ANION EXCHANGE CHROMATOGRAPHY OF TRANSITION METALS IN TARTRATE MEDIUM*

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INTRODUCTION

Tartrate medium has been used for a number of anion exchange studies[1-3]. Recently the separation of manganese, cobalt, zinc, copper and iron in tartrate medium was reported[4]. It was also found that the tartrate system was convenient for the quantitative separation of iron(II) and iron(III)[5].

In the present work, equilibrium studies were made on the tartrate complexes of chromium, molybdenum, nickel, silver, cadmium and mercury. On the basis of the data obtained for these metals and the data for manganese, cobalt, zinc and iron[4], a number of column separations were developed.

EXPERIMENTAL

Reagents and apparatus

Dowex 2X-8-anion exchange resins were converted to the tartrate form using *d*-tartaric acid obtained from J. T. Baker Chemical Company, Phillipsburgh, N.J. Batch determinations were made with 50–100 mesh resin since it was more convenient for this work than the finer mesh resin. Mesh size 200–400 was selected for column operation because it reaches equilibrium faster. A comparison of the distribution coefficients of chromium on the two mesh size resins was made and no significant difference was found.

The isotopes used in this investigation were chromium-51, manganese-54, iron-59, cobalt-60, nickel-63, zinc-65, molybdenum-99, silver-110, cadmium-115 and mercury-187. All of the above isotopes except manganese-54 were obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn. The manganese-54 was obtained from Nuclear Science and Engineering Corporation, Pittsburg, Pa.

Nearly all isotopes were obtained as either the chloride or nitrate salt and could be used without modification. However, molybdenum-99 was obtained as ammonium molybdate in ammonium hydroxide solution. It was necessary to convert this to molybdic acid in order to form a complex ion with tartaric acid[6]. This was accomplished by heating the active ammonium molybdate at 800° F for one hour as described by KILLEFFER[7]. Molybdic acid solutions were made slightly basic to prevent precipitation as the isopoly acid.

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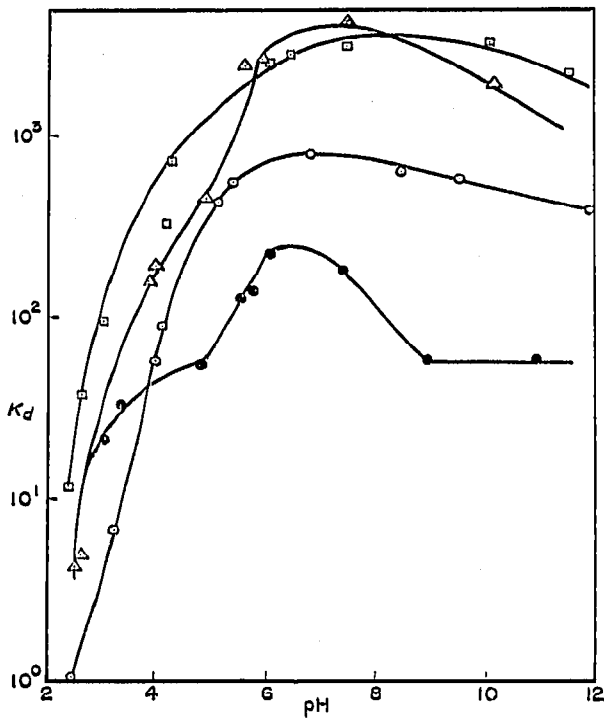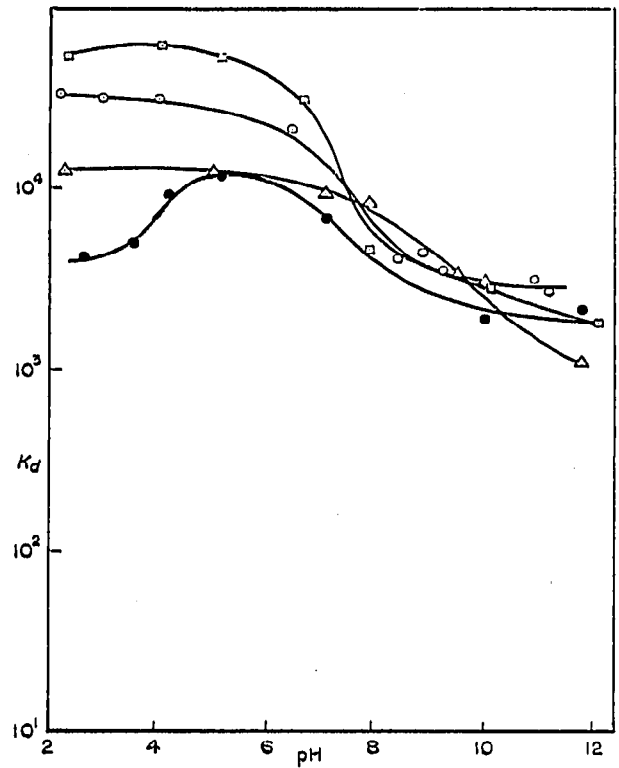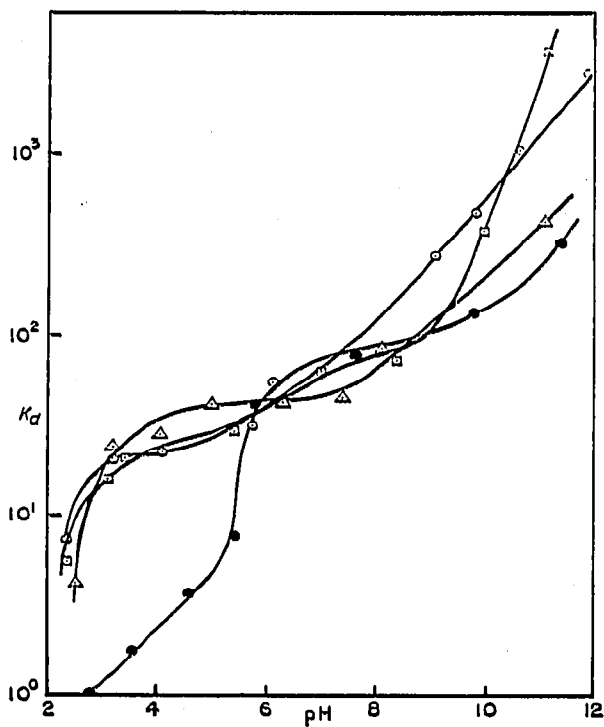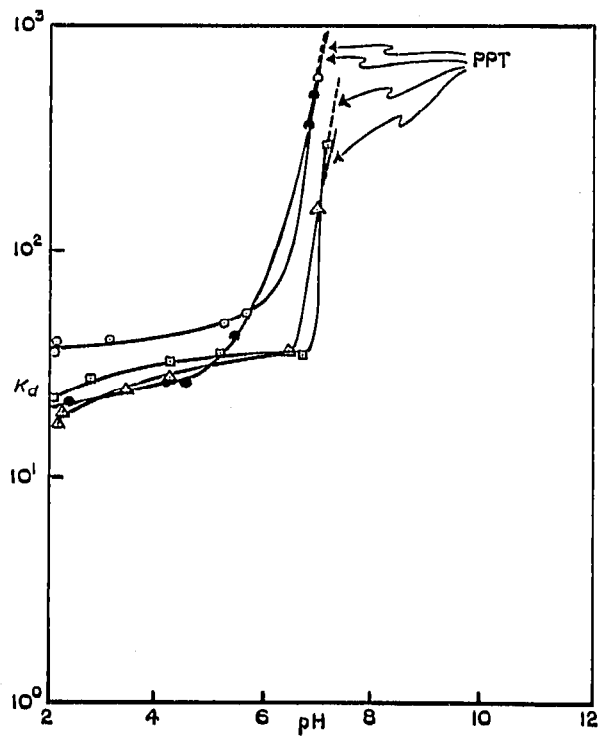
Fig. 1. Chromium.

Fig. 2. Molybdenum.

Fig. 3. Nickel.

Fig. 4. Silver.

Figs. 1–4. Distribution coefficients for metals. Effect of pH and concentration. $\odot$ – in $8.5 \cdot 10^{-2}$ M tartrate; $\boxdot$ – in $4.25 \cdot 10^{-2}$ M tartrate; $\triangle$ – in $2.12 \cdot 10^{-2}$ M tartrate; $\bullet$ – in $2.12 \cdot 10^{-3}$ M tartrate.
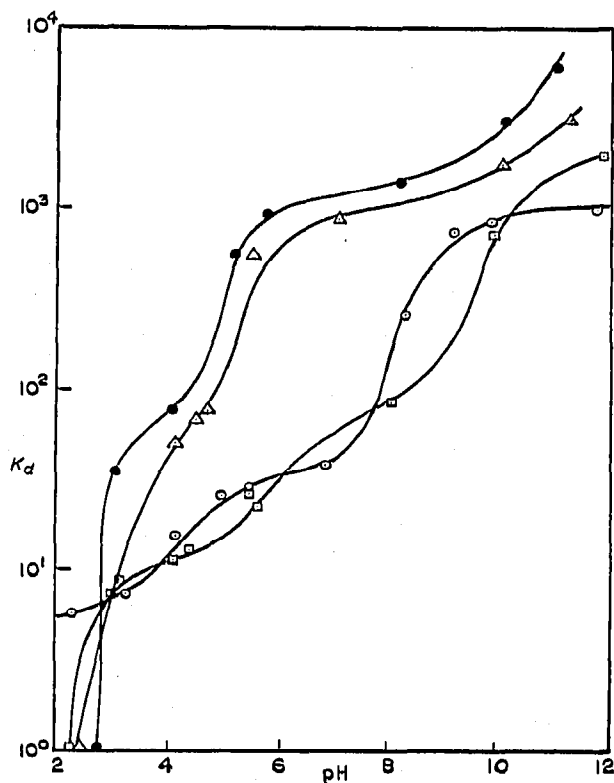
Fig. 5. Cadmium.

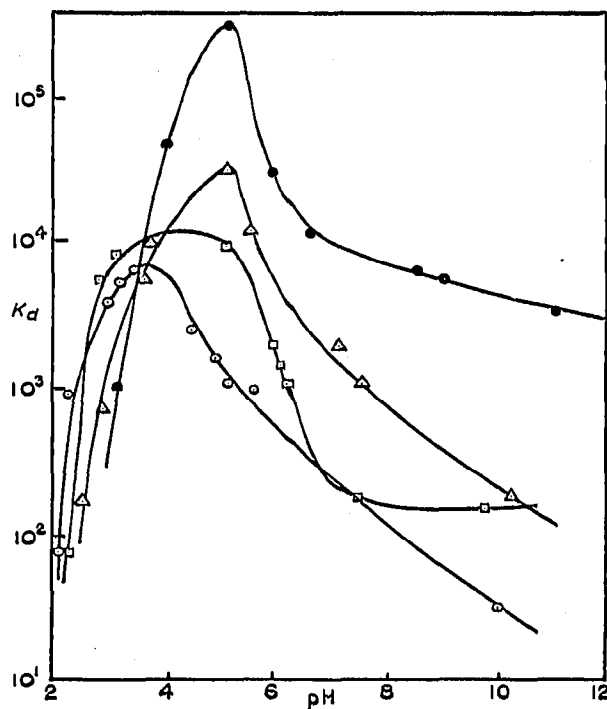Fig. 6. Mercury.

Figs. 5–6. Distribution coefficients for metals. Effect of pH and concentration. $\odot$ – in $8.5 \cdot 10^{-2}$ M tartrate; $\boxdot$ – in $4.25 \cdot 10^{-2}$ M tartrate; $\triangle$ – in $2.12 \cdot 10^{-2}$ M tartrate; $\bullet$ – in $2.12 \cdot 10^{-3}$ M tartrate.

Nickel-63 activity was measured with a windowless gas flow counter since it is a weak beta emitter of 0.067 MeV. The instrument employed was a Nuclear Chicago Model D-47 gas flow detector equipped with a time interval printer.

All other apparatus and reagents used were described in a previous publication[4].

Procedure

Distribution coefficients. The distribution coefficients for $4.25 \cdot 10^{-4}$ M solutions as a function of pH and tartrate concentration were determined by the batch equilibration method described in an earlier communication[4].

After the solution and the resin had reached equilibrium in the batch determinations, aliquots were withdrawn by pipet and the activity was measured. Five ml samples of all solutions except nickel were placed in vials for scintillation counting. Since nickel-63 is a weak β emitter, 1 ml portions of it were withdrawn and placed in planchets and allowed to dry. Activity measurements for these samples were obtained using a windowless gas flow counter.

The pH of the remaining solution was measured and recorded as the equilibrium pH. The activity of the 5 or 1 ml portion was compared to the activity of an equal portion of the original solution to obtain the activity on the resin. Cadmium-115 and molybdenum-99 have relatively short half lives and it was necessary to correct for the decay of these isotopes.

The distribution coefficient, K_d, for each metal was calculated using the following formula:

$$K_d = \frac{\text{c.p.m. in resin phase per gram of resin}}{\text{c.p.m. in solution phase per ml of solution}}$$

Column separations

After preparing a resin bed of the desired depth in a 0.8 cm I.D. column, the resin was brought to the pH and tartrate concentration necessary for the separation. This was accomplished by passing a tartrate solution of the proper pH through the column until the effluent pH matched the eluent pH.

After preparation of the column, a 2 ml sample containing the radioactive metals to be separated was introduced at the top of the column with a pipet. After this portion had passed into the resin, a 125 ml separatory funnel containing the eluting agent was fitted to the top of the column and the flow was started. The effluent was allowed to flow into a fraction collector which collected 2 ml portions. With the exception of nickel-63, these 2 ml portions were viewed qualitatively with a 200 channel pulse height analyzer and were counted on a R.I.D.L. scintillation counter. Nickel was detected by adding 5 drops of concentrated sodium hydroxide and 5 drops of dimethylglyoxime to each 2 ml portion of the effluent and the solutions were observed for a red precipitate. Concentrated hydrochloric acid was then added to dissolve the precipitate and the solutions were diluted to 3 ml. A 1 ml portion was taken from each vial, placed on a planchet, dried, and counted on a windowless flow counter.

RESULTS AND DISCUSSION

The data resulting from the batch equilibrations are shown in Figs. 1–6. These distribu-

TABLE I

CONDITIONS FOR SEPARATIONS

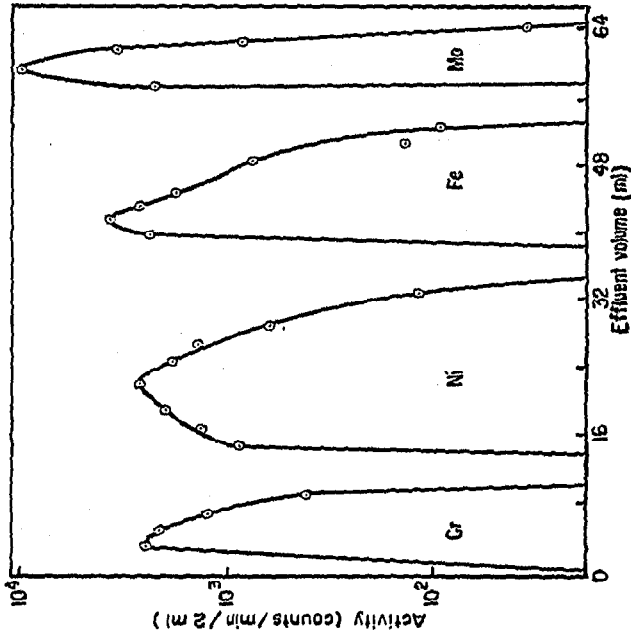| Separation	Column	Sample	Flow rate	Eluting agent
Mn, Co, Ni, Fe, Mo	8.0 cm long, treated with $8.5 \cdot 10^{-2}$ M tartaric acid at pH 4.0	9 μg Mn, 10 μg Fe, 10 μg Co, 16 μg Mo, 10 μg Ni in $8.5 \cdot 10^{-2}$ M tartrate at pH 4.0	3 drops/min	$8.5 \cdot 10^{-2}$ M tartrate solution at pH 4.0 for Mn and Co; tartaric acid in 0.1 M HCl for Fe; 3 M NaOH for Mo
Cr, Ni, Fe, Mo	5.0 cm long, treated with $8.5 \cdot 10^{-2}$ M tartaric acid at at pH 3.5	11 μg Cr, 12 μg Ni, 12 μg Fe, 20 μg Mo in $8.5 \cdot 10^{-2}$ M tartrate at pH 3.5	4 drops/min	$8.5 \cdot 10^{-2}$ M tartrate at pH 3.5 for Cr and Ni; $8.5 \cdot 10^{-2}$ M tartaric acid in 0.1 M HCl for Fe; 3 M NaOH for Mo
Mn, Cr, Fe, Mo	3.5 cm long, treated with $4.24 \cdot 10^{-2}$ M tartaric acid at pH 3.0	12 μg Mn, 11 μg Cr, 12 μg Fe, 20 μg Mo in $4.25 \cdot 10^{-2}$ M tartrate at pH 3.0	5–6 drops/min	$4.25 \cdot 10^{-2}$ M tartrate at pH 3.0; 1 M HCl for Fe; 3 M NaOH for Mo
Zn, Cd, Hg	4.5 cm long, treated with 100 ml 3 M HNO$_3$, then $8.5 \cdot 10^{-2}$ M tartrate at pH 2.5	18 μg Zn, 32 μg Cd, 57 μg Hg in $8.5 \cdot 10^{-2}$ M tartrate at pH 2.5	4 drops/min	$8.5 \cdot 10^{-2}$ M tartrate at pH 2.5; 1 M HNO$_3$ for Hg

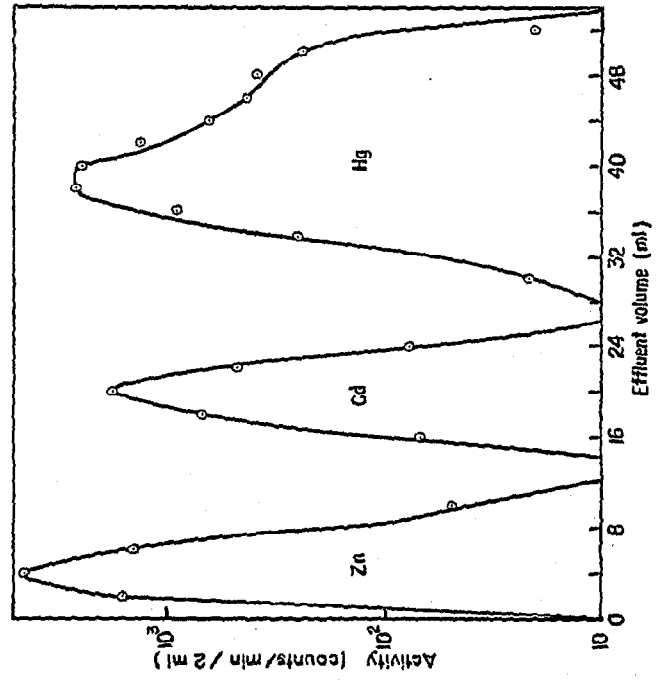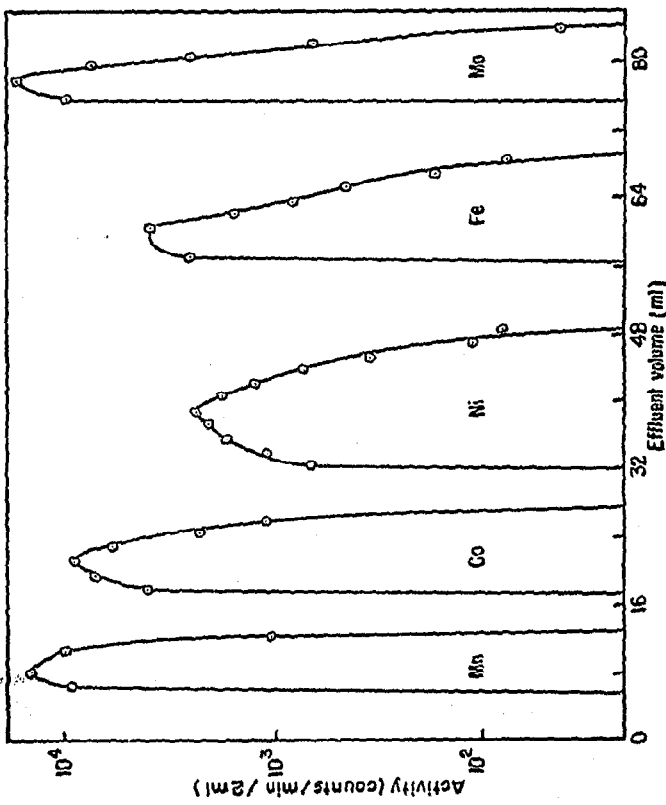Fig. 7. The separation of manganese, cobalt, nickel, iron and molybdenum.

Fig. 8. The separation of chromium, nickel, iron and molybdenum.
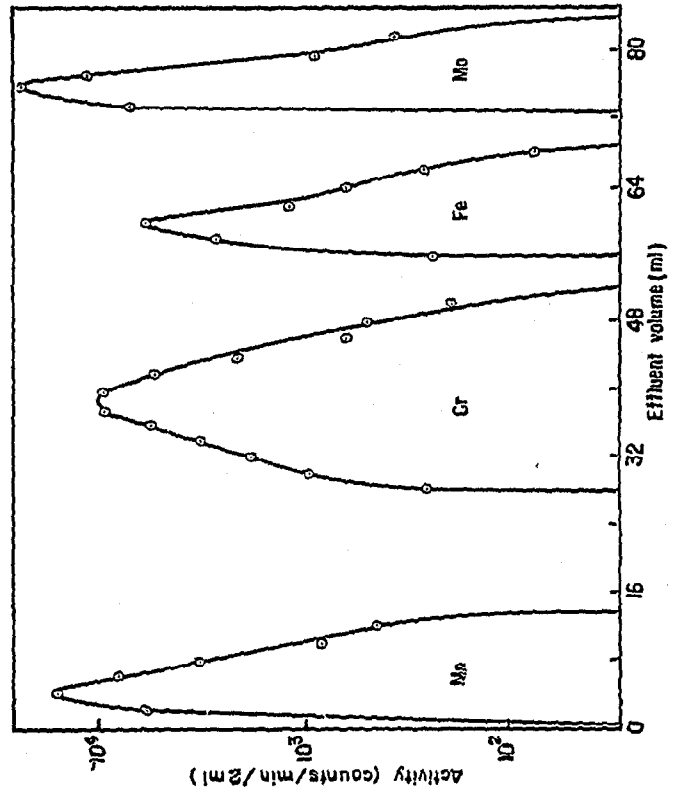
Fig. 9. The separation of manganese, chromium, iron and molybdenum.

Fig. 10. The separation of zinc, cadmium and mercury.

tion coefficients and those reported in an earlier publication[4], were used to determine conditions for several column separations. Four of these are shown in Figs. 7–10. The conditions for these separations are given in Table I.

SUMMARY

The tartrate complexes of chromium, molybdenum, nickel, silver, cadmium and mercury were studied by the batch equilibration method on Dowex 2X-8 anion exchange resin. From the distribution coefficients obtained for the above metals and for manganese, cobalt, zinc and iron, several column separations were developed. Radioisotopes were used in the batch equilibration studies and in the chromatographic separations.

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