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CHROMATOGRAPHIC SEPARATION OF METAL IONS ON MACRO-RETICULAR ANION-EXCHANGE RESINS OF A LOW CAPACITY

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SUMMARY

The capacity of anion-exchange resins is a useful variable in devising practical analytical separations. Metal ions that form anionic chloro complexes are more weakly retained on resins of very low exchange capacity. Palladium(II), platinum(IV), gold(III), bismuth(III) and mercury(II) are retained on a column of 0.21 mequiv./g XAD-4 anion-exchange resin from 0.2 *M* hydrochloric acid and base metals pass through. The metals are then selectively eluted by various higher concentrations of hydrochloric acid. Batch distribution data are used to show the effect of capacity and to predict what separations are possible.

INTRODUCTION

The separation of metals in the form of chloro complexes from aqueous hydrochloric acid solutions using anion exchange columns is a well established analytical technique[1–7]. Hydrochloric acid has been a useful medium because it can be used to dissolve a large number of metals. Equally important, it is a useful reagent for the quantitative spectrophotometric determination[8] of many metals that may be automated with the use of a flow cell[9,10]. The very strong sorption of chloro complexes of several metal ions on conventional anion-exchange resins makes it difficult or impossible to elute these metal ions. In some cases elution has been accomplished by mixing perchloric acid with the hydrochloric acid eluent[10].

Recently it was shown that the distribution coefficients of simple inorganic anions decrease with decreasing capacity of the anion-exchange resin[11]. Fritz and Story[12,13] have reported a similar effect for cations on cation-exchange resins of lower capacity. In the present investigation a series of macroporous anion-exchange resins of very low capacity was prepared and the exchange behavior of anionic metal chloride complexes studied. Distribution coefficients on the new anion-exchange resins are significantly lower, and many analytical separations of metal ions have been obtained that would be impossible to achieve on conventional resins of high capacity.

EXPERIMENTAL

Apparatus

Most of the work was done with a liquid chromatograph that has been described previously[14]. The system employs automatic detection with a Tracor 970 variable-wavelength detector. All detection was done at 225 nm unless otherwise stated. Various concentrations of hydrochloric acid were used as the dye. Flow-rates of the eluent and dye were 1.5 ml/min. Sample loop size was 200 μl. A 80 × 2 mm column was used for the platinum–gold and palladium–gold separations. For the bismuth–mercury and for the tin separations a 25 × 2 mm column with 20 × 2 mm ends was used. Both columns used Altex 200-28 glass connectors.

The copper, palladium and platinum separation required a longer column. The resulting higher back pressure made the liquid chromatograph described above unsuitable. The chromatograph used for this separation is outlined in Fig. 1. This chromatograph was designed to allow only glass, PTFE, Kel-F or Tefzel plastic to come into contact with the mobile phase.

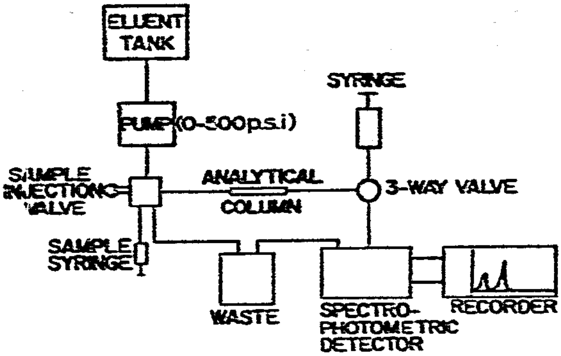


Fig. 1. Schematic diagram of the liquid chromatograph.

The eluent tank was a 500 ml glass reagent bottle. The mobile phase was pumped from the eluent tank by a CMP-2 Cheminert metering pump. The pump is rated 0–500 p.s.i. It employs a three piston design to reduce pressure and flow pulsation. The pump can be adjusted to flow-rates of 2.4–120 ml/h. All experiments were done at a flow-rate of 60 ml/h. Flow control is provided by pneumatically actuated three-way valves which control the filling and draining of each piston. The sample injection system is a three-way and four-way valve modeled after an Altex 201-56 sample injection valve. All work was performed using a 56.3 μl sample loop. The three-way valve between the column and detector allowed the removal of bubbles in the flow cell by rapidly forcing water through the system with a syringe. Two 500 × 2 mm glass columns were connected in series. The columns were individually slurry packed with a syringe. The resin was 0.04 mequiv./g XAD-1 (150–160 mesh), a strong base anion-exchange resin. The detector used was the same as for the other separations.

Measurement of distribution coefficients

Approximately 0.15 g of dried resin was accurately weighed into a 50 ml glass stoppered flask. The metal salt–hydrochloric acid solution was pipetted into the flask and the mixture was left for 6–12 h, with occasional shaking. Generally 15 ml of solution were used, however smaller and larger amounts of solution were used for extremely small and large distribution coefficients. The resin was filtered off and the metal content of the solution was determined by the absorbance at an appropriate wavelength. Distribution coefficients, D, were calculated by assuming all the metal gone from the solution was sorbed on on the resin where D is defined as

$$D = \frac{\text{amount of metal per g of dry resin}}{\text{amount of metal per ml of solution}}$$

Reagents

The copolymer material used for the synthesis of low capacity anion-exchange resins was macroreticular poly(styrene–divinylbenzene)beads. XAD-1 and XAD-4 were obtained from Rohm & Haas (Philadelphia, Pa., U.S.A.). The synthesis has been described in another paper[11]. The beads are highly cross-linked and have excellent chemical and mechanical stability.

Reagent grade metal chlorides were used when available. The stock silver solution was made from silver perchlorate. Platinic chloride solutions were made by diluting a 10% stock solution obtained from Fisher Scientific (Pittsburgh, Pa., U.S.A.) with the appropriate concentration of hydrochloric acid.

RESULTS

The distribution coefficients for several metal ions were determined as a function of aqueous hydrochloric acid concentration for low capacity anion-exchange resins. The metal ions chosen for study form chloro complexes that are tenaciously held by conventional anion-exchange resins. The results in Fig. 2 show distribution coefficients that are significantly lower for the new resins than for conventional anion-exchange resins of high capacity. Furthermore, the distribution coefficients tend to decrease more rapidly at the very low capacities, as shown by the behaviour of platinum(IV) in Fig. 2.

The distribution coefficients in Fig. 2 suggest that by suitable selection of hydrochloric acid concentration, column separations of some of the metal ions in Fig. 2 from other metals and from each other should be possible. Several actual separations are reported below using the chromatographic and detection systems outlined in Experimental.

Separation of platinum(IV) or palladium(II), gold(III) and base metals

A separation of chromium(III), platinum(IV) and gold(III) on 0.21 mequiv./g XAD-4 is shown in Fig. 3. The sample is dissolved in *ca.* 0.2 M hydrochloric acid and injected on the column with eluent 0.2 M hydrochloric acid. Chromium(III) and other base metals are eluted under these conditions. Platinum(IV) is removed with 3.5 M hydrochloric acid. Gold(III) is eluted with 1.0 M hydrochloric acid in methanol. A

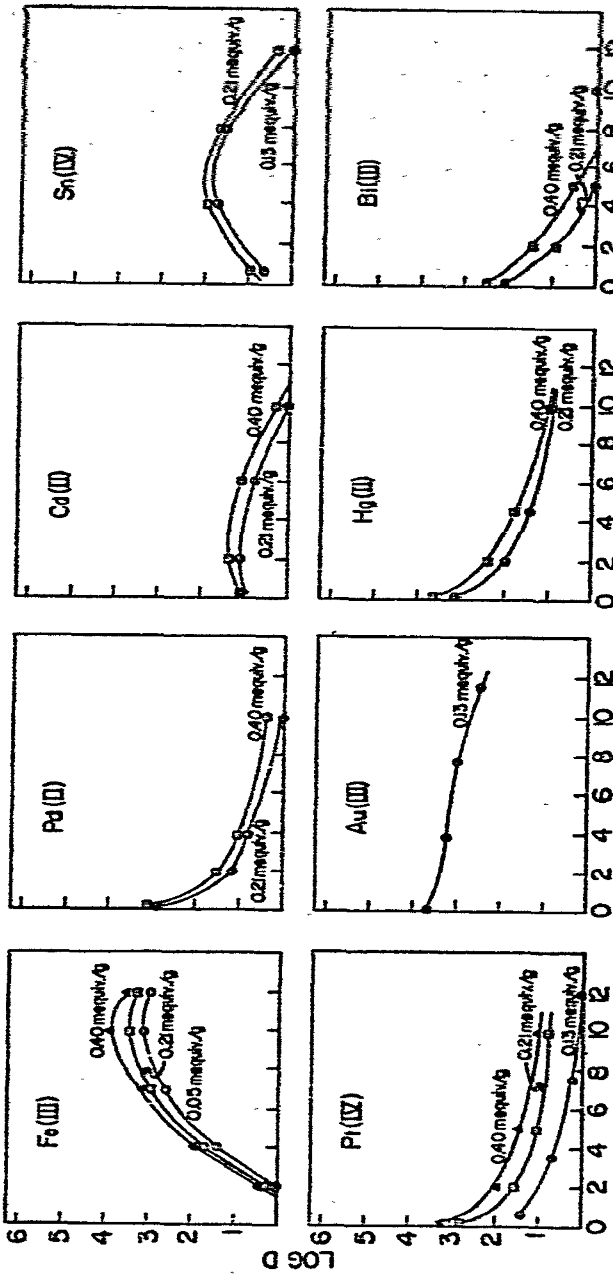
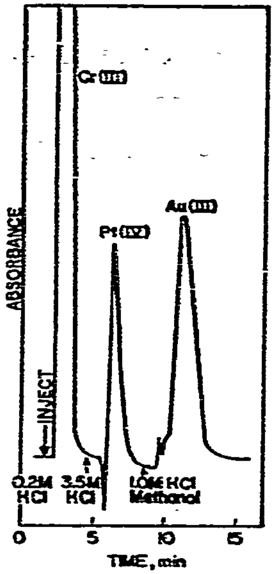


Fig. 2. XAD-4 anion-exchange distribution coefficients (*D*) of various metals as a function of HCl concentration and capacity.



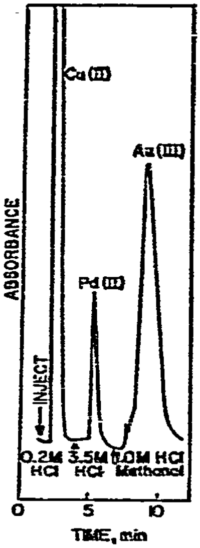


Fig. 3. Separation of 2.0 mg chromium(III), 39 μg platinum(IV) and 7.8 μg gold (III).
Fig. 4. Separation of 1.3 mg copper(II), 2.1 μg palladium(II) and 9.8 μg gold(III).

separation of copper(II), palladium(II) and gold(III) on 0.21 mequiv./g XAD-4 is shown in Fig. 4. The same procedure is used to carry out the separation.

The negative peak directly preceding platinum(IV) in Fig. 3 is a solvent change peak and is typical in a step gradient elution from a low concentration to a high concentration of hydrochloric acid. The small peak right ahead of the gold(III) peak is also a solvent change peak. None of the solvent change peaks interfered with the peak heights of the metals analyzed. Standard solutions of platinum, palladium and gold of various concentrations gave linear calibration curves of peak height *vs.* μg of metal ion.

TABLE I

DETERMINATION OF PLATINUM AND GOLD IN THE PRESENCE OF FOREIGN METALS

Foreign metal	*Pt (IV)*		*Au(III)*	
	Molar excess foreign metal	*Recovery % (av. of 2)*	*Molar excess foreign metal*	*Recovery (%) (av. of 2)*
Mn(II)	200	100.8	1000	99.1
Fe(III)	200	99.2	1000	79.0
Fe(III)	—	—	500	98.2
Cr(III)	200	96.9	1000	99.8
Ni(II)	200	97.1	1000	99.0
Cu(II)	200	97.0	1000	98.7
Sr(II)	200	98.3	1000	99.2
Co(II)	200	97.7	1000	99.6
	Average range 2.3%		Average range 1.1%	

TABLE II

DETERMINATION OF PALLADIUM AND GOLD IN THE PRESENCE OF FOREIGN METALS

Foreign metal	*Pd(II)*		*Au(III)*	
	Molar excess foreign metal	*Recovery (%) (av. of 3)*	*Molar excess foreign metal*	*Recovery (%) (av. of 3)*
Mn(II)	1000	96.5	400	99.7
Fe(III)	1000	96.6	400	99.6
Cr(III)	1000	98.0	400	99.8
Ni(II)	1000	96.0	400	99.6
Cu(II)	1000	97.6	400	99.7
Sr(II)	1000	96.7	400	99.8
Co(II)	1000	98.8	400	100.0
	Average range 1.7%		Average range 0.4%	

Tables I and II show there is little or no interference with the foreign metals tested.

Separation of bismuth(III) and mercury(II) from other metals

Bismuth(III) and mercury(II) also form stable anion complexes but are somewhat difficult to elute with aqueous hydrochloric acid from ordinary anion-exchange resins. In the chromatogram shown in Fig. 5 bismuth(III) and mercury(II) are separated from each other and iron(III) on 0.21 mequiv./g XAD-4. The sample is injected onto the column with an eluent of 0.2 *M* hydrochloric acid. After the major metal ion [iron(III)] has eluted, bismuth(III) is eluted with 2.2 *M* hydrochloric acid. Mercury(II) is eluted with 8.5 *M* hydrochloric acid. A larger column was used for

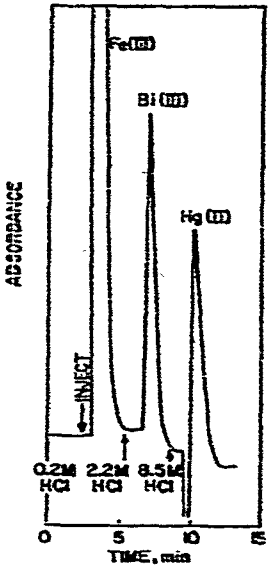


Fig. 5. Separation of 2.2 mg iron(III), 4.2 μg bismuth(III) and 4.0 μg mercury(II).

TABLE III

DETERMINATION OF BISMUTH AND MERCURY IN THE PRESENCE OF FOREIGN METALS

Foreign metal	*Bi(III)*		*Hg(II)*	
	Molar excess foreign metal	*Recovery (%) (av. of 3)*	*Molar excess foreign metal*	*Recovery (%) (av. of 3)*
Cu(II)	1000	99.7	1000	99.8
Cr(III)	1000	100.1	1000	100.6
Fe(III)	1000	101.9	1000	100.0
Mn(II)	1000	99.2	1000	100.2
Sr(II)	1000	99.3	1000	99.6
Ni(II)	1000	100.0	1000	100.9
Co(II)	1000	100.5	1000	100.7
Zn(II)	1000	100.1	1000	102.7
Cd(II)	1000	99.7	1000	101.1
Sn(IV)	100	98.8	100	101.9
As(III)	100	98.9	100	100.2
Pb(II)	20	101.2	20	101.3
Sb(III)	20	100.6	20	104.4
Ag(I) $\lambda = 225$	1	>150	1	99.9
Ag(I) $\lambda = 327$	1	99.0	1	—
	Average range 1.3%		Average range 1.5%	

this separation, which permitted samples to be dissolved in up to 2 *M* hydrochloric acid with no premature bleeding of the bismuth(III).

The results in Table III show the method is quite selective. Samples containing antimony(III) and tin(IV) have a different baseline shift which is caused by bleeding of the residue metals. However, this effect is not serious and recovery is still good. Silver(I) interferes with bismuth(II) when detection is at 225 nm. Changing to 327 nm eliminates this interference because silver(I) no longer absorbs.

Separation of tin(IV) from other metals

Satisfactory separations of tin(IV) and nickel(II) have been obtained on 0.21 mequiv./g XAD-4. The sample is dissolved in *ca.* 5 *M* hydrochloric acid and is

TABLE IV

DETERMINATION OF TIN IN THE PRESENCE OF FOREIGN METALS

Foreign metal	*Sn(IV)*	
	Molar excess foreign metal	*Recovery (%) (av. of 3)*
Cu(II)	100	100.9
Cr(III)	100	100.5
Ni(II)	100	100.6
Zn(II)	100	99.7
As(III)	100	interfers
Sb(III)	100	interfers
	Average range 1.3%	

injected on the column. Nickel(II) and other metals are eluted with 5.0 *M* hydrochloric acid. Tin(IV) is eluted with 1.0 *M* hydrochloric acid. There is a solvent change peak preceding the tin(IV) peak, but a linear calibration curve peak height *vs.* μg of tin(IV) was obtained nevertheless. Data for determination of tin(IV) in the presence of other metal ions are given in Table IV.

Separation of copper(II), palladium(II) and platinum(IV)

When a column with higher performance is used, palladium(II) and platinum(IV) can be easily separated from each other and a non-retained metal such as copper(II). The chromatogram in Fig. 6 shows this separation on 0.04 mequiv./g XAD-1. The peaks given by platinum represent two different complexes of platinum(IV).

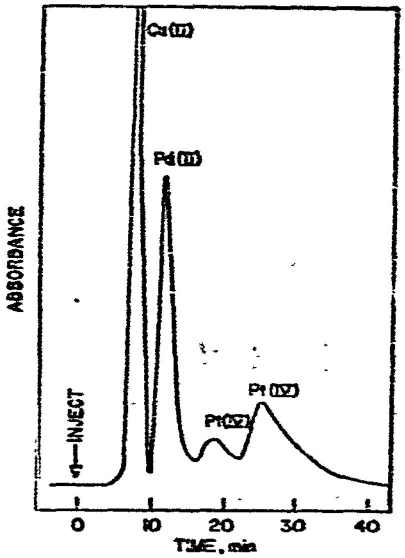


Fig. 6. Separation of copper(II), palladium(II) and platinum(IV).

CONCLUSION

Ion-exchange resin capacity can be easily varied and a parameter to be considered when devising analytical separations. Low capacity anion-exchange resins permit elution of many metal chloro complexes that previously were difficult or impossible to elute. XAD anion-exchange resins have excellent mechanical and chemical stability and lend themselves well to a forced flow system with automatic detection.

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