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Ion-exchange elution sequences with chelating eluants

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ION-EXCHANGE ELUTION SEQUENCES
WITH CHELATING ELUANTS

by

Dean B. James

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry⁶⁶

Approved:

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1960

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INTRODUCTION

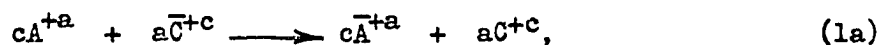
Ion exchange may be broadly defined as any exchange of ions, reversible or irreversible, between any two phases. However, in this dissertation ion exchange shall have the limited definition of a reversible exchange of ions between a solid phase consisting of a synthetic ion-exchange resin and an aqueous phase. Other terminology pertaining to this field are used as defined by Arden (1).

The cation-exchange resin used was Amberlite IR-120-X8, a sulfonated copolymer of divinylbenzene and styrene, supplied by Rohm and Haas Company, Philadelphia, Pennsylvania. The anion-exchange resin used was Amberlite IRA-400, also supplied by Rohm and Haas, which has a quaternary ammonium group on a polystyrene lattice.

All the ion-exchange separation processes used in this work were vertical column operations (see Appendix B), using downward flow of the solution phase. The temperature was about 25° C, unless otherwise specified.

Chromatographic Ion-Exchange Separations

In all ion-exchange separations the material to be separated is loaded on the resin by displacing the replaceable ion, hereafter called the retaining ion. Differences in resin selectivity may cause some separation during the loading operation. The load is then developed by elution with an appropriate eluant. The exchangeable ion A^{+a} in the eluant displaces the ions, B^{+b} and C^{+c} , of the mixture absorbed on the resin as in the reactions:



where the bars indicate components in the resin phase. These reactions are forced to the right by one or more of the following causes:

- (1) a greater affinity of the resin for A^{+a} than for B^{+b} or C^{+c} ,
- (2) simple mass action, and
- (3) any of the conventional solution phase phenomena which drive equilibrium reactions to completion, such as complex formation or the formation of a new phase.

As the eluant, which now contains at least some \bar{B}^{+b} and \bar{C}^{+c} , passes over the rest of the mixture of \bar{B}^{+b} and \bar{C}^{+c} , the reaction,



can proceed to the right or left according to three factors similar to those given above. These are

- (1') differences in the resin affinity for B^{+b} and C^{+c} ,
- (2') simple mass action, and
- (3') formation of complexes of B^{+b} and C^{+c} to varying degrees in the aqueous phase, which alter the relative availabilities of B^{+b} and C^{+c} for exchange.

This action, coupled with the initial displacement, is what effects the separation. Ion-exchange separation processes can be divided into two general categories, namely, elution and displacement chromatography.

Elution chromatography

If factor 2 is the only one applicable during the displacement, that is, the resin has a greater affinity for B^{+b} and C^{+c} than for A^{+a} and none of the aqueous phenomena of factor 3 occur, then the initial exchange of A^{+a} for B^{+b} or C^{+c} will be poor; and the solution that passes over the absorbed band of \bar{B}^{+b} and \bar{C}^{+c} will contain much A^{+a} . As the solution passes over this resin, however, more and more of \bar{B}^{+b} and \bar{C}^{+c} are removed, depending on factors 1', 2' and 3'. When this solution strikes the retaining ion \bar{D}^{+d} , which is absorbed ahead of the separating mixture, the opposite of reactions (1) and (1a) occur,



Factors similar to 1, 2 and 3 govern these exchanges also. If, as before, factor 2 is the only important one, the exchanges will be poor. Curves of the concentration of the separating ions versus volume of eluate take on a bell-shaped appearance. These "bells" separate completely from one another and become more flat as elution proceeds.

Displacement chromatography

If either or both of the factors 1 and 3 apply during the displacement step, then a displacement chromatogram results. At this point the concentration of A^{+a} in the aqueous phase drops sharply to near zero, and the total of the equivalent concentrations of B^{+b} and C^{+c} rises to near the original equivalent concentration of A^{+a} . The factors affecting separation can be any of all of 1', 2' or 3'. The retaining ion D^{+d} can be such that its displacement by the separating band is governed by any

or all of factors similar to 1, 2, and 3. If these factors allow the equilibrium (2) to lie further to the right, then B^{+b} will precede C^{+c} down the column. Two bands within the total separating band will result. However, these two bands will not separate from one another as in the case of elution chromatography, and the overall band will not increase in length after having progressed one or two band lengths.

The Separation of the Rare Earths by Ion Exchange

A classical problem that was solved by the use of ion-exchange chromatography was the separation of the rare-earth elements. The initial work was carried on at this laboratory (2,3,4,5,6) and elsewhere (7,8,9,10,11,12,13,14). The eluant was a 5% solution of citric acid-ammonium citrate in the pH range of 3 to 5. The retaining ion was hydrogen. With a high concentration of hydrogen ions in the eluant the complexing action of the citrate ion was impaired. The initial displacement from the resin was due, for the most part, to simple mass action, since most of the citric acid was undissociated. Therefore, typical "bell-shaped" elution chromatograms resulted, even though sufficient citrate ion was present to allow for some complexing of the rare-earth ions in the aqueous phase and to effect some separation. This method required the elution of the absorbed band for relatively great distances. Even then many of the separations were poor for macro-quantities of rare earths. Trace quantities of rare earths, such as those resulting from nuclear reactions, are easily separated by this method. In this case the initially absorbed band of rare earths is short compared to the column dimensions and elution for many

band lengths is easy and quick. Also, the bands of individual rare earths are separated from one another by hydrogen and ammonium ions. A displacement chromatogram with its "head-to-tail" separation would be impractical with such short bands.

When Spedding and his co-workers raised the pH of the eluant to higher values, finally choosing 8.0, better and more easily attainable separations were possible (15,16,17,18,19,20,21,22). Under these conditions the eluant displaces the rare-earth ions from the resin, due to the formation of the stable citrate complexes in the aqueous phase. Separations are possible in a shorter distance because the separation factor is due, for the most part, to the differences in the stability of these complexes. A sharp boundary is maintained at the front edge of the rare-earth band, due to the formation of the undissociated citric acid when the rare-earth-citrate complexes contact the hydrogen-form resin. A typical displacement chromatogram results.

Even better separations were attained when the chelating eluant was changed to ethylenediaminetetraacetic acid (EDTA) at a pH of 8.4 with ammonium hydroxide (23). As in the high pH case with ammonium citrate, a sharp boundary is maintained at the rear edge of the rare-earth band, due to the formation of stable rare-earth-EDTA complexes;



where \bar{R}^{+3} stands for the rare-earth ion and Y^{-4} for the EDTA anion.

As this reaction takes place, the pH drops from 8.4 to about 2.3. At this pH the species HRY is about 90% dissociated. These details will

receive further consideration later. Once again, the major factor affecting the separation is the differences in stability of the EDTA complexes formed with the rare earths. Since the free acid of EDTA is quite insoluble, hydrogen ion cannot be used successfully as a retaining ion. However, any metal ion which forms a more stable complex with EDTA than the rare earths form would suffice. When the rare-earth-EDTA complex contacts this metal ion on the resin, exchange occurs because of the formation of the more stable complex. However, the resin has a greater affinity (selectivity coefficient of approximately 10^2) for the trivalent ion than the divalent ion. This, coupled with other factors which are a major topic of this thesis, allows the use of divalent metal ions whose complexes with EDTA are less stable than those of the rare earths. The first retaining ion tried was ferric ion (24), but it has two serious limitations. First, because of the insolubility of ferric hydroxide, the range of the pH of the eluant is rather limited. Second, the iron (III) complex with EDTA is quite easily reduced to the iron (II) complex. Since $\overline{\text{Fe}^{+2}}$ will retain only Nd, Pr, Ce, and La, iron "trails" into the rare-earth band as far back as Nd.

Cupric ion was used as a retaining ion for all of the rare earths although its stability constant is over ten times smaller than that of the most stable rare-earth complex (25). This ion proved to be nearly ideal, and the process has been developed to such an extent that it is now possible to separate half-ton quantities of rare-earth mixtures in one elution. However, the pressing need for pure rare earths has caused the technology to develop faster than the theory, and the optimum conditions of 0.015 molar EDTA at a pH of 8.4 were determined, more or

less, by trial and error (26,27).

Another chelating agent has proved successful in the separation of the rare earths by ion exchange. The differences of the stability constants of the heavy rare earths with N-hydroxyethyl-N,N',N'-ethylenediaminetriacetic acid (HEDTA) are smaller than for EDTA, but kinetic factors allow faster flow rates and consequently easier separations (28,29). Separation of the elements Ho through Sm is difficult with this eluant, and light rare earths separate with about the same ease enjoyed with EDTA. The free acid of HEDTA is much more soluble than that of EDTA, which allows hydrogen ion to be used as a retaining ion. This fact makes the use of HEDTA more desirable, since the Cu-EDTA complex, resulting from elution with EDTA, is difficult to break without destroying the chelating agent. If this were possible, the cupric ion and the EDTA could be recycled. Recycling the free HEDTA requires only the addition of ammonium hydroxide.

With EDTA the concentration of the eluant is dictated by the low solubility of the Cu-EDTA complexes. With HEDTA the low solubility of the heavy rare-earth complexes requires the eluant concentration to be less than 5 grams per liter, but the concentration can be raised to 10 grams per liter when the light rare earths are being eluted. The optimum pH for HEDTA is 7.5.

Powell and Spedding have presented a workable theory for describing these separations (29). These systems can be conveniently compared to a two-phase counter-current separation with the solution moving downward and the resin "moving" upward. The separation factor is conventionally defined as the ratio of the concentrations of the separating species

in one phase, divided by this ratio in the other phase. Therefore, the separation factor α shall be defined as,

$$\alpha = \frac{[\bar{R}_1^{+3}] [R_{T2}]}{[R_2^{+3}] [R_{T1}]} \quad (4)$$

where $[\bar{R}_i^{+3}]$ stands for the mole fraction of the i th rare earth in the resin phase and $[R_{T_i}]$ stands for the total concentration in moles per liter of the i th rare earth in the aqueous phase, which is given by,

$$[R_{T_i}] = [R_i^{+3}] + [R_i Y^-] + [HR_i Y] + [R_i Y(OH)^{-2}]. \quad (5)$$

It has been shown that no hydrolytic species appear below a pH of seven (30). Since the pH of the eluate is approximately three, $[R_i Y(OH)^{-2}]$ is probably insignificant. Because of the extreme stability of the complexes, $[R_i^{+3}]$ is also probably insignificant. As will be indicated in a later portion, $[HR_i Y]$ may be significant; but its contribution to $[R_{T_i}]$ is probably so nearly the same for adjacent rare earths that it does not affect the ratio $[R_{T_2}]/[R_{T_1}]$ appreciably. Therefore, Powell and Spedding assume that,

$$\frac{[R_{T_2}]}{[R_{T_1}]} = \frac{[R_2 Y^-]}{[R_1 Y^-]} \quad (6)$$

Since the resin is not appreciably selective as far as two adjacent rare earths are concerned, they further assume that the selectivity coefficient is unity. Then,

$$\frac{[\bar{R}_1^{+3}]}{[\bar{R}_2^{+3}]} = \frac{[R_1^{+3}]}{[R_2^{+3}]} \quad (7)$$

A combination of equations (6) and (7) with equation (4) yields,

$$\alpha = \frac{[R_1^{+3}] [R_2 Y^-]}{[R_2^{+3}] [R_1 Y^-]} \quad (4a)$$

If the stability constant for a metal-EDTA complex is defined in general as,

$$K_{MY^{(n-4)}}^{M^{+n}} = \frac{[MY^{(n-4)}]}{[M^{+n}] [Y^{-4}]} \quad (8)$$

then equation (4a) becomes,

$$\alpha = \frac{K_{R_2 Y^-}^{R_2^{+3}}}{K_{R_1 Y^-}^{R_1^{+3}}} \quad (4b)$$

From the separation factor α by a calculation similar to that used with all counter-current systems, Powell and Spedding predict theoretical plate heights and necessary elution distances in good agreement with experiment. The stability constants which they used were determined at an ionic strength of one-tenth, but the eluant concentration was 0.015 molar. They assumed that ionic-strength changes would affect both constants to the same extent and that the change would be cancelled when a ratio of stability constants was considered. Since the stability constants for the rare-earth-EDTA complexes increase directly with

atomic number, the rare earths elute in reverse order of their atomic numbers with yttrium between dysprosium and terbium.

Several factors have prompted the author to extend these investigations to include common divalent and trivalent cations. These ions are also chelated to varying degrees by EDTA. According to their stability constants, resin affinities, and other factors, they may elute ahead of the rare earths, as do Cu^{+2} and Fe^{+3} , behind them, or even sandwiched between two rare earths.

Because the initial separations of the rare earths from other common elements occurring in their ores are not perfect, trace amounts of these elements may be loaded on the resin with the rare earths. If these elements elute among the rare earths, they contaminate the final product. If the elution sequence were completely established, it would be obvious which ions could be used as retaining ions. Vickery has suggested that if a common element elutes between two rare earths, then large amounts of that element could be added to the rare-earth mixture to act as a wedge, allowing faster and easier separation of the two adjacent rare earths (31).

ELUTION SEQUENCES

During the past ten years, the technology involved in the separation of the rare earths by ion-exchange elution with chelating eluants has developed to the point that large quantities of spectrographically-pure individual rare earths are now available. This technology would be furthered if the elution sequences of all cations were known under the conditions used for the separation of the rare earths. Analysis for non-rare-earth contamination in the final product would be easier, other retaining ions might be suggested, and non-rare-earth cation "wedges" might be used to aid the separation of troublesome mixtures.

Three chelating agents, EDTA, HEDTA and citric acid, have gained considerable use for the separation of large amounts of the rare earths. The author has determined the complete sequences for these eluants. Nitritotriacetic acid (NTA) and diethylenetriamine-N,N,N',N',N''-pentaacetic acid (DTPA) have found some use, and the partial elution sequences, as determined by other workers in this laboratory, are given for these chelating agents.

All the experiments reported in this work were carried out in glass columns with inside diameters of one inch. The resin beds were approximately four feet long, and the columns were connected in series. The mixtures to be separated were prepared from appropriate salts or oxides, and they contained an equal amount of each element on an equivalent basis. Between three and ten elements were loaded in each run in order to facilitate the final analysis. Usually one tenth of an equivalent of each element was used. This produced separated

individual bands about three inches long. The total absorbed band was eluted approximately three band lengths in each run. This distance was usually adequate to effect a separation of sufficient quality to make the order of elution obvious. The eluate was caught in successive, approximately equal fractions. A detailed description of these methods and the methods of analysis is given in Appendix B.

Complete Sequences under Pilot-Plant Conditions

EDTA

The optimum eluant for the separation of the rare earths with EDTA appears to be a 0.015M solution, raised to a pH of 8.4 with ammonium hydroxide. Therefore, the elution sequence was determined under these conditions. Eleven runs were made with this eluant, and the results are given in Table 1. The ions in parentheses were not sufficiently separated to allow positive identification of the order. The retaining ion was Cu^{+2} unless otherwise specified.

The Fe (II) complex with EDTA is easily oxidized to the Fe (III) complex. When Fe^{+2} was investigated in run V, most of it was air oxidized to Fe^{+3} . Since Fe^{+3} is not retained by Cu^{+2} , most of it was lost. However, this oxidation is slow; and some iron was present throughout the samarium band back as far as UO_2^{+2} , which eluted between Sm^{+3} and Nd^{+3} . Therefore, it was concluded that Fe^{+2} elutes between Sm^{+3} and UO_2^{+2} . Aluminum was very poorly separated from the rare earths, but it was found very slightly concentrated before Ho^{+3} in run VI and behind Cd^{+2} in run I. The Co(II) complex is also air oxidized to the Co(III) complex, but not as easily as Fe(II) to Fe(III). The divalent

Table 1. Sequence determination runs for EDTA

Run number	Elution sequence
I	$\text{Cu}^{+2}, \text{Pb}^{+2}, \text{Zn}^{+2}, \text{Co}^{+2}, \text{Cd}^{+2}, \text{Al}^{+3}$
II	$\text{Th}^{+4}, \text{Pb}^{+2}, \text{Lu}^{+3}, \text{Yb}^{+3}$
III	$\text{Yb}^{+3}, \text{Zn}^{+2}, \text{Tm}^{+3}, \text{Co}^{+2}, \text{Er}^{+3}, \text{Cd}^{+2}, \text{Ho}^{+3}$
IV	$\text{Dy}^{+3}, \text{Y}^{+3}, \text{Sm}^{+3}, \text{UO}^{+2}, \text{Nd}^{+3}$
V	$\text{Sm}^{+3}, \text{Fe}^{+2}, \text{UO}^{+2}, \text{Nd}^{+3}$
VI	$\text{Al}^{+3}, \text{Ho}^{+3}, \text{Dy}^{+3}, \text{Y}^{+3}$
VII	$\text{Cu}^{+2}, \text{Ni}^{+2}, \text{Th}^{+4}$
VIII ^a	$(\text{Co}^{+3}, \text{Bi}^{+3}), \text{Fe}^{+3}, \text{Sc}^{+3}, \text{Cu}^{+2}, \text{Co}^{+2}$
IX ^b	$\text{Co}^{+3}, \text{Bi}^{+3}$
X	$\text{La}^{+3}, \text{Ca}^{+2}, \text{Mg}^{+2}, \text{Be}^{+2}, \text{Sr}^{+2}, \text{Ba}^{+2}$
XI	$\text{Nd}^{+3}, \text{Pr}^{+3}, \text{Mn}^{+2}, \text{Ce}^{+3}, \text{La}^{+3}$

^a Retaining ion was Fe^{+3}

^b Retaining ion was Bi^{+3}

complex of cobalt is a barn red, while the trivalent complex is a very intense purple. Although a large portion of the cobalt which was originally loaded remains as Co^{+2} and forms a well-characterized band, cobalt was found in all the eluate ahead of the Co^{+2} band. Under the conditions of this eluant, Co^{+3} along with Sc^{+3} , Fe^{+3} and Bi^{+3} was not retained by Cu^{+2} . When any of these elements were loaded in a mixture, they did not appear in the eluate if Cu^{+2} were used as a retaining ion. Of course, cobalt could not be loaded as $\text{Co}(\text{III})$, for this ion is not stable in aqueous solution in an uncomplexed form. A solution of

Co(III)-EDTA was prepared by oxidizing a boiling solution equal-molar of cobalt (II) nitrate and the disodium salt of EDTA with 3% hydrogen peroxide. The resulting deep-purple solution was adjusted to a pH of about three with ammonium hydroxide. When the solution was passed over a column containing Bi⁺³, no cobalt was retained by the resin. This established the order Co⁺³, Bi⁺³. When a mixture of Bi⁺³, Sc⁺³, Cu⁺² and Co⁺² was eluted in run VIII with Fe⁺³ as the retaining ion, only Co⁺³ and Bi⁺³ were not retained. The reaction of Cr⁺³ with EDTA is kinetically too slow for it to be eluted under these conditions. The results in Table 1 completely establish the elution sequence for 0.015M EDTA at a pH of 8.4:

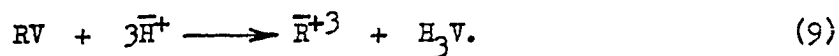
Co⁺³, Bi⁺³, Fe⁺³, Sc⁺³, Cu⁺², Ni⁺², Th⁺⁴,
 Pb⁺², Lu⁺³, Yb⁺³, Zn⁺², Tm⁺³, Co⁺², Er⁺³,
 Cd⁺², Al⁺³, Ho⁺³, Dy⁺³, Y⁺³, Tb⁺³, Gd⁺³,
 Sm⁺³, Fe⁺², UO₂⁺², Nd⁺³, Pr⁺³, Mn⁺², Ce⁺³,
 La⁺³, Ca⁺², Mg⁺², Be⁺², Sr⁺², Ba⁺².

HEDTA

The conditions used by Powell and Spedding (29) for elutions with HEDTA were a 0.018M solution, raised to a pH of 7.5 with ammonium hydroxide. The elution sequence for HEDTA was determined under these conditions. When hydrogen ion is used as a retaining ion for elutions with HEDTA, a phenomenon which is foreign to other chelating agents of this type occurs.

The separating mixture is redeposited at the front edge of the absorbed band when the HEDTA complexes contact the hydrogen ion on the resin. This happens because the hydrogen ion associates with the HEDTA

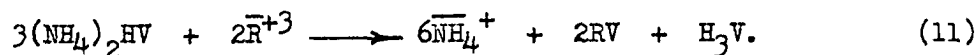
anion, hereafter indicated as V^{-3} , to form a more stable species than the rare-earth-complexes;



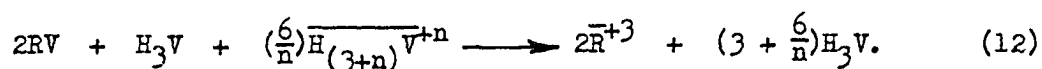
The free HEDTA then passes over more hydrogen ion which is absorbed on the resin. It immediately associates with the hydrogen ion to form on the resin a species of the form $\overline{H_{(3+n)}V^{+n}}$;



Since HEDTA, neutralized to a pH of 7.5 with ammonium hydroxide, is approximately the diammonium salt, reaction (11) occurs as the rare earths are desorbed:



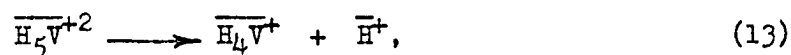
One mole of free acid is formed for each two moles of rare earth chelated because of the greater affinity of the resin for ammonium ion than hydrogen ion, and the greater affinity of V^{-3} for hydrogen ion than ammonium ion. At the front edge of the rare-earth band reaction (12) occurs;



Inspection of reactions (11) and (12) indicates that the concentration of HEDTA in the solution passing over this unknown band is greater than that in the eluant by an additive factor of $2/n$. If n is greater than zero, the band of this unknown species $\overline{H_{(3+n)}V^{+n}}$ will grow in length as elution proceeds. Its rear boundary will move at the same rate as the

rare-earth band, which stays at a constant length. However, the front boundary will move at a rate which is $(n + 2)/n$ times faster, and pure water will pass from the column until this front boundary passes from the column. This is what is observed.

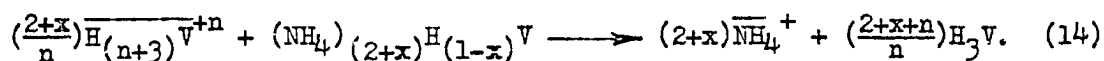
The value of n was determined. Since the concentration of the eluate is about two times that of the eluant, n is approximately two. That is, the unknown resin species is probably $\overline{H_5V^{+2}}$. It must be kept in mind, however, that the exact position of the equilibrium,



cannot be determined without disturbing it; it occurs entirely within the resin phase. But the very fact that it cannot be detected means it has no effect on the manner in which this resin will behave. In subsequent discussions, therefore, the assumption will be made that the species $\overline{H_4V^+}$ and $\overline{H^+}$ cannot "exist" together, since they might as well be considered as $\overline{H_5V^{+2}}$.

In successive experiments eluants of different concentrations, all nearly $(NH_4)_2HV$, were passed over resin beds in the hydrogen form. After the band of $\overline{H_{(3+n)}V^{+n}}$ began to pass from the column, the concentration of H_3V in the eluate was measured in every case. A detailed description of these experiments can be found in appendix B.

Of course, it is difficult to prepare eluants that have an exact ammonium ion concentration equivalent to that of $(NH_4)_2HV$. If x is the amount of ammonium ion exceeding a concentration equivalent to that of $(NH_4)_2HV$, then,



The ratio of the concentration of HEDTA in the eluant to that in the eluate is,

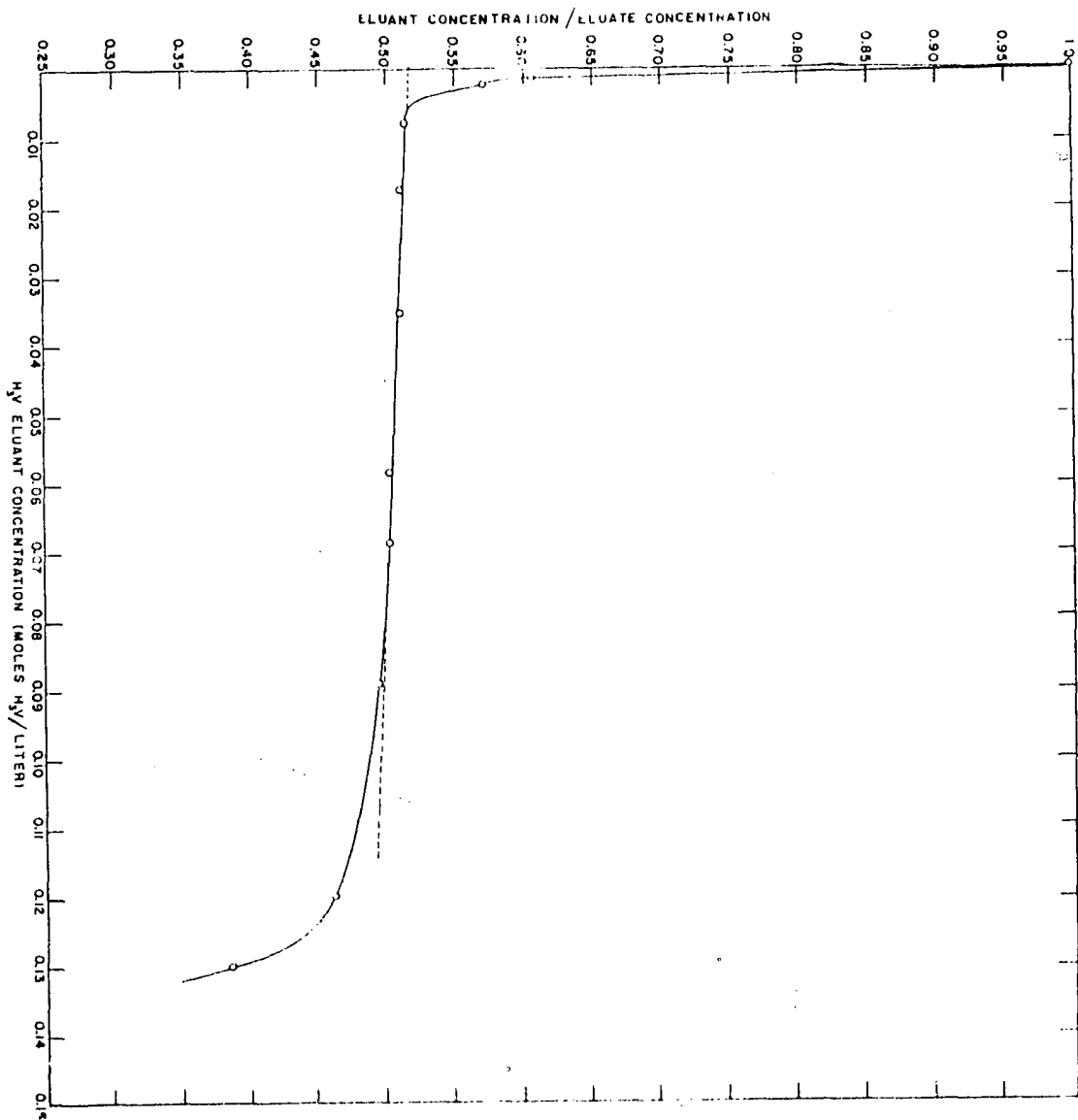
$$r = \frac{n}{2 + x + n}. \quad (15)$$

The experimental determination of r and x allowed the calculation of n for various eluate concentrations according to the relationship.

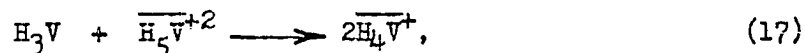
$$n = \frac{r(2+x)}{r-1}. \quad (16)$$

Figure 1 is a plot of r versus the concentration of the eluant in which r has been corrected to the value it would assume if x were zero. Over a range of eluant concentrations of 0.006M to 0.08M, r assumes the nearly constant value of one half, giving n a value of two in this range, within the experimental error. The slight slope of the curve in this region is probably an ionic strength effect. At low eluant concentrations r approaches unity because of mass action, indicating that the resin in the $\overline{H_5V}^{+2}$ form can be restored to the hydrogen form by simply washing the resin with water. At high concentrations of the eluant the value of r drops below one half because mass action begins to force the molecules of HEDTA to occupy only one site on the resin lattice. The occupancy of two sites would be expected if one assumes that both nitrogen atoms in the HEDTA molecule can accept a proton. This is not unreasonable, since the hydrogen ion "concentration" is very high within the resin lattice. However, the species H_3V is uncharged and, therefore, relatively free to migrate into the resin lattice. High concentrations

Figure 1. Eluant to eluate concentration ratio verses eluant concentration for elutions with 0.018M $(\text{NH}_4)_2\text{HV}$.



of H_3V force the reaction,

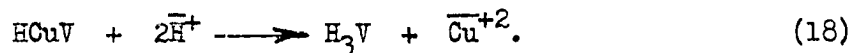


to the right. At the concentrations used to separate the rare earths, the resin species is most certainly $\overline{H_5V}^{+2}$.

Twelve runs were made in order to determine the elution sequence with HEDTA. Hydrogen ion was used as a retaining ion, unless otherwise stated. The results of these experiments are given in Table 2. The ions within the parentheses were not sufficiently separated to allow positive identification of the order.

As is the case with EDTA, the cobalt(II) complex is air-oxidized to the cobalt(III) complex. Co^{+3} , Bi^{+3} , Cu^{+2} and Ni^{+2} were not retained by the acid form of the resin when eluted with HEDTA. The exact nature of the interaction of these metal-ion complexes with the band of $\overline{H_5V}^{+2}$ was determined.

A solution of $HCuV$ was added to a known number of equivalents of oven-dried resin in the hydrogen form. The preparation and properties of metal-chelate compounds, such as $HCuV$, are discussed in a later portion of this dissertation. After equilibrium was reached, the amount of replaceable hydrogen in the solution was determined. The amount of hydrogen ion in the aqueous phase was greater than that introduced by adding $HCuV$. Reaction (18) explains this result;



Reaction (18) is driven to the right by the stability of H_3V and the greater affinity of the resin for Cu^{+2} than for H^+ .

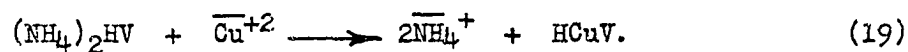
Table 2. Sequence determination runs for HEDTA

Run number	Elution sequence
I	Lu ⁺³ , Yb ⁺³ , Th ⁺⁴ , Tm ⁺³
II	Zn ⁺² , Pb ⁺² , Co ⁺² , Cd ⁺²
III	Ca ⁺² , Lu ⁺³
IV	(Yb ⁺³ , Er ⁺³ , Al ⁺³ , Dy ⁺³ , Sm ⁺³), Nd ⁺³ , La ⁺³
V	Sm ⁺³ , (UO ₂ ⁺² , Nd ⁺³), Pr ⁺³
VI	Sm ⁺³ , Nd ⁺³ , Pr ⁺³ , Ce ⁺³ , Mn ⁺² , La ⁺³
VII	H ₅ V ⁺² , Fe ⁺³ , Cr ⁺³ , Zn ⁺² , Pb ⁺² , Co ⁺² , Cd ⁺²
VIII	Yb ⁺³ , Tm ⁺³ , Al ⁺³ , Er ⁺³ , Ho ⁺³ , Dy ⁺³
IX	Sm ⁺³ , Y ⁺³ , Nd ⁺³ , Pr ⁺³
X	La ⁺³ , Ca ⁺² , Mg ⁺² , Be ⁺² , Sr ⁺² , Ba ⁺²
XI ^a	Bi ⁺³ , Cu ⁺² , Ni ⁺²
XII ^b	Co ⁺³ , Bi ⁺³

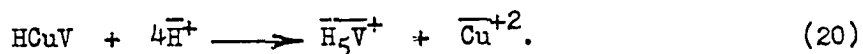
^aRetaining ion of Cu⁺²

^bRetaining ion of Bi⁺³

Similar to the case of the rare earths in reaction (11), when $\overline{\text{Cu}^{+2}}$ is eluted on a hydrogen form resin with the diammonium salt of HEDTA,



However, when HCuV strikes the $\overline{\text{H}_5\text{V}^{+2}}$ band, no reaction occurs. It passes over this band and remains intact until it strikes the free hydrogen form resin ahead of the growing $\overline{\text{H}_5\text{V}^{+2}}$ band;



The band that forms is a mixture of $\overline{\text{Cu}}^{+2}$ and $\overline{\text{H}_5\text{V}}^{+2}$ and not $\overline{\text{H}_3\text{CuV}}^{+2}$, for if this species were formed, the experiment described by reaction (18) would have yielded no excess hydrogen ion. This mixed band grows to twice the length which would be expected from the amount of copper in the original separating mixture because half of it is $\overline{\text{H}_5\text{V}}^{+2}$. The mixed $\overline{\text{Cu}}^{+2}$ - $\overline{\text{H}_5\text{V}}^{+2}$ band then remains a constant length and moves at the same rate as the front boundary of the pure $\overline{\text{H}_5\text{V}}^{+2}$ band. The copper is removed from the mixed band at the rear edge by the reaction,



and then redeposited at the front edge by reaction (20). Comparable reactions must apply to nickel, since it behaves similarly. Since Bi^{+3} and Co^{+3} are immediately displaced from the column, reaction (20) probably does not apply to them.

To determine the order of the four ions which were not retained by hydrogen ion, Cu^{+2} was used as a retaining ion; and in run XI a mixture of Bi^{+3} and Ni^{+2} was eluted with HEDTA. Only Ni^{+2} was retained. Co(III)-HEDTA was prepared in a manner similar to that described for the preparation of Co(III)-EDTA in the preceding section. The Co(III)-HEDTA complex was not retained by a resin in the Cu^{+2} form or one in the Bi^{+3} form. Thus the order, Co^{+3} , Bi^{+3} , H^+ , Cu^{+2} , Ni^{+2} and H_5V^{+2} , was established.

Chromium(III) was loaded as the chloride, forming a green band on the resin. As elution proceeded, this green band was slowly removed;

and a violet Cr(III)-HEDTA complex was formed and appeared to concentrate just behind Fe⁺³. However, the separation is quite poor; Cr(III) was detected throughout the remaining band of ions.

Th⁺⁴ elutes between Yb⁺³ and Tm⁺³, but the separation is quite poor. Any Th⁺⁴ that is present will contaminate both of these rare earths, especially the Yb⁺³.

The separation of Al⁺³ from the rare earths was also very poor. It was always detected throughout the rare-earth band, and it was difficult to determine any position that Al⁺³ preferred. A slight increase in the concentration of aluminum between Tm⁺³ and Er⁺³ indicated that this may be the position that Al⁺³ seeks.

The separation of UO₂⁺² from the light rare earths was poorer, but a definite increase in the concentration of uranium between Sm⁺³ and Y⁺³ established the order.

From the data in Table 2 it can be seen that the elution sequence with 0.018M HEDTA at a pH of 7.4 with ammonium hydroxide is:

Co⁺³, Bi⁺³, H⁺, Cu⁺², Ni⁺², H₅V⁺², Fe⁺³, Cr⁺³, Zn⁺², Pb⁺²,
 Co⁺², Cd⁺², Lu⁺³, Yb⁺³, Th⁺⁴, Tm⁺³, Al⁺³, Er⁺³, Ho⁺³,
 Dy⁺³, Tb⁺³, Gd⁺³, Eu⁺³, Sm⁺³, UO₂⁺², Y⁺³, Nd⁺³, Pr⁺³,
 Ce⁺³, Mn⁺², La⁺³, Ca⁺², Mg⁺², Be⁺², Sr⁺², Ba⁺².

Citric acid

For the separation of all the rare earths with citric acid the optimum eluant is a 0.0052M solution, raised to a pH of 8.0 with ammonium hydroxide. Therefore, the elution sequence was determined under these conditions. Seven runs were made with this eluant, and the results are given in Table 3. Ions within the parentheses were not sufficiently separated to allow determination of their relative order. The retaining

Table 3. Sequence determination runs for citric acid

Run number	Elution sequence
I	Fe ⁺³ , Cr ⁺³ , UO ₂ ⁺² , (Cu ⁺² , Al ⁺³), Yb ⁺³ , Ni ⁺² , Zn ⁺² , Co ⁺² , Pb ⁺² , La ⁺³
II	Fe ⁺³ , Cr ⁺³ , UO ₂ ⁺² , Be ⁺² , Th ⁺⁴ , Al ⁺³ , Cu ⁺²
III	Al ⁺³ , Yb ⁺³ , Dy ⁺³ , (Sm ⁺³ , Ni ⁺² , Zn ⁺² , Co ⁺² , Pb ⁺²), La ⁺³
IV	Be ⁺² , Mn ⁺² , Cd ⁺² , Mg ⁺² , Ca ⁺² , Sr ⁺² , Ba ⁺²
V	Ni ⁺² , Sm ⁺³ , Nd ⁺³ , Zn ⁺² , Pr ⁺³ , Co ⁺² , Ce ⁺³ , Pb ⁺²
VI	Er ⁺³ , Ho ⁺³ , Ni ⁺² , Dy ⁺³ , Y ⁺³
VII	Ce ⁺³ , Pb ⁺² , La ⁺³ , Mn ⁺² , Cd ⁺² , Mg ⁺²

ion was hydrogen ion in all cases.

The elements, Mn⁺², Cd⁺², Mg⁺², Ca⁺², Sr⁺² and Ba⁺², which were found to follow the rare earths, eluted only very slowly with citric acid. The initial band of elements lengthened about threefold, and sufficient separation took place to indicate their relative order. However, the concentration of these elements in the eluate was very low. The analysis was made by removing the resin bed from the columns in fractions, ashing the resin, and analyzing the oxide residues. This inefficient separation is probably due to the weak complexes formed by these elements with citric acid (25). These complexes are in the same order of magnitude as the difference in resin affinity for these metal ions and the ammonium ion. The initial displacement is not sharp; ammonium ion overruns these ions; an elution chromatogram results.

The elution sequence for 0.0052M citric acid at a pH of 8.0 with

ammonium hydroxide is:

Fe^{+3} , Cr^{+3} , UO_2^{+2} , Th^{+4} , Be^{+2} , Al^{+3} , Cu^{+2} , Lu^{+3} , Yb^{+3} , Tm^{+3} , Er^{+3} ,
 Ho^{+3} , Ni^{+2} , Dy^{+3} , Y^{+3} , Tb^{+3} , Gd^{+3} , Sm^{+3} , Nd^{+3} , Zn^{+2} , Pr^{+3} , Co^{+2} ,
 Ce^{+3} , Pb^{+2} , La^{+3} , Mn^{+2} , Cd^{+2} , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} .

NTA

The use of nitrilotriacetic acid has not been so widespread as the use of the three eluants described in the preceding pages. A review of the use of this reagent was given by Powell (32). No specific set of eluant conditions can claim superiority. Powell and Farrell (33) have determined a partial elution sequence for 0.015M NTA at a pH of 9.0 with ammonium hydroxide. The sequence found is:

Cu^{+2} , Th^{+4} , Ni^{+2} , Pb^{+2} , Al^{+3} , Zn^{+2} , Lu^{+3} , Yb^{+3} , Tm^{+3} , Er^{+3} , Cd^{+2} ,
 Ho^{+3} , Dy^{+3} , Tb^{+3} , Gd^{+3} , Eu^{+3} , Y^{+3} , UO_2^{+2} , Sm^{+3} , Nd^{+3} , Pr^{+3} , Ce^{+3} ,
 La^{+3} , Mn^{+2} , Ca^{+2} , Mg^{+2} , Be^{+2} , Sr^{+2} , Ba^{+2} .

DTPA

The use of this chelating agent has likewise been limited. The stability of the rare-earth complexes with this chelating agent increases with increasing atomic number and then decreases again in the neighborhood of dysprosium (34). Powell and Larson (35) have determined this partial elution sequence for five-gram-per-liter DTPA at a pH of 8.74 with ammonium hydroxide:

Cu^{+2} , Th^{+4} , Ni^{+2} , UO_2^{+2} , Zn^{+2} , Dy^{+3} , Ho^{+3} , Er^{+3} , Yb^{+3} , Sm^{+3} , Y^{+3} ,
 Co^{+2} , Cd^{+2} , Pb^{+2} , Nd^{+3} , Pr^{+3} , Ce^{+3} , La^{+3} , Mn^{+2} , Al^{+3} , Fe^{+2} , Ca^{+2} ,
 Mg^{+2} , Be^{+2} , Sr^{+2} , Ba^{+2} .

Although the relative orders have been established, the quality of the separations has not been considered. All counter-current separations

depend not only on the separation factor but also on the height equivalent to a theoretical plate (HETP). If the separation factor is large, the cations will separate quickly and easily. However, in displacement chromatography, the amount of overlap between consecutive bands after a steady state is reached is directly proportional to the HETP (29). The HETP is dependent on such factors as flow rate, resin-particle size, temperature, and any significant kinetic parameters in either phase.

The significance of these elution sequences will be discussed in the following section.

Technology Suggested by the Sequences

Separation of thorium from the rare earths

As indicated by the elution sequences, when thorium is present in the mixture to be separated, it will contaminate the lutecium fraction if EDTA is used as the eluant and the ytterbium and thulium fractions if HEDTA is used as the eluant. Since thorium is commonly found in rare earth minerals, the separation of thorium from these elements is an analytical problem of considerable interest.

The elution order with citric acid is H^+ , Th^{+4} , Cu^{+2} and the rare earths. This suggests that if a thorium-rare-earth mixture were loaded behind a short band of Cu^{+2} and if this system were eluted with citric acid down a bed of hydrogen ion, the thorium would form a band ahead of the copper; but the rare earths would remain behind it and separate into a band sequence completely free of thorium.

This hypothesis was verified by treating 1200 grams of an oxide mixture of thorium and ytterbium which had resulted from previous

separations with HEDTA. Elution of the absorbed mixture just one and one-half band lengths was sufficient to effect the separation. At this point the system was divided at the middle of the copper band. About 40 grams of thorium, some of it contaminated with copper, were recovered from the front portion. The rear portion of the band, which contained ytterbium preceded by copper, was eluted down a hydrogen-ion form resin bed with HEDTA. Since copper is not retained by the resulting H_5V^{+2} band, 1150 grams of pure Yb_2O_3 were recovered from the column.

The copper could have been removed from the contaminated thorium by any one of a number of methods had there been enough thorium to warrant its recovery in pure form. Elution of the hydrogen-thorium-copper band with HEDTA a short distance would remove the copper from the system as in the recovery of ytterbium above.

Half-ton quantities of rare-earth mixtures, which contain considerable thorium, are now being processed in this laboratory. After elution with EDTA for three band lengths, a band of heavy rare earths and thorium is cut from the front of the separating mixture. If a small portion of the copper retaining ion were included, the thorium could be removed at this point by elution with citrate. Then the final separation of the heavy rare earths with HEDTA would not be hampered by the presence of thorium. The thorium itself could be recovered, as outlined above, if there were enough to make this practical.

Other retaining ions

Any of the ions which precede the rare earths with a given eluant could be used as a retaining ion for rare-earth separations with that

eluant. With EDTA the list includes Bi^{+3} , Fe^{+3} , Cu^{+2} , Ni^{+2} and Pb^{+2} . With HEDTA the list includes all these ions, plus H^{+} , Zn^{+2} , Co^{+2} and Cd^{+2} . With citric acid Fe^{+3} , Cr^{+3} , Be^{+2} , Al^{+3} and Cu^{+2} are possibilities, while Cu^{+2} , Ni^{+2} , Pb^{+2} , Al^{+3} and Zn^{+2} are suggested by the sequence for elutions with NTA, and Cu^{+2} and Ni^{+2} may be practical for elutions with DTPA.

For separations involving large quantities of rare earths, economics may be an important factor. As elution proceeds, large volumes of a solution of the complex of the retaining ion are produced. To be economical a separation process certainly must include a method for cleaving this complex without destroying the chelating agent. The uncomplexed cation could then be used to regenerate the resin beds which were left in the ammonium-ion form by prior operations. Ammonium hydroxide could be added to the recovered chelating acid to prepare it for reuse as eluant. The complex has not been economically broken in the case of Cu-EDTA. The loss of EDTA because it is not recycled is a major factor in the cost of producing pure individual rare earths. The disadvantages of the use of iron as a retaining ion for EDTA elutions were given in the introduction to this work. However, it would seem that the ions, Bi^{+3} , Ni^{+2} and Pb^{+2} , should be evaluated as retaining with consideration given to the ease with which they might be recycled.

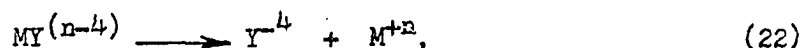
After an initial separation of the rare earths into light and heavy fractions by using EDTA as the eluant and Cu^{+2} as the retaining ion, zinc, cobalt and cadmium should be effective as retaining ions for separating the light-rare-earth mixture. Brazilian workers (36) have suggested the use of zinc as a retaining ion, but they used it for all

the rare earths. They recovered the heavy rare earths, which are not retained, from the solution of Zn-EDTA complex. These elements are apparently separated to some extent by an elution-chromatographic mechanism. They broke the Zn-EDTA complex and precipitated free EDTA by acidification. This is not possible with the Cu-EDTA complex. The use of zinc as a retaining ion for light rare earths is currently being investigated in this laboratory. Wolf and Massonne (37,38) have used zinc as a retaining ion when separating rare earths with NTA.

Analytical applications

The sequences, given in the preceding section, should prove to be of great value to the rare-earth analyst. The rare earths which neighbor a common element in a particular sequence should be suspected of containing trace amounts of that element if these rare earths were separated with the eluant to which the sequence belongs. If even the barest traces of a common element are present in the eluant, that element will accumulate to significant quantities at its normal position in the sequence. Therefore, it is of paramount importance that the many gallons of water which are required for large-scale separations be completely free of heavy-metal ions. Elements, such as iron, calcium, zinc and lead, have proved to be troublesome at this laboratory.

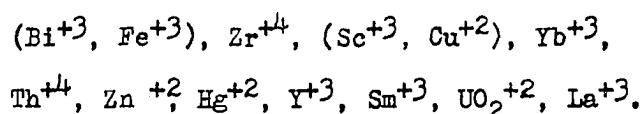
Several investigators (39,40,41,42,43,44) have separated various metal ions by selectively removing them from cation-exchange resin with EDTA solutions at a controlled pH. The equilibrium,



is forced to the right as the pH is lowered, due to competition of

hydrogen ion for Y^{-4} . The pH range in which the equilibrium shifts from an insignificant amount of M^{+n} to an insignificant amount of $MY^{(n-4)}$ depends, for the most part, on the size of the equilibrium constant for reaction (22). At a given pH, an EDTA solution will remove from the resin those metal ions, \bar{M}^{+n} , whose complexes with EDTA are stable at this pH. However, either hydrogen ion or ammonium ion must replace \bar{M}^{+n} on the resin. Therefore, $MY^{(n-4)}$ must be sufficiently stable to overcome the greater affinity of the resin for M^{+n} than for hydrogen or ammonium ions.

Fritz (44) obtains the following sequence when the metal ions are listed in the order of increasing pH at which they are removed from the resin:



This partial sequence is nearly identical with the elution sequence which was given for EDTA in the preceding section.

In addition to the competition between metal ions and hydrogen ion for EDTA, Takitatsu (45) has used the competition between one metal cation and another for EDTA to effect similar separations. He passed a 0.015M solution of Pb-EDTA, at a pH of 3.0, over a mixture of cerium and thorium sorbed on a cation resin. The lead ion exchanged with thorium ion, but not with cerium ion. Th-EDTA then passed from the column, leaving a mixture of lead and cerium on the resin.

Of course, neighboring elements in the EDTA elution sequence cannot be easily separated by these methods because there is a range of about one and one-half pH units over which equilibrium (22) shifts from

left to right; the differences in the pH's at which neighboring elements are completely retained by the resin are fractions of a pH unit. If a retaining ion of hydrogen were placed ahead of the mixture and the eluant well-buffered at the correct pH, an elution-chromatographic separation of neighboring elements might be effected.

A discussion of the use of common-ion "wedges" will be deferred until the next chapter where it will be discussed in connection with the theory presented there.

A Limited Theory for the Sequences

In the introduction the method of Powell and Spedding for calculating the separation factor for two rare earths in separations with EDTA was presented. They found that the separation factor was simply the ratio of the stability constants of the individual rare-earth complexes with EDTA. Since many assumptions were made, based on the chemical similarity of the rare earths, the theory does not necessarily apply to separations where non-rare-earth cations are included.

In Tables 4, 5, 6 and 7 the stability constants of metal-chelate complexes are listed in the order in which the metal ions elute. The values for EDTA are those of Schwarzenbach, Gut and Anderegg (46). The values for HEDTA are given in references (47,48); for NTA, in references (25,49); for DTPA, in references (50,51).

If an arbitrary number is added to the logarithms of the stability constants for the divalent metals for each eluant, a list of the metal ions in decreasing order of these "corrected" stability constants is identical with the elution sequence. This additive correction is 2.6

Table 4. Stability constants of metal-EDTA complexes

Metal ion	$\text{Log } K_{MY}^{M^{+n}(n-4)}$	$\text{Log } K_{MY}^{M^{+n}(n-4)}$ with 2.6 added to all divalent metal constants
Co ⁺³	36	36
Fe ⁺³	25.7	25.7
Sc ⁺³	23.1	23.1
Cu ⁺²	18.8	23.3
Ni ⁺²	18.6	23.1
Th ⁺⁴	23.2	23.2
Pb ⁺²	18.0	22.6
Lu ⁺³	19.9	19.9
Yb ⁺³	19.8	19.8
Zn ⁺²	16.5	19.1
Tm ⁺³	19.3	19.3
Co ⁺²	16.3	18.9
Er ⁺³	18.9	18.9
Cd ⁺²	16.4	19.0
Al ⁺³	16.1	16.1
Ho ⁺³	18.7	18.7
Dy ⁺³	18.3	18.3
Y ⁺³	18.1	18.1
Tb ⁺³	17.9	17.9
Gd ⁺³	17.4	17.4
Sm ⁺³	17.1	17.1
Fe ⁺²	14.3	16.9
Nd ⁺³	16.6	16.6
Pr ⁺³	16.4	16.4
Mn ⁺²	14.0	16.6
Ce ⁺³	16.0	16.0
La ⁺³	15.5	15.5
Ca ⁺²	10.7	13.3
Mg ⁺²	8.7	11.3
Sr ⁺²	8.6	11.2
Ba ⁺²	7.8	10.4

Table 5. Stability constants of metal-HEDTA complexes

Metal ion	Log $K_{MV(n-3)}^{M+n}$	Log $K_{MV(n-3)}^{M+n}$ with 3.0 added to all divalent metal constants
Cu+2	17.4	20.4
Ni+2	17.0	20.0
Fe+3	19.6	19.6
Zn+2	14.5	17.5
Co+2	14.4	17.4
Cd+2	13.0	16.0
Lu+3	15.8	15.8
Yb+3	15.6	15.6
Th+4	15.4	15.4
Tm+3	15.4	15.4
Er+3	15.2	15.2
Ho+3	15.1	15.1
Dy+3	15.1	15.1
Tb+3	15.1	15.1
Gd+3	15.1	15.1
Eu+3	15.2	15.2
Sm+3	15.1	15.1
Nd+3	14.7	14.7
Pr+3	14.4	14.4
Ce+3	14.1	14.1
Mn+2	10.7	13.7
La+3	13.2	13.2
Ca+2	8.0	11.0

for EDTA, 3.0 for HEDTA, 1.8 for NTA and 3.6 for DTPA.

The combination of equations (4) and (6) in the introduction yields,

$$\alpha = \frac{[\bar{R}_1^{+3}] [R_2 Y^-]}{[\bar{R}_2^{+3}] [R_1 Y^-]} \quad (23)$$

Table 6. Stability constants of metal-NTA complexes

Metal ion	Log $K_{MN}^{M+n}(n-3)$	Log $K_{MN}^{M+n}(n-3)$ with 1.8 added to all divalent metal constants
Cu ⁺²	13.0	14.8
Ni ⁺²	11.5	13.3
Pb ⁺²	11.4	13.2
Zn ⁺²	10.7	12.5
Lu ⁺³	12.1	12.1
Yb ⁺³	12.0	12.0
Tm ⁺³	11.8	11.8
Er ⁺³	11.7	11.7
Cd ⁺²	9.8	11.6
Ho ⁺³	11.6	11.6
Dy ⁺³	11.5	11.5
Tb ⁺³	11.4	11.4
Gd ⁺³	11.3	11.3
Eu ⁺³	11.1	11.1
Y ⁺³	11.4	11.4
Sm ⁺³	11.2	11.2
Nd ⁺³	11.0	11.0
Pr ⁺³	11.0	11.0
Ce ⁺³	10.7	10.7
La ⁺³	10.4	10.4
Mn ⁺²	7.4	9.2
Ca ⁺²	6.4	8.2
Mg ⁺²	5.4	7.2
Sr ⁺²	5.0	6.8
Ba ⁺²	4.8	6.6

The selectivity coefficient of the resin for a pair of rare-earth ions is,

$$K_s = \frac{[\bar{R}_1^{+3}] [R_2^{+3}]}{[\bar{R}_2^{+3}] [R_1^{+3}]} \quad (24)$$

Spedding and Powell assumed that K_s is unity for the rare earths.

According to data supplied by Surls and Choppin (52) for tracer quantities

Table 7. Stability constants of metal-DTPA complexes

Metal ion	Log $K_{MD}^{M+n}(n-5)$	Log $K_{MD}^{M+n}(n-5)$ with 3.6 added to all divalent metal constants
Cu+2	21.1	24.7
Ni+2	20.2	23.8
Dy+3	23.5	23.5
Er+3	23.2	23.2
Yb+3	23.0	23.0
Sm+3	22.8	22.8
Y+3	22.4	22.4
Cd+2	18.9	22.5
Co+2	18.4	22.0
Nd+3	22.2	22.2
Pr+3	21.9	21.9
La+3	20.0	20.0
Mn+2	15.1	18.7
Fe+2	16.5	20.1
Ca+2	10.1	13.7

of rare earths, values of K_s range from 1.0 to 1.18 for adjacent pairs of rare earths. For divalent-trivalent mixtures K_s is far from unity. Vickery (53) and Fritz (44) have suggested that the additive correction which is required to amend the logarithms of the stability constants is $\log K_s$. This is reasonable, since the combination of equations (8), (23) and (24) yields

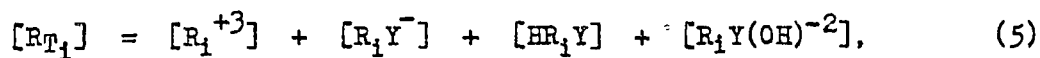
$$\alpha = \frac{K_{R_2}^{R_2+3} K_{R_2 Y^-}}{K_{R_1}^{R_1+3} K_{R_1 Y^-}} K_s. \quad (25)$$

The resin used in all the sequence determinations was the same.

Therefore, K_s should not vary from eluant to eluant. Also, K_s for the

thorium-rare-earth system should be at least as large as that for the divalent-trivalent systems. Yet, for EDTA and HEDTA no number is needed to correct the logarithm of the thorium-EDTA stability constant, and thorium behaves as though it were trivalent. It is also worthy of note that the order for the divalent metals, Cu^{+2} , Ni^{+2} , Zn^{+2} , Cd^{+2} , Mn^{+2} , Ca^{+2} , Mg^{+2} , Be^{+2} , Sr^{+2} , Ba^{+2} , is preserved with all four eluants.

The other assumption of Powell and Spedding is that all but one of the species on the right of equation (5),



are insignificant. This assumption is not valid when ions of different charge are considered. Since this introduces a considerable number of complications in the theory, further discussion will be left to the next chapter in which a complete theory is presented.

Metal-Chelate Compounds

In the course of studying elution sequences, a few miscellaneous metal-chelate compounds were prepared and their properties studied. In general, to prepare such compounds equivalent amounts of a metal carbonate and the free acid of the chelating agent were dissolved in a minimum of boiling water, and the metal-chelate compound was crystallized from the cooled solution. If the solubility of either the metal carbonate or the free chelating agent was near that of the metal-chelate compound, it was difficult to prepare pure metal-chelate compound by crystallization from water. It soon became apparent that such compounds were all strong acids. If they could be prepared in pure form, they

might be used as primary standards for alkalimetry.

Th-DTPA

Attempts to dissolve thorium carbonate or thorium hydroxide in DTPA failed. A solution of the compound was prepared by dissolving thorium nitrate in an equivalent amount of DTPA and raising the pH to approximately two with ammonium hydroxide. This method introduces ammonium nitrate into the solution. A glassy mass was obtained from this solution only after it was concentrated to 300 grams per liter.

Bi-EDTA

Attempts to dissolve bismuth carbonate in an EDTA solution failed.

Co(III)-EDTA

A few drops of a 30% hydrogen peroxide solution were added to a boiling Co(III)-EDTA solution, prepared from the carbonate. After the addition of peroxide, the color of the solution immediately changed from a pale rust red to an extremely intense purple. Purple crystals formed when the solution was concentrated to about 1000 grams per liter. The crystals were dried at 110°C, and a solution of them was titrated potentiometrically with potassium hydroxide. A slight break at a pH of 2.7 indicated the presence of either free EDTA or Co(II)-EDTA. The acid HCoY appears to be nearly as strong as hydrochloric acid.

Cu-HEDTA

Crystals of Cu-HEDTA were dried at 110°C before a solution of them was potentiometrically titrated with KOH. These titrations indicated the dried crystals were pure monohydrate. An experiment, using a thermobalance, indicated that the compound began to decompose at about 170°C before all of the hydrate water was lost. The monohydrate is

soluble to the extent of 11.7 grams per liter in water at 25°C. It is a strong acid, and solutions of it are deep blue in color. The monohydrate is hygroscopic, removing water from a 50%-humidity atmosphere at the rate of 0.4 milligrams of water per gram of sample per minute.

Pb-HEDTA

A solution of this compound was prepared and concentrated to over 1000 grams per liter without crystallization. The solution became extremely syrupy; and when it was allowed to evaporate slowly at room temperature, it solidified finally in a colorless, hard, glassy mass.

Ni-HEDTA

Crystallization from a 500-gram-per-liter blue solution required several weeks. After drying the aqua crystals at 100°C, potentiometric titrations with potassium hydroxide indicated that they contained a small amount of excess nickel.

Mn-HEDTA

Crystals with a pink tinge were obtained from a solution whose concentration was approximately 100 grams per liter. Potentiometric titrations of a solution of oven-dried crystals indicated that they still contained some free HEDTA. HMnV is obviously a weaker acid than HCuV or HNiV.

Zn-HEDTA

This material appears to have a solubility near that of HCuV. The white crystals were dried at 110°C, and the molecular weight was determined by titration with potassium hydroxide. The value obtained was 346.8, compared to the theoretical value of 341.6. The high molecular weight indicated the presence of excess zinc, and it

remained high after repeated recrystallizations.

Cd-HEDTA

HCdV is very easily prepared and purified. It is virtually non-hygroscopic, is stable and has a high molecular weight. It is a very strong acid with an ionization constant of 2.7×10^{-3} in a 0.1M potassium chloride solution; its density is 1.07 grams per milliliter. Its solubility is given in Table 8. It slowly decomposes at 240°C in air yielding pure cadmium oxide. A description of the use of this compound as a primary standard for alkalimetry and chelometry is given in Appendix A. A more detailed description of the experiments described in this section can be found in Appendix B.

Table 8. Solubility of HCdV in water

Temperature (°C)	Solubility (g/l)
0	5.3
25	8.6
60	20.3
95	57.8

THE SEPARATION FACTOR IN ION-EXCHANGE ELUTIONS WITH CHELATING ELUANTS

If there is a sharp, efficient exchange of the separating ions between resin phase and the aqueous phase at both the front and rear edges of the separating mixture, a displacement-chromatographic separation will result. Such separations are conveniently described by a model similar to that used in two-phase, counter-current separations. The separation factor α , which measures the ease with which separations occur, is defined as the ratio of the concentrations of the separating ions in one phase, divided by the ratio of these concentrations in the other phase. For the ion-exchange separation of B^{+b} from C^{+c} , using a chelating eluant, the separation factor takes the form,

$$\alpha = \frac{\bar{x}_B/\bar{x}_C}{[B_T]/[C_T]}, \quad (26)$$

where \bar{x}_i is the mole fraction of i in the resin phase and $[i_T]$ is the total concentration of i in the aqueous phase. If α is unity, no separation can occur. The absolute magnitude of the difference of α from unity,

$$|\epsilon| = |\alpha - 1|, \quad (27)$$

is a measure of the ease with which the separation can be effected. The smaller is $|\epsilon|$, the greater will be the number of band lengths that the separating mixture must be eluted before an equilibrium condition is reached. Then the degree of overlap of the two separated bands is determined by the height equivalent to a theoretical plate (HETP)

whose magnitude depends upon temperature, flow rate and any significant kinetic factors in either phase.

Both the separation factor and the HETP are of interest when considering the merits of a specific separation. The HETP, with its relation to this type of separation, is discussed in a dissertation by Sellers (54). The nature of the separation factor is the topic of this chapter.

The algebraic sign of ϵ determines the order of elution of the separating bands of B^{+b} and C^{+c} . Because of the arbitrary definition of the separation factor, if ϵ is greater than zero, C^{+c} will precede B^{+b} ; if ϵ is less than zero, B^{+b} will precede C^{+c} .

The Separation Factor for a Mixture of Divalent and Trivalent Ions

Equation (26) is applicable to any mixture of two ions, regardless of their charge. For a mixture of a divalent ion D^{+2} and a trivalent rare earth R^{+3} equation (26) becomes

$$\alpha = \frac{\bar{X}_D [R_T]}{\bar{X}_R [D_T]} . \quad (26a)$$

In this discussion all complexes except the one-to-one complexes will be assumed to be insignificant. For the divalent metals which exhibit some tendency toward a coordination number of four, the two-to-one complex, D_2Y , is certainly possible. In this section only the general trend of the separation factor will be considered. The effect of this species will be considered for the quantitative calculations in a later section of this chapter. It has been shown that no hydroxylated

species exist below a pH of seven (30). Therefore, at the low pH's of the eluate in these separations equations (28) and (29) apply.

$$[R_T] = [R^{+3}] + [RY^-] + [HRY]; \quad (28)$$

$$[D_T] = [D^{+2}] + [DY^{-2}] + [HDY^-] + [H_2DY]. \quad (29)$$

In the subsequent discussions many reactions of the form,



will be considered. A stability constant for these associations will have the general form,

$$K_{RS}^R = \frac{[RS]}{[R][S]}.$$

Any such constants used in quantitative calculations were determined at the appropriate ionic strength of 0.015M. In these dilute solutions the principle of constancy of activity coefficients in systems of constant ionic strength is assumed to apply.

By substitution of the appropriate stability constants equations (28) and (29) become

$$[R_T] = [R^{+3}] \left\{ 1 + K_{RY}^R [Y^{-4}] (1 + K_{HRY}^H [H^+]) \right\} \quad (28a)$$

and

$$[D_T] = [D^{+2}] \left\{ 1 + K_{DY}^D [Y^{-4}] (1 + K_{HDY}^H [H^+] + K_{HDY}^H K_{H_2DY}^H [H^+]^2) \right\}. \quad (29a)$$

In dilute solutions of constant ionic strength the functions within the parentheses in equations (28a) and (29a) depend only upon the hydrogen-

ion concentration. For simplicity these equations may be written,

$$[R_T] = [R^{+3}] \left\{ 1 + K_{RY}^R F_R(H) [Y^{-4}] \right\} \quad (28b)$$

and

$$[D_T] = [D^{+2}] \left\{ 1 + K_{DY}^D F_D(H) [Y^{-4}] \right\}, \quad (29b)$$

where,

$$F_D(H) = 1 + K_{HDY} [H^+] + K_{HDY}^H K_{H_2DY}^H [H^+]^2 \quad (30)$$

and

$$F_R(H) = 1 + K_{HRY}^H [H^+]. \quad (31)$$

The equilibrium exchange of a divalent and a trivalent ion on cation-exchange resin is



The equilibrium "constant" for this reaction,

$$K_R^D = \frac{[D^{+3}]^2 \bar{X}_R^3}{[R^{+2}]^3 \bar{X}_D^2}, \quad (32)$$

will be shown to be a true constant for the case of zinc and thulium if the ionic strength of the aqueous phase remains constant. It is assumed in this general discussion that this is true for all exchanges between divalent and rare-earth ions.

The combination of equations (26a), (28b) and (29b) yields

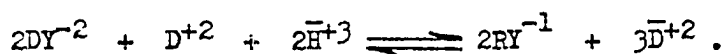
$$\alpha = \sqrt{\frac{[D^{+2}]}{K_R^D \bar{X}_D} \frac{1 + K_{RY}^R F_R(H) [Y^{-4}]}{1 + K_{DY}^D F_D(H) [Y^{-4}]}}. \quad (33)$$

It is difficult to analyze this expression to determine the effects of such factors as pH and mole fraction of divalent elements in the aqueous phase. For the sake of such an analysis it is assumed that the terms, $K_{DY}^D F_D(H)[Y^{-4}]$ and $K_{RY}^R F_R(H)[Y^{-4}]$, are of sufficient magnitude that they are not appreciably affected by the addition of unity. Since they are both greater than one, the error is not as large when their ratio is considered. However, it is shown in the next section that in the case of the zinc-thulium system this assumption would introduce as much as a ten-percent error in the calculation of the separation factor. This assumption is the same as assuming that $[R^{+3}]$ and $[D^{+2}]$ are not significant in equations (28) and (29).

With this assumption equation (33) becomes

$$\alpha = \sqrt{\frac{[D^{+2}]}{K_R^D \bar{X}_D}} \frac{K_{RY}^R F_R(H)}{K_{DY}^D F_D(H)}. \quad (33a)$$

When some divalent ions are present in the separating mixture, there are always some uncomplexed divalent ions in the eluate. This is probably due to the exchange of these ions for rare-earth ions is dictated, for the most part, by the equilibrium,



As long as divalent ions are present in the separating mixture, $[D^{+2}]$ remains constant at about ten percent of the eluant concentration. This fact is demonstrated in the next section where a specific system is treated on a quantitative basis. If all the "constants" of equation (33a) are combined, this equation takes the form,

$$\alpha = \overline{KX_D}^{-1/2} \frac{F_R(H)}{F_D(H)}. \quad (33b)$$

The ratio, $F_R(H)/F_D(H)$, is greatly influenced by pH. Therefore, the separation factor in these systems should depend upon the pH of the eluate. The pH of the eluate can be changed by changing the pH of the eluant. Identical mixtures which are eluted with eluants with different pH's may be separated in different orders; or one eluant may effect no separation if it has a pH which causes the separation factor to be unity.

According to equation (33b) the separation factor and, therefore, the elution order should be dependent upon the composition of the resin, which in turn depends upon the composition of the eluate or the separating mixture. For an eluant of a given pH there is a resin composition $\overline{X_D^0}$ which will cause the separation factor to be unity. Then $\overline{X_D^0} = X_D^0$; and no separation will result, regardless of how many band lengths the mixture is eluted.

If the composition of the mixture were such that

$$\overline{X_D} = \overline{X^0} + \overline{x}, \quad 0 < \overline{x} < 1 - \overline{X_D^0}$$

then the separation factor would be different from unity. If, in this case, the separation factor is greater than unity and is defined as in equation (26a), the elution order will be R^{+3} preceding D^{+2} . However, as R^{+3} separates from D^{+2} , $\overline{X_R}$ will approach $1 - \overline{X_D^0}$ in the front portion of the band, and the separation factor will approach unity. When

$$\overline{X_R} = 1 - \overline{X_D^0} = \overline{X_R^0},$$

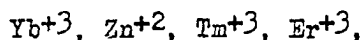
the separation factor will be identically unity; and no further separation can be effected. At the same time \bar{K} will have been reduced to zero in the front portion of the band. In the rear portion of the band X_D will have grown to unity. There will be some pure D^{+2} at the rear of the band, but the rest of the band will contain a mixture which will not separate.

The results of quantitative experiments which verify these predictions are given in the three sections which follow.

The Effect of the pH of the Eluant

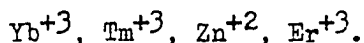
The dependence of the elution sequence upon the pH of the eluant was studied.

One-tenth of an equivalent of each of the elements, ytterbium, thulium, erbium and zinc, was eluted with 0.015 molar EDTA, raised to a pH of 8.0 with ammonium hydroxide. The pH of the eluate was approximately 2.0. The elution sequence,



was observed. This is identical to the order, given in the last chapter, which resulted from the use of an eluant with a pH of 8.5.

However, when one-tenth of an equivalent of each of these elements was eluted with the same eluant, raised to a pH of 8.65, the following order was obtained:



The pH of the eluate was approximately 2.4.

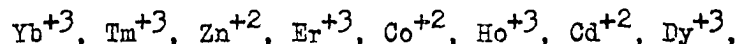
These results indicate that the separation factor between zinc and thulium,

$$\alpha = \frac{\bar{X}_{Zn} [Tm_{Tl}]}{\bar{X}_{Tm} [Zn_{Tl}]},$$

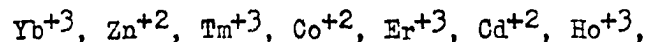
was changed from a value greater than unity to a value less than unity by changing the pH of the eluant used in the two runs.

The logarithm of the first acid association constant for the ion DY^{-2} can be calculated from data, given in Bjerrum, Schwarzenbach and Sillen (25), for several divalent metals. Values computed from these data are given in Table 9. If the second acid association constants are as similar as the first acid association constants, $F_D(H)$ should not differ markedly for the various divalent metal-ion-EDTA complexes in solutions of the same pH. The chemical similarity of the rare earths might cause the same effect with $F_R(H)$. If this is so, $F_D(H)/F_R(H)$ would remain nearly constant during the separation of several rare earths and several divalent elements. Only the position of the rare earth sequence would change with respect to the sequence of the divalent elements as the pH of the eluant is changed.

The 0.015M EDTA with a pH of 8.65 was used to separate one-tenth of an equivalent each of ytterbium, thulium, erbium, holmium, dysprosium, zinc, cobalt, and cadmium. The elution sequence,



was observed. Run III (see Table 1) indicated the order,



when a similar mixture was eluted with an eluant with a pH of 8.5.

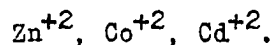
In these elutions the order of the trivalent rare earths was always identical with that predicted by Powell and Spedding. In spite of

Table 9. The logarithm of the first acid association constant of divalent-metal-EDTA complexes

Metal ion	Log K_{HDY}^H
Cu ⁺²	3.00
Co ⁺²	3.10
Cd ⁺²	2.90
Pb ⁺²	2.83
Zn ⁺² ^a	3.21
Ni ⁺²	3.20
Fe ⁺²	2.79
Mn ⁺²	3.12
Ca ⁺²	3.07

^aThis datum was determined by the author. See the following section.

changes in pH the order of the divalent ions was always



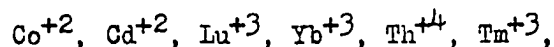
This result would be expected if, for the reasons given above, the ratio, $F_D(H)/F_R(H)$, is much less dependent upon the identity of D^{+2} or R^{+3} than upon the hydrogen-ion concentration.

A major portion of the pH-dependence of $F_D(H)/F_R(H)$ is due to $F_D(H)$. This is because the species HRY is an acid of considerable strength ($K_{HRY}^H \cong 30$). When the eluant is changed to HEDTA, $F_R(H)$ becomes unity. With this eluant

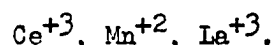
$$F_D(H) \cong 1 + K_{HDY}^H[H^+].$$

The acid HDV is nearly as strong as HRY ($K_{HDV}^H \cong 400$). Therefore, with HEDTA the pH-dependence of the elution sequence should be much less.

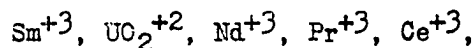
No change in the previously established order,



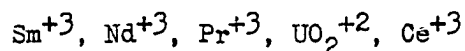
was observed when a 0.018M HEDTA solution with a pH of 4.2 or one with a pH of 9.0 was used. These eluants also produced no change in the order,



The order,



which was that found with 0.018M HEDTA, raised to a pH of 7.5 with ammonium hydroxide, was changed to

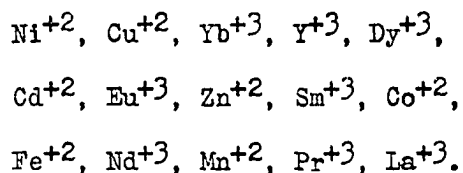


by the eluant with the low pH. The chemical difference of UO_2^{+2} from the non-hydrolyzed divalent-metal ion probably accounts for this shift.

The effect of the composition of the separating mixture on the elution sequence is considered in the next section.

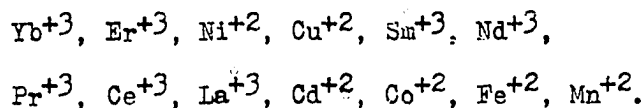
The Effect of the Composition of the Separating Mixture on the Elution Sequence

Vickery (53) has given the following partial sequence for the elution of a mixture of rare earths and some divalent elements with EDTA:

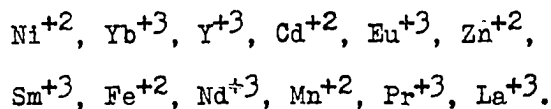


However, he did not give the conditions of the eluant which he used. Another paper by Vickery (31), published at the same time, may indicate that he used a low pH eluant with ammonium ion as a retaining ion for separating tracer quantities of material. These conditions would give an elution-chromatographic separation with considerable hydrogen and ammonium ion in the resin phase. The expression for the separation factor, derived at the beginning of the chapter, would not apply under these conditions.

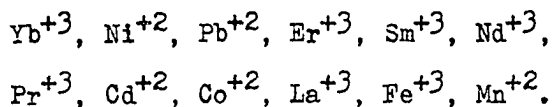
Vickery also noted that the elution sequence was dependent upon the composition of the mixture to be separated. With a large mole fraction of the total divalent ions he found the order:



With a large mole fraction of the total trivalent ions he found the order:



With the equivalent fractions of the total di- and trivalent ions the same, Vickery finds the order:



Although comparison of these sequences with those of the displacement-chromatographic system is probably not warranted because of the dissimilarity of the systems, it should be noted that the order of the trivalent ions is unchanged throughout Vickery's sequences, as is the order of the divalent ions.

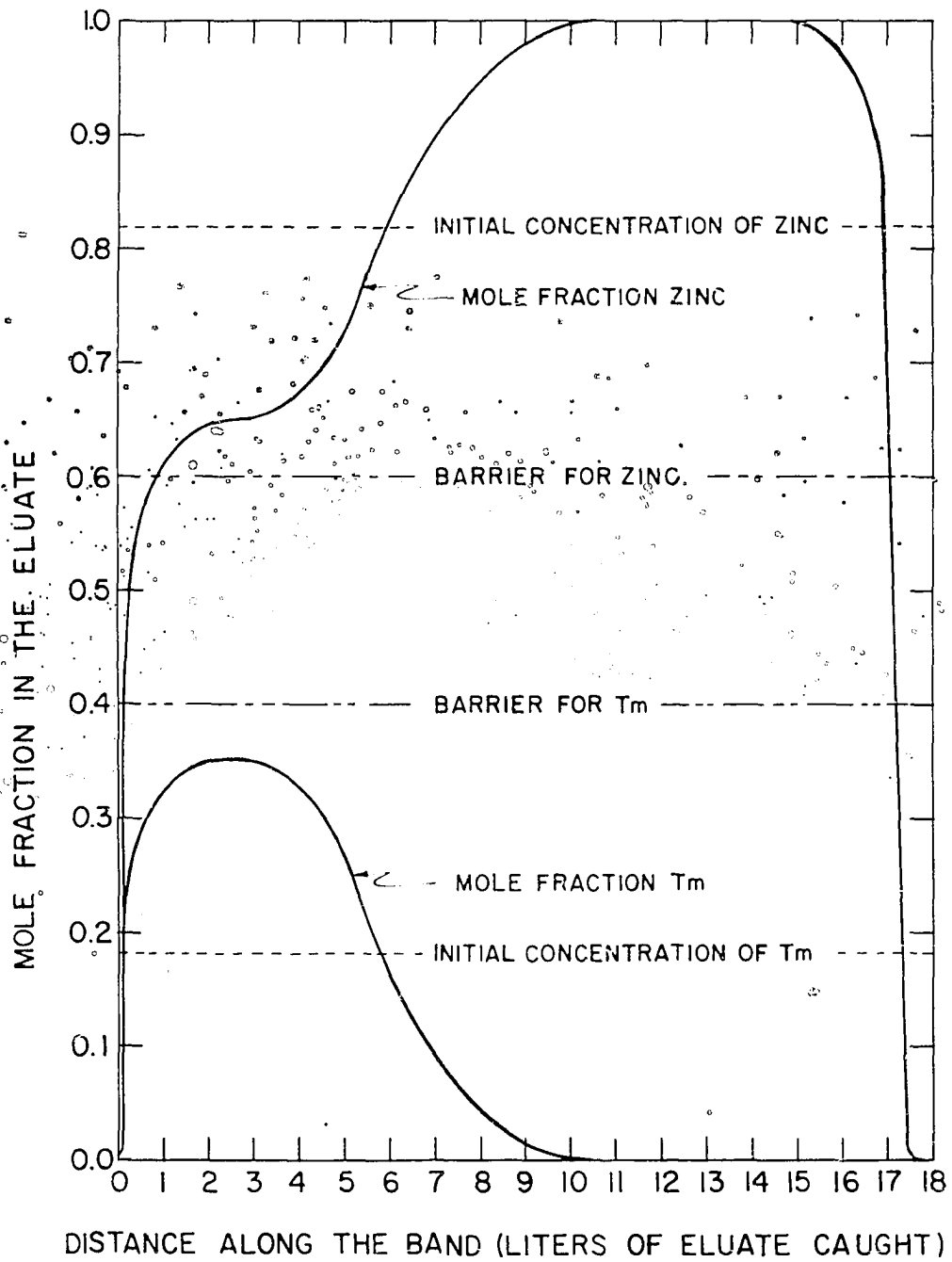
The effect of the composition of the separating mixture on the elution sequence was investigated by the author. Three runs were made with a 0.01703M EDTA solution, raised to a pH of 8.00 with ammonium hydroxide. In each experiment a mixture of zinc and thulium, containing a total of six-tenths of an equivalent of metal ions, was separated.

The first run contained three-tenths of an equivalent each of zinc and thulium ($X_{Zn} = 0.6$). Although this composition was chosen only because it was a convenient starting point for the investigations, the mixture showed no signs of separating after elution of over sixty band lengths. Mere chance had produced that composition for which no separation occurs with an eluant whose pH is 8.00.

The second run contained an equivalent fraction of 75% zinc ($X_{Zn} = 0.82$). This mixture was partially separated by the eluant having a pH of 8.0. The results of this separation are shown in Figure 2. \bar{X}_{Zn}^0 for these elements and this eluant is six-tenths, as indicated by the previous experiment. For a separation factor, as defined in equation (26a), that is greater than unity thulium should precede zinc. As the separation proceeded, the mole fraction of thulium increased in the initial portion of the separating band. As the mole fraction of thulium approached $X_{Tm}^0 = 0.4$, the separation factor in this portion of the band approached unity. At the same time X_{Zn} was approaching $X_{Zn}^0 = 0.6$ from above. The separation could not proceed beyond this "barrier".

A third run contained an equivalent fraction of 40% zinc ($X_{Zn} = 0.50$). This mixture was partially separated by the eluant

Figure 2. Separation of a mixture of zinc and thulium containing seventy-five equivalent percent zinc with 0.015M EDTA with a pH of eight.



whose pH was 8.00. The results are shown in Figure 3. If the separation factor was greater than unity in the previous run, it should have been less than unity for this run, since the initial composition was on the other side of the "barrier". This means that zinc should precede thulium; this result is observed in Figure 3. The composition which would not separate remained, $X_{Zn}^0 = 0.6$, for the eluant was not changed. The mole fraction of zinc in the eluate approached six tenths in the front portion of the band. Although the approach was from below in this run, the "barrier" of $X_{Zn}^0 = 0.6$ was still present. Similarly, X_{Tm}^0 approached, but did not pass, the "barrier" of $X_{Tm}^0 = 0.4$.

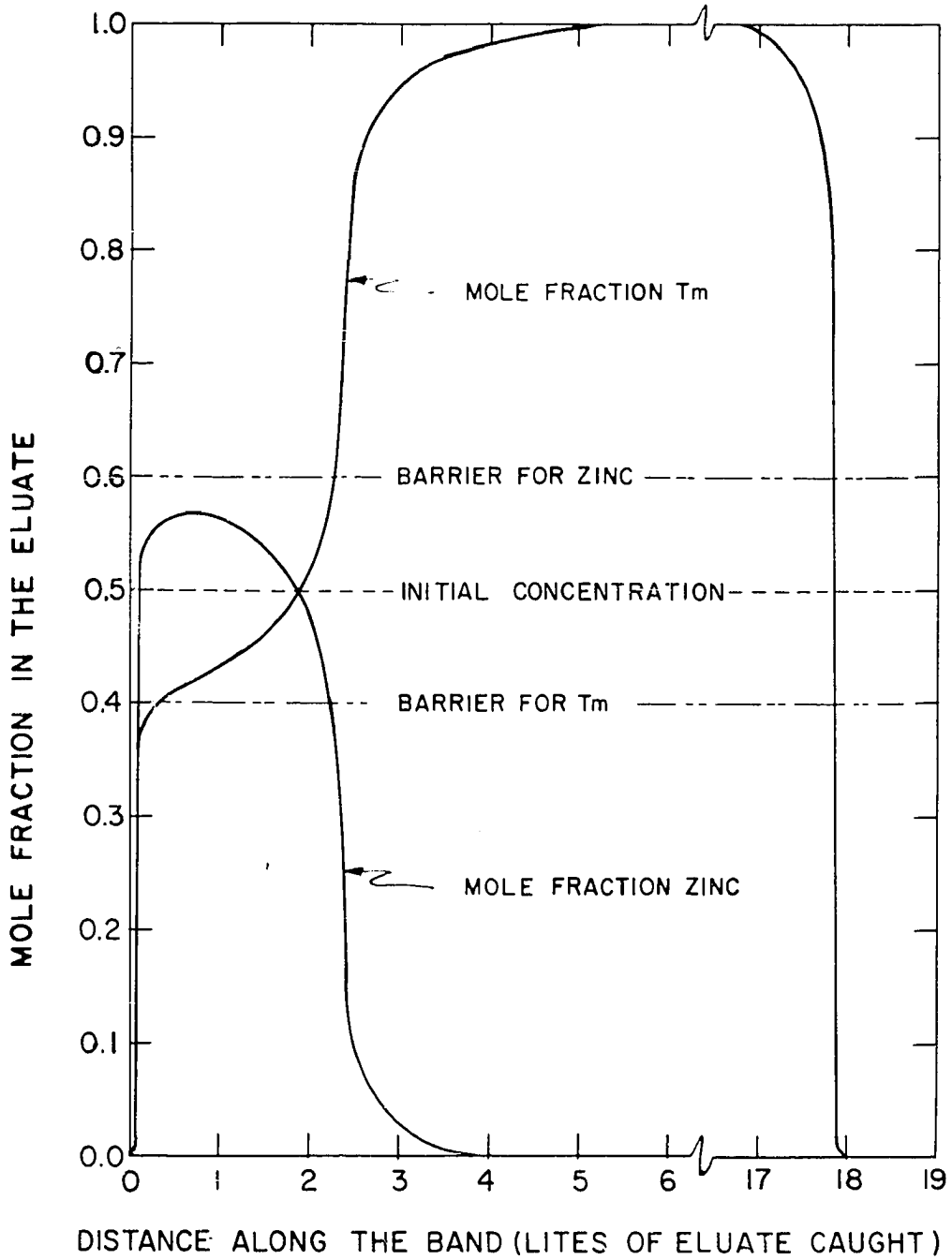
Thulium, which contains small amounts of zinc, could be purified by elution with 0.015M EDTA, raised to a pH of 8.0; however, a portion of the thulium would become badly contaminated with zinc, and this mixture would not be separable with this eluant.

The value of X_{Tm}^0 depends, to a very great degree, upon the pH of the eluant. As the pH of the eluant is raised, the ratio $F_D(H)/F_R(H)$ would decrease. According to equation (33b), the value of X_{Zn}^0 which is required to keep the separation factor unity would have to increase proportionately. The barrier for the mole fraction of thulium in the zinc band (see Figure 3) would decrease. Therefore, a complete separation of these two elements, using an eluant with a higher pH, may be possible.

The Calculation of the Separation Factor

For each run the pH of the eluate and its composition were measured. These data allow the calculation of the separation factor as a function

Figure 3. Separation of a mixture of zinc and thulium containing fifty equivalent percent zinc with 0.015M EDTA with a pH of eight.



of the distance along the band according to equation (33). The term $[Y^{-4}]$ can be evaluated by using the fact that the total concentration of all the species containing the EDTA anion in the eluate must be exactly the concentration of EDTA in the eluant. That is,

$$[Y_T] = [RY^-] + [HRY] + [DY^{-2}] + [HDY^-] + [H_2DY] + [Y^{-4}] + [HY^{-3}] + [H_2Y^{-2}] + [H_3Y^-] + [H_4Y]. \quad (34)$$

The substitution of appropriate stability constants yields

$$[Y_T] = [Y^{-4}] \left\{ [R^{+3}] K_{RY}^R F_R(H) + [D^{+2}] K_{DY}^D F_D(H) + Y(H) \right\}, \quad (34a)$$

where,

$$Y(H) = 1 + K_{HY}^H [H^+] + K_{HY}^H K_{H_2Y}^H [H^+]^2 + K_{HY}^H K_{H_2Y}^H K_{H_3Y}^H [H^+]^3 + K_{HY}^H K_{H_2Y}^H K_{H_3Y}^H K_{H_4Y}^H [H^+]^4, \quad (35)$$

A rearrangement of equations (28b) and (29b) yields

$$[R^{+3}] = [R_T] / (1 + K_{RY}^R F_R(H) [Y^{-4}]), \quad (28c)$$

and

$$[D^{+2}] = [D_T] / (1 + K_{DY}^D F_D(H) [Y^{-4}]). \quad (29c)$$

The substitution of equations (28c) and (29c) into equation (34a) yields

$$\frac{[Y_T]}{[Y^{-4}]} = \frac{[R_T] K_{RY}^R F_R(H)}{1 + K_{RY}^R F_R(H) [Y^{-4}]} + \frac{[D_T] K_{DY}^D F_D(H)}{1 + K_{DY}^D F_D(H) [Y^{-4}]} + Y(H). \quad (34b)$$

This equation is a cubic in $[Y^{-4}]$, and it has only one real positive root.

The term $[D^{+2}]$ in equation (33) can then be evaluated by using equation (29c). The term \bar{X}_D in equation (33) can also be evaluated by determining $[R^{+3}]$ from equation (28c) and using the cubic relation,

$$1 - 2\bar{X}_D + \bar{X}_D^2 - \frac{[R^{+3}]^2 K_R^D}{[D^{+2}]^3} \bar{X}_D^3 = 0, \quad (35)$$

which has only one real positive root. Equation (35) is obtained from equation (32) when the relation,

$$\bar{X}_D + \bar{X}_R = 1, \quad (36)$$

is assumed. The only species of significance in the resin phase must be positively charged. A neutral species, which is within the resin matrix but not absorbed there, cannot be considered as being in the resin phase, according to the model used in this discussion. The only possible species which could be in the resin phase in these systems are D^{+2} , R^{+3} , H^+ and NH_4^+ . The much greater affinity on the resin for the di- or trivalent ion probably makes equation (36) a valid assumption.

With the measurement of $[D_T]$, $[R_T]$ and $[H^+]$ and the evaluation of $F_D(H)$, $F_R(H)$, $[D^{+2}]$, $[Y^{-4}]$ and \bar{X}_D , the separation factor was determined as a function of the distance along the band, or the liters of eluate caught, in the three runs discussed above. The constants needed for this calculation were determined at an ionic strength of 0.015. A detailed description of the methods used for their determination is given in Appendix B.

The calculation of the separation factor requires many multiplications and divisions and the solution of two cubics. These operations

cause the errors in the numbers used to be magnified to such an extent that the error in the separation factor may be large enough to make its calculated value ridiculous. The errors in the determination of $[D_T]$ and $[R_T]$ are probably no larger than one percent, since they are measured by titration. The error in the determination of $[H^+]$ may be as high as ten percent, since it is measured with a pH meter. The values of the constants required for the calculation are given in Table 10. An estimation of their possible errors is included. Using the formulas,

$$\begin{aligned}(a \pm E_a) + (b \pm E_b) &= (a + b) \pm (E_a + E_b), \\(a \pm E_a) - (b \pm E_b) &= (a - b) \pm (E_a - E_b), \\(a \pm E_a)(b \pm E_b) &= ab + [E_a E_b \pm (aE_b + bE_a)], \\(a \pm E_a)/(b \pm E_b) &= (a \pm E_a)(b \pm E_b)/(b \pm E_b)^2,\end{aligned}$$

where E_i is the absolute possible error in i , and the data from the first run in which the separation factor should be very near unity, it can be shown that the calculated separation factor could be in error by as great a factor as thirty! However, this large possible error is due, for the most part, to the possibility of large errors in the three constants, K_{RY}^R , K_{DY}^D and K_R^D . The data for the mixture which would not separate yield a separation factor of 0.067, rather than unity. This calculated value is in error by a factor of fifteen. An error of this magnitude is probably due to constants. Therefore, as long as the measured numbers do not change greatly, an empirical correction factor of fifteen might be expected to apply. The significant terms in the calculation of the separation factor in various portions of the eluate

Table 10. Stability and acid association constants at an ionic strength of 0.015.

Constant	Magnitude	Estimated possible error
K_{TmY}^{Tm}	6.46×10^{19}	50%
K_{ZnY}^{Zn}	6.92×10^{17}	50%
$K_{Zn_2Y}^{Zn}$	646	10%
K_{HTmY}^H	26.5	10%
K_{HZnY}^H	2,390	10%
$K_{H_2ZnY}^H$	270	5%
K_{HY}^H	4.19×10^{10}	10%
$K_{H_2Y}^H$	2.57×10^6	5%
$K_{H_3Y}^H$	776	5%
$K_{H_4Y}^H$	181	5%
K_{Tm}^{Zn}	139	30%

from the three runs are given in Table 11. In the qualitative discussions in the first section of this chapter it was assumed that $[D^{+2}]$ remains approximately constant as long as some divalent ion is present in the mixture. This rough approximation is confirmed by Table 11. In this thesis it was assumed that the species D_2Y is not significant in these systems. The effect of Zn_2Y would be the addition of the product of $[D^{+2}]$ and $K_{Zn_2Y}^{Zn}$ (see Table 10) to $F_D(H)$. This product is approximately seven-tenths; therefore, it becomes significant at the higher pH's. The introduction of the term $[Zn_2Y]$ in equation (29) complicates the calculations tremendously, and the results become

Table 11. Calculation of the separation factor for zinc and thulium.

Run number	Liters of eluate caught	X_D	pH	$F_D(H)$	$F_R(H)$	$Y(H) \times 10^{-12}$	$[D^{+2}] \times 10^3$	$[R^{+3}] \times 10^5$	α	α (corrected)
I	1.1	0.600	2.57	13.9	1.081	1.55	1.34	13.8	0.066	1.05
II	1.00	0.604	2.53	16.0	1.088	1.95	1.25	14.2	0.060	0.96
II	1.50	0.625	2.56	14.4	1.083	1.62	1.15	10.6	0.061	0.98
II	2.00	0.649	2.59	13.0	1.078	1.39	1.16	8.84	0.063	1.01
II	3.00	0.651	2.59	13.0	1.078	1.39	1.07	8.04	0.062	0.99
II	4.00	0.667	2.60	12.5	1.076	1.29	0.86	5.75	0.058	0.93
II	5.00	0.724	2.70	9.4	1.061	0.75	1.02	3.96	0.068	1.09
II	6.00	0.832	2.80	7.3	1.048	0.44	1.09	1.75	0.070	1.12
II	7.00	0.896	2.92	5.4	1.037	0.24	1.07	0.74	0.075	1.20
II	8.00	0.951	2.98	4.8	1.033	0.17	1.09	0.30	--	--
III	1.00	0.564	2.38	27.1	1.125	5.02	1.61	81.3	0.283	0.91
III	1.50	0.483	2.29	38.8	1.153	9.33	1.00	89.9	0.276	0.88
III	2.00	0.028	2.10	87.5	1.238	36.31	0.05	11.1	0.001	0.003

ridiculous. This is probably due to the large possible errors in the constants.

In Figure 4 the corrected separation factor is given as a function of distance along the band in the second run. The mole fraction of zinc in the eluate is also given for comparison. The low value of the separation factor at the very front of the band is probably due to the influence of the copper retaining ion. The separation factor is approximately unity in the region where X_{Zn} is nearly six tenths. As X_{Zn} increases, the separation factor increases also. This is in complete agreement with the theory and the results shown in Figure 2.

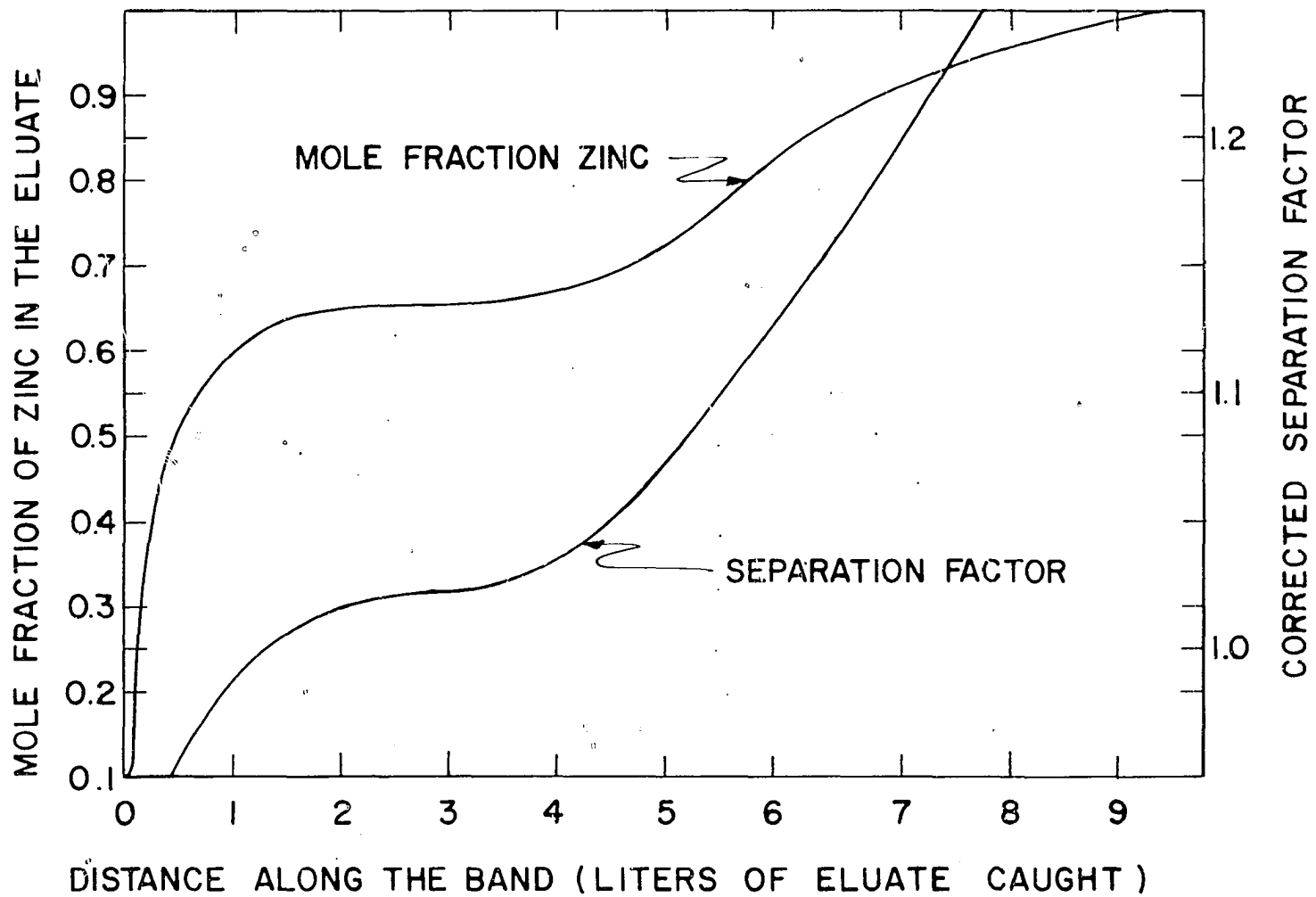
A similar treatment of the data from the third run required an empirical correction factor of 3.2 to bring to unity those separation factors which were calculated in the region where the composition is near the barrier. With this correction the calculated separation factor becomes smaller as X_{Tm} increases at the rear of the band. This is also in complete agreement with the theory and the results shown in Figure 3.

Conclusions

The ion-exchange elution sequences have been established for some di- and trivalent ions in elutions with those eluants commonly used for the separation of macroquantities of rare earths. The sequences suggest some possible alternate retaining ions. For separating all of the rare earths with EDTA, the possibilities include Bi^{+3} , Ni^{+2} and Pb^{+2} . For separating just the light rare earths, Zn^{+2} , Co^{+2} or Cd^{+2} might be used.

The elution sequence obtained with citric acid is quite different

Figure 4. The change in the separation factor with the degree of separation as calculated from run two.



from the general character of the sequences obtained with the amino-polycarboxylic acid chelating agents. This difference makes citric acid valuable in removing non-rare-earth contaminants which result from the separation of the rare earths with the more efficient chelating agents. A method was described for the removal of thorium from the heavy rare earths. The same method could be used to remove aluminum or uranium.

It does not appear feasible to add a large amount of a common element to a rare-earth mixture in order to improve the separation. While this ion may "wedge" between two rare earths, the separation factor between the rare earths is not changed. The mixture would have to be eluted the same number of band lengths to separate the rare earths, but the addition of the common ion would lengthen the band. The separation would require more eluant and a greater length of resin bed. The preceding discussion indicated that the common ion may not separate completely from either or both of the rare earths after an equilibrium condition is reached.

There would be the added problem of removing the common ion from the separated rare earths. However, the results of the preceding section also indicate that this final step might be effected by cutting the common-ion band in the middle where it is free from either rare earth. Appropriate eluants with different pH's might then be used to obtain a normal separation of the common ion from the rare earth in each of the resulting bands. However, there would always be a slight overlapping region.

The separation factor in these systems appears to depend upon

two conditions which are not significant in the separation of a mixture of rare earths alone. Even with elements of the same valence, the pH of the eluant should affect the separation factor. The chemical similarity of the rare earths reduces this effect to insignificance. When ions of different valence are considered, the ion-exchange "equilibrium constant" introduces a dependence of the separation factor upon the mole fraction of the total ions of one valence in the separating mixture. As separation proceeds and the composition changes, this effect is changed.

Until methods are developed for determining the required stability constants with a greater degree of certainty, it appears that the theory presented in this thesis will be of little value in predicting the efficiency of separations. However, the theory does qualitatively explain the phenomena observed in the ion-exchange elution of polyvalent cation mixtures with chelating eluants.

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APPENDIX A - HCdV AS A PRIMARY STANDARD

Cadmium acid N-hydroxyethyl-N,N',N'-ethylenediamine-triacetate (HCdV) is an excellent primary standard. It is easily prepared and purified. Because it is stable and virtually non-hygroscopic and has a high molecular weight, molal amounts can be accurately measured by weight. It is a stronger acid than most alkalimetric primary standards. Boiling a few minutes with aqueous persulfate destroys the chelation, rendering the cadmium ion available for chelometric standardizations.

General Properties of HCdV

If a material is to be used as a primary standard, it must be possible to accurately measure molal quantities which must react stoichiometrically with the material to be standardized; and it must be possible to detect the completion of the reaction.

Preparation of HCdV

HCdV can be prepared from reagent grade cadmium carbonate and HEDTA. A 70% yield is obtained by dissolving, portionwise, a dry mixture which contains 0.444 parts of cadmium carbonate and 0.716 parts of HEDTA in 18 parts of boiling water. Filter the resulting solution while it is hot, using a sintered-glass filter. Allow the filtrate to cool to room temperature while stirring it mechanically. Since the crystallization is slow, it should be continued overnight for a maximum yield. Collect the crystalline product on a sintered-glass filter and wash the fine crystals with water. Dissolve these crystals in 15 parts of boiling water; and filter the clear, colorless solution if necessary.

Crystallize the acid as before; filter, wash and spread the product on a flat dish of borosilicate glass; and dry it for a few hours at 110°C. Powder the product and dry it overnight at 110°C. This procedure produces about 0.70 parts of HCdV. The yield can be improved to about 0.75 parts by crystallizing at 0°C.

Density of HCdV

The density of the dry, crystalline powder was determined pycnometrically in dry benzene. A value of 1.07 g/ml was obtained.

Ionization constant of HCdV

The ionization constant of HCdV in a solution with a total ionic strength of 0.10 was determined potentiometrically by titration with potassium hydroxide. A complete discussion of this method is given in Appendix B. The value obtained was 2.7×10^{-3} .

Solubility of HCdV

The solubility of HCdV in water is given in Table 8 in the second chapter of this work.

Stability of HCdV

A one-gram sample of HCdV showed no detectable loss in weight after being heated at 110°C for over 200 hours. The temperature of a 0.2-gram sample was slowly increased from 110°C to 240°C over a period of 22 hours on a thermobalance with no detectable loss in weight. At 240°C the acid very slowly decomposed over a period of two weeks, leaving a residue of cadmium oxide. On the basis of the cadmium oxide thus obtained, the decomposition appears stoichiometric. Several other samples were likewise decomposed, and the results are reported in Table 12. The large average deviation is probably due to the presence

of a reducing atmosphere during the decomposition.

Table 12. Decomposition of HCdV .

Batch number	Calculated molecular weight of CdO
2	128.17
2	128.30
3	128.34
3	128.60
4	127.93
4	129.10
Average	128.41
Correct value	128.41
Average deviation	0.3%
Assay	100.00%

Hygroscopic character of HCdV

The hygroscopic character of HCdV was determined on a thermobalance at 25°C with a chamber designed to allow a circulation of air at a constant humidity. Various humidities were obtained by bubbling the air through appropriate sulfuric acid-water mixtures. The results are reported in Table 13. The rate of moisture uptake was essentially linear during the first hour.

Table 13. Hygroscopic character of HCdV (25°C).

Percent humidity	Rate of moisture uptake (%/min.)
20	≈ 0.0004
40	~ 0.001
50	~ 0.002
60	0.021
80	0.032

HCdV as an Alkalimetric Primary Standard

The effect of repeated crystallization on the purity of HCdV was determined by comparative titrations with potassium hydroxide. A potassium hydroxide solution, about 0.1N and free of carbon dioxide, was prepared by the method of Powell and Hiller (55). The exact normality of this solution was determined by using dry samples of the unrecrystallized, once- and twice-recrystallized HCdV and by using National Bureau of Standards sample 84f, potassium acid phthalate. The titrations were performed with a weight buret, and all weights were corrected to weight in vacuum. The crushed, one-gram samples were dissolved in carbonate-free distilled water and titrated potentiometrically to the theoretical end-point. This occurs at a pH of 8.6 for the conversion of potassium acid phthalate to di-potassium phthalate and a pH of 7.4 for the conversion of HCdV to KCdV. The value of 7.4 was calculated from the ionization constant. The data, summarized in Table 14, show that the purity of the material is not improved by

recrystallization.

Table 14. Comparison of NaOH molality using potassium acid phthalate and HCdV as primary standards.

	NBS 84f KHP	HCdV		
		Not recryst	Once recryst	Twice recryst
	0.10669	0.10669	0.10668	0.10673
	0.10670	0.10671	0.10673	0.10665
	0.10664	0.10674	0.10667	0.10673
Average	0.10668	0.10671	0.10669	0.10670
Combined average	0.10668		0.10670	
Av. stand. deviation of HCdV samples			±0.03%	
Calculated assay	99.99%		100.01%	

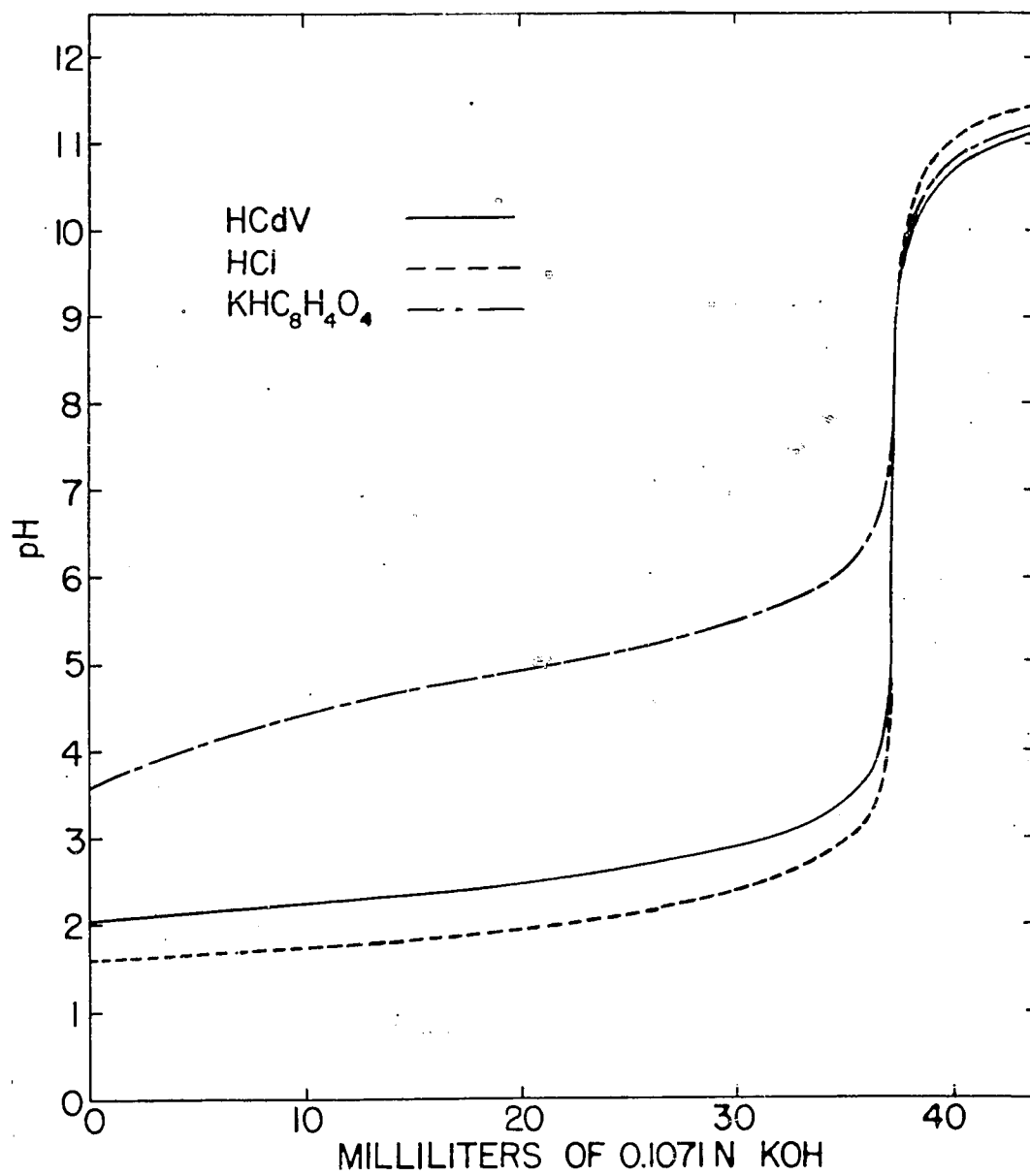
A sample of HCdV was analyzed spectrographically; the only metallic impurities detected were Hg and Pb, both to an extent of less than 0.002%. Addition of silver nitrate and barium chloride to 0.01 molar HCdV solutions indicated the absence of chloride and sulfate with a lower detection limit of less than one ppm.

A comparison of the titration curves of HCdV, hydrochloric acid and potassium acid phthalate is given in Figure 5.

HCdV as a Chelometric Primary Standard

The Russian investigators, Smirnov-Avern, Krot, and Sokolov (56) have reported that the chelating properties of EDTA can be destroyed by

Figure 5. The titration curves of HCdV, HCl and $\text{KHC}_8\text{H}_4\text{O}_4$.



boiling the solution with a two-fold excess of ammonium persulfate. Boiling a solution of HCdV with potassium persulfate will also destroy the CdV^- complex. The variable factors involved in this decomposition seem to be (1) the molar ratio $[\text{S}_2\text{O}_8^{2-}]/[\text{HCdV}]$, (2) the concentration of HCdV, (3) the boiling time, and (4) the acidity. A series of experiments was conducted in which one variable was varied while the others were held constant, in order to determine the optimum conditions.

In each experiment the degree of decomposition of HCdV was determined by a titration of liberated cadmium ion with a standard EDTA solution.

Results of these experiments indicated that a two-fold excess of potassium persulfate is necessary to effect decomposition of the HCdV. Greater amounts of persulfate may intensify the pale yellow color of the resulting solution. The solution should be about 0.003M in HCdV. The decomposition is complete after 2 to 3 minutes boiling. Best results were obtained by heating the HCdV solution to boiling before addition of the persulfate. Some added acid is essential to the decomposition. Good results were obtained when the solution was acidified to a pH of about 1.3 with concentrated sulfuric acid.

In order to evaluate HCdV as a primary standard for chelometry, a solution of EDTA was standardized against HCdV. All titrations were carried out using weight burets. Although the visual end-point is sharp, more precise location of the end-point is possible using a photometric end-point. The EDTA solution used was also standardized against pure zinc metal using weight burets with both visual and spectrophotometric end-point detection. Results, given in Table 15, show excellent

Table 15. Comparison of EDTA molality using zinc metal and HCdV as primary standards.

Spectrophotometric end points				Visual end points			
Zinc		HCdV		Zinc		HCdV	
Soln No.	Molality of EDTA Solution I	Batch No.	Molality of EDTA Solution I	Soln No.	Molality of EDTA Solution II	Batch No.	Molality of EDTA Solution II
1	0.04795	2	0.04793	1	0.04967	2	0.04968
1	0.04793	3	0.04795	1	0.04962	2	0.04958
1	0.04787	3	0.04796	1	0.04965	2	0.04964
2	0.04791	4	0.04793	1	0.04963	2	0.04962
2	0.04789	4	0.04793	1	0.04968	2	0.04958
2	0.04795	4	0.04792	2	0.04960	2	0.04967
		4	0.04795	2	0.04961	2	0.04961
				2	0.04964		
Av. molality		Av. molality		Av. molality		Av. molality	
0.04792		0.04794		0.04963		0.04963	
Std. deviation		Std. deviation		Std. deviation		Std. deviation	
0.06%		0.03%		0.06%		0.08%	

agreement between the HcdV and zinc primary standards. Using spectrophotometric end-points, the precision was better using HcdV than it was with zinc as a primary standard. The chelometric indicator was naphthyl azoxine (57). The color changes from yellow or pale orange to deep pink at the end-point. The pH of the solutions was adjusted to the range, 5.5 to 6.0, by adding several milliliters of pyridine and ammonium hydroxide prior to each titration.

APPENDIX B - MATERIALS, APPARATUS AND METHODS

Materials

Chemicals

EDTA The pure acid form of EDTA (H_4Y) was supplied by Geigy Industrial Chemicals, Cranston, Rhode Island. It was stated to be 99 percent pure. The disodium salt (Na_2H_2Y) was supplied by Hach Chemical Company, Ames, Iowa.

HEDTA The HEDTA which was used in this work was obtained from Geigy Industrial Chemicals. This material was stated to be 98 percent pure and was recrystallized once from water before it was used.

DTPA The DTPA was also supplied by Geigy Industrial Chemicals.

Rare-earth oxides The rare earths which were used in this work were supplied by the rare-earth separation group under the direction of Dr. J. E. Powell at the Ames Laboratory of the Atomic Energy Commission. For investigations concerning individual rare earths, oxides of a spectrographic purity of better than 99.9 percent were used. For the preparation of rare-earth mixtures at least 98 percent pure oxides were used.

Other chemicals The mineral acids and ammonium hydroxide were Baker and Adamson C.P. grade and were supplied by the General Chemical Division of Allied Chemical and Dye Corporation, New York, New York. All common salts and organic chemicals were Baker Analyzed Reagent grade and were supplied by the Baker Chemical Company, Phillipsburg, New Jersey.

Thorium and uranium Uranyl nitrate, thorium carbonate and thorium hydroxide were obtained from the supplies at the Ames Laboratory.

Resin

Cation resin The cation-exchange resin was Amberlite 1R-120, 40 to 50 mesh with approximately 8 percent cross linking. This is a sulfonated copolymer of styrene and divinylbenzene, supplied by Rohm and Haas Company, Resinous Products Division, Philadelphia, Pennsylvania.

Anion resin The anion-exchange resin which was used in this work was Amberlite 1R-400A, a polymer of styrene and divinylbenzene with quaternary-ammonium ions.

Water

Distilled water, demineralized by passage through a mixed-bed ion exchanger, was used in all the experiments.

Apparatus

pH meter

A Beckman model H2 meter, standardized against Beckman pH-seven buffer, was used for all pH measurements. Beckman Instruments, Fullerton, California, supplied both the meter and the buffer.

Columns

The cation-exchange columns which were used for all elution experiments were assembled from flanged, six-foot lengths of Pyrex-glass pipe with an inside diameter of one inch. A three-inch circle of one-inch polystyrene, fitted with a Saran screen to support the four-foot resin bed, was bolted to the bottom of each column. The bore was conically reduced to 3/8-inch in this polystyrene block. A three-inch circle of 1/2-inch polystyrene with a 1/4-inch cylindrical bore was bolted to the top of each column. The columns were connected in series by 3/8-inch

Saran tubing and Saran connectors. The flow was due to a ten-foot head and was controlled by a stopcock at the outlet end of the system.

The cation-exchange columns, which were used for resin equilibrium-constant measurements, and the anion-exchange column were made from coarse, fritted-glass, sealing tubes with one end drawn to a five-millimeter nipple. The inside diameter was one centimeter; and the top of the tube was fitted with a one-hole stopper, holding a short piece of five-millimeter glass tubing. Eighth-inch surgical tubing was used to carry solution to and from the columns.

The resin was loaded into all resin columns from a water slurry. It was then raised in mass by an upward flow of water. When the flow of water was stopped, the resin slowly settled to the bottom of the column. This "backwashing" operation produced a uniform packing, which was necessary to obtain level band fronts during elution.

Methods

Elution sequence determinations

For use with HEDTA or citric acid, the columns were placed in the hydrogen-ion form by treatment with a dilute solution of sulfuric acid. For elutions with EDTA the columns were placed in the copper-ion form by treatment with a dilute solution of copper sulfate. The columns were then rinsed with water. The mixture to be separated was prepared from appropriate oxides or salts. One-tenth of an equivalent of each element was measured by weight. The mixture was loaded on the first column from a dilute aqueous solution. This produced about three inches of band for each element loaded. The band was eluted about five band

lengths with a flow rate of five to ten milliliters per minute. The eluate was collected in consecutive liter fractions.

Determination of the character of $\overline{H_5V^{+2}}$

Solutions of various concentrations of $(NH_4)_2HV$ were prepared by adding ammonium hydroxide to solutions of H_3V . The pH of each solution was adjusted to 7.5 after its concentration was determined by the titration of an aliquot with standard potassium hydroxide. The total concentration of ammonium ion was determined by a Kjeldahl analysis. These analyses were performed by the analytical service group under the direction of Dr. C. V. Banks at the Ames Laboratory.

In each run the eluant was percolated through a column in the hydrogen-ion form. When HEDTA began passing from the bottom of the column, consecutive, appropriately-sized fractions were caught and analyzed by an alkalimetric titration. In each run the concentration of H_3V rose to a plateau value which was chosen as the equilibrium condition.

Analysis methods

HEDTA solutions All solutions which contained the acid H_3V were analyzed by an alkalimetric titration. Metal-HEDTA solutions were not analyzed for their HEDTA content, but the determination of their metal-ion content is described below.

EDTA solutions The concentration of all uncomplexed EDTA solutions was determined by a titration with a secondary-standard zinc nitrate solution. This solution was standardized against a standard Na_2H_2Y solution which was standardized with $HClV$.

Metal-chelate eluate solutions The metal-chelate eluate solutions were analyzed by various means, depending upon the character of the metal ions involved and the nature of the analysis required. The consecutive fractions from the sequence determination runs were boiled to dryness with nitric acid and hydrogen peroxide and then transferred to crucibles for ignition to oxide. A qualitative emission spectrographic analysis of these oxide samples was performed by the analytical service group, directed by Dr. V. A. Fassel, at the Ames Laboratory.

The zinc-thulium-EDTA solutions, resulting from the composition effect studies, required a quantitative determination of $[Zn_T]$ and $[Tm_T]$. An aliquot from each of these solutions was titrated with a standard EDTA solution to determine the amount of uncomplexed metal ion present. After the pH was measured, a second aliquot was made two molar in hydrochloric acid and then passed through an anion-exchange column, previously saturated with a two molar hydrochloric acid solution. Under these conditions the zinc was completely absorbed by the resin as $ZnCl_4^{-2}$. The thulium-EDTA solution was washed from the column with more of the two molar hydrochloric acid solution. The zinc was stripped from the resin with a dilute ammonium hydroxide solution. A titration with the standard EDTA solution yielded $[Zn_T]$. A combination of this result with the amount of uncomplexed metal ion and the concentration of EDTA in the eluate allowed $[Tm_T]$ to be calculated. The concentration of EDTA in the eluate was assumed to be the same as its concentration in the eluant. This was 0.01703M in all the studies, as determined by a chelometric titration with the standard zinc nitrate solution.

The determination of constants

The values of the constants in Table 10 were all determined in solutions of an ionic strength of 0.015. The ionic strength was controlled by an excess of potassium nitrate. All measurements were made at the laboratory room temperature, $23 \pm 3^\circ\text{C}$.

$$\frac{K_{\text{Zn}}}{K_{\text{Tm}}}$$

The resin "equilibrium constant" for the reaction,



was found to be a true constant for all aqueous solutions of these two metals of ionic strength 0.015. Of course, potassium nitrate could not be used to control the ionic strength in the aqueous phase, for the potassium ion would certainly influence the constant. This makes the column experiment more favorable than the batch experiment.

The exact capacities of ten equivalents of resin in each of two short columns with an inside diameter of one centimeter were determined by displacing hydrogen-ion from the resin with an excess of potassium nitrate. The amount of hydrogen-ion released was determined by an alkalimetric titration.

Solutions with varying amounts of zinc and thulium nitrates, but always a total ionic strength of 0.015, were prepared from a measured amount of the standard zinc nitrate solution and an accurately weighed amount of thulium oxide, which had been dissolved in nitric acid; this mixture was accurately diluted to the required volume. In each experiment one of these eluate solutions was simultaneously passed through each of the two short columns, one of which was initially in the zinc-ion form, the other initially in the thulium-ion form. After a ten-fold

excess of metal ion had passed through both columns, as much of the solution as possible was removed from the resin by drawing a partial vacuum below the column. The resin was then rinsed with water. It was assumed that this operation had no effect on the composition of the resin. Both ions were then stripped from both columns by an EDTA solution. The amount of zinc in these solutions was determined, as described in a previous section. The amount of thulium on the resin was determined by difference. These results allowed the calculation of \bar{X}_{Zn} and \bar{X}_{Tm} for each of the various eluates of known composition. K_{Tm}^{Zn} was then calculated from the relation,

$$K_{Tm}^{Zn} = \frac{[Zn^{+2}]^3 \bar{X}_{Tm}^{-2}}{[Tm^{+3}]^2 \bar{X}_{Zn}^{-3}}$$

K_{Tm}^{Zn} was found to have the value 139 ± 4 .

$\frac{H}{K_{HTmY}}$ The acid association constant of the thulium-EDTA anion, TmY^{-} , was determined in a solution whose ionic strength was 0.015 with potassium nitrate. A solution was prepared that was exactly 0.001M in thulium nitrate and 0.001M in Na_2H_2Y . Sufficient potassium nitrate was added to raise the ionic strength to 0.015. This solution was titrated with a standard potassium hydroxide solution which was 0.015M in potassium nitrate. The course of the titration was followed by measuring the pH. These pH-meter readings were converted to hydrogen-ion concentration by a pH-correction factor of -0.05. This value of pY_{H+} for a solution of ionic strength 0.015 was interpolated from data given by Harned and Owen (58).

In this titration the following relations apply:

$$[Y_T] = [Tm_T] = [HTmY] + [TmY^-],$$

and

$$[H_T] = [HTmY] + [H^+] + B,$$

where B is the moles of base added per liter of solution. A combination of these equations with the expression for K_{HTmY}^H yields the relation,

$$K_{HTmY}^H = \frac{[H_T] - [H^+] - B}{[H^+]([Y_T] - [H_T] + [H^+] + B)}.$$

Sufficiently high pH's were used in the calculation so that uncomplexed species of EDTA were not significant. An average value of K_{HTmY}^H was taken from the treatment of several points along the titration curve.

K_{HZnY}^H and $K_{H_2ZnY}^H$ This system was treated in a manner similar to that described in the preceding section. In this case the following relations apply;

$$[Y_T] = [H_2ZnY] + [HZnY^-] + [ZnY^{-2}],$$

and

$$[H_T] = 2[H_2ZnY] + [HZnY^-] + [H^+] + B.$$

The combination of these relations with the expressions for K_{HZnY}^H and $K_{H_2ZnY}^H$ yields the relations,

$$K_{HZnY}^H = \frac{2[Y_T] - 2[ZnY^{-2}] - [H_T] + [H^+] + B}{[H^+] [ZnY^{-2}]}$$

and

$$K_{H_2ZnY}^H = \frac{[H_T] - [Y_T] + [ZnY^{-2}] - 1/2([H^+] + B)}{[H^+](2[Y_T] - 2[ZnY^{-2}] - [H_T] + [H^+] + B)}.$$

The term $[ZnY^{-2}]$ was eliminated from these equations by the simultaneous treatment of two points along the titration. The results from several sets of points along the titration curve were averaged.

$K_{Zn_2Y}^{Zn}$ A solution of ionic strength 0.015 was prepared. It was 0.001M in Na_2H_2Y , 0.002M in zinc nitrate and contained sufficient potassium nitrate. This system was treated in a manner similar to that described in the preceding two sections. In this case the following relations apply;

$$[Zn_T] = 2[Y_T] = [Zn^{+2}] + [ZnY^{-2}] + [HZnY^{-}] + [H_2ZnY] + 2[Zn_2Y],$$

$$[Y_T] = [ZnY^{-2}] + [HZnY^{-}] + [H_2ZnY] + [Zn_2Y]$$

and

$$[H_T] = [Zn_T] = [HZnY^{-}] + 2[H_2ZnY] + [H^+] + B.$$

The combination of these equations with the expression for K yields the relation,

$$K_{Zn_2Y}^{Zn} = \frac{F_{Zn}(H)}{4[Y_T]} \left\{ \frac{[2[Y_T](1 + K_{HZnY}^H K_{H_2ZnY}^H [H^+]^2) - F_{Zn}(H)([H^+] + B)]^2 - 1}{F_{Zn}(H)([H^+] + B - 2[Y_T])} \right\}.$$

As before, the results from several points along the titration curve were averaged.

The acid association constants of Y^{-4} The four acid association constants of the EDTA anion, Y^{-4} , at an ionic strength of 0.015 were determined by interpolating values of the logarithms of these constants, given by Matson (59), for various ionic strengths in the range of 0.015. Values for an ionic strength of 0.015 were taken from plots of $\log K_{H_1Y}^H$

versus ionic strength ($i = 1, 2, 3, 4$).

$\frac{K_{ZnY}^{Zn}}{K_{TmY}^{Tm}}$ and K_{TmY}^{Tm} The values of the stability constants for the Zn-EDTA and Tm-EDTA complexes were determined at an ionic strength of 0.015, using a method described by Reilley and Schmid (60) and used by Schwarzenbach and Anderegg (61). The potential of a mercury electrode was measured against a standard calomel cell. This potential is given by the equation,

$$E = E_0 + 0.0291 \log[Hg^{+2}],$$

where E_0 is a sum of three potentials:

- (1) the standard potential of a Hg^{+2}/Hg cell, measured against a standard calomel cell;
- (2) the liquid junction between a 0.1N KCl solution and a 0.015M KNO_3 solution; and
- (3) the liquid junction between a 0.015M KNO_3 solution and the test solution.

The coefficient 0.0291 arises from RT/nF with $T = 293^\circ K$ and $n = 2$.

A solution of mercuric nitrate and Na_2H_2Y was prepared with

$$[Hg_T] = [Hg^{+2}] + [HgY^{-2}] \cong [HgY^{-2}] = 0.0001M$$

and with

$$[Y_T] = [HgY^{-2}] + [Y^{-4}]Y(H) = 0.0002M$$

and with sufficient potassium nitrate to make the ionic strength 0.015.

Then

$$K_{HgY}^{Hg} = \frac{[Hg_T]Y(H)}{[Hg^{+2}]([Y_T] - [Hg_T])} = \frac{Y(H)}{[Hg^{+2}]}$$

Due to the function $Y(H)$, the potential of the cell was a function of the pH of this solution. That is,

$$E(H) = E_0 + 0.0291 \log \frac{Y(H)}{K_{Hg}^{HgY}}$$

The solution was titrated with a standard potassium hydroxide solution which contained 0.015M potassium nitrate. The titration was followed by measuring the pH of the solution and the potential of the cell. An average value of

$$\log K_{Hg}^{HgY} - \frac{E_0}{0.0291} = \log Y(H) - \frac{E(H)}{0.0291}$$

was determined from several combinations of these data. Neither $\log K_{Hg}^{HgY}$ nor $E_0/0.0291$ was determined, for only their difference was needed for the subsequent determination of the stability constants of the Zn-EDTA and Tm-EDTA complexes.

Solutions of each metal ion which contained Hg^{+2} and sufficient EDTA to complex all the mercuric ion, but not all the metal ion, were prepared. The mercuric ion was entirely complexed because K_{Hg}^{HgY} is much larger than either K_{Zn}^{ZnY} or K_{Tm}^{TmY} . Therefore, the following relations apply to these solutions:

$$[Hg_T] \cong [HgY^{-2}];$$

$$[M_T] \cong [M^{+n}] + [MY^{(n-4)}];$$

$$[Y_T] \cong [Hg_T] + [MY^{(n-4)}] + [Y^{-4}]Y(H).$$

At pH's high enough to make the term $[Y^{-4}]Y(H)$ insignificant

$$\frac{[\text{Hg}_T]([\text{M}_T] - [\text{Y}_T] + [\text{Hg}_T])K_{MY}^M}{([\text{Y}_T] - [\text{Hg}_T])K_{\text{HgY}}^{\text{Hg}}}$$

When the potential of the cell is measured with the mercury electrode in contact with this solution, the desired constant can be calculated from the relation,

$$\log K_{MY}^M = \frac{E}{0.0291} - \log \frac{[\text{Hg}_T]([\text{M}_T] - [\text{Y}_T] + [\text{Hg}_T])}{[\text{Y}_T] - [\text{Hg}_T]} + \log K_{\text{HgY}}^{\text{Hg}} - \frac{E_0}{0.0291}$$

The large probable error in these constants, as reported in Table 10 in Chapter 3, is due to a large range of values for the difference,

$$\log K_{\text{HgY}}^{\text{Hg}} - \frac{E_0}{0.0291}$$

It was found to have a value of 5.56 ± 0.30 .