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By
Raymond David Szidon
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May 1961

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Ames, Iowa

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ABSTRACT

Attempts were made to separate components of metal ion mixtures on columns of iminodiacetate type chelating resin. Distribution coefficients of metal ions in the presence of sulfosalicylic acid and citric acid were calculated in order to determine the proper pH for the most efficient separations. Separations of metal ion mixtures using citric acid or sulfosalicylic acid solutions as eluting agents were, for the most part, successful, although incomplete elution was observed in some cases.

Fluoride solutions were also found to be effective eluting agents for the separation of metal ions on columns of chelating resin. Separations of metal ion mixtures using either a 0.1 M hydrofluoric acid-0.1 M sodium fluoride solution at pH 4.0 or a 0.1 hydrofluoric acid solution at pH 5.5 as the eluting agent were accomplished

INTRODUCTION

Ion exchange resins have in recent years become well established as tools for the chemist. The analytical chemist, in particular, has found in ion exchange an excellent method for separating components of mixtures, for concentrating trace amounts of substances, and for removing interfering substances prior to analysis. The properties of ion exchange resins and related substances and the factors involved in their use have been discussed by Kunin (1). Those aspects of ion exchange resins of particular interest to the analytical chemist have been well reviewed in Analytical Chemistry (2, 3, 4).

The most widely used ion exchange resins at present are insoluble crosslinked styrene-divinylbenzene polymers containing acidic or basic functional groups. The cation exchange resins normally contain sulfonic acid or carboxylic acid groups while the anion exchange resins contain amine or quaternary ammonium functional groups. The ions associated with these functional groups are free to exchange with ions in solution.

These conventional ion exchange resins exhibit different affinities for different ions, and separations of ions from one another can sometimes be accomplished solely by selective absorption. In general, however, these intrinsic differences are not sufficiently great to be of use.

Therefore, chromatographic procedures are often necessary, and complexing agents are often employed in the case of cation exchange to enhance the differences in affinities. Some degree of selectivity can be accomplished by increasing the degree of crosslinking of the resin; however, this results in a decrease in the rate of exchange. Since the applicability of ion exchange resins depends largely on the extent to which they exhibit selective absorption, the relative affinities of different ions for the resin are of prime importance.

Another approach to the problem involves alteration of the functional groups of the resin. Properties of the conventional ion exchange resins indicate that the affinity of cations for such resins is greatly influenced by the nature of the functional groups on the resin. Resins containing weakly acidic functional groups exhibit a high affinity for the hydrogen ion. Lithium exhibits a higher affinity for phosphonic acid and carboxylic acid resins than do sodium or potassium whereas the opposite is true in the case of sulfonic acid resins (5). Cupric ions are absorbed by weakly basic anion exchange resins as a result of complex formation (6).

Resins containing chelating groups which can form stable complexes with cations are known as chelating resins. Such resins might be expected to exhibit specific or

selective behavior toward particular ions in a manner simi-
lar to that shown by complexing agents in solution.

It is evident that the development of chelating resins
as analytical tools for the chemist and as industrial re-
agents has lagged far behind that of the conventional ion
exchange resins. However, many chelating resins have been
prepared, and their properties have been studied to various
degrees. D. K. Hale (7) and M. Okawara (8) have adequately
reviewed the literature concerned with the preparation and
properties of the resins. Kunin (1) has included a short
section dealing with this subject in his book.

More recently Seidl and Stamberg (9) have described an
exchanger containing 1,2-dioxime groups which is selective
for nickel, a resin with o-hydroxyaldoxime groups selective
for copper, a resin synthesized from resorcyl aldehyde,
aniline, and formaldehyde selective for copper, an ion ex-
changer containing o-o'-dihydroxyazo groups which is capable
of absorbing copper and magnesium at pH 3, and a chelate
resin prepared from fluorone derivatives and formaldehyde
selective for germanium even in concentrated acid solutions.

Nakamura and Yanagita (10) have prepared polystyrene
resins containing acetylacetone or 8-quinolinol chelating
groups.

Turse and Rieman (11) have used Dowex Chelating Resin
A-1 to concentrate trace amounts of copper from concentrated

4

ammonium chloride solutions.

The purpose of this research was to use Dowex Chelating Resin A-1 (12) for the separation of metal cations by selective absorption. Dowex Chelating Resin A-1 is physically similar to conventional ion exchangers since it has the same styrene-divinylbenzene matrix. Iminodiacetate functional groups on the matrix, however, impart specific chemical properties to the resin causing it to show unusually high selectivity for certain cations. The resin exhibits an affinity for heavy metal cations over such ions as sodium, potassium, and calcium. A higher affinity for alkaline earths than for alkali metals is also shown.

Further selectivity of absorption has been obtained in this research by selective complexing of one of a mixture of metal cations in solution to form a neutral or anionic complex and subsequent separation of the components of the mixture on columns of the chelating resin by the single-pass method. The aspects of the single-pass method of ion exchange separations and literature involving its use have been reviewed by Oliver and Fritz (13).

EXPERIMENTAL

Apparatus

Glassware: Kimble "Kimax burets were used for all titrations throughout this work. All volumetric glassware was class A. Glass columns used for the metal ion separations by sulfosalicylic and citric acid elution consisted of tubing 1.1 cm. inside diameter and 20 cm. in length equipped with a coarse glass frit approximately 2 cm. from the bottom. A medicine dropper was attached to the bottom of the column by a short length of teflon tubing. A section of glass tubing 2.2 cm. inside diameter and 3 cm. long was attached to the top of the column. A rubber stopper holding a long stem funnel which served as a reservoir was inserted into this top section.

Plastic ware: Polyethylene tubing 1.2 cm. inside diameter inserted in glass tubing for support was used as columns for the separation of metal ions by fluoride elutions. Orlon cloth, held between the column and a polyethylene funnel tip by a band of teflon tubing, supported the resin in the column. Plastic funnels inserted in the column top were used as reservoirs.

pH meter: All pH measurements were made with a Beckman Model G pH meter equipped with a Beckman 1190-80 glass electrode and a Beckman 1170 calomel reference electrode.

Shaker: A Burrell shaker was used in the study of distribution coefficients.

Spectrophotometer: A Beckman Model B spectrophotometer was used for all spectrophotometric measurements involved in the distribution coefficient measurements.

Reagents and Solutions

Chelating resin: Dowex Chelating Resin A-1, 50-100 mesh, sodium form, obtained from The Dow Chemical Company, was used for the measurement of metal ion distribution coefficients. Approximately two bed volumes of 2 M hydrochloric acid were passed through one pound of resin to remove any cation impurities in the resin. Water was passed through the resin until a test for chloride in the effluent was negative, and 1.5 bed volumes of 1 M sodium hydroxide were passed through the resin to convert it back to the sodium form. The resin was again washed with water to remove any excess sodium hydroxide. The resin was then air dried before use.

Analytical grade Chelex 100 Chelating Resin, 100-200 mesh, sodium form, obtained from the Bio-Rad Laboratories, was used for the separations of metal ion mixtures. The procedure used for purification and regeneration of the resin was identical to that given above.

EDTA [disodium dihydrogen (ethylenedinitrilo) tetra-acetate dihydrate]: Eastman Organic Chemicals white label grade EDTA was used for the titrimetric analysis of the metals.

Zinc metal: 99.99 per cent pure primary standard zinc metal, obtained from Platt Brothers and Company, Waterbury, Connecticut, was used for standardization of EDTA solutions.

All other reagents were reagent grade laboratory chemicals.

Metal ion solutions (0.05 M): The required amount of metal nitrate or perchlorate salt was dissolved in water or dilute acid, as required, and diluted to 1 liter with water.

Sulfosalicylic acid, pH 9.5 (0.1 M): 25.4 gm. of sulfosalicylic acid dihydrate was dissolved in water. The resulting solution was adjusted to pH 9.5 with concentrated ammonium hydroxide and diluted to 1 liter.

Citric acid, pH 9.5 (0.1 M): 29.4 gm. of sodium citrate dihydrate was dissolved in water. After 10 ml. of concentrated ammonium hydroxide was added, the pH was adjusted to 9.5 with concentrated perchloric acid, and the solution was diluted to 1 liter.

Citric acid, pH 6.0 (0.1 M): 29.4 gm. of sodium citrate dihydrate was dissolved in water. After 10 ml. of pyridine was added the pH was adjusted to 6.0 with concentrated perchloric acid, and the solution was diluted to

l liter.

Hydrofluoric acid, pH 5.5 (0.1 M): 3.5 ml. of 48 per cent hydrofluoric acid was dissolved in water. Pyridine was added to pH 5.5, and the resulting solution was diluted to 1 liter.

Hydrofluoric acid (0.1 M)-sodium fluoride (0.1 M), pH 4.0: 3.5 ml. of 48 per cent hydrofluoric acid and 4.2 gm. of sodium fluoride were dissolved in water, and the resulting solution was diluted to 1 liter.

Analytical Procedures

EDTA: EDTA solutions were standardized by titration of standard zinc (II) solution using naphthylazoxine as the indicator as described by Fritz et al. (14).

Copper(II), nickel(II), zinc(II), cobalt(II), and cadmium(II): These metals were analyzed by titration with EDTA using naphthylazoxine indicator (14). Copper was also determined colorimetrically, using neocuproine as reported by Diehl and Smith (15). The colorimetric procedure used for zinc was that of Rush and Yoe (16).

Uranium(VI): Analysis of uranium was accomplished by titration with standard sulfatoceric acid solution after passage through a lead reductor as described by Sill and Peterson (17) or by the colorimetric method of Fritz and

Richard (18).

Iron(III): Samples of iron were washed through a lead reductor by 1 M hydrochloric acid and titrated with standard sulfatoceric acid using ferroin as the indicator.

Aluminum(III): Samples containing aluminum were analyzed by backtitration of excess EDTA with zinc(II) in 50 per cent alcohol using dithizone indicator according to the method of Wänninen and Ringbom (19).

Zirconium(IV): Analysis of zirconium was made by backtitration of excess EDTA with bismuth(III) using xylenol orange as the indicator as described by Kinnunen and Wennerstrand (20).

Measurement of Distribution Coefficients

In order to measure the metal ion distribution coefficients, approximately 1 gm. of air dried chelating resin was accurately weighed into a 125 ml. glass stoppered Erlenmeyer flask. A 25 ml. aliquot of a buffered solution 0.02 M in metal ion and 0.2 M in complexing agent was added to the resin. Twenty-five ml. of water was added, and the resulting mixture was shaken on a Burrell automatic shaker for five hours or more. If the amount of metal ion in the aqueous phase was to be determined, aliquots of that phase were taken, the complexing agent was wet oxidized by a mixture of

concentrated nitric and perchloric acids, and the metal was analyzed by either a titrimetric or a colorimetric method. If the metal absorbed by the resin was to be determined, the equilibrated system was poured into a glass column equipped with a frit, and suction was applied at the bottom of the column to remove the aqueous phase. The resin was rapidly washed several times with water, and the metal on the resin was eluted with 50 ml. of 2 M hydrochloric acid. The excess acid was evaporated from the eluate before analysis.

The dry weight of the resin was calculated from the weight of air dried resin and the moisture content of the resin. The moisture content of the resin was determined by drying a weighed sample of the air dried resin in an oven at 100°C and placing the resin in a vacuum desiccator for five hours or more. These operations were repeated until a constant weight was obtained on two successive measurements.

Separation of Metal Ion Mixtures

For the separation of mixtures of metal ions a slurry of Chelex 100 Chelating Resin, 100-200 mesh, sodium form, was poured into a column which contained approximately 5 ml. of water until the resin column was 8 cm. high. The water was allowed to drain until the liquid level was approximately 1 cm. above the resin bed. A rubber stopper and

funnel were fitted into the column, and 50 ml. of eluting solution was added. When the level of this solution neared the top of the resin, a 25 ml. sample 0.01 M in each metal to be separated and 0.1 M in complexing agent (citric acid, sulfosalicylic acid, or hydrofluoric acid) which had been adjusted to the proper pH wereadded to the column at a 1 cm./sec. flow rate. Three 5 ml. portions of eluting solution were used to wash out the sample container and were added to the column when the level of the preceding portion of eluent neared the top of the resin bed. The separation was completed with 25 ml. of eluting solution. The metal which remained on the column was eluted with 25 ml. of 1 N hydrochloric acid for the elution of copper(II), nickel(II), cobalt(II), iron(III), and uranium(VI) or with 100 ml. of 1 M hydrochloric acid in the case of zinc(II) and cadmium (II).

The sulfosalicylic acid and citric acid solutions collected from the column were wet oxidized with nitric and perchloric acids prior to the analysis. The solutions of metals eluted by 25 ml. of hydrochloric acid were titrated directly after an adjustment to the proper pH. Solutions of those metals eluted by 100 ml. of hydrochloric acid were evaporated to dryness before the analysis.

DISCUSSION OF DISTRIBUTION COEFFICIENT DATA

In order to determine the optimum conditions for metal
ion separations, batch distribution coefficients for copper
(II), zinc(II), iron(III), aluminum(III), and uranium(VI) in
the presence of Dowex Chelating Resin A-1 and a water solu-
ble complexing agent were determined. If the quantity of
metal ion absorbed by the resin and that remaining in solu-
tion of an equilibrated system are known, the batch distri-
bution coefficient, D, can be calculated by Equation 1.

$$D = \frac{\text{amount of metal on resin/gm. of dry resin}}{\text{amount of metal in solution/ml. of solution}} \qquad (1)$$

This batch distribution coefficient is related to the
column distribution coefficient, D_v, by Equation 2.

$$D_v = D\rho \qquad (2)$$

where ρ is the density of the resin bed. The column distri-
bution coefficient can be used to determine the volume of
eluent required to elute the metal to the maximum of the
elution curve by calculating Equation 3.

$$D_v = \frac{v}{Ad} - i \qquad (3)$$

In this case, v is the volume of eluent (ml.) required to
move the metal band a distance d (cm.) down a column of
cross sectional area A (cm.^{2}) and of fractional interstitial

volume i.

For the purpose of this work it was sufficient to find conditions under which one component of a metal ion mixture exhibited a batch distribution coefficient near to or less than unity while that for the other component was as large as possible. If the difference in distribution coefficients of the two components is sufficiently large, column separations should be quantitative and rapid.

Distribution coefficients for copper(II), zinc(II), uranium(VI), iron(III), and aluminum(III) in the presence of sulfosalicylic acid are given in Table 1. Coefficients for these metals in the presence of citric acid are given in Table 2. The systems were buffered by glycine, formic acid, pyridine, and ammonium hydroxide at pH 2.5, 4.5, 6.0, and 8.0 and 9.5, respectively.

Table 1. Distribution coefficients of metal ions in the presence of sulfosalicylic acid

pH	Metal ion				
	Cu(II)	Zn(II)	Fe(III)	UO_2(II)	Al(III)
2.5	8,100	41	210	6,600	26
4.5	56,600	1,800	95	7,600	22
6.0	42,400	27,000	57	1,300	13
8.0	22,700	56,000	6.2	320	0.2
9.5	4,200	2,900	1.1	85	0.8

Table 2. Distribution coefficients of metal ions in the
presence of citric acid

pH	Metal ion				
	Cu(II)	Zn(II)	Fe(III)	UO_2(II)	Al(III)
2.5	5,400	95	8.3	80	13
4.5	2,000	50	1.4	18	4.7
6.0	4,500	81	5.6	10	0.0
8.0	2,200	330	2.6	2.9	0.3
9.5	42,500	25,500	5.3	0.4	6.4

There are many factors which influence the affinities
of the metal ions for the chelating sites on the resin in
the systems used for the measurements of the distribution
coefficients. The resin itself exhibits an intrinsic order
of selectivity for the metal ions similar to that of imino-
diacetic acid (12). The qualitative order of selectivity of
the resin has been reported to be Pd(II) > Cu(II) >>
Fe(II) > Ni(II) > Pb(II) > Mn(II) >> Ca(II) ≅ Mg(II) >>>
Na(I).

The nature of the complexes of the metal cations with
sulfosalicylic and citric acid under the conditions employed
in these studies would greatly influence the value of the
distribution coefficients. A neutral or negatively charged
complex would be more effective in reducing the magnitude of

the distribution coefficients than would a positively charged complex, which might be absorbed by the resin in the complex form. In addition, the larger the formation constant of a complex, the smaller should be the distribution coefficient of the complexed metal.

Banks and Singh (21, 22) have reported that copper(II) forms 1:1, $CuSSA^{-1}$, and 1:2, $Cu(SSA)_2^{-4}$, complexes with sulfosalicylic acid at pH 5.5 and 8.5, respectively. Log step-wise stability constants were reported to be 9.52 and 6.93. Turner and Anderson (23) found that the 1:1 complex was present in the pH range 3.0 to 5.5.

Agren (24) has found by potentiometric and photometric measurements that iron(III) forms 1:1, FeSSA, 1:2, $Fe(SSA)_2^{-3}$, and 1:3, $Fe(SSA)_3^{-6}$, complexes with sulfosalicylic acid at pH 2, 4, and 6 to 7, respectively. He reports the equilibrium constants for the reaction,

$$Fe^{+3} + nSSAH^{-2} \rightleftharpoons nH^+ + Fe(SSA)_n^{3-3n} \qquad (4)$$
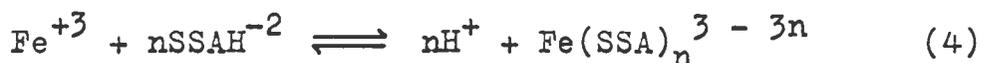
to be 480, 50, and 0.011 for n = 1, 2, and 3, respectively. Banks and Patterson (25) reported that a 1:3 complex exists in neutral and alkaline solution. They determined polarographically that three triply ionized sulfosalicylic acid ions are coordinated to each iron and estimated the log equilibrium constant for the reaction,

$$Fe^{+3} + 3SSAH^{-2} + 3OH^- \rightleftharpoons Fe(SSA)_3^{-6} + 3H_2O \qquad (5)$$
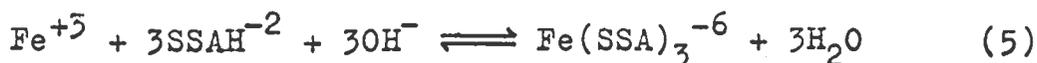
to be 42. Foley and Anderson (26), however, have shown that a 1:1 complex is stable up to pH 7.75 in phthalate and bicarbonate buffered solution.

Uranium(VI) forms 1:1, UO_2SSA^{-1}, and 1:2, $UO_2(SSA)_2^{-4}$, complexes with sulfosalicylic acid at pH 4.5 and 7.5 (22). The 1:2 complex forms only in the presence of a large excess of sulfosalicylic acid and tends to hydrolyze. Log stepwise stability constants for the complexes are 11.14 and 8.06. Foley and Anderson (27) state that the maximum stability of the 1:1 complex occurs at pH 4.5 to 4.7 and that dissociation of the complex at higher pH may result from the formation of UO_2OH^+.

Banks and Singh (22) also found that aluminum(III) forms 1:1, AlSSA, 1:2, $Al(SSA)_2^{-3}$, and 1:3, $Al(SSA)_3^{-6}$, complexes at pH 3.8, 5.5, and 8.5, respectively, with stepwise log stability constants of 13.20, 9.63, and 6.06. The 1:3 complex, however, forms only in the presence of excess sulfosalicylic acid.

Warner and Weber (28) by spectrophotometric and titrimetric methods determined that copper(II) forms a 1:1 chelate with citric acid at pH 6 to 7 in which four protons have been displaced from the citric acid. They also state that at lower pH values other 1:1 complexes exist in which fewer than four protons have been displaced. The log formation constant for the complex was found to be approximately

18. Parry and DuBois (29) found that for high citrate concentrations (30:1) at pH 2.9 a complex of the form $Cu(HCit)(H_2Cit)^-$ is stable with a log formation constant of 7.3. At lower citrate concentrations copper(II) adds to the complex with the liberation of a single proton to form $Cu_2(HCit)_2$. At very low citrate concentrations (1:2) $Cu_2C_6H_4O_7$, an insoluble solid, forms.

Li et al. (30) and Schubert et al. (31) calculated the log stability constant for a 1:1 zinc(II) citrate complex to be 4.85 and 4.71, respectively.

Hamm et al. (32) by a titrimetric procedure found that complexes of the form $FeHCit^{+1}$, $FeCit$, $FeOHCit^{-1}$, and $Fe(OH)_2Cit^{-2}$ exist in solutions containing a 1:1 ratio of complexing agent to metal, the dominant species depending upon the basicity of the solution. Log stability constants for the above species were found to be 6.3, 11.8, 9.4, and 1.9, respectively. Warner and Weber (28), however, report that a 1:1 chelate exists at about pH 3 in which four protons have been displaced from citric acid. The log stability constant for this complex was estimated to be 25.

Uranium(VI) was reported by Li et al. (30) to form a 1:1 complex of the form UO_2Cit^{-1} with citric acid in the pH range 1.9 to 2.5 with a log stability constant of 8.5. Feldman et al. (33) found that, in the presence of excess citric acid, a 1:1 tridentate complex exists as a dimer at

pH 3.5 to 4.5 in which two carboxyl groups and one hydroxyl group act as the coordinating groups.

Another important factor which influences the value of the distribution coefficients is the pH of the system in which the exchange is taking place. Since the functional groups on the chelating resin are salts of weak acids, the resin exhibits a high affinity for the hydrogen ion. It has been shown (12) that the resin will not appreciably absorb cations from a solution of pH less than 1. The affinity of metal ions for the resin increases sharply from pH 2 to 4, and most metals are quantitatively absorbed at pH values above 4.

Since the complexing agents used in this work are weak acids, an increase in basicity of the metal ion solution would also lead to more complete complexing of the metal. This phenomenon would tend to lower the value of the distribution coefficients.

In highly alkaline solutions many metal complexes hydrolyze to some extent. This could result either in the formation of different complex species as has been indicated for the iron(III) citrate complex or in the complete dissociation of the complex as has been reported for the uranium(VI) citrate complex.

The initial increase of the distribution coefficients in the lower pH region found in the copper(II) and zinc(II)

sulfosalicylic acid systems is probably caused by the increasing affinity of the chelating resin for cations in the pH range 2 to 4. The subsequent decline of distribution coefficients at the higher pH region for these metals may be the result of the increased association of the sulfosalicylic acid complexes. The tendency of zinc(II) to hydrolyze in alkaline solution to form the zincate ion would also contribute to the sharp decline of that distribution coefficient.

Iron(III), uranium(VI), and aluminum(III) exhibit a uniform decrease of distribution coefficient with increase in basicity, which indicates an increased stability of the sulfosalicylic acid complexes in the higher pH region.

The high stability of the citric acid complexes of iron(III), uranium(VI), and aluminum(III) is indicated by the relatively low distribution coefficients of the corresponding systems at all pH values above that at which the resin shows maximum absorption.

The sharp increase of distribution coefficient of the copper(II) and zinc(II) citrate systems at pH 9.5 may be caused by hydrolysis of the metal ion complexes to form species of the type $CuOH^{+1}$ and $ZnOH^{+1}$ (31).

RESULTS OF METAL ION SEPARATIONS

The distribution coefficients which were determined for citric acid and sulfosalicylic acid solutions indicate that iron(III) should be rapidly eluted from a column of chelating resin by a sulfosalicylic acid solution at pH 9.5 or by a citric acid solution at pH 4.5. Similar conditions for elution of uranium(VI) exist for citric acid elutions at pH 9.5. Aluminum(III) should be eluted rapidly by sulfosalicylic acid at pH 8.0 or 9.5 or by citric acid at pH 6.0 or 8.0. Under all of these conditions, the distribution coefficients indicate that weakly complexed metal ions such as copper(II) or zinc(II) should be absorbed by the resin strongly enough to permit separation of a mixture of these cations.

The results of separations which have been performed on columns of Chelex 100 Chelating Resin using a 0.1 M sulfosalicylic acid solution at pH 9.5 as eluting agent are given in Table 3. Separations utilizing 0.1 M citric acid at pH 6.0 and 9.5 as eluting agents are included in Table 4.

For the most part, iron(III) was rapidly eluted by sulfosalicylic acid at pH 9.5. However, considerable tailing of the iron occurred and traces of iron were found to remain on the column after the elution was completed. No measurable gain in iron recovery resulted from the use of an additional 25 ml. of eluting agent.

Table 3. Separation of metal ions by sulfosalicylic acid
elution, pH 9.5

Separation of M_1 from M_2	Mg. M_1 taken	Mg. M_1 found	Mg. M_2 taken	Mg. M_2 found
Cu-Fe	17.08	17.14	14.40	14.27
Ni-Fe	14.90	15.08, 15.08	14.40	14.22, 14.25
Zn-Fe	17.80	17.86, 17.96	14.51	14.10, 14.59
Cd-Fe	28.60	28.65, 28.48	14.51	14.17, 14.29
Cu-Al	17.08	17.08, 17.11	6.82	6.77, 6.84
Ni-Al	14.90	15.02, 15.08	6.82	6.86, 6.88

Table 4. Separation of metal ions by citric acid elution

Separation of M_1 from M_2	pH	Mg. M_1 taken	Mg. M_1 found	Mg. M_2 taken	Mg. M_2 found
Cu-Al	6.0	17.08	16.51, 16.48	6.77	6.66, 6.70
Ni-Al	6.0	14.90	14.84, 14.79	6.82	6.81, 6.58
Zn-Al	6.0	17.80	17.64, 17.48	6.82	6.84, 6.81
Cd-Al	6.0	28.60	27.82, 27.65	6.82	6.88, 6.94
Cu-U	9.5	17.08	17.08, 17.08	60.97	57.19, 57.91
Ni-U	9.5	14.90	14.87, 14.56	60.97	57.67, 57.91

Only 95 per cent of the uranium(VI) was rapidly eluted by citric acid at pH 9.5, and further elution with an additional 25 ml. of citric acid did not produce a measurable increase in the uranium recovery. A light yellow band observed near the top of the resin column was assumed to be the remainder of the uranium.

Under both of the above conditions, copper(II), zinc(II), cadmium(II), and nickel(II) were quantitatively retained as narrow bands at the top of the resin columns.

Partial elution of copper(II) by citric acid at pH 6.0 was observed as a blue color in the first fractions of eluent from the column. Most of the copper, however, was retained as a sharp band at the top of the column.

Zinc(II), cadmium(II), and nickel(II) are quantitatively absorbed by the resin during elutions with citric acid at pH 6.0, while aluminum(III) is eluted either by these conditions or by sulfosalicylic acid elutions at pH 9.5.

Cobalt(II) was very slowly eluted by citric acid at pH 6.0 and penetrated throughout the length of the column. Elutions with citric acid and sulfosalicylic acid at pH 9.5 resulted in a splitting of the cobalt so that part was rapidly eluted from the column while the remainder was strongly absorbed at the top of the column. Because of this erratic behavior, no attempt was made to include cobalt in these separations.

Since the fluoride ion is a very selective complexing agent, it was assumed that solutions of fluoride would be good eluting agents for the separation of metal ion mixtures using columns of chelating resin. Upon elution with a 0.1 M hydrofluoric acid-0.1 M sodium fluoride solution at pH 4.0, it was found that copper(II), nickel(II), zinc(II), and cadmium(II) were quantitatively absorbed by a column of chelating resin while iron(III) and uranium(VI) are rapidly eluted. Although the results for the analysis of zirconium(IV) in the fluoride eluent were erratic, successful analysis of those metals absorbed by the resin indicates that the elution of zirconium is essentially quantitative, since more than trace amounts of zirconium interfere in the procedure used for the analysis (14). Cobalt(II) and aluminum(III) are only partially eluted under these conditions. Results of separations attempted by this procedure are given in Table 5.

If a 0.1 M hydrofluoric acid solution at pH 5.5 is employed as the eluting agent, cobalt(II), iron(III), and uranium(VI), in addition to those reported above, are quantitatively absorbed by the resin. No zirconium(IV) or aluminum(III) was found in the hydrochloric acid eluent in this case, although erratic results were once again obtained in attempts to analyze for these metals in the fluoride eluent. Results of separations by this procedure are given in

Table 6.

Table 5. Separation of metal ions by elution with 0.1 M
          hydrofluoric acid-0.1 M sodium fluoride, pH 4.0

Separation of M_1 from M_2	Mg. M_1 taken	Mg. M_1 found	Mg. M_2 taken	Mg. M_2 found
Cu-Fe	17.08	17.11	14.46	14.38
Ni-Fe	14.84	14.93	14.46	14.46
Cu-U	17.08	17.02, 17.08	60.87	60.46, 60.15
Ni-U	14.84	14.99	60.87	60.72
Cu-Zr	17.08	16.98, 17.08	--	--
Ni-Zr	14.84	14.96	--	--
Zn-Zr	17.83	17.90, 17.96	--	--
Cd-Zr	28.60	28.38, 28.38	--	--

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Table 6. Separation of metal ions by elution with 0.1 M
hydrofluoric acid, pH 5.5

Separation of M_1 from M_2	Mg. M_1 taken	Mg. M_1 found
Cu-Zr	17.08	17.08, 17.02
Ni-Zr	14.84	14.93, 14.84
Co-Zr	14.44	14.50, 14.50
Zn-Zr	17.83	17.90, 17.86
Fe-Zr	14.51	14.54, 14.54
U -Zr	61.03	60.82, 61.55
Zn-Al	17.83	17.80
Cd-Al	28.60	28.31
Co-Al	14.44	14.56, 14.44
Fe-Al	14.46	14.56, 14.36

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