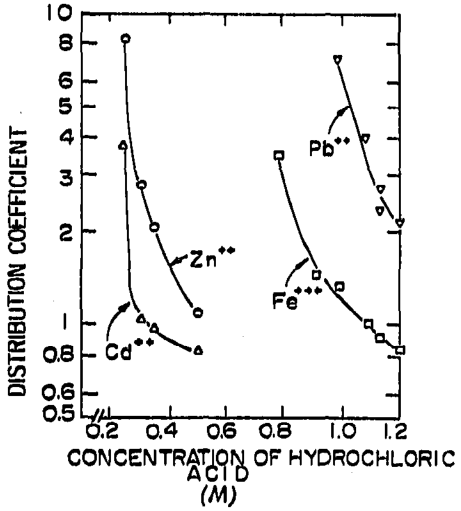
TABLE I

SEPARATION AND DETERMINATION OF METAL IONS

Solvent of color-forming reagent solution: deionized water for PAR; Mixture of water–2-propanol (3:2) Length of column; A-15 (Amberlyst 15), 175 mm; A-200 (Amberlite 200), 166 mm or 138 mm.

Metal ion	*Eluent*		*Color-forming reagent solution*		*Resin*	*Wave-length (nm)*
	Solvent	*Hydrochloric acid (M)*	*Ammonium hydroxide (M)*	*Reagent (%)*		
Cd^{2+}, Zn^{2+}	90% 2-propanol	0.25^{a}, 0.30^{b}	0.5	PAN 0.20	A-15	552
		0.35^{b}, 0.51^{b}	1.0	PAN 0.015		
	57–60% acetone	0.64^{c}	0.64	PAR 0.02	A-200	520
	60–70% acetone		0.6	PAR 0.0125		
Fe^{3+}, Pb^{2+}	90% 2-propanol	0.59–1.14^{c}	0.6	PAR 0.01	A-15	
	80% acetone	0.61–0.71^{c}	0.6	PAR 0.0125	A-15, A-200	525
Cu^{2+}, Co^{2+}	90–91% acetone	0.64^{c}	0.6	PAR 0.125	A-200	520
Co^{2+}, Mn^{2+}	92.5–96.5% acetone	0.64–0.77^{c}	0.6	PAR 0.125	A-200	520

[a] Volume of sample loop, 5.13 ml.
[b] Volume of sample loop, 38 µl.
[c] Volume of sample loop, 56.3 µl.



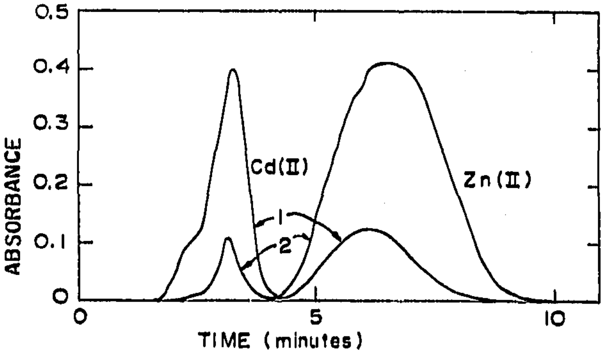


Fig. 2. Distribution coefficients as a function of hydrochloric acid concentration in 90% 2-propanol.

Fig. 3. Elution curve using 90% 2-propanol–0.30 M hydrochloric acid as the eluent. 1 = 3.42 µmoles Cd and 0.38 µmole Zn; 2 = 0.38 µmole Cd and 3.42 µmole Zn.

zinc(II) completely, with a resolution of 1.5. However, the eluent containing 0.3 *M* hydrochloric acid is more useful for the rapid separation, as shown in Fig. 3 where the resolution is 1.2. The flow-rate of the eluent affects the height equivalent to a theoretical plate (HETP) of the column as shown in Fig. 4, where 7.6×10^{-7} *M* cadmium(II) and zinc(II) are separated with 90% 2-propanol–0.3 *M* hydrochloric acid. The HETP plate increases slightly with the increase of the flow-rate. This indicates that macroreticular resin is useful for the separation of metal ions, partially in non-aqueous solution. A calibration plot is obtained by using the peak height in absorbance or the peak area of the elution curve. The peak area gives greater linearity against the metal amount than the peak height does, as shown in Fig. 5.

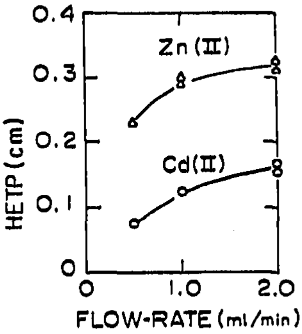


Fig. 4. HETP *vs.* flow-rate.

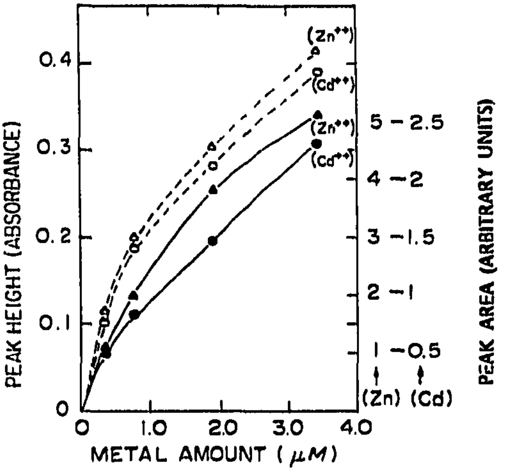


Fig. 5. Calibration curve of cadmium(II) and zinc(II). ○ and ●, cadmium; △ and ▲, zinc. ———, peak area; — — —, peak height.

Cadmium(II) and zinc(II) are separated with 50–60% acetone–0.64 *M* hydro-

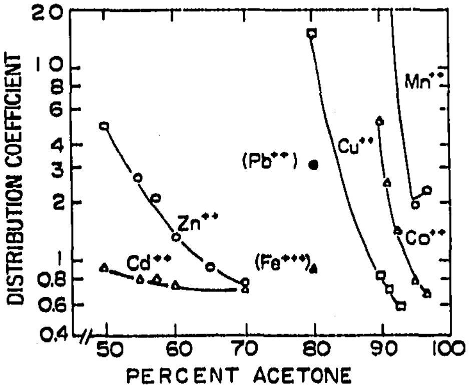


Fig. 6. Distribution coefficients as a function of acetone concentration in 0.64 *M* hydrochloric acid.

TABLE II

SEPARATION OF CADMIUM AND ZINC WITH 57% ACETONE–0.64 *M* HYDROCHLORIC ACID

Metal ion	*Metal amount* (10^{-9} *M*)	*HETP* (*cm*)	*Resolution*	*No. of curve in Fig. 7*
Cd^{2+}	563.0	0.127	1.09	1
Zn^{2+}	11.3	—		
Cd^{2+}	56.3	0.032	1.62	2
Zn^{2+}	56.3	0.135		
Cd^{2+}	11.3	—	1.34	3
Zn^{2+}	563.0	0.254		
Cd^{2+}	11.3	0.021	1.84	
Zn^{2+}	11.3	0.079		

chloric acid on a column of Amberlite 200. The effect of acetone upon the distribution coefficient may be seen in Fig. 6. The separation factor increases when the acetone concentration of the eluent becomes less than 60%. The results of the chromatographic separations are shown in Table II where 57% acetone containing 0.64 *M* hydrochloric acid is used as the eluent. Fig. 7 shows the curve of cadmium(II) and zinc(II) eluted with 57% acetone–0.64 *M* hydrochloric acid. The number in the elution curve corresponds to that in Table II, where the metal amount of the sample is shown. Linear calibration plots are obtained for the determination of cadmium(II) up to 6 µg (absorbance, 0.63) and zinc(II) up to 3 µg (absorbance, 0.45).

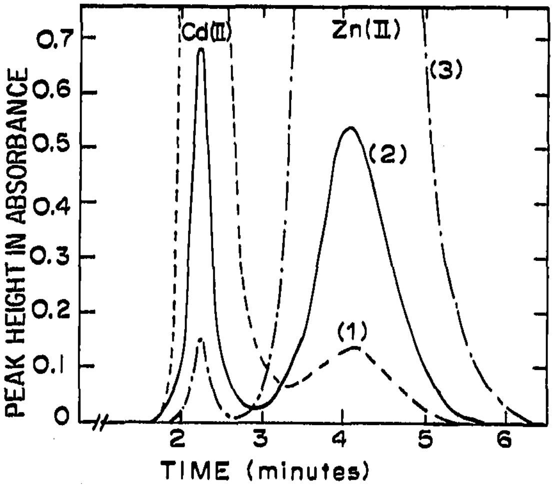
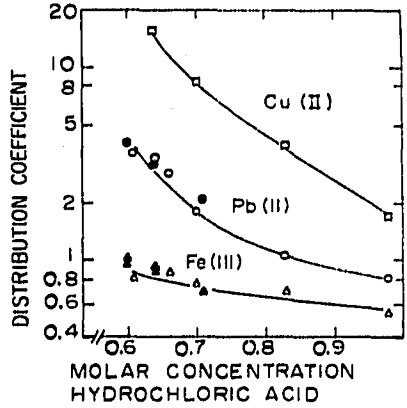


Fig. 7. Elution curves using 57% acetone–0.64 *M* hydrochloric acid.

Iron and lead

Small amounts of iron(III) and lead(II) are separated with 90% 2-propanol containing 0.91–1.2 *M* hydrochloric acid on a column of Amberlyst 15. The effect of the hydrochloric acid concentration upon the distribution coefficients may be seen in Fig. 2. 90% 2-propanol–1.08 *M* hydrochloric acid is the most useful eluent for the rapid separation of iron(III) and lead(II). The separation requires 12 min and a



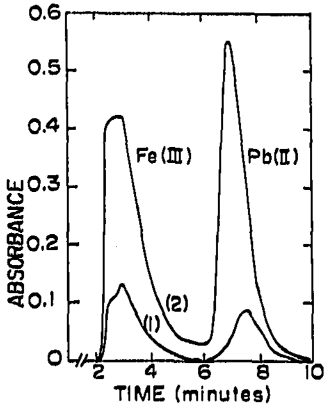
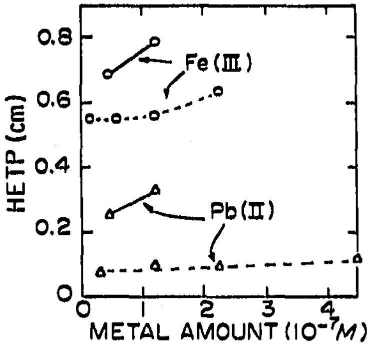


Fig. 8. Distribution coefficients as a function of hydrochloric acid concentration in 80% acetone. □, ○ and △, Amberlyst 15; ● and ▲, Amberlite 200.

Fig. 9. Elution curves for iron(III) and lead(II) mixtures.

resolution of 1.2 is obtained for the separation of 4.5 × 10^{-7} M iron(III) and lead(II). However, no simple relation is found between the peak height in absorbance and the metal amount in the chromatographic studies using this eluent. In addition, large amounts of each metal ion caused tailing to some extent.

Iron(III) and lead(II) are separated with 80% acetone containing 0.6–0.71 M hydrochloric acid on the column of Amberlyst 15 or Amberlite 200. Fig. 8 shows the distribution coefficients of iron(III), lead(II) and copper(II) onto Amberlyst 15 or



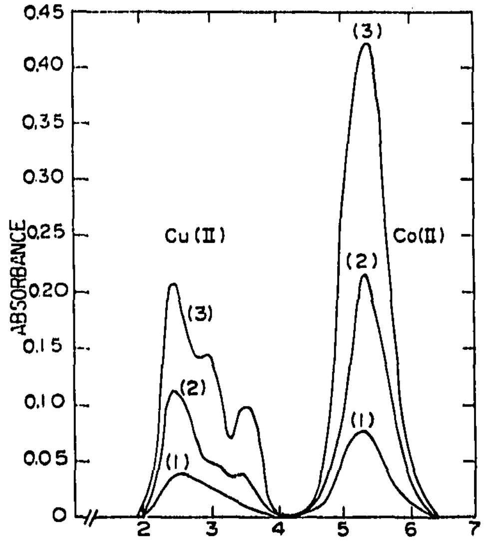


Fig. 10. HETP using 80% acetone–0.64 M hydrochloric acid eluent. ———, Amberlyst 15; — — —, Amberlite 200.

Fig. 11. Elution curve for copper and cobalt. 1 = 0.56 × 10^{-8} M; 2 = 1.41 × 10^{-8} M; 3 = 2.82 × 10^{-8} M.

Amberlite 200 from 80% acetone containing hydrochloric acid. Fig. 9 shows the elution curve of iron(III) and lead(II) which are separated with 80% acetone–0.64 M hydrochloric acid on a column of Amberlite 200. Linear calibration plots are obtained for the determination of iron(III) up to 1.1×10^{-7} M (absorbance, 0.92) and lead(II) up to 2.3×10^{-7} M (absorbance, 1.0). Amberlite 200 gives more (5–30%) peak height in absorbance for the same amount of the metal ion than Amberlyst 15. The HETP of each column is plotted against the metal amount as shown in Fig. 10. The smaller height equivalent is obtained on the column of Amberlite 200.

Copper, cobalt and manganese

Copper(II), cobalt(II) and manganese(II) are eluted with 90%–96.5% acetone containing 0.64–0.77 M hydrochloric acid on a column of Amberlite 200. The effect of acetone upon the distribution coefficient may be seen in Fig. 6. The peak of copper (II) has shoulders and the peak of manganese(II) is split in the chromatographic separation, so the major peak (which exhibits maximum absorption) of each metal ion is used for the calculation of the distribution coefficient.

These metal ions are eluted more rapidly by 91% acetone–0.64 M hydrochloric acid. The elution curve is shown in Fig. 11. The HETP is 0.05 cm for the separation of cobalt(II) and 0.3–0.6 cm for the separation of copper(II). Linear calibration plots are obtained for the determination of copper(II) up to 5.6×10^{-8} M (absorbance, 0.41) and cobalt(II) up to 2.8×10^{-8} M (absorbance, 0.42).

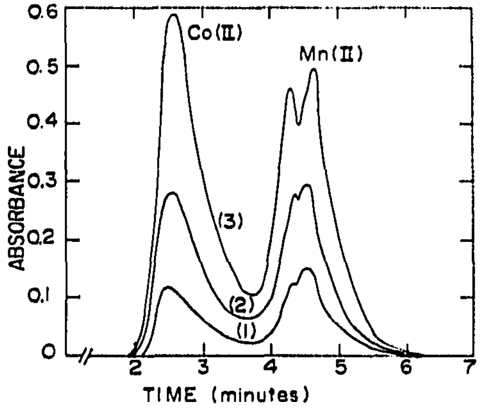


Fig. 12. Elution curve of cobalt and manganese (95% acetone–0.64 M hydrochloric acid). 1 = 1.13×10^{-8} M; 2 = 2.282×10^{-8} M and 3 = 5.63×10^{-8} M.

Cobalt(II) and manganese(II) are rapidly separated with 95% acetone including 0.64–0.77 M hydrochloric acid or 96.5% acetone containing 0.64 M hydrochloric acid on a column of Amberlite 200 (see Fig. 6). Fig. 12 shows the elution curve of these metal ions eluted with 95% acetone–0.64 M hydrochloric acid, which gives the best resolution for the separation. Manganese(II) always gives the two peaks in the chromatographic separation. As the first peak fails to give a linear calibration plot against the metal amount, the second peak (which exhibits the higher absorbance) is used for the calibration. Linear calibration plots are obtained for the determination of cobalt(II) up to 6×10^{-8} *M* (absorbance, 0.6) and manganese(II) up to 3×10^{-8} *M* (absorbance, 0.3).

Cadmium, zinc, iron, lead, copper, cobalt and manganese

Seven metal ions were separated rapidly from each other by the stepwise elution chromatography, as shown in Fig. 13. Successive elution conditions were chosen so that two metal ions are eluted by each eluent. In this separation, the percentage of acetone in the eluent is varied, while the concentration of hydrochloric acid in the eluent is kept constant at 0.64 *M*. Before the elution, Amberlite 200 resin of the column is equilibrated with 0.06 *M* hydrochloric acid aqueous solution while the metal ions are taken up by the column. Each metal amount of the sample is as follows: Cadmium(II) and zinc(II), each 2.25×10^{-8} *M*; iron(II) and copper(II), each 2.82×10^{-8} *M*; lead(II), 6.76×10^{-8} *M*; cobalt(II) and manganese(II), each 1.41×10^{-8} *M*. Constant air pressure is applied to the reservoir of color-forming reagent solution, causing it to flow through the mixing chamber. As the concentration of acetone in the eluent is changed, the baseline on the chromatogram shifts as shown in Fig. 13. Transformation from a partially non-aqueous elution medium to an aqueous medium and then back to a partially non-aqueous medium does not hinder the performance of the column. The present chromatographic method may be used also for the analysis of water containing the metal ions.

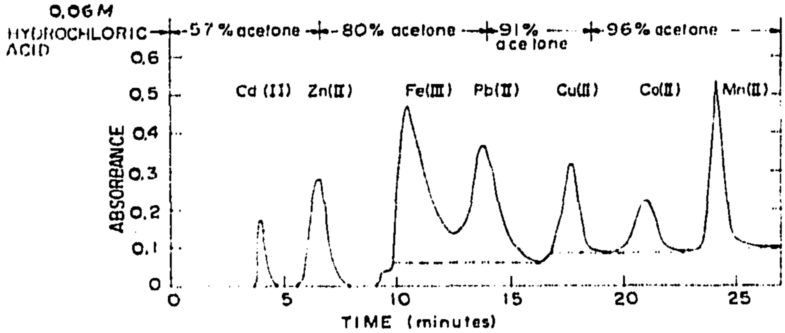


Fig. 13. Elution curve for a seven-component mixture. All eluents are 0.64 *M* in hydrochloric acid.

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