1955

The use of chelating agents in the separation of the rare earth elements by ion-exchange methods

Earl J. Wheelwright
Iowa State College

Recommended Citation

Wheelwright, Earl J., "The use of chelating agents in the separation of the rare earth elements by ion-exchange methods " (1955). *Retrospective Theses and Dissertations*. 12734.
https://lib.dr.iastate.edu/rtd/12734

THE USE OF CHELATING AGENTS IN THE SEPARATION OF THE RARE EARTH ELEMENTS BY ION-EXCHANGE METHODS

by

Earl J. Wheelwright

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

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1955

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

11/26--

TABLE OF CONTENTS

INTRODUCTION

The group of elements with atomic numbers 58 through 71 are commonly known as the rare earths. Element 57, lanthanum, though not possessing a 4f electron, is the first element to have the rare earth like $5d^1\ 6s^2$ outermost electronic configuration and consequently is included in the rare earth family by most authors. Because of its trivalent character, ionic size, chemical properties, and existence as a major constituent in many rare earth ores, the element yttrium is also included in many systematic studies of the rare earths. While most of the rare earths having odd atomic numbers are quite scarce, it must be pointed out that many members of the series are sufficiently abundant to permit production in technical quantities if important uses develop. As a family, the rare earth elements account for 0.01% of the igneous rock of the earth's crust.

At present, the greatest demand for pure rare earth elements, other than lanthanum, cerium, and perhaps neodymium, is for fundamental scientific research. Since the rare earth atoms differ from each other essentially only by the number of electrons contained in the shielded 4f subshell and the number of protons in the nucleus, their unique physical and chemical properties, such as ionic size, make them valuable tools for testing many of the theories that have been proposed in physics and chemistry.

Even though these elements are relatively abundant in nature, they are usually found in quite low concentrations in their ores, and are always associated with each other. Their similar chemical properties make it extremely difficult to isolate them individually in pure form by classical physical chemical methods such as fractional crystallization and precipitation. In recent years, however, ion-exchange techniques have been applied with great success to this separation problem, and all of the rare earths are now available in kilogram quantities with a purity of 99.99% or greater. The ion-exchange methods which have proven most successful involve the use of an organic chelating agent as the eluant. The successful separation of the rare earth elements by such a method depends for the most part upon the differences in the stability of the complexes formed between individual rare earth elements present in a given mixture and the chelating agent in the eluant.

The research described in this thesis was undertaken in order to accomplish two main objectives. The first objective was to measure carefully the stability of the complexes formed by each of the trivalent rare earth cations with ethylenediaminetetraacetic acid, abbreviated EDTA, and with N-hydroxyethylethylenediaminetriacetic acid, abbreviated HEDTA; both of which are known to form quite stable metal chelates. Such a series of constants would provide both theoretical information concerning the influence of the size of a cation upon its physical and chemical properties, and also would indicate the effectiveness of such a chelating agent in separating the individual rare earths by ion-exchange or other means. The second objective of this research was to find methods for using the two chelating agents in conjunction with an ion-exchange resin for separating the rare earths.

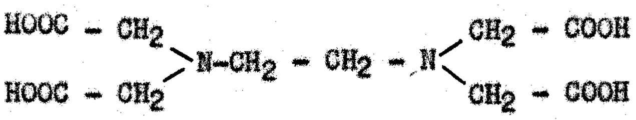
MEASUREMENT OF THE STABILITY OF THE RARE EARTH COMPLEXES WITH ETHYLENEDIAMINETETRAACETIC ACID AND WITH N-HYDROXYETHYLETHYLENEDIAMINETRIACETIC ACID

Historical Review

Methods used to detect the presence of metal chelates

When a metal ion combines with an electron donor, the resulting substance is said to be a metal complex, or coordination compound. If the molecule which combines with the metal contains two or more donor groups, one or more rings are formed. The resulting substance is called a chelate compound, and the donor containing molecule is said to be a chelating agent. The electron-pair bond formed between the metal and the donor group may vary in type from essentially ionic to essentially covalent, depending upon the metal and the chelating agent. Morgan and Drew (1) were the first to use the term chelation to describe this type of coordination structure.

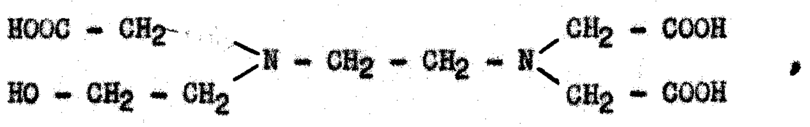
The chelating agent ethylenediaminetetraacetic acid, which has the structural formula



$$\begin{array}{l}HOOC-CH_2\\HOOC-CH_2\end{array}\!\!>N-CH_2-CH_2-N<\!\!\begin{array}{l}CH_2-COOH\\CH_2-COOH\end{array},$$

was prepared first by Fick and Ulrich (2). These authors describe a method in which ethylenediamine and hydrogen cyanide are reacted with formaldehyde in aqueous solution at a pressure of one atmosphere and room temperature to give the tetranitrile, which can then be converted to EDTA or its tetra sodium salt by acidic or basic hydrolysis.

N-Hydroxyethylethylenediaminetriacetic acid, with the structure



$$\begin{matrix}\mathrm{HOOC-CH_2} \\ \mathrm{HO-CH_2-CH_2}\end{matrix}\!\!>\mathrm{N-CH_2-CH_2-N}<\!\!\begin{matrix}\mathrm{CH_2-COOH} \\ \mathrm{CH_2-COOH}\end{matrix} \quad ,$$

was first described by Chaberk and Bersworth (3) in 1953. These workers have not as yet published a description of the method used for the preparation of this compound. Only two papers have been published describing any of the chemistry of HEDTA.

There are a great many methods which various workers have used to show evidence for the existence of metal chelates. No attempt will be made to review all of these, but a few which apply to EDTA and HEDTA complexes will be briefly described. This section contains only those methods which have been used in a qualitative manner. The methods which have been used to give a quantitative measurement of the stability constants are described in a later section.

The isolation, purification, and chemical analysis of crystalline compounds is a widely used method of indicating the presence of chelates. Britzinger, Thiele, and Miller (4) were able to isolate some lavender-colored crystals which a chemical analysis showed to be the tetrahydrate of sodium-(ethylenediaminetetracetato)-cobaltate III. Strong evidence for a hexadentate chelate structure was obtained when dehydration of the lavender-colored crystals at 150°C removed all of the water but did not change the color of the crystals.

A second method for detecting the formation of metal chelates is the alteration of the normal chemical behavior of a metal ion in solution.

For example, calcium carbonate will not precipitate from a solution containing calcium ions when an excess of the sodium salt of EDTA has been added. Oxalate will not precipitate calcium from a calcium-EDTA complex in a solution whose pH is above 10. Dimethylglyoxime will not precipitate nickel from the nickel-EDTA complex in a solution of pH 6.5. Chaberek and Bersworth (3) report that the iron III-HEDTA chelate is stabilized against hydrolysis to the extent that the chelate is completely stable against alkali hydroxide precipitation.

The color of chelate compounds is generally accepted as being so significant that colors are carefully described in reports of chemical investigation of these substances. The intensification of color is usually considered an indication that a chelate is present. These color changes were strikingly illustrated during the preparation of one of the solutions for this research. The color of a copper II chloride solution changed from blue-green to a very deep blue upon the addition of the disodium salt of EDTA. Moeller and Brantley (5) have shown that essentially all of the absorption bands in the neodymium spectrum are altered by the presence of EDTA, the most striking effects occuring in the 5780 Å region. Similar effects were also found in the spectra of tripositive gadolinium, holmium, and erbium.

The effective disappearance of ions in solution by the formation of metal chelates may be followed by electrical-conductance measurements. Martell (6) used this method to follow the titration of ethylenediaminetetraacetic acid with sodium hydroxide and with calcium hydroxide. He found that with the sodium hydroxide titration, a simple minimum was found when the conductance was plotted as a function of the equivalents of base added; indicating that a simple neutralization had taken place and that the metal ion was not strongly chelated. The conductance curve for the titration with calcium hydroxide paralleled the sodium hydroxide curve to the minimum value of the latter. Once the mono-calcium diacid salt was formed, further addition of calcium hydroxide did not increase the conductance until after the complete addition of a full mole of calcium hydroxide. The calcium results are interpreted as involving a simple neutralization reaction, followed by a chelation reaction. The conductance remains practically constant during the second reaction because the addition of calcium hydroxide results in the replacement of one bivalent ion with another of practically the same size.

It should be pointed out that an investigator might be in error in assuming chelate formation on the basis of one or perhaps two of the methods which have been described, as alternate interpretations of the physical chemical phenomenon are possible in some cases. It is necessary, therefore, to enmasse as much independent evidance as possible before stating that the existence of a chelate is proven.

Nature and structure of the metal complexes of EDTA

It is possible for the anion of EDTA to serve as a tetra-, penta-, or hexadentate chelating agent, depending upon the specific metal ion involved. The hexadentate structure is shown as an octahedral configuration, utilizing both nitrogen atoms and all four carboxyl groups. In most chelates such a structure would involve a good deal of strain so an alternate structure, in which one of the carboxyl groups is displaced in the coordination sphere by a water molecule or some other donor group, has been postulated. The literature indicates that either structure may exist, depending upon the specific ion involved and the conditions of the solution.

Pfeiffer and co-workers (7,8,9) have described the preparation and some of the physical and chemical properties of compounds that are formed between EDTA and the alkaline earth elements and copper. At about the same time, Brintzinger and co-workers (4,10,11) conducted similar experiments with EDTA complexes of some of the heavy metals, some light rare earths, lithium, beryllium, thorium, and uranium. Both of these workers attempted to elucidate the nature or structure of the various compounds which they had prepared on the basis of physical properties, stability toward various precipitating agents, solubility, and color. Brintzinger reported the preparation of the tetrahydrate of sodium-(ethylenediaminetetracetato)-cobaltate III and found that the color of the deep lavender crystals was not altered by complete dehydration at 150°C. Such a color stability is good evidence that EDTA serves as a hexadentate chelating agent and that water is not involved in the primary coordination structure.

Schwarzenbach (13) prepared a number of cobalt III complexes containing pentadentate EDTA and a second donor substituent. The removal of the second group then yielded a hydrate of the hexadentate complex. It was demonstrated that when a water molecule is actually coordinated, a reversible color change from red to blue takes place as the pH is increased. This is attributed by Schwarzenbach to the conversion of the monoaquo complex to monohydroxy complex. The monoaquo species may be converted into the red hexadentate species by boiling, as evidenced by the fact that the reversible color change no longer occurs.

Perhaps the best evidence for the existence of a cobalt III complex in which EDTA is hexadentate has been found in the infrared spectrum of some pentadentate and hexadentate species by Busch and Bailor (12). They prepared the pentadentate complexes bromo-(ethylenediaminetetraacetato)-cobaltate III, and nitro-(ethylenediaminetetraacetato)-cobaltate III. The hexadentate complex was prepared from the bromo complex by triturating with silver oxide. The infrared spectra for the pentadentate complexes exhibited two carbonyl bands. The stronger band was attributed to the presence of three coordinated carboxyl groups while the weaker band was associated with the free carbonyl group. Only one carbonyl band appeared in the infrared spectrum of the hexadentate chelate, thus indicating the equivalence of the four coordinated carboxyl groups.

Klemm and Raddatz (14) measured the magnetic susceptibility of the nickel II-EDTA complex which Brintzinger and Hesse had prepared. Since the salt was not diamagnetic but exhibited paramagnetic properities of the same order of magnitude as the uncomplexed nickel II ion, and since the salt was blue, these authors concluded that the complex was either tetrahedral or octahedral rather than the covalent planer type and was predominately ionic. Two years later Klemm (15) published data on the magnetic properties of the EDTA complexes with iron III, cobalt III, and chromium III. The data on the chromium complex were inconclusive because the covalent and ionic complexes have the same susceptibility. The iron III complex was found to be ionic and the cobalt complex was found to have covalent octahedral bonding.

Work on the iron III complex of EDTA indicates clearly that in the case of the complex FeY^-, where Y is used to indicate the various anionic species of EDTA, there is no free carboxyl group present. Jones and Long (16) prepared the solid compound HFeY of high purity and concluded from an analysis of C, H, N, and Fe that there was no water in the coordination sphere of the acid. This fact was confirmed by a titration of the acid with standard base. The authors point out that HFeY behaves exactly like a completely strong monobasic acid to pH 7. However, at a higher pH a second inflection occurs, accompanied by a color change due to the formation of the deep orange $Fe(OH)Y^{-2}$; indicating that $Fe(OH)Y^{-2}$ is probably pentadentate. This was pointed out earlier by Schwarzenbach and Heller (17) who indicated that the iron III complex, $Fe(OH)_2Y^{-3}$, as well as the iron II complexes, $Fe(OH)Y^{-3}$ and $Fe(OH)_2Y^{-4}$, can be formed. These hydroxo complexes are formed by the stepwise decomposition of the hexadentate complexes, with hydroxyl ions replacing the carbonyl groups in the coordination sphere of the metal ion. Schwarzenbach and Biedermann (18) report the formation of hydroxo complexes with Al III and Cr III at high pH values.

At the present time, no direct investigation of the structure of these various chelates using the techniques of electron or X-ray diffraction has been reported. When such studies are made, the true nature and structure of the chelates will be better understood.

Methods which have been used to determine the stability constants of the EDTA and HEDTA complexes

Potentiometric (pH). The pH of a solution is always directly affected by chelate formation because all chelating agents are either acids or bases. Consequently, one of the most widely used methods for the determination of chelate stability constants has been the potentiometric measurement of the hydrogen ion concentration of a reaction mixture.

Method A. Schwarzenbach and his co-workers (19,20) have determined the stability of the complexes that are formed between the alkaline earth metal ions and EDTA. The process involved the titration of EDTA with standard potassium hydroxide in the presence of a fifteen-fold excess of an alkaline earth metal ion. The titrations were carried out at a constant ionic strength in the presence of 0.1 M potassium chloride. The pH was measured from the potential of the hydrogen electrode versus the silver-silver chloride electrode. In order to satisfactorily explain the titration results which were obtained in the presence of excess calcium II, it was found necessary to assume the formation of complexes between calcium II and two specific anionic species of EDTA according to the equation:

$$M^{+2} + H_2Y^{-2} \rightleftharpoons MHY^{-} + H^{+} \qquad (I)$$

and

$$M^{+2} + HY^{-3} \rightleftharpoons MY^{-2} + H^{+} \; . \qquad (II)$$

The two desired stability constants were defined as follows:

$$K_1 = \frac{[MHY]}{[M]\,[HY]} \tag{1}$$

and

$$K_2 = \frac{[MY]}{[M]\,[Y]}\ . \tag{2}$$

Schwarzenbach proposed a graphical procedure for computing these stability constants from the total concentration of EDTA, total concentration of the specific alkaline earth present in solution, the amount of KOH added, and the pH of the solution. Martell and Calvin (6) have proposed an algebraic method which accomplishes the same objective.

This method proved satisfactory for measuring complexes of low to intermediate stability. For very strong complexes, such as those formed with the rare earths (21), the equilibria in equations I and II lie too far to the right to permit accurate calculation of the equilibrium concentrations of the various ionic species from the pH measurements.

Method B. Vickery (22) used a modification of the above procedure to determine the rare earth-EDTA stability constants. The titrations were carried out at 20°C in a solution whose ionic strength was adjusted to a value of 0.10 with KCl. The solution pH was determined by a saturated calomel-glass electrode system. The constants were calculated from the pH titration curves by a modification of Bjerrum's stepwise equilibrium theory. Vickery has been criticized (21,23) for errors in this particular paper. He defined the stability constants by the equation

$$K = \frac{[MHY]}{[M]\,[HY]}\ .$$

It has been pointed out by critics that complexes of the composition MHY, containing a proton and a rare earth cation simultaneously, do not occur in the equilibrium mixtures. In spite of the obvious errors in the paper itself and the large experimental errors involved in determining the stability constants of very stable complexes by direct methods, the constants reported by Vickery are of about the right order of magnitude indicating that equation (16) must have been important in his calculations.

Method C. The simple titration procedure described under method A has been considerably modified by Schwarzenbach and his co-workers (24,25,26) so as to be applicable to the measurement of the stability constants of very stable complexes. This method involves the use of two chelating agents competing with each other for possession of a heavy metal ion (M) and a second auxiliary metal (Me) which forms a very stable complex with one of the chelating agents but does not complex with the second chelating agent. Since this method was employed in the present research to measure the rare earth complexes that are formed with EDTA and with HEDTA, it is described in a later section.

Potentiometric (Redox). Two general types of non-pH potentiometric methods have been used to determine chelate stability constants. In one method, the oxidized or reduced form of a cation is potentiometrically titrated with an oxidizing or reducing titrant in the presence of an excess of the chelating agent. The second method involves measuring the emf of a cell in which the cell reaction can be directly related to the formation of the desired chelate.

Method A. Schwarzenbach and Heller (17) made a study of the oxidation-reduction equilibrium systems for the EDTA complexes of iron II and iron III. The procedure involved the use of a gold electrode to follow the titration of iron II sulfate with iodine in the presence of an excess of EDTA. All measurements were conducted at 20°C in solutions whose ionic strength was maintained at 0.10 with KCl. Various buffer systems were used in order to extend the investigation to pH values ranging from 2.3 to 8.4. By using a rather complex graphic and algebraic analysis of the experimental data, Schwarzenbach and Heller were able to calculate the stability constants for the normal iron II and iron III complexes, FeY^{-2} and FeY^{-}. They also calculated equilibrium constants for the reactions by which the various hydroxy complexes are formed from FeY^{-} and from FeY^{-2}.

Method B. In a recent series of papers, Carnie and Martell (27,28,29) have described a method for measuring the true thermodynamic equilibrium constants for the reactions between M^{+2}(aq) and Y^{-4}(aq) where M^{+2} is an alkaline earth ion and Y^{-4} is, of course, the anion of EDTA. The experimental method consists of measuring the hydrogen-ion activities in solutions consisting of an alkaline earth metal ion, EDTA, and an inert supporting electrolyte, under equilibrium and reversible conditions. This was accomplished by measuring the emf of the cell.

$Pt\text{-}H_2$, $K^{+}(m_1)$, $M^{+2}(m_2)$, $Cl^{-}(m_3)$, $H_nY^{n-4}(m_4)$, AgCl-Ag, where n may be varied from 0 to 2. The emf data is taken for various cell temperatures from 0 to 30°C and various concentrations of m_1, m_2, m_3, and m_4. It is required that the ratio $(m_{M^{+2}})(m_{H_nY^{n-4}}) : (m_{MY^{-2}})(m_{Cl^{-}})$ be constant by the method employed to extrapolate the emf data to infinite dilution for each experimental temperature. The standard free energy change, ΔF°, was calculated at each experimental temperature for the reaction

$$M^{+2}(aq) + Y^{-4}(aq) \rightleftharpoons MY^{-2}(aq)$$

from the extrapolated data. The extrapolation was made with the Debye-Hückel limiting law and the values of ΔH°, ΔS°, and the thermodynamic equilibrium constants were calculated by the usual equations.

Polarographic. Two general methods for the determination of chelate stability constants are known in polarography. The first method evaluates the stability constant in terms of the displacement of the half-wave metal reduction potential that is produced by the addition of a chelating agent to the metal-ion solution. This method can be applied only if the electrode process is reversible and the equilibrium between the free metal ions and the complex is completely mobile. If, however, the rate of formation and dissociation of the complex is sufficiently low, then although the equilibrium in the vicinity of the electrode is disturbed by the electrode process, the restoration of the equilibrium does not proceed at a sufficient rate to contribute to the wave height. In this case another method can be applied because the free and complexed ions almost always have different electro-deposition potentials and thus give rise to separate waves. The height of each wave is proportional to the concentration of the wave-producing species in the solution.

Method A. As was previously stated, the characteristic half-wave potential ($E_{1/2}$) of a simple metal ion is shifted when the metal ion is complexed by a chelating agent. The magnitude of this shift varies with the concentration of the chelating agent. Thus, by measuring the shift of $E_{1/2}$ values as a function of the concentration of the chelating agent, it is possible to obtain information concerning the formula and stability of the metal chelate. If the oxidized form of the metal ion is denoted by Ox, the reduced form by Red, the chelating agent by X, the coordination number of the oxidized form of the cation by p and the reduced form by q, the following equations and their respective stability or equilibrium constants can be written:

$$\mathrm{Ox} + p\mathrm{X} \rightleftharpoons \mathrm{OxX}_p$$

$$\mathrm{Red} + q\mathrm{X} \rightleftharpoons \mathrm{Red\ X}_q$$

and

$$K_{\mathrm{Ox}} = \frac{[\mathrm{OxX}_p]}{[\mathrm{Ox}]\ [\mathrm{X}]^p} \qquad (3)$$

$$K_{\mathrm{Red}} = \frac{[\mathrm{Red\ X}_q]}{[\mathrm{Red}]\ [\mathrm{X}]^q}\ . \qquad (4)$$

If equations (3) and (4) are solved for [Ox] and [Red] and these values are substituted into the well-known Nernst equation, the following is obtained:

$$E = E^\circ - \frac{0.059}{n} \log \frac{K_{\mathrm{Red}}\ [\mathrm{OxX}_p]\ [\mathrm{X}]^q}{K_{\mathrm{Ox}}\ [\mathrm{Red\ X}_q]\ [\mathrm{X}]^p}\ . \qquad (5)$$

Equation (5) can be simplified by remembering that the half-wave potential, $E_{1/2}$, is the potential at which half of all of the oxidized form which reaches the electrode is reduced to the corresponding reduced form. Therefore, when:

$$E = E_{1/2}$$

then

$$[OxX_p] = [Red\ X_q]$$

and equation (5) reduces to

$$E_{1/2} = E^\circ + \frac{0.059}{n} \log \frac{K_{Red}}{K_{Ox}} \quad [X]^{q-p} \quad . \qquad (6)$$

Equation (6) shows that the half-wave potential is a function of the ratio of the two stability constants, the number of groups coordinated to the oxidized and reduced ions, and the concentration of the complexing agent.

Equation (6) can be modified in a variety of ways to give the desired results. If equation (6) is differentated with respect to log [X], (p-q) values can be calculated from the slope of the straight line obtained by plotting measured values of $E_{1/2}$ versus concentrations of X, expressed as log [X]. The ratio K_{Ox}/K_{Red} can be calculated from equation (6) by substituting the experimental value of $E_{1/2}$ found at [X] = 1 and solving the equation. Thus, if one constant is known the other can be calculated. In the special case, when the complex is reduced to the metal amalgam at the mercury cathode, no reduced form of the complex exists, so equation (6) can be simplified to give equation (7).

$$E_{1/2} = E^\circ - \frac{.059}{n} \log K_{Ox} \qquad (7)$$

Equation (7) gives the single stability constant directly in terms of the value of $E_{1/2}$ when the concentration of the uncomplexed chelate is unity.

Using a modification of this procedure and a streaming mercury electrode, Koryta and Kossler (30) evaluated the nitrilotriacetic acid complexes of cadmium, zinc, and lead at various ionic strengths. An attempt to measure the EDTA complexes of the same metal cations failed because the constants were more stable than the upper limits of the polarographic method that was used. In a later publication, Matyska and Kössler (31), using a slightly different modification, evaluated the formation constants of three mercury EDTA complexes, HgY^{-2}, $HgHY^{-}$, and $HgOHY^{-3}$ at 20°C and an ionic strength of 0.10.

<u>Method B</u>. The basic principle of this method was stated in the polarographic introduction. In a solution containing free ions and complexed ions, each species is reduced at the mercury electrode at a different potential. Thus, each species will contribute its own individual wave. The height of the wave, which is a reflection of the electrode diffusion current, is a direct measure of the concentration of the species in the solution. The polarograph serves merely as an analytical tool for measuring the concentrations of the reactants and products of a chemical reaction. This method was used to measure the HEDTA and EDTA complexes of the rare earths in the present research. An exact description of the procedure and a derivation of all of the equations are presented in a later section of this thesis.

The mechanism of the reaction between copper II and the cadmium-EDTA complex was studied by Ackermann and Schwarzenbach (32) using the above method. They found that the reaction proceeds simultaneously via four different reaction paths brought about through the collision of the copper II ion with CdY^{-2}, $CdHY^{-}$, HY^{-3}, and H_2Y^{-2} which are all in permanent equilibrium with each other.

The EDTA complexes of titanium III and titanium IV have been studied by Blumer and Kolthoff (33). They report that complexes of the probable formula TiY^{-} and TiY are formed at pH values less than 2.5. At higher values, the electrode processes are irreversible and dependent upon the solution pH. The authors assumed such pH dependence to be caused by the formation of hydroxy complexes. A value for the stability constant of the TiY complex was calculated.

Pecsok and Maverick (34) found that the titanium III and titanium IV EDTA complexes yield well formed reversible polarographic waves. Below pH 2 the half-wave potential is independent of pH and above 2.5 the dependence is linear. As the pH is increased, the waves become more irreversible, the diffusion currents are dimminished, and the solution becomes colloidal. They found that the diffusion current of the wave is a direct measure of the concentration of the complex in the presence of either an excess of titanium or of EDTA. Measurements of the pH, total titanium, total EDTA, and the diffusion current indicate that TiY is reduced to TiY^{-} below pH 2. The stability constants for the complexes TiY^{-}, $TiOY^{-2}$, and TiY were calculated from known total EDTA and titanium concentrations, and four acid dissociation constants of EDTA, and the diffusion current data.

A series of stability constant ratios have been evaluated by Bril and Krumholz (35) using a displacement method. They investigated the systems copper-EDTA with nickel, lead, cadmium, and zinc; cadmium-EDTA with zinc; and lead-EDTA with zinc. From the polarographically measured equilibrium concentration of the metal M^{+2} and the known total analytical concentrations, an equilibrium constant can be calculated for equation (III).

$$Me^{+2} + MY^{-2} \rightleftharpoons MeY^{-2} + M^{+2} \qquad \text{(III)}$$

This equilibrium constant is, of course, the ratio of the two individual chelate stability constants. All measurements were carried out at 20°C and in solutions maintained at an ionic strength of 0.10 with KNO_3. Actual thermodynamic constants were determined by extrapolating the data to infinite dilutions.

This polarographic method has been used very extensively by Schwarzenbach and his co-workers (36,37) to evaluate heavy metal stability constants of EDTA and also of cyclohexanediaminetetraacetic acid (CDTA). They report measurement of the stability constants of the vanadium complexes VY^{-2}, VY^{-}, VHY^{-}, $V(OH)Y^{-2}$, VOY^{-2}, and $VOHY^{-}$. A second paper reports the measurement of the stability constants of thirty one metals with EDTA and twenty five metals with CDTA. The procedure used was identical to that used to measure the rare earth stability complexes in the present research except that Schwarzenbach used several auxiliary metals in place of the single metal, copper, which was used in the rare earth research.

Spectrophotometric. The stability of the EDTA complex with iron III has been determined by Kolthoff and Auerback (38) from spectrophotometric measurements at four different wave lengths in the 370 to 400 millimicron region. Because of the great stability of the iron III chelate, it was found necessary to make the measurements in 0.6 to 1 molar perchloric acid so as to suppress the ionization of H_4Y and H_3Y^- and prevent the reaction from going to completion with all iron in the form of a chelate. The concentration of the uncomplexed iron III was determined by the difference between the known total iron concentration and the spectrophotometrically determined equilibrium concentration of FeY^-. The concentration of Y^{-4} was computed from the known total EDTA concentration, its four acid dissociation constants, and the pH. This data enabled the authors to calculate the desired constant from the equation

$$K_{FeY} = \frac{[FeY^-]}{[Fe^{-3}]\,[Y^{-4}]} = \frac{[FeY]}{[Fe]\,[Y]} \quad .$$

Because of the necessity of using highly acidic solutions, pH measurements and the calculated equilibrium concentration of Y^{-4} were subject to considerable error. The error was, of course, carried over into the final stability constant calculations.

Martell and his co-workers (39,40) have employed a competition reaction method to determine the stability constants of several heavy metal-EDTA complexes. The experimental method consisted of reacting equal molar amounts of the complexing agent and two cations. Thus, assuming the usual 1:1 ratio, only half of the total number of metal ions are complexed. Depending upon the various buffers that were employed, the uncomplexed form of the metal either remained in solution or precipitated out as a solid phase. In some cases, several weeks of constant shaking were required to insure equilibrium with the solid phase. The individual reactants and products were determined by spectrophotometric analysis.

Only stability constant ratios could be determined by this method. However, if one of the constants was known independently, then the other one could be calculated from the ratio. The results reported by the authors do not agree very well with the constants obtained by other people. Two possible sources of error are immediately obvious. The existence of a solid phase in the reacting mixture introduces many complications which are not very well understood. Also, no correction was made for possible complex formation between the free cations and the buffers used to maintain a constant pH value.

Radioactive exchange. In an acid solution, the complex ion MY^{4-n}, formed from a metal ion and the conjugate base of a weak acid, will undergo partial dissociation due to the formation of some undissociated free acid. If the ionization constants of the weak acids that are formed are known, the stability constant of the chelate complex can be calculated from the concentration of M^{+n} ions present in an equilibrated MY^{4-n} solution of known acidity. The M^{+n} ion concentration can be determined by use of a radioactive indicator. It is necessary that the exchange of the uncomplexed ions with the complexed ions take place slowly. This is usually true for highly stable chelates.

In the procedure used by Cook and Long (41) to measure the stability of the nickel II-EDTA complex, Ni^{+2} ions are added to an acidified and equilibrated solution of $\overset{*}{N}iY^{-2}$; prepared from nickel containing some Ni^{63}. In such a mixture, the exchange

$$\overset{*}{N}iY^{-2} + Ni^{+2} \rightleftharpoons NiY^{-2} + \overset{*}{N}i^{+2}$$

takes place. Aliquots are removed from the resulting mixture at measured time intervals after mixing. The uncomplexed ions in the various aliquots are immediately separated from the complexed ions by a rapid hydroxide precipitation of the nickel II ions and the specific activity is measured. The increase of the specific activity with time is a function of the moles of added Ni^{+2} and of that present as such in the original solution before mixing.

The fraction of exchange, x, in each aliquot is given by the ratio of the specific activity of the separated ions to that of the separated ions from an aliquot removed from the reaction mixture after equilibrium has been reached, i.e.,

$$x_t = S_t/S_\infty \ .$$

A plot of log $(1-x_t)$ against time, extrapolated to zero time, gives the value of the instantaneous exchange, x_0, the exchange due to mixing of the dissociated $\overset{*}{Ni}{}^{+2}$ ions from the complex with the inactive Ni^{+2} that are added.

If $[NiY]_0$ represents the total of the complex ion in the original solution, α the degree of fractional dissociation of the complex ion, A the total moles of nickel atoms in the original solution and B the total moles of added nickel ions, the relationship between α and x_0 is given by the equation

$$\alpha = \frac{x_0 B}{A(1-x_0) + B} \ .$$

In the original equilibrated complex ion solution,

$$[Ni] = [Y] + [HY] + [H_2Y] + [H_3Y] + [H_4Y] = [Y]\,\phi$$

where $\phi = 1 + [H]\,K_{HY} + [H]^2\,\overline{K}_{H_2Y} + [H]^3\,\overline{K}_{H_3Y} + [H]^4\,\overline{K}_{H_4Y}$

and

$$[Ni] = \alpha\,[NiY]_0 \quad .$$

Two other equations can also be written:

$$[Y] = \frac{[Ni]}{\phi} = \frac{\alpha\,[NiY]_0}{\phi}$$

and

$$[NiY] = \frac{(1-\alpha)\;[NiY]_0}{1 + [H]/K_A} \quad .$$

The term K_A represents the second ionization constant of the weak acid H_2NiY. It is necessary because the species $HNiY^-$ must be considered. The above equations can be combined to give equation (8) from which the desired constant can be obtained

$$K_{NiY} = \frac{[NiY]}{[Ni]\;[Y]} = \frac{(1-\alpha)\;\phi}{\alpha^2\;[NiY]_0\;(1 = [H]/K_A)} \quad . \tag{8}$$

Cook and Long reported a value of 10^{19} for the nickel II-EDTA stability constant. This value does not compare too favorably with the value of $10^{18.45}$ reported by Schwarzenbach and Freitag (26) for the same complex. Using a similar procedure, Jones and Long (42) obtained a value of 10^{24} for the iron III-EDTA stability constant. This is a little lower than the value of 10^{25} reported by Schwarzenbach and Biedermann (18).

Ion exchange. The ion-exchange method depends upon the fact that the quantity of a cation bound to a definite amount of cation exchanger at equilibrium is proportional to the concentration of free cations in the solution over a wide range of concentrations. This proportionality holds true even in the presence of a chelating agent.

Fulda and Fritz (43) have determined the stability of the chelates formed between HEDTA and uranium VI, calcium II, zirconium IV, thorium IV, and lanthanum III by an ion-exchange method.

A solution containing the metal ion and a known excess of chelating agent was intimately mixed with a known amount of cation-exchange resin for a period of three hours. At the end of the equilibration period, the exchange constant (slope of the adsorption isotherm) for the metal with the resin was determined by analysis of the liquid phase for the metal by an appropriate method. In an exactly analogous manner, the exchange constant in the absence of a chelating agent was determined. Then the stability constant for the metal complex was calculated from the equation

$$K = \frac{\frac{\lambda_0}{\lambda} - 1}{[V^{-3}]} ,$$

where λ_0 = the distribution constant when no chelating agent is present

λ = the distribution constant when chelating agent is present.

The experiments were carried out at room temperature and with solutions adjusted to an ionic strength of 0.1 with KCl. Since λ and λ_0 were measured in two separate solutions, it was essential that the ionic strength of these solutions be adjusted to the same value.

Derivation of the Experimental Methods Used to Measure the Stability Constants

The stability of the complexes formed between each of the rare earth cations and the anions of two separate polydentate organic chelating agents has been measured. These measurements have been accomplished by the use of two separate independent experimental methods. Because of the similarity in the types of rare earth chelates formed by EDTA and HEDTA, it is found that the equations which describe the EDTA systems are directly applicable to the HEDTA systems. Therefore, the two experimental methods will be derived in terms of the EDTA systems. It should be remembered that the same equations, except for a change of one in the ionic charge of a few of the ionic species, describe the HEDTA chelate formation equally well.

The potentiometric method

If equal molar quantities of the copper complex of EDTA, Na_2CuY, a rare earth salt, MCl_3, and the trihydrochloride of β , β', β'' triaminotriethylamine, $N(CH_2\text{-}CH_2\text{-}NH_2)_3$, designated as "tren", are mixed together, the reaction shown below takes place (26).

$$CuY^{-2} + H_3tren^{+3} + M^{+3} \rightleftharpoons MY^{-} + Cutren^{+2} + 3H^{+} \qquad \text{(IV)}$$

If such a mixture is titrated with NaOH, three formula weights of the base are used in a buffer region between pH 4 and 5.5.

The tri-(β -aminoethyl)-amine, "tren", is a strong triprotonic base with pK values of 10.29, 9.59, and 8.56. These ionization constants can be expressed as follows:

$$\bar{K}_{H_3tren} = \frac{[H_3tren]}{[H]^3\ [tren]} = K_{Htren} \cdot K_{H_2tren} \cdot K_{H_3tren} = 10^{28.44} \quad (9)$$

The amine, "tren", forms a very stable complex with the copper II ion (44).

$$K_{Cutren} = \frac{[Cutren]}{[Cu]\ [tren]} = 10^{19.1} \quad (10)$$

This stability constant was determined from the equilibrium constant of reaction (V) which exhibits a buffer action in the pH range 3.9 to 4.8.

$$Cu^{+2} + H_3tren^{+3} \rightleftharpoons Cutren^{+2} + 3H^{+} \quad (V)$$

Because of the greater proton affinity of the base "tren" compared to the anion "Y", the complex $Cutren^{+2}$ is less stable than the complex CuY^{-2} in a pH range below 8.5. If NaOH is added to an equivalent mixture of CuY^{-2} and H_3tren^{+3}, a buffer region is observed in the pH range 8.5 to 9.5 during which the copper exchanges from the "Y" to the "tren". Such a reaction is expressed as follows:

$$CuY^{-2} + H_3tren^{+3} \rightleftharpoons Cutren^{+2} + HY^{-3} + 2H^{+} . \quad (VI)$$

If a second cation capable of being complexed by the chelating agent "Y" is added during the neutralization, not only two, but three hydrogen ions can be neutralized in a buffer region much lower than that observed for reaction VI. If the second cation is a rare earth, the buffer region exists between pH 4 and 5.5 and the reaction is expressed by equation IV. The chemical reaction expressed by equation IV is the basic reaction involved in the potentiometric determination of the rare earth-EDTA stability constants.

The equilibrium constant for reaction IV can be expressed as follows:

$$K_{IV} = \frac{[MY]\ [Cutren]\ [H]^3}{[CuY]\ [H_3tren]\ [M]} = \frac{K_{Cutren}\ K_{MY}}{K_{H_3tren}\ K_{CuY}} \quad . \qquad (11)$$

The quantity "a" which will be used subsequently, denotes the number of equivalents of sodium hydroxide added to the reaction expressed by equation IV per mole of rare earth in the solution. Before K_{IV} can be calculated, the equilibrium concentration of five of the six concentration terms expressed in equation (11) must be evaluated. The hydrogen ion concentration is measured directly.

Five material balance equations can be written as follows:

$$\left.\begin{aligned}
&[Cu]_t = c = [Cutren] + [CuY] + [Cu] && (a)\\
&[M]_t = c = [MY] + [Mtren] + [M] && (b)\\
&[Y]_t = c = [CuY] + [MY] + [H_4Y] + [H_3Y] && \\
&\qquad\qquad + [H_2Y] + [HY] + [Y] && (c)\\
&[tren]_t = c = [Cutren] + [Mtren] + [H_3tren] && \\
&\qquad\qquad + [H_2tren] + [Htren] + [tren] && (d)\\
&[H]_t = c(3-a) = [H] + 3[H_3tren] + 2[H_2tren] && \\
&\qquad\qquad + [Htren] + 4[H_4Y] + 3[H_3Y] + 2[H_2Y] && \\
&\qquad\qquad + [HY] \quad . && (e)
\end{aligned}\right| \qquad (12)$$

These five equations express the concentrations of all possible species involved in the reaction represented by equation IV. As will be demonstrated later, many of them are insignificantly small and can be neglected.

If equation (9) is solved for [tren] and this value substituted into equation (10), the result can be expressed as

$$[\mathrm{Cu}] = \frac{[\mathrm{Cutren}]\,[\mathrm{H}]^3\,\overline{K}_{\mathrm{H_3tren}}}{K_{\mathrm{Cutren}}\,[\mathrm{H_3tren}]} ,$$

which can be substituted into equation (12a) to give the following:

$$[\mathrm{Cu}]_t = c = [\mathrm{CuY}] + [\mathrm{Cutren}] + \frac{[\mathrm{Cutren}]\,[\mathrm{H}]^3\,\overline{K}_{\mathrm{H_3tren}}}{K_{\mathrm{Cutren}}\,[\mathrm{H_3tren}]}$$

or

$$[\mathrm{Cu}]_t = c = [\mathrm{CuY}] + \alpha\,[\mathrm{Cutren}] \tag{13}$$

where $$\alpha = 1 + \frac{[\mathrm{H}]^3\,\overline{K}_{\mathrm{H_3tren}}}{[\mathrm{H_3tren}]\,K_{\mathrm{Cutren}}} . \tag{14}$$

The rare earth stability constants and the copper-EDTA constant can be expressed as follows:

$$K_{\mathrm{Mtren}} = \frac{[\mathrm{Mtren}]}{[\mathrm{M}]\,[\mathrm{tren}]} \tag{15}$$

$$K_{\mathrm{MY}} = \frac{[\mathrm{MY}]}{[\mathrm{M}]\,[\mathrm{Y}]} \tag{16}$$

and

$$K_{CuY} = \frac{[CuY]}{[Cu]\,[Y]} \quad . \qquad (17)$$

When equation (15) is solved for [Mtren], equation (9) for [tren], and the two results substituted into equation (12b), the latter equation can be simplified to give:

$$[M]_t = c = [MY] + [M] + \frac{K_{Mtren}\,[M]\,[H_3tren]}{\bar{K}_{H_3tren}\,[H]^3}$$

or

$$[M]_t = c = [MY] + [M]\left\{1 + \frac{1}{\theta - 1}\right\} \quad , \qquad (18)$$

where

$$\theta = 1 + \frac{[H]^3\,\bar{K}_{H_3tren}}{[H_3tren]\,K_{Mtren}} \quad . \qquad (19)$$

The acid association equilibria of EDTA can be expressed by four equations.

$$K_{HY} = \frac{[HY]}{[H]\,[Y]} \qquad \bar{K}_{H_2Y} = \frac{[H_2Y]}{[H]^2\,[Y]}$$

$$\bar{K}_{H_3Y} = \frac{[H_3Y]}{[H]^3\,[Y]} \qquad \bar{K}_{H_4Y} = \frac{[H_4Y]}{[H]^4\,[Y]}$$

These four equations and equation (17) can be solved for the quantities $[H_4Y]$, $[H_3Y]$, $[H_2Y]$, $[HY]$ and $[Y]$.

$$\left.\begin{array}{ll}[HY] = K_{HY}\,[Y]\,[H] & \text{(a)} \\ [H_2Y] = \bar{K}_{H_2Y}\,[Y]\,[H]^2 & \text{(b)} \\ [H_3Y] = \bar{K}_{H_3Y}\,[Y]\,[H]^3 & \text{(c)} \\ [H_4Y] = \bar{K}_{H_4Y}\,[Y]\,[H]^4\;. & \text{(d)}\end{array}\right|\quad (20)$$

Upon substitution of these quantities into equation (12c), the latter may be simplified to the following:

$$[Y]_t = c = [MY] + [CuY]\;\cdot \left\{1 + \frac{1 + [H]\,K_{HY} + [H]^2\,\bar{K}_{H_2Y} + [H]^3\,\bar{K}_{H_3Y} + [H]^4\,\bar{K}_{H_4Y}}{[Cu]\,K_{CuY}}\right\}$$

or

$$[Y]_t = c = [MY] + [CuY]\left\{1 + \frac{\phi}{[Cu]\,K_{Cuy}}\right\}\;, \qquad (21)$$

where

$$\phi = 1 + [H]\,K_{HY} + [H]^2\,\bar{K}_{H_2Y} + [H]^3\,\bar{K}_{H_3Y} + [H]^4\bar{K}_{H_4Y}\;. \qquad (22)$$

The acid association equilibria of H_3tren can be expressed by three equations.

$$K_{Htren} = \frac{[Htren]}{[H]\,[tren]} \qquad\qquad K_{H_2tren} = \frac{[H_2tren]}{[H]\,[Htren]}$$

$$K_{H_3tren} = \frac{[H_3tren]}{[H]\,[H_2tren]}$$

The following expressions can be obtained from the above three equations and from equation (15):

$$[\text{Mtren}] = \frac{[\text{M}]\,[\text{H}_3\text{tren}]\,K_{\text{Mtren}}}{[\text{H}]^3\,\overline{K}_{\text{H}_3\text{tren}}} \tag{23}$$

$$[\text{tren}] = \frac{[\text{H}_3\text{tren}]}{[\text{H}]^3\,\overline{K}_{\text{H}_3\text{tren}}} \tag{24}$$

$$[\text{Htren}] = \frac{[\text{H}_3\text{tren}]}{[\text{H}]^2\,K_{\text{H}_2\text{tren}}\,K_{\text{H}_3\text{tren}}} \tag{25}$$

and

$$[\text{H}_2\text{tren}] = \frac{[\text{H}_3\text{tren}]}{[\text{H}]\,K_{\text{H}_3\text{tren}}} \quad . \tag{26}$$

It will be noted that equations (23), (24), (25), and (26) express the concentration of the various "tren" species in terms of known constants, the single concentration $[\text{H}_3\text{tren}]$, and the hydrogen ion concentration. Equation (12d) can, therefore, be simplified considerably by substitution of equations (23) through (26).

$$[\text{tren}]_t = c = [\text{Cutren}] + \frac{[\text{H}_3\text{tren}]}{[\text{H}]^3\,\overline{K}_{\text{H}_3\text{tren}}} + \frac{[\text{H}_3\text{tren}]}{[\text{H}]^2\,K_{\text{H}_2\text{tren}}\,K_{\text{H}_3\text{tren}}}$$

$$+ \frac{[\text{H}_3\text{tren}]}{[\text{H}]\,K_{\text{H}_3\text{tren}}} + \frac{K_{\text{Mtren}}\,[\text{M}]\,[\text{H}_3\text{tren}]}{\overline{K}_{\text{H}_3\text{tren}}\,[\text{H}]^3} + [\text{H}_3\text{tren}]$$

or

$$[\text{tren}]_t = c = [\text{Cutren}] + \gamma\,[\text{H}_3\text{tren}] + [\text{M}]\left\{\frac{1}{\theta - 1}\right\} \tag{27}$$

where

$$\gamma = 1 + \frac{1}{[H]^3\ \bar{K}_{H_3tren}} + \frac{1}{[H]^2\ K_{H_2tren}\ K_{H_3tren}} + \frac{1}{[H]\ K_{H_3tren}} \ . \quad (28)$$

The three "tren" terms in equation (12e) can be combined by the use of equations (25) and (26) to the following simplified expression:

$$[Htren] + 2[H_2tren] + 3[H_3tren] = \delta\,[H_3tren] \quad (29)$$

where

$$\delta = 3 + \frac{1}{[H]^2\ K_{H_2tren}\ K_{H_3tren}} + \frac{2}{[H]\ K_{H_3tren}} \ . \quad (30)$$

By the use of equations (17) and (20), the last four terms in equation (12e) can be simplified as follows:

$$[HY] + 2[H_2Y] + 3[H_3Y] + 4[H_4Y] = \frac{K_{HY}\ [H]\ [CuY]}{[Cu]\ K_{CuY}}$$

$$+ 2\,\frac{\bar{K}_{H_2Y}\ [CuY]\ [H]^2}{K_{CuY}\ \ [Cu]} \qquad + 3\,\frac{\bar{K}_{H_3Y}\ [CuY]\ [H]^3}{K_{CuY}\ [Cu]}$$

$$+ 4\,\frac{\bar{K}_{H_4Y}\ [CuY]\ [H]^4}{K_{CuY}\ \ [Cu]}$$

or

$$= \frac{[CuY]\ \rho}{[Cu]\ K_{CuY}} \quad (31)$$

where

$$\rho = [H]\ K_{HY} + 2[H]^2\ \bar{K}_{H_2Y} + 3[H]^3\ \bar{K}_{H_3Y} + 4[H]^4\ \bar{K}_{H_4Y} \ . \quad (32)$$

Then by combining equations (29) and (31) with equation (12e) the latter can be simplified to give the expression

$$[H]_t = c(3-a) = [H] + \delta\,[H_3\text{tren}] + \frac{[\text{CuY}]\,\varphi}{[\text{Cu}]\,K_{\text{CuY}}} \quad . \tag{33}$$

The five material balance equations, in a more usable form are grouped together below.

$$\left.\begin{aligned}
&[\text{Cu}]_t = c = [\text{CuY}] + \alpha\,[\text{Cutren}] && \text{(a)}\\
&[\text{M}]_t = c = [\text{MY}] + [\text{M}]\left\{1 + \frac{1}{\theta - 1}\right\} && \text{(b)}\\
&[\text{Y}]_t = c = [\text{MY}] + [\text{CuY}]\left\{1 + \frac{\phi}{[\text{Cu}]\,K_{\text{CuY}}}\right\} && \text{(c)}\\
&[\text{tren}]_t = c = [\text{Cutren}] + \gamma\,[H_3\text{tren}] + [\text{M}]\left\{\frac{1}{\theta - 1}\right\} && \text{(d)}\\
&[H]_t = c(3-a) = [H] + \delta\,[H_3\text{tren}] + \frac{[\text{CuY}]\,\varphi}{[\text{Cu}]\,K_{\text{CuY}}} \quad . && \text{(e)}
\end{aligned}\right| \tag{34}$$

The coefficients in the above equations are defined in the following equations.

$$\left.\begin{aligned}
&\alpha = 1 + \frac{[H]^3\,\bar{K}_{H_3\text{tren}}}{[H_3\text{tren}]\,K_{\text{Cutren}}} && \text{(a)}\\
&\theta = 1 + \frac{[H]^3\,\bar{K}_{H_3\text{tren}}}{[H_3\text{tren}]K_{\text{Mtren}}} && \text{(b)}\\
&\phi = 1 + [H]\,K_{HY} + [H]^2\,\bar{K}_{H_2Y} + [H]^3\,\bar{K}_{H_3Y} + [H]^4\,\bar{K}_{H_4Y} && \text{(c)}
\end{aligned}\right| \tag{35}$$

$$\left.\begin{aligned}
\rho &= [H]\,K_{HY} + 2[H]^2\,\bar{K}_{H_2Y} + 3[H]^3\,\bar{K}_{H_3Y} + 4[H]^4\,\bar{K}_{H_4Y} && \text{(d)}\\
\gamma &= 1 + \frac{1}{[H]^3\,\bar{K}_{H_3\text{tren}}} + \frac{1}{[H]^2\,K_{H_2\text{tren}}\,K_{H_3\text{tren}}}\\
&\quad + \frac{1}{[H]\,K_{H_3\text{tren}}} && \text{(e)}\\
\delta &= \frac{1}{[H]^2\,K_{H_2\text{tren}}\,K_{H_3\text{tren}}} + \frac{2}{[H]\,K_{H_3\text{tren}}} + 3 && \text{(f)}
\end{aligned}\right|\quad (35)$$

The equations (34a) to 34e) are very general, but they can be simplified considerably because of the experimental conditions (such as the pH range and the magnitude of the various constants involved) encountered in the measurements of the rare earth complexes with both EDTA and HEDTA. Each equation will be discussed individually.

Equation (34a) is valid if no complexes are formed in which both "tren" and "Y" are bound to the same copper ion. Since "tren" is tetradentate and "Y" is hexadentate, each is capable of individually satisfying the coordination number of copper and it seems unlikely that mixed complexes would form.

In order to solve unambiguously equation (34b) it would be necessary to know the stability constants of the possible complexes formed between the rare earths and "tren", as defined by equation (15). These constants have not been measured. However, since no one has been able to measure any very stable rare earth-ammonium type complexes, it seems very unlikely that any rare earth-tren complexes that might exist would be more stable than the Mntren^{+2} or Fetren^{+2} complexes which have stability constants of $10^{5.8}$ and $10^{8.8}$ respectively. Because the constant K_{Mtren} can affect equation (34b) only through "θ", and because K_{Mtren} occurs in equation (35b) as a term in the denominator, the numerator of which contains the extremely large constant $\bar{K}_{H_3tren}$ (see equation 9), it can be shown that under the experimental conditions involved, K_{Mtren} would have to be larger than 10^{12} in order to make the concentration of the complex $Mtren^{+3}$ exceed 10^{-5}, which is 1% of $[M]_t$. This means that "θ" is a very large term compared to unity. Consequently, the expression $\left\{1 + \frac{1}{\theta - 1}\right\}$ is very nearly equal to one and equation (34b) is reduced to two terms, [MY] and [M].

Because of the pH range involved, there is very little, if any, uncomplexed "Y". Consequently, the term $\left\{\frac{\phi}{[Cu]\ K_{CuY}}\right\}$ in equation (34c) was found to insignificantly small compared to unity. The right side of equation (34c), therefore, is simplified to two terms, [MY] and [CuY].

Equation (34d) also can be simplified to two terms. The " γ " term was shown by calculation of the experimental data to be essentially unity. This is that the terms $[H_2tren]$, [Htren], and [tren] are so small that they can be neglected in the pH range concerned. Since "θ" is very large, the term $\left\{\frac{1}{\theta - 1}\right\}$ is a very small fraction. This makes the product term $[M]\left\{\frac{1}{\theta - 1}\right\}$ insignificantly small and reduces equation (34d) to the two terms [Cutren] and $[H_3tren]$.

Because of the magnitude of φ compared to the large value of K_{CuY}, the last term in equation (34e) is also very small. This can be shown by evaluating the term directly from the experimental data. The term "δ" was found to equal three for all of the rare earth measurements. Thus, equation (34e) also reduces to two terms, [H] and 3[H_3tren].

It is now possible to write all of the material balance equations as they apply to the EDTA and HEDTA complexes of the rare earths.

$$\left.\begin{array}{lr}
[Cu]_t = c = [CuY] + \alpha [Cutren] & (a) \\
[M]_t = c = [MY] + [M] & (b) \\
[Y]_t = c = [MY] + [CuY] & (c) \\
[tren]_t = c = [Cutren] + [H_3tren] & (d) \\
[H]_t = c(3-a) = [H] + 3[H_3tren] & (e)
\end{array}\right| \quad (36)$$

The reactants in equation IV were all initially present in 0.001 M concentrations. Consequently, the "c" term in equation (36) had a value of 0.001. The experimental data consisted of five "a" values and five corresponding pH values for each rare earth constant measured. Since only one "a" value with its corresponding pH value is necessary to calculate a stability constant, this method provides five checks on each constant determined. The method of calculation is quite simple. From the known values of "c", the experimentally determined values of "a" and [H], equation (36e) is solved for the quantity [H_3tren]. This quantity is then substituted into equation (35a) and "α" is calculated. Then equations (36d), (36a), (36c), and (36b) are solved in that order. The quantities [MY], [Cutren], [H], [CuY], [H_3tren] and [M] are substituted into equation (11) and solved for K_{IV}. Since the values of the constants K_{Cutren}, $\overline{K}_{H_3tren}$ and K_{CuY} are known from previous measurements, the desired constant K_{MY} is readily obtained from equation (11).

The polarographic method

This method is based upon the fact that it is possible to measure the concentration of free uncomplexed copper II ions in the presence of the copper complex, CuY^{-2}, by polarographic means. If equal molar amounts of the disodium copper salt of EDTA, Na_2CuY, and rare earth nitrate, $M(NO_3)_3$, are allowed to equilibrate, the rare earth ion competes with the copper ion for the complexing agent.

$$CuY^{-2} + M^{+3} \rightleftharpoons Cu^{+2} + MY^{-} \qquad \text{(VII)}$$

In such a solution, two separate individual polarographic waves are produced by the reduction of Cu^{+2} and of CuY^{-2}. The first of these has the shape of a two-electron wave with $E_{1/2} = -0.04$ V vs SCE (versus saturated calomel electrode). It is due to the reduction of Cu^{+2} to the metal at the surface of the mercury drop. The second is due to the reduction of the complex CuY^{-2}, its $E_{1/2}$ being -0.32 V (for the copper HEDTA complex, the $E_{1/2}$ occurs at about -0.2 V vs SCE). Between the two waves the diffusion current, i_d, remains constant and is proportional to the concentration of free uncomplexed copper II present in the solution. Reference i_d values were obtained for 100% uncomplexed copper and for 100%

complexed copper by obtaining polarograms of solutions containing $CuSO_4$ and Na_2CuY respectively. The percentage of uncomplexed copper was calculated from a comparison of the i_d value for each of the rare earth solutions with the i_d values for the two reference solutions.

Since the reactants were initially present in equal molar quantities, it is obvious from equation VII that

$$[MY] = [Cu]$$

and

$$[CuY] = [M] = c - [Cu] \quad .$$

where "c" is the initial concentration of both reactants. The equilibrium constant for equation VII can be written as follows:

$$K_{VII} = \frac{[Cu]\,[MY]}{[CuY]\,[M]} = \frac{[Cu]^2}{(c - [Cu])^2} \quad . \qquad (37)$$

Division of equation (16) by equation (17) gives

$$\frac{K_{MY}}{K_{CuY}} = \frac{[MY]\,[Cu]}{[M]\,[CuY]} = K_{VII} \quad ,$$

therefore,

$$K_{MY} = K_{CuY} \frac{[Cu]^2}{[c - [Cu])^2} = K_{CuY} \frac{(\%\ Cu)^2}{(100 - \%\ Cu)^2} \quad . \qquad (38)$$

It is obvious that the stability constants for the rare earth complexes can be calculated by substituting the polarographically measured percentage of uncomplexed copper and the known stability constant for the copper complex into equation (38).

$c^2 - 2c[Cu] - [Cu]^2$

Determination of the acid association constants of HEDTA

A knowledge of the acid association constants of a chelating agent is necessary before the stability of the complex formed between the chelating agent and a metal ion can be determined by the potentiometric method. The constants of EDTA have been determined by Schwarzenbach (45) at 20°C and an ionic strength of 0.10. Since the stability constants of the rare earths with EDTA were measured at 20°C and an ionic strength of 0.10, Schwarzenbach's values were used in the calculations.

Values of the acid association constants of HEDTA have been reported in the literature (46), but they were measured at 29.6°C. It was, therefore, deemed necessary to determine these constants under the same conditions as were used to measure the rare earth-HEDTA stability constants; namely, 25°C and a solution ionic strength of 0.10.

Determination of K_1 and K_2. The titration curve of HEDTA with standard KOH is typical of a dibasic acid of moderate strength, having two separate inflection points at $\underline{a} = 1$ and $\underline{a} = 2$, where $\underline{a}$ represents the fraction of the total replacable hydrogen that has been titrated. The third inflection point is absent due to the extensive hydrolysis of the trivalent anion. Because of the separation in the inflection points corresponding to K_1 and K_2, the problem of determining these two constants is very similar to that for determining K_A for a simple monobasic weak acid.

In the vicinity of $\underline{a} = 0.5$, only the species H_3V and H_2V^- need be considered. Likewise, only the species H_2V^- and HV^{-2} need be considered in the region around a = 1.5. Therefore, the two acid association constants can be expressed as

$$K_1 = \frac{[H_3V]}{[H]\,[H_2V]} = \frac{\text{(fraction untitrated)}}{[H]\ \text{(fraction titrated)}} \tag{39}$$

$$K_2 = \frac{[H_2V]}{[H]\,[HV]} = \frac{\text{(fraction untitrated)}}{[H]\ \text{(fraction titrated)}} \tag{40}$$

where "V" represents the anion of HEDTA. These two equations can be simplified.

$$K_1 = \frac{(1-\underline{a})}{[H]\ \underline{a}} \qquad\qquad K_2 = \frac{(2-\underline{a})}{[H]\ (\underline{a}-1)}$$

Upon converting to logarithms,

$$\log K_1 = -\log[H] + \log \frac{(1-\underline{a})}{\underline{a}} \tag{41}$$

$$\log K_2 = -\log[H] + \log \frac{(2-\underline{a})}{(\underline{a}-1)} \quad . \tag{42}$$

The first association constant, as defined by equation (39), can be calculated from a titration curve of HEDTA by substituting one or more pH values with their corresponding a values (obtained from the region around a = 0.5) into equation (41). Equation (42) can be used in exactly the same manner to calculate the second association constant from experimental data in the region of a = 1.5.

The determination of K_3. The determination of K_3 is complicated by the hydrolysis of the very weak acid V^{-3}. The third association constant can be defined as

$$K_3 = \frac{[HV]}{[H]\,[V]} \quad , \tag{43}$$

and the hydrolysis of V^{-3} as

$$V^{-3} + H_2O \rightleftharpoons HV^{-2} + OH^{-} \quad . \tag{44}$$

With no hydrolysis occuring, the concentration of V^{-3} could be calculated by merely subtracting the amount of KOH added. Since two molecules of KOH are needed for every one molecule of HV^{-2} produced, the concentration of V^{-3} would be given by

$$[V] = (\underline{a} - 2)\ C_V \quad , \tag{45}$$

where C_V = the total molar concentration of HEDTA. When hydrolysis does take place, one V^{-3} molecule is consumed for every hydroxyl ion produced (see equation 44). Therefore, the total concentration of [V] is given as

$$[V] = (\underline{a} - 2)\ C_V - [OH] \ . \tag{46}$$

The only ionic species of HEDTA present in the alkaline region beyond $\underline{a}$ = 2 are HV^{-2} and V^{-3}. Therefore,

$$C_V = [V] + [HV]. \tag{47}$$

A combination of equations (46) and (47) gives

$$[HV] = (3 - \underline{a})\ C_V + [OH] \quad . \tag{48}$$

Substitution of equations (46) and (48) into (43) gives

$$K_3 = \frac{(3 - \underline{a})\ C_V + [OH]}{[H]\ (\underline{a} - 2)\ C_V - [OH]} \quad . \tag{49}$$

Equation (49) permits the calculation of K_3 from the experimental values of C_V, pH, and a for all points on the titration curve from a = 2 to a = 3.

Materials and Equipment

Preparation of stock solutions

Carbonate-free sodium hydroxide solution (0.1 N). A standard solution of sodium hydroxide[*] was prepared and allowed to stand until the supernatant liquid had become clear. Approximately 25 ml of the clear solution was carefully removed from the saturated solution and added to three liters of freshly deionized water. The resulting solution was stored in a Pyrex bottle fitted with a siphon for withdrawing solution and with a gas-train, consisting of an Ascarite tube and a small bubbler containing dilute potassium hydroxide, to protect the stock solution from carbon

---

[*] All chemicals were reagent grade unless otherwise specified.

dioxide. The sodium hydroxide solution was standardized against dried potassium acid phthalate by titration.

Carbonate-free potassium hydroxide solution (0.1 N). The potassium hydroxide solution was prepared by the silver oxide method. A hot solution containing about 9 grams of sodium hydroxide in 200 ml of water was slowly added to an equal volume of a hot solution containing 36 grams of silver nitrate. After a few minutes, the silver oxide coagulated, was filtered from the hot solution on a fine sintered glass funnel, and was washed about fifteen times with hot deionized water. The silver oxide and 1600 ml of freshly deionized water, containing 16 grams of potassium chloride, were then transfered to a dry-box. In the dry-box, under a nitrogen atmosphere, the silver oxide was added to the potassium chloride solution. The resulting mixture was allowed to stand (with occasional shaking) for 48 hours. Then, the clear supernatant liquid was filtered through a very fine sintered glass funnel, transfered into a Pyrex bottle, and stored in the same manner as the sodium hydroxide solution. The potassium hydroxide solution was also standardized against potassium acid phthalate by titration.

Triaminotriethylamine trihydrochloride (0.0100 M). A sample of triaminotriethylamine trihydrochloride (obtained from Chemicals Procurement Co.) was carefully purified by a double recrystallization. The amine salt was first dissolved in a minimum amount of warm water and then crystalized from the water with 95 per cent ethanol. The crystals were filtered each time in a sintered glass crucible and washed repeatedly with cold absolute ethanol. Finally, the crystals were dried at 100°C under a reduced pressure for 24 hours. A two liter 0.0100 molar solution of the amine was prepared by dissolving 5.1126 grams of the dried crystals in pure water and diluting to the mark in a 2000-ml volumetric flask.

Potassium chloride (1.00 M). A two liter 1.00 molar solution of potassium chloride was prepared by dissolving 149.11 grams of previously dried KCl in pure water and diluting to 2000 ml. The salt had been dried at 115°C for 24 hours.

Potassium nitrate (1.00 M). A two liter 1.00 molar solution of potassium nitrate was prepared by dissolving 202.21 grams of dried KNO_3 in pure water and diluting to 2000 ml. This salt was also dried at 115°C for 24 hours.

Sodium acetate (0.100 M). Two liters of 0.100 molar sodium acetate were prepared by dissolving 16.408 grams of dried (at 180°C for 18 hours) anhydrous sodium acetate in pure water and diluting to 2000 ml.

Acetic acid (0.100 M). A two liter stock solution (approximately 0.5 M) of acetic acid was prepared by diluting glacial acetic acid. Careful standardization of the stock solution by potentiometric titration with standard sodium hydroxide disclosed its concentration to be 0.4990 molar. Thus, two liters of 0.100 molar acetic acid were prepared by diluting 400.8 ml of 0.4990 M acetic acid to 2000 ml.

Disodium copper ethylenediaminetetraacetate (0.0100 M). A solution of exactly 0.100 M $CuCl_2$ was prepared. A solution of approximately 0.1 M Na_2H_2Y was prepared by dissolving a weighed amount of crystaline disodium dihydrogen ethylenediaminetetraacetate dihydrate (secured from the Hach Chemical Co.) in pure water. A ten ml aliquot of the standardized copper II chloride solution was titrated with the tetraacetate solution after the addition of 5 ml of concentrated ammonium hydroxide and diluting to 300 ml. Murexide was used as the indicator. Following the standardization of the tetraacetate solution, 200 ml of the copper solution was mixed with 204 ml of the tetraacetate. In such a mixture the following reaction takes place:

$$Cu^{+2} + H_2Y^{-2} \rightleftharpoons CuY^{-2} + 2H^+ \ .$$

Therefore, the solution was carefully neutralized to a pH of 6 with sodium hydroxide and diluted to 2000 ml.

The copper tetraacetate solution described above contained a considerable quantity of chloride. Because chloride ions gave trouble during the polarographic determinations, it was found necessary to prepare a second copper tetraacetate solution starting with copper II nitrate rather than copper II chloride. The method of preparation was exactly the same as that described above.

N-Hydroxyethylethylenediaminetriacetic acid (0.1 M). The HEDTA (secured from Geigy Chemical Co.) was further purified by two operations. The acid was first dissolved in a small amount of warm water and filtered. Then 95% ethanol was added and the solution allowed to cool. The acid crystals were filtered on a sintered glass funnel, washed three times with cold absolute ethanol, then once again dissolved in warm water, recrystalized, filtered and washed. A triple leaching with cold water followed by drying at 100°C under a reduced pressure for 24 hours completed the purification. A solution of the purified product was tested for sulfate with barium chloride and for sodium with a flame spectrophotometer. No barium sulfate precipitate could be detected. The flame test indicated 0.1 ppm of sodium.

A two liter solution of HEDTA was prepared by dissolving 55.652 grams of the solid in water and diluting to 2 liters. The acid solution was standardized by three independent methods; titration against a standard zinc II chloride solution using Eriochromschwartz T as the indicator, titration against a standard copper chloride solution using Murexide as the indicator, and a potentiometric titration of the free acid with standard sodium hydroxide. The three methods gave values of 0.0992, 0.0989, and 0.0994 for the molar concentration of the HEDTA stock solution.

Sodium copper hydroxyethylethylenediaminetriacetate (0.0100 M). A copper II chloride solution was prepared by dissolving $CuCl_2 \cdot 2H_2O$ in water. Electrolytic analysis of the solution showed its concentration to be 0.1001 molar. Therefore, 199.8 ml of the copper solution were added to 201.82 ml of the stock HEDTA solution and the resultant acid solution neutralized with sodium hydroxide. The neutral copper triacetate solution was diluted to 2000 ml.

A copper triacetate solution, containing nitrate rather than chloride, was prepared by mixing 193.2 ml of a 0.1035 molar copper II nitrate solution with 201.8 ml of the standard HEDTA solution, neutralizing with sodium hydroxide to the neutral equivalents point, and diluting the resultant solution to 2000 ml.

Rare earth salt solutions (0.0100 M). The rare earths used in this research were separated from all other elements and from each other on ion-exchange columns according to the methods developed in the Ames Laboratory (47,48,49,50,51,52,53,54,55,56,57). With the exception of cerium and terbium, all of the rare earth solutions were prepared in the same manner. As with the other solutions previously described, the rare earths were prepared in both chloride and nitrate solutions. Sufficient freshly ignited pure rare earth oxide was dissolved in a slight excess of acid, HCl or HNO_3, to give a solution containing 0.005 of a mole of M^{+3}. A part of this solution was then potentiometrically titrated with sodium hydroxide to a point just past the neutral equivalence point. The pH of a neutral rare earth solution was then located from a graph of ΔpH/Δ ml against ml of base added to the solution. These pH values ranged from 5.2 to 4.8. After titration, the two solutions were recombined, adjusted to the equivalence point pH with hydroxide and diluted to 500 ml.

The composition of terbium oxide depends upon the ignition temperature. In order to correct this uncertainty, a sample of the oxide was reduced to sesquioxide by heating it for 8 hours at 900°C in a stream of hydrogen. The sesquioxide was then weighed out and dissolved in an acid as described above.

It is virtually impossible to dissolve quantitatively a small amount of cerium oxide, even with the help of hydrogen peroxide. Consequently, a larger amount of oxide was dissolved in acid, the solution filtered, and diluted to volume. Then the cerium stock solution was standardized by withdrawing an aliquot, precipitating the cerium with oxalic acid, igniting, and weighing the ignited oxide. Once the concentration of the solution was known, 0.005 of a mole was removed and prepared in the same manner as the other rare earth salt solutions.

Description of equipment

pH Meter. All pH measurements concerned with the determination of the stability constants of the rare earths with EDTA were made with a Beckman Model G pH meter. The electrode system consisted of a fiber type saturated calomel electrode and a "General Purpose" glass electrode. Both electrodes were of the shielded type for use external to the pH meter.

The pH measurements necessary for the determination of the stability constants of the rare earths with HEDTA were made with the more accurate Beckman Model GS pH meter. The same type of electrodes were used.

Microburette. A Pyrex microburette graduated in 0.01 ml subdivisions (obtained from Scientific Glass Apparatus Co.) was used to dispense the sodium and potassium hydroxide solutions needed for the stability constant measurements. The calibrations of the microburette were rechecked at 0.5 ml intervals for delivery of 0.1 normal sodium hydroxide by weighing the amount of 0.1 normal base actually delivered.

Experimental Procedures and Results

Determination of the acid association constants of HEDTA

As was pointed out earlier, a knowledge of the acid association constants of a chelating agent is necessary before the stability of the complex that is formed between the chelating agent and a metal ion can be determined by the potentiometric method. The more accurate scale on the Beckman Model GS pH meter is limited to a range of only three pH units. It was necessary, therefore, to potentiometrically titrate one solution for the evaluation of K_1 and K_2 and a second solution for the evaluation of K_3. Two other solutions were titrated to check the results from the first two. The titrations were carried out in a double-walled titration cell. Water from a constant temperature bath maintained at 25.00 ± 0.02°C was pumped through the jacketed compartment of the titration cell. An atmosphere of pure nitrogen was maintained above the liquid in the titration cell.

In the first titration, Run I, a solution containing 3 ml of 0.0991 M HEDTA, 3.2 ml of 1.00 M KCl and 43.8 ml of deionized water was titrated with standard KOH. The values of K_1 and K_2 were calculated from the pH values in the regions of $\underline{a} = 0.5$ and $\underline{a} = 1.5$, respectively, by the use of equations (41) and (42). The experimental results and calculated values for K_1 and K_2 are given in Table 1.

In Run II a solution of exactly the same concentration as that used for Run I was again titrated with standard KOH. These results and the calculated values of K_1 and K_2 are presented in Table 2.

Table 1

Titration of HEDTA with Potassium Hydroxide (Run I)*

a	Corrected pH	log K_1	a	Corrected pH	log K_2
0.390	2.807	3.001	1.324	5.089	5.409
0.428	2.841	2.967	1.363	5.165	5.409
0.467	2.878	2.934	1.402	5.237	5.411
0.506	2.916	2.906	1.442	5.309	5.411
0.545	2.958	2.880	1.480	5.381	5.416
0.584	3.002	2.856	1.519	5.454	5.422
0.623	3.050	2.833	1.558	5.527	5.426
		Av. = 2.91	1.597	5.604	5.433
			1.636	5.689	5.447
					Av. = 5.42

---

*Temperature = 25.00 ± 0.02°C; ionic strength = 0.10.

Table 2

Titration of HEDTA with Potassium Hydroxide (Run II)*

a	Corrected pH	log K_1	*a*	Corrected pH	log K_2
0.390	2.803	2.995	1.324	5.078	5.398
0.467	2.869	2.925	1.402	5.228	5.402
0.545	2.950	2.872	1.480	5.368	5.403
0.632	3.038	2.821	1.558	5.515	5.414
		Av. = 2.90	1.636	5.671	5.429
					Av. = 5.41

---

*Temperature = 25.00 ± 0.02°C; ionic strength = 0.10.

A value for K_3 was obtained by titrating a solution containing 2 ml of 0.0991 M HEDTA, 3.81 ml of 1.00 M KCl, and 40 ml of water with standard KOH. Values of K_3 were calculated from the region of $\underline{a} = 2.3$ to $\underline{a} = 2.7$ by the use of equation (49). The experimental and calculated results for Run III are presented in Table 3. Run IV was an exact repetition of Run III. The results from this run are also given in Table 3.

The pH meter was standardized with Beckman pH 4 buffer for Runs I and II. A standardization with Beckman pH 9 buffer was necessary to cover the pH range required for Runs III and IV.

Since the pH as obtained from the pH meter thus standardized is defined in terms of the hydrogen-ion activity, while hydrogen-ion concentrations are needed for the calculations, it is necessary to correct each pH meter reading. Three solutions were independently prepared, each containing 0.000802 M HCl and 0.100 M KCl. These solutions should have pH values of 3.096 based upon concentrations at an ionic strength of 0.100. The pH meter was standardized in the conventional manner using Beckman buffers and then two separate pH determinations were made upon the three solutions. The results are presented in Table 4. It is evident that a correction of 0.071 units must be subtracted from each pH meter reading before the hydrogen-ion concentration of the solutions are calculated.

Table 3

Titration of HEDTA with Potassium Hydroxide (Runs III and IV)*

Run III			Run IV		
a	Corrected pH	log K_3	*a*	Corrected pH	log K_3
2.279	9.489	9.920	2.366	9.663	9.922
2.337	9.596	9.908	2.395	9.710	9.918
2.396	9.693	9.900	2.425	9.756	9.914
2.454	9.793	9.903	2.454	9.801	9.910
2.512	9.883	9.898	2.483	9.840	9.900
2.571	9.966	9.886	2.512	9.887	9.900
2.629	10.046	9.872	2.542	9.932	9.897
2.788	10.128	9.856	2.571	9.973	9.890
			2.600	10.015	9.885
		Av. = 9.89	2.629	10.056	9.879
			2.658	10.096	9.871
			2.688	10.138	9.862
					Av. = 9.90

---

*Temperature = 25.00 ± 0.02°C; ionic strength = 0.10.

Table 4

Data for Correction of pH Values

Sample #	pH
1-a	3.166
1-b	3.168
2-a	3.167
2-b	3.167
3-a	3.167
3-b	3.168
	Av. = 3.167

Potentiometric determination of stability constants

Exactly the same procedure was used to determine the rare earth-HEDTA stability constants as was used to determine the rare earth-EDTA stability constants. A description of the experimental procedure is given, using the rare earth-EDTA stability constant determinations as an example.

When equal molar quantities of Na_2CuY, MCl_3, and H_3tren^{+3} are mixed together, a chemical reaction described by equation IV takes place. If the reaction mixture is potentiometrically titrated with standard sodium hydroxide, a normal acid-base neutralization curve is obtained with a large pH increase occuring at "a" = 3 ("a" being used to designate the equivalents of sodium hydroxide added per mole of rare earth atoms in solution). If the reaction proceeded as fast as the neutralization of a strong acid with a strong base, a direct potentiometric titration could be carried out. In such a case, the rare earth stability constant could be calculated from any value of "a" and pH picked from the buffer region of the neutralization curve (roughly from "a" = 0.4 to 1.9) by the use of equations (35a), (36), and (11). Such a direct approach cannot be used because the reaction is slow; usually 25 to 30 minutes are required for the pH of the reaction mixture to reach a stationary value after each addition of base. It was found necessary to prepare five individual solutions; each one with the same equal molar amounts of Na_2CuY, MCl_3, and H_3tren^{+3}, but with different amounts of standard sodium hydroxide so as to correspond to five different positions across the buffer region of a normal neutralization curve. These five solutions were allowed to equilibrate for 24 hours in a constant temperature water bath adjusted to

20.00 ± 0.02°C (25.00 ± 0.02°C for the HEDTA determinations). At the end of that period, the pH of each solution was measured.

The five solutions were made up in 100-ml volumetric flasks, each containing 10 ml of 0.0100 M disodium copper ethylenediaminetetraacetate, 10 ml of 0.0100 M triaminotriethylamine trihydrochloride, 10 ml of 0.0100 M rare earth chloride, enough 1.00 M KCl to give the solutions an ionic strength of 0.10 when diluted to 100 ml (9.00 ml of KCl for the EDTA determinations and 9.10 ml of KCl for the HEDTA determinations), and different predetermined amounts of 0.1 N NaOH. After diluting to the mark and mixing the solutions, they were suspended in a water bath from a specially constructed rack. The rack was fabricated so as to suspend ten 100-ml volumetric flasks and ten 40 x 80 mm ground-glass stoppered weighing bottles in the water bath.

A standardized procedure was followed for determining the pH of the solutions. At the end of a 16-hour equilibration period, about 50 ml of solution was transfered from each of the five 100-ml volumetric flasks to 5 separate clean dry weighing bottles. Both the tightly covered weighing bottles and the 100-ml volumetric flasks were immersed in the water bath for eight hours. Then the pH of the solutions in the weighing bottles was determined directly; with the bottles still immersed in the water bath. The solutions remaining in the 100-ml flasks were used to rinse the electrodes in going from one solution to the next. The pH meter was standardized with Beckman pH 4 buffer and also checked with Beckman pH 9 buffer before each series of determinations.

Because of the procedure adopted, the experimental results consisted of five separate pH and "a" values for each rare earth. It was thus possible to calculate five values for K_{IV} for each rare earth by use of equations (35a), (36) and (11). An average value for K_{IV} was then used to calculate the EDTA and HEDTA stability constants for each of the rare earths. The experimental data and calculated results are presented in Tables 5 and 6. Table 7 gives the numerical values of the various constants that are necessary for the calculations.

Check determinations were made allowing 48 hours for equilibration for the EDTA determinations with praseodymium, neodymium, samarium and yttrium and for the HEDTA determinations with dysprosium, gadolinium and ytterbium. Since the results were the same as those obtained with 24-hour equilibration, the practice was discontinued for the rest of the series.

Polarographic determination of stability constants

The polarographic determinations of the stability constants of the rare earth elements with EDTA and HEDTA were accomplished much easier than the corresponding potentiometric determinations. The theoretical basis for the method and the necessary equations have been described. It is necessary to describe only the preparation of the reaction mixtures, the technique used to take the polarograms, and the experimental results.

Solutions were prepared by mixing 10 ml of 0.0100 M sodium copper chelate, 10 ml of 0.0100 M rare earth nitrate, 10 ml of 0.10 M sodium acetate, 10 ml of 0.10 M acetic acid, 9.1 ml of 1.00 M KNO_3 (to adjust the ionic strength to a value of 0.10), and diluting the solution to

Table 5

Results for the Potentiometric Determination of the Rare Earth-EDTA Stability Constants*

Rare Earth	"a"	Corrected pH	-log K_{IV}	Av.-log$_{IV}$	log K_{MY}
La^{+3}	0.50	4.92	13.05	13.02	15.14
	0.85	5.12	13.00		
	1.20	5.29	13.00		
	1.50	5.44	13.02		
	1.75	5.56	13.01		
Ce^{+3}	0.50	4.71	12.29	12.35	15.81
	0.85	4.92	12.39		
	1.20	5.08	12.35		
	1.50	5.21	12.33		
	1.75	5.36	12.40		
Pr^{+3}	0.50	4.60	12.04	11.99	16.17
	0.85	4.80	12.02		
	1.20	4.92	11.87		
	1.55	5.15	12.05		
	1.75	5.22	11.98		
Nd^{+3}	0.51	4.51	11.70	11.68	16.48
	0.84	4.70	11.72		
	1.20	4.86	11.68		
	1.50	5.00	11.68		
	1.75	5.10	11.62		
Sm^{+3}	0.50	4.36	11.17	11.19	16.97
	0.85	4.54	11.18		
	1.20	4.72	11.23		
	1.55	4.85	11.14		
	1.75	4.97	11.21		

16.2

---

*Temperature = 20.00 ± 0.02°C; ionic strength = 0.10; supporting electrolyte = KCl.

Table 5 (continued)

Rare Earth	"a"	Corrected pH	-log K_{IV}	Av.-log$_{IV}$	log K_{MY}
Eu^{+3}	0.50	4.33	11.04	11.05	17.11
	0.85	4.50	11.03		
	1.20	4.65	11.01		
	1.50	4.81	11.09		
	1.75	4.93	11.09		
Gd^{+3}	0.50	4.32	11.00	11.04	17.12
	0.85	4.50	11.03		
	1.20	4.63	10.93		
	1.55	4.83	11.07		
	1.75	4.94	11.12		
Tb^{+3}	0.50	4.21	10.46	10.49	17.67
	0.85	4.36	10.46		
	1.20	4.52	10.53		
	1.50	4.64	10.51		
	1.75	4.74	10.47		
Dy^{+3}	0.50	4.15	10.05	10.17	18.01
	0.85	4.29	10.31		
	1.20	4.44	10.20		
	1.50	4.55	10.17		
	1.75	4.65	10.13		
Ho^{+3}	0.50	4.14	10.00	10.07	18.1
	0.85	4.28	10.04		
	1.20	4.40	10.08		
	1.55	4.55	10.08		
	1.75	4.65	10.13		
Er^{+3}	0.50	4.09	9.61	9.76	18.4
	0.85	4.22	9.67		
	1.20	4.37	9.86		
	1.55	4.49	9.81		
	1.75	4.58	9.84		
Tm^{+3}	0.50	4.03	8.95	9.15	19.0
	0.85	4.15	9.02		
	1.20	4.26	9.06		
	1.50	4.39	9.32		
	1.75	4.49	9.38		

Table 5 (continued)

Rare Earth	"a"	Corrected pH	-log K_{IV}	Av. -log$_{IV}$	log K_{MY}
Yb^{+3}	0.50	4.03	8.95	9.06	19.1
	0.85	4.13	8.76		
	1.20	4.26	9.06		
	1.55	4.39	9.32		
	1.75	4.46	9.19		
Lu^{+3}	0.50	4.00	8.42	8.68	19.5
	0.85	4.12	8.60		
	1.20	4.23	8.71		
	1.50	4.33	8.76		
	1.75	4.44	8.92		
Y^{+3}	0.49	4.15	10.10	10.36	17.80
	0.84	4.31	10.22		
	1.19	4.48	10.39		
	1.59	4.67	10.48		
	1.79	4.80	10.59		

Table 6

Results for the Potentiometric Determination of the Rare Earth-HEDTA Stability Constants*

Rare Earth	"a" ×10^{-3} equiv of/mole	Corrected pH	$-\log K_{IV}$	Av. $-\log K_{IV}$	$\log K_{MV}$	
La^{+3}	0.697	5.112	13.24			
	0.930	5.257	13.30	13.29	13.22	
	1.162	5.364	13.27			
	1.394	5.482	13.29			
	1.627	5.611	13.34			
Ce^{+3}	0.697	4.847	12.44			
	0.930	4.970	12.42			
	1.162	5.087	12.43	12.43	14.08	
	1.394	5.196	12.43			
	1.627	5.316	12.45			
Pr^{+3}	0.697	4.730	12.07			
	0.930	4.859	12.08			
	1.162	4.980	12.11	12.12	14.39	
	1.394	5.097	12.13			
	1.627	5.226	12.18			
Nd^{+3}	0.697	4.637	11.78			
	0.930	4.762	11.78			
	1.162	4.876	11.79	11.80	14.71	
	1.394	4.991	11.81			
	1.627	5.122	11.86			
Sm^{+3}	0.697	4.495	11.31			
	0.930	4.616	11.32			
	1.162	4.735	11.35	11.36	15.15	15.3
	1.394	4.850	11.38			
	1.627	4.977	11.42			
Eu^{+3}	0.697	4.480	11.26			
	0.930	4.600	11.27			
	1.162	4.718	11.30	11.30	15.21	
	1.394	4.832	11.32			
	1.627	4.959	11.35			

---

*Supporting electrolyte = KCl; temperature = 25.00 ± 0.02°C; ionic strength = 0.10.

Table 6 (continued)

Rare Earth	"a"	Corrected pH	$-\log K_{IV}$	Av. $-\log K_{IV}$	$\log K_{MV}$	
Gd^{+3}	0.697	4.517	11.39	11.41	15.10	15,90
	0.930	4.636	11.39			
	1.162	4.754	11.41			
	1.394	4.885	11.38			
	1.627	4.998	11.47			
Tb^{+3}	0.697	4.517	11.39	11.41	15.10	
	0.930	4.637	11.39			
	1.162	4.755	11.41			
	1.394	4.863	11.41			
	1.627	4.989	11.45			
Dy^{+3}	0.697	4.517	11.39	11.43	15.08	15,30
	0.930	4.640	11.40			
	1.162	4.758	11.42			
	1.394	4.873	11.44			
	1.627	5.001	11.49			
Ho^{+3}	0.697	4.524	11.41	11.45	15.06	15,46
	0.930	4.645	11.41			
	1.162	4.764	11.44			
	1.394	4.881	11.47			
	1.627	5.008	11.52			
Er^{+3}	0.697	4.489	11.29	11.33	15.17	15.40
	0.930	4.608	11.30			
	1.162	4.729	11.33			
	1.394	4.842	11.35			
	1.627	4.971	11.40			
Tm^{+3}	0.697	4.432	11.09	11.13	15.38	15,50
	0.930	4.549	11.10			
	1.162	4.664	11.12			
	1.394	4.778	11.15			
	1.627	4.903	11.19			
Yb^{+3}	0.697	4.358	10.81	10.87	15.64	[illegible]
	0.930	4.474	10.84			
	1.162	4.584	10.86			
	1.394	4.697	10.89			
	1.627	4.823	10.95			

Table 6 (continued)

Rare Earth	"a"	Corrected pH	$-\log K_{IV}$	Av. $-\log K_{IV}$	$\log K_{MV}$	
Lu^{+3}	0.697	4.322	10.68			
	0.930	4.429	10.68			
	1.162	4.539	10.71	10.72	15.79	16.00
	1.394	4.652	10.74			
	1.627	4.775	10.80			
Y^{+3}	0.697	4.701	11.98			
	0.930	4.827	11.99			
	1.162	4.952	12.02	12.02	14.49	14.80
	1.394	5.066	12.03			
	1.627	5.194	12.08			

Table 7

Source and Numerical Value of Constants Used in Calculations

Constant	log K	Temperature degrees C	Reference
K_{Cutren}	19.1	20	(44)
"	19.1	25	(23)
K_{CuY}	18.8	20	(37)
K_{CuV}	17.4	29.6	(46)
$\overline{K}_{H_3tren}$	28.44	20	(24)
"	28.24	25	(23)
K_{H_4Y}	2.0	20	(45)
K_{H_3Y}	2.67	20	(45)
K_{H_2Y}	6.16	20	(45)
K_{HY}	10.26	20	(45)

100 ml in 100-ml volumetric flasks. After mixing, the solutions were allowed to equilibrate for 24 hours in a constant temperature water bath (20.00 ± 0.02°C for the EDTA chelates and 25.00 ± 0.02°C for the HEDTA chelates). The acetic acid-sodium acetate buffer buffered the solutions to a pH of approximately 4.65. The two reference solutions contained the same concentrations of acetic acid, sodium acetate, and potassium nitrate; but did not contain rare earth nitrate. One reference solution contained 10 ml of 0.0100 M sodium copper chelate and the other one contained 10 ml of 0.0100 M copper sulfate or copper nitrate.

The measurements were made with a Sargent Model XXI polarograph. An H type cell was used, with the dropping mercury electrode in one side and a saturated calomel electrode in the other side; contact being made through a porus plug. Two drops of basic fuchsin (0.2%) were added to the solutions in the electrolytic cell andpure nitrogen was bubbled through the solutions (to remove any oxygen) for 20 minutes before each polarogram was taken. The stability constants were calculated from the experimental i_d values by the use of equation (38). These results are given in Tables 8 and 9.

Discussion and comparison of results

Acid association constants of HEDTA.

After the acid association constants were measured, it was found that they were not needed for the potentiometric calculations because of the very small contribution of H_3V, H_2V^-, and HV^{-2} to the total concentration of HEDTA in reaction IV. It was necessary to make the measurements so as to validate the potentiometric method, since it was impossible to predict their

Table 8

Polarographic Determination of the Rare Earth-EDTA Stability Constants*

Rare Earth	% Uncomplexed copper	log K_{MY}
La^{+3}	uncertain	- - -
Ce^{+3}	4.1	16.0
Pr^{+3}	4.6	16.2
Nd^{+3}	5.9	16.4
Sm^{+3}	8.7	16.7
Eu^{+3}	10.4	16.9
Gd^{+3}	11.9	17.0
Tb^{+3}	24.1	17.80
Dy^{+3}	32.5	18.17
Ho^{+3}	48.1	18.73
Er^{+3}	55.0	18.97
Tm^{+3}	68.8	19.49
Yb^{+3}	76.3	19.81
Lu^{+3}	81.3	20.07
Y^{+3}	28.1	17.98

[*] Temperature = 20.00 ± 0.02°C; ionic strength = 0.10; supporting electrolyte = KNO_3.

Table 9

Polarographic Determination of the Rare Earth-HEDTA Stability Constants*

Rare Earth	% Uncomplexed copper	log K_{MV}
Sm^{+3}	7.7	15.3
Gd^{+3}	9.0	15.4
Dy^{+3}	8.1	15.3
Ho^{+3}	8.6	15.4
Er^{+3}	9.5	15.4
Tm^{+3}	10.5	15.5
Yb^{+3}	14.4	15.8
Lu^{+3}	17.2	16.0
Y^{+3}	4.8	14.8

*Temperature = 25.00 ± 0.02°C; ionic strength = 0.10; supporting electrolyte = KNO_3.

quantitative effect with exactness. Table 10 shows a comparison of the values obtained in this research with the only other value reported in the literature. Considering the difference in temperature, the values agree very well. The agreement is certainly as good, if not better, than that for the EDTA acid association constants that are reported in the literature.

Table 10

HEDTA Acid Association Constants

K_1	K_2	K_3	Temp. °C	Ionic strength	Reference
2.90	5.41	9.89	25.0	0.10	this research
2.6	5.33	9.73	29.6	0.10	(46)

The EDTA stability constants. It should be noted that no uncertainty has been given to the values of K_{MY} in Table 5 or Table 8. The reason for this is that these constants are directly dependent upon the values for the constants K_{CuY}, $\overline{K}_{H_3tren}$, and K_{Cutren}. Uncertainties have been reported in the literature for these constants, but the constants themselves have been changed much more than the reported uncertainties. This is particularly true of K_{CuY}, which Schwarzenbach has changed from his original value of $10^{18.38}$ to $10^{18.80}$. However, because of the ion-exchange applications of the chelating agents, the relative values of the rare earth stability constants are more important than absolute values. If the constants reported in Table 7 are assumed to be correct, then a number of interesting observations can be drawn from the experimental data.

There are two sources of error in the potentiometric determinations. The least important source of error is that associated with the inability to measure the solution pH values more accurately than ± 0.02 units. Any error in the pH determination influences the value of " α ", because the hydrogen-ion concentration enters into equation (35a) as $[H]^3$. Equation (11) also contains a third power term, $[H]^3$. The errors inherent in the pH measurements cause an error of ± 0.06 units in K_{MY}.

The second source of error is more serious. As soon as the stability of the rare earth complex MY^- is no longer smaller than the stability of the copper complex CuY^{-2}, reaction VIII will take place to a considerable extent as soon as Na_2CuY and MCl_3 are mixed together.

$$CuY^{-2} + M^{+3} \rightleftharpoons MY^- + Cu^{+2} \qquad \text{VIII}$$

In case of a complete displacement of the equilibrium of equation VIII to the right side ($K_{MY} \gg K_{CuY}$), the complex MY^- would be formed to 100% during the initial mixing process and the neutralization of the solution with NaOH would not be influenced by the formation of the rare earth complex. It would be impossible to obtain any information as to the stability of the complex MY^- from pH measurements of such a reaction. As the stability of MY^- increases, equilibrium VIII is shifted more and more to the unfavorable right side. The magnitude of this shift is shown by the inconsistency of the values of $-\log K_{IV}$ in Table 5 for each rare earth. The inconsistency increases toward the heavy rare earths.

The values in Table 5 indicate that the constants, K_{MY}, are fairly accurate up to the element terbium. Only very approximate values can be obtained for the last six elements by this method. Figure 1 shows the potentiometric values with an uncertainty estimated on the basis of the facts presented.

Only one source of error is apparent in the polarographic determinations namely, the error made in the determination of the percentage of uncomplexed copper. This error amounts to about ± 2% and should be the same for all of the determinations. When these limits are introduced into equation (38), larger errors are found for the light rare earth stability constants and smaller errors for the heavy rare earth constants. The values range from ± 0.4 units for the cerium complex to ± 0.12 units for lutetium. These relative errors are also represented in data given in Figure 1. From the data presented, it is quite evident that the polarographic method gives better values for the heavy rare earths and less accurate values for the light rare earths. Thus, the potentiometric andpolarographic values supplement each other.

The uncertainty ranges of the values obtained by the two independent methods overlap up to the element dysprosium. The polarographic values are definitely higher than the potentiometric values. This difference may be real, in spite of the large errors inherent in the potentiometric values for the heavy rare earths. If this is so, the difference may be due to the change in the supporting electrolyte, i.e., resulting from substitution of KNO_3 for KCl. These differences can be explained if we assume that the

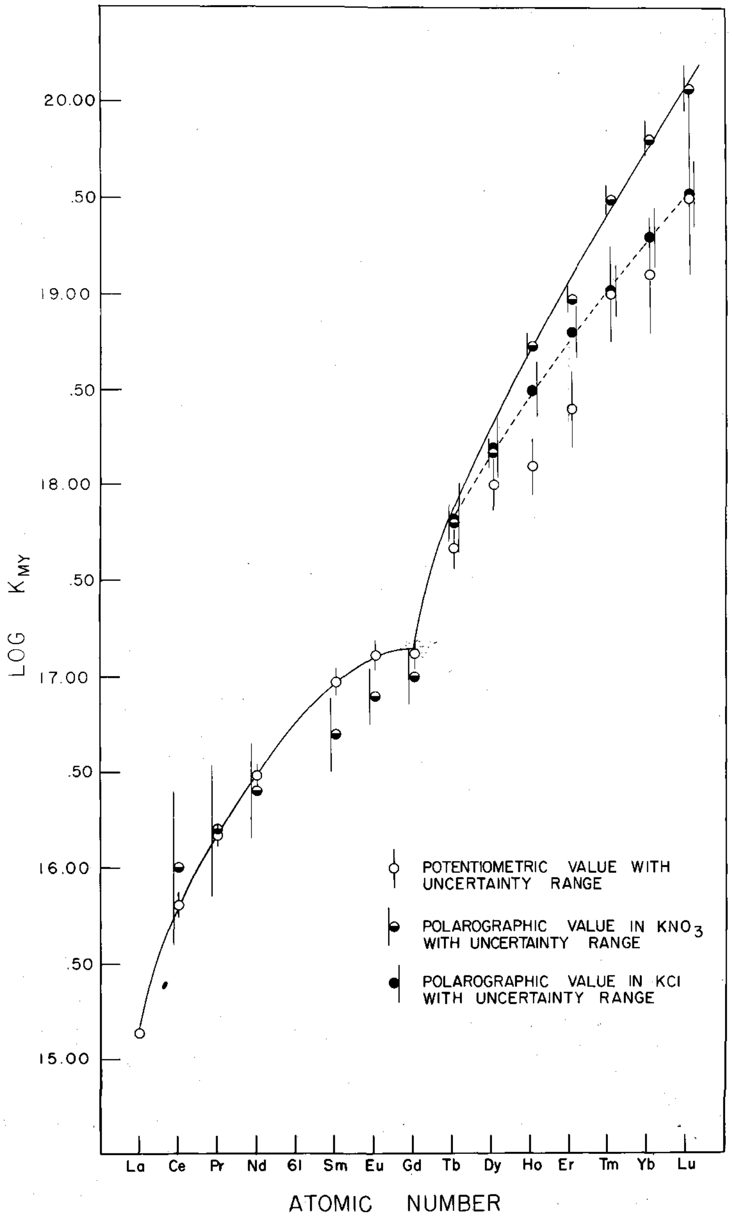


Figure 1. Rare Earth-EDTA Stability Constants

rare earth cations form chloro complexes to a slight extent in 0.1 M KCl, thus reducing the apparent formation constant of the complex MY^-. If only the most simple of such chloro complexes with the composition MCl^{+2} are considered, the stability constant can be calculated from the difference between the two values found for K_{MY} in 0.1 M KCl and 0.1 M KNO_3. The value of 28 for the stability constant of $LuCl^{+2}$ explains quantitatively the difference found for K_{LuY}. The chloro complexes would be less stable for the other rare earths.

In order to prove this assumption, the polarographic method was applied to solutions containing chloride in place of the previously used nitrate. The method and solution concentrations were exactly the same as previously stated except for the chloride to nitrate shift. Instead of the original two-electron wave with $E_{1/2} = 0.04$ V, two one-electron waves due to the stepwise reduction of uncomplexed copper Cu II to Cu I and Cu I to Cu° are found. The first wave is situated to the left and the second to the right of the original two-electron wave observed in KNO_3. The first wave lies in the positive potential range and overlaps with the anodic oxidation of mercury. The height of the second wave is proportional to the concentration of uncomplexed copper, but it is impossible to measure this height exactly because of partial overlapping of the first wave and some interference from the wave representing the reduction of the complex CuY^{-2}. The errors involved in the determination of the concentration of uncomplexed copper are about ± 4%. This eliminates application of the method to the light rare earths. The results for the heavy rare earths are consistent with the potentiometric measurements. The polarographic chloride values are given in Table 11

Table 11

Polarographic Determination of Rare Earth-EDTA Stability Constants*

Rare Earth	% Uncomplexed copper	log K_{MY}
Gd^{+3}	16	17.4
Tb^{+3}	24	17.8
Dy^{+3}	33	18.2
Ho^{+3}	40	18.5
Er^{+3}	50	18.8
Tm^{+3}	57	19.0
Yb^{+3}	64	19.3
Lu^{+3}	69	19.5

---

*Temperature = 20.00 ± 0.02°C; ionic strength = 0.10; supporting electrolyte = KCl.

and are also represented in Figure 1.

The assumption of the formation of rare earth chloro complexes was rechecked by determining the ytterbium value with perchlorate as the supporting electrolyte. This value was found to identical with the polarographic nitrate value. The stability constants of the rare earth-EDTA complexes have been measured by two other groups of workers. Vickery's work (22) was published in May, 1952, and became accessible about the time the author had completed the potentiometric and polarographic measurements of the rare earth-EDTA stability constants. The results obtained by Schwarzenbach (37) were published a year after those of the author (21). All of the values are shown in Table 12 for comparison.

The HEDTA stability constants. The accuracy of the HEDTA stability constants depends directly upon the accuracy of K_{CuY}. This constant was determined at 29.6°C. However, its magnitude would probably not be changed much more than the experimental error with a temperature change of only 4.6°C. Schwarzenbach reports a value of 18.8 for K_{CuY}, measured at 20°C, while Loomis gives a value of 18.6 for the same constant measured at 25°C.

Since the rare earth-HEDTA complexes are all considerably weaker than the copper-HEDTA complex, a reaction such as that represented by equation VIII does not occur in the rare earth-HEDTA systems. This is substantiated by the consistency of the $-\log K_{IV}$ values for given rare earths (see Table 6).

A Beckman Model GS pH meter was used for the HEDTA potentiometric measurements. The pH values obtained with such an instrument are more

Table 12
Stability Constants of the Rare Earth-EDTA Complexes*

Rare Earth	This research log K_{MY}		log K_{MY} Schwarzenbach (37)	log K_{MHY} Vickery (22)
	(Potentiometric)	(Polarographic)	(Polarographic)	(Potentiometric)
La^{+3}	15.14	- - -	15.50	15.30
Ce^{+3}	15.81	16.0	15.98	16.05
Pr^{+3}	16.17	16.2	16.40	16.55
Nd^{+3}	16.48	16.4	16.61	16.75
Sm^{+3}	16.97	16.7	17.14	17.2
Eu^{+3}	17.11	16.9	17.35	- - -
Gd^{+3}	17.12	17.0	17.37	17.2
Tb^{+3}	17.67	17.80	17.93	- - -
Dy^{+3}	18.0	18.17	18.30	17.75
Ho^{+3}	18.1	18.73	- - -	- - -
Er^{+3}	18.4	18.97	18.85	18.15
Tm^{+3}	19.0	19.49	19.32	- - -
Yb^{+3}	19.1	19.81	19.51	18.70
Lu^{+3}	19.5	20.07	19.83	- - -
Y^{+3}	17.8	17.98	18.09	18.0

*All values were measured at 20°C and at an ionic strength of 0.10.

accurate than the buffer used to standardize the meter. Since sufficient buffer solution was prepared at the beginning of the experiments to standardize the pH meter with the same buffer each time, the pH measurements have an absolute accuracy of only ± 0.01 pH units, but have a relative accuracy of ± 0.0025 pH units, the limit of the pH meter. no!

Thus, errors in determining the pH of the various solutions have an effect upon stability constant of only ± 0.03 units. Because of the uncertainty of the values of other constants, $\bar{K}_{H_3tren}$, K_{CuV}, and K_{Cutren}, the values of log K_{MV} reported in Table 6 probably have an absolute uncertainty of about ± 0.2 units. The relative values of the constants within the rare earth series are probably of the order of ± 0.06 units or less.

The uncertainty in the values of the polarographically determined rare earth-HEDTA stability constants is much larger. This is a direct result of the instability of K_{MV} compared to K_{CuV}. The equilibrium in equation VIII is shifted predominately toward the left. As a result, less than 20% of the total copper is uncomplexed. Since an error of ± 2% is committed in measuring the copper, the constant K_{MV} is accurate to only ± 0.2 to ± 0.4 units. With a relative error of this magnitude, a comparison of values of K_{MV} given in Tables 6 and 9 shows that the values determined by two independent methods do agree reasonably well. The errors are so great that the light rare earth constants could not be measured by polarography. Figure 2 shows the potentiometric and the polarographic values with uncertainties estimated on the basis of information given above.

Only one other rare earth-HEDTA stability constant is available for comparison. Fulda and Fritz (43) report a value of 13.0 ± 0.4 for

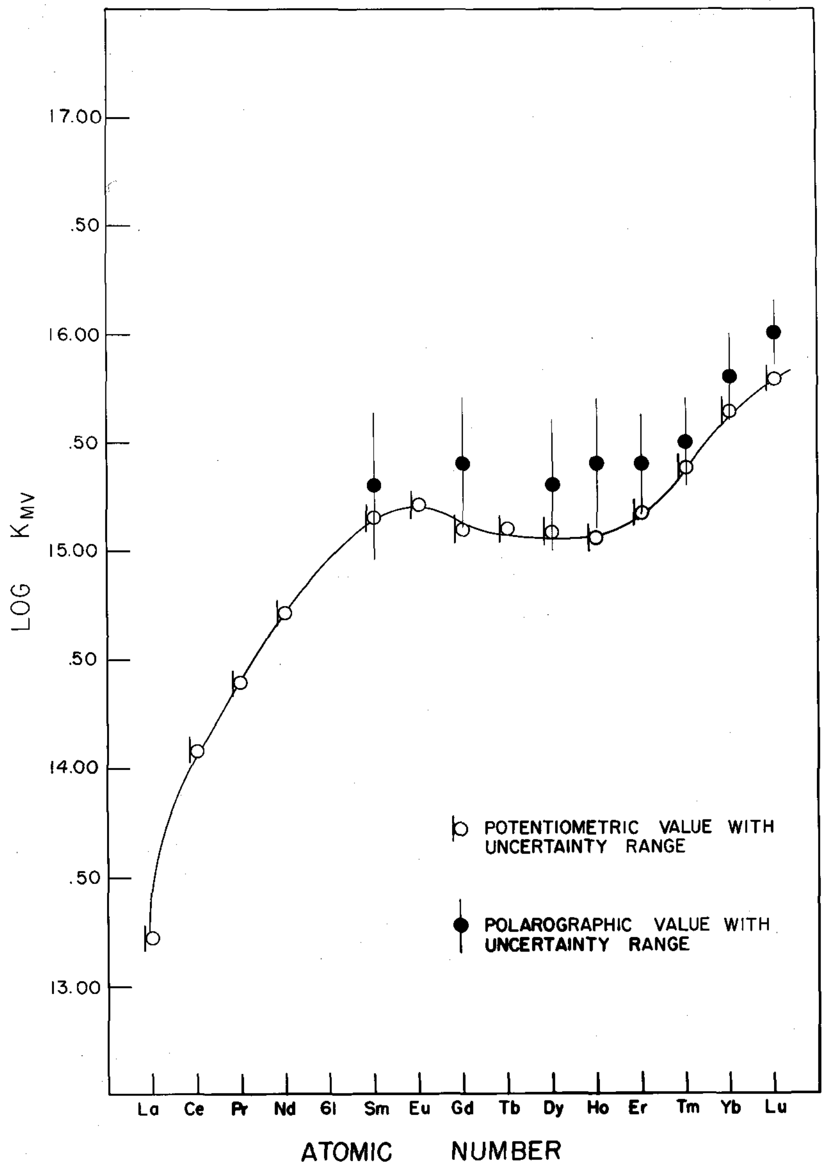


Figure 2. Rare Earth-HEDTA Stability Constants

log K_{LaV}. This value compares favorably with the value of 13.22 reported in Table 6. It is unfortunate that the value reported by Fulda and Fritz has such a large uncertainty.

Summary and Conclusions

1. The stability constants of the complexes formed between the rare earth metal ions and the anion of ethylenediaminetetraacetic acid have been measured at a temperature of 20.0°C and an ionic strength of 0.10 by two independent methods. The two methods are shown to supplement each other, one being more accurate for the lighter rare earths and the second method more accurate for the heavy rare earths.

2. In the first method, the rare earth-EDTA stability constants were calculated from measurements of the equilibrium constants of reactions involving competition between EDTA and a polyamine chelating agent, triaminotriethylamine, for the rare earth ions. The equilibrium constants were calculated from pH measurements upon the various reaction mixtures.

3. The second method is based upon the fact that it is possible to measure the concentration of free uncomplexed copper II ions in the presence of the copper complex, CuY^{-2}, by polarographic means. The rare earth-EDTA stability constants are determined by measuring the amount of copper II ions liberated when equal molar quantities of the copper-EDTA complex and a rare earth salt are mixed together.

4. The acid association constants of N-hydroxyethylethylenediaminetriacetic acid were measured from pH titration curves obtained by potentiometrically titrating the acid with standard KOH at 25.0°C and

an ionic strength of 0.10.

5. The stability constants of the complexes formed between the rare earths and the anion of N-hydroxyethylethylenediaminetriacetic acid were measured at a temperature of 25.0°C and an ionic strength of 0.10. The methods used were those described in paragraphs 2 and 3. The potentiometric method is shown to give more accurate constants with these particular chelates.

SEPARATION OF THE RARE EARTHS BY ION-EXCHANGE METHODS

Historical Review

No attempt has been made to review the extensive literature dealing with the separation of the rare earths by non ion-exchange methods, since they have little or no application to the work described in this thesis. The separation of any of the trivalent rare earths in pure form by the early fractionation methods required a great amount of time and labor. Consequently, it became obvious to those concerned with the problem that if the pure rare earths were to become available in useful quantities, a method or methods would have to be developed whereby the thousands of fractional operations needed could be performed rapidly and automatically. The development of ion-exchange techniques has provided a means of accomplishing this task.

Any separation that is achieved by chromatography or ion exchange results from repeated application of the equilibria described in simplified form by equation (IX) and equation (X)

$$uM_s^{+v} + vN_r^{+u} \rightleftharpoons vN_s^{+u} + uM_r^{+v} \tag{IX}$$

$$K_{IX} = \frac{[N_s]^v\ [M_r]^u}{[M_s]^u\ [N_r]^v} \tag{50}$$

$$M^{+3} + NY^{-1} \rightleftharpoons MY^{-1} + N^{+3} \tag{X}$$

$$K_X = \frac{[MY]\,[N]}{[M]\,[NY]} \qquad (51)$$

Equation (IX) represents the simple exchange of a cation in solution for a different cation on the resin. K_{IX} will usually be different for each pair of cations considered. In some cases K_{IX} will have a value very close to unity. This means that the resin exhibits very little selectivity between the two cations considered. When K_{IX} has a value significantly different from unity, the two cations can usually be separated by a simple elution down the exchange medium by a third cation.

Equation (X) represents the exchange of one rare earth ion in solution for a different rare earth ion in a chelate complex which is also in the solution phase. Since it is difficult to represent unambigiously all possible chelate exchange reactions by a simple general equation, the rare earth ethylenediaminetetraacetate exchange is given as an example. K_X has a different value for each of the rare earths. This means that in a mixture of two different rare earth ions, the chelating agent prefers to complex with one rather than the other. This preference provides a second means of separating the ions.

For ions of the same charge, the absolute magnitude of K_X is usually much greater than the absolute magnitude of K_{IX}. Some rare earth enrichments have been achieved by the use of the simple exchange represented by equation (IX), but more of the successful separation methods involve the use of a complexing agent. In such processes, both K_{IX} and K_X are involved. Since it is possible to have equation (IX) enrich in one direction and equation (X) in the opposite direction, care must be exercised in the choice of operating conditions, the exchange medium, and the chelating agent. A reverse enrichment by equation (IX) can be tolerated if, and only if, $\left| K_X \right| \gg \left| K_{IX} \right|$.

Separations reported prior to the year 1945

The first attempt to separate rare earths by a chromatographic technique was made by Land and Nagel (58) in 1936. They proposed a method which depends upon the difference in adsorbability (in K_{IX}). A chromatogram was developed with pure solvent. Then, the whole adsorbent phase was extruded bodily from the column and the individual concentration zones isolated by excision. These workers were able to obtain some slight enrichments, but no separation of any rare earths.

Five years elapsed before any other attempts at rare earth chromatographic separations were reported. In 1941, Finnich and Italian papers describing work with alumina columns were published. Erätmetsä and his co-workers (59,60) passed mixtures consisting of commercially available yttrium and erbium nitrates of known composition through an alumina column at different pH values. Effluent fractions were examined by spectrographic and othermethods of analysis. The yttrium group was, in general, more strongly adsorbed than the cerium group, and the enrichments seemed to be fairly independent of the pH. No quantitative evaluation of the concentrates was obtained. It is of special interest that these workers developed chromatograms of the citric acid complexes of the rare earths, and that a reversal of the usual adsorption series for the light rare earths then took place; indicating that the equilibrium described by equation (X) became dominant over that described by equation (IX).

Craotto (61) developed a chromatogram of a binary mixture consisting of trivalent lanthanum and cerium on a column of activated alumina. He reported only that cerium was more strongly adsorbed than lanthanum.

The use of ion-exchange materials for the attempted separation of the rare earth elements was reported for the first time in 1943 by Russell and Pearce (62). They carried out single and multiple stage operations. Various ion exchangers were tested and columns fifty feet long, containing crystallite No. 20 as exchanger, were used in the multiple stage experiments. These authors did not use chelating agents in their experimental work. The rare earth ions of decreasing ionic radius were, therefore, attached more firmly to the zeolite lattice than the larger ions. By regeneration of the base exchanger, the rare earth ions were differentially removed; the largest ions tending to be removed first. Russell and Pearce obtained some enrichments, but were not able to separate any adjacent rare earths into pure components.

Development of the citric acid procedures

The occurance of rare earth elements in the fission products provided great impetus to the development of ion-exchange separations within the Manhatten Project. This effort has been briefly reviewed by Johnson, Quill, and Daniels (63). Two separate ion-exchange projects were carried out; the development of methods for separating the fission products on a radio-tracer scale, and the development of methods whereby macro quantities of the pure rare earths could be separated. The latter separations were necessary before the physical and chemical properties of the individual pure rare earths could be investigated. Both projects were tremendously aided by the development of various high-capacity synthetic organic ion-exchange resins.

Resin properties and column techniques.* Most of the successful rare earth ion-exchange separations have been carried out on high-capacity nuclear sulfonated styrene-divinylbenzene copolymer type resins. These resins are sold under such trade names as Nalcite HCR, Dowex-50, and Amberlite IR-120.

The hydrogen ions from the acidic groups can be replaced by other cations. If hydrogen is attached to these groups, the resin is said to be in the hydrogen state or cycle and, similarly, if ammonium or sodium ions are attached, the resin is said to be in the ammonium or sodium cycle.

Due to the porous structure of the resin particles, positive ions and neutral molecules can diffuse throughout the resin as long as electrical neutrality is maintained. Whenever a positively charged ion enters into the resin lattice, it is necessary that an anion accompany it or that another positive ion leave the resin phase. If the ionic strength of the solution outside of the resin particles is kept low, negative ions are effectively prevented from entering into the resin phase by the relatively high concentration of fixed negative sulfonic acid groups within the resin particles. It has been clearly shown by many experiments that each

---

*A preliminary description of ion-exchange resins and ion-exchange column operations is presented prior to a review of the citrate processes for the benefit of the reader who may be unfamiliar with such operations.

gram of dry resin has a fixed number of acid groups, depending upon the manufacturing conditions. Thus, if the ionic strength of the external solution is kept relatively low, the resin will exchange an equivalent number of positive charges, whether they are associated with hydrogen, ammonium, calcium, rare earth, or any other cation.

An ion-exchange column is prepared by washing the appropriate resin particles into a glass tube; open at one end and containing a filtering device such as glass wool or a sintered glass disk at the other end so as to support the resin bed within the tube. The column is fabricated in such a manner that the solution can be withdrawn from the column, below the filter support, through a small tube, and the flow rate regulated by a pinch clamp. Usually a number of columns are prepared and used simultaneously.

The resin beds are backwashed with water, prior to use, in order to eliminate any fine particles which were not removed by previous screening and to obtain a uniformly packed bed. If rare earths are to be separated, mixed rare earth oxides are dissolved in hydrochloric acid and a known quantity of the acid solution is poured into the column--the amount depending upon the length of adsorbed band desired and the diameter of the bed. The rare earth ions displace an equivalent quantity of ions from the resin and form a saturated band of rare earths at the top of the column. The associated anions and the displaced cations are washed from the resin by pure water. The column, prior to elution, consists of an absorbed band of rare earths at the top of the exchange bed and an absorbed band of hydrogen or ammonium ions below it, with a very sharp and level band front between them.

The elution process is accomplished by passing a solution containing an ammonia-buffered chelating agent downward through the column at a controlled rate. As the band of rare earths is displaced down the column, separation is achieved by the competition of the resin and the chelating agent for the rare earth ions. Since some rare earth ions form stronger chelates, they tend to concentrate toward the front of the rare earth band; leaving the rare earths which form weaker chelates to concentrate toward the back of the band. Break-through occurs when the rare earth ions first appear in the eluate solution. The separation process is completed by fractionating the rare earth containing eluate solution as it flows from the column.

Elution with 5% citric acid at low pH. The process by which rare earth ions are eluted down an ion-exchange resin bed in the hydrogen cycle—in a few specific cases in the ammonium cycle—with a solution of 5% citric acid, buffered to a pH of 2.5 to 3.2 with ammonium hydroxide, was developed during and immediately after World War II at the Ames Lab (47,48,49) and simultaneously and independently at Oak Ridge (64,65,66, 67,68,69). Spedding and his co-workers were primarily interested in developing a process for separating macroscopic quantities of rare earths in pure form, while the scientists at Oak Ridge were interested primarily in rare earth separations on a radio-tracer scale.

When a band of adsorbed rare earth ions is eluted with 5% citric acid at a pH of 2.5 to 3.2, the band spreads out asit progresses down the resin bed and continues to expand as long as it is on the column. Analyses of the resin show that the mole fraction of rare earth to ammonia continually varies throughout the adsorbed band. The concentration of rare earth per unit length is not constant across the length of the band, but is greatest in the center. Consequently, as the rare earth band moves off the bottom of the column, a bell-shaped elution curve--concentration versus volume--is observed. As a consequence of the continually lengthening band, the longer the column through which a band is eluted, the flatter will be the bell-shaped elution curve. The ammonium ion of the eluant constantly overrides the rare earth band front; resulting in the elution of the rare earth band down an ammonium resin. A number of experiments were performed at Oak Ridge using ammonium-cycle resins. The results obtained were practically the same as with a hydrogen-cycle resin. The individual rare earth bands travel at different rates so that their maxima grow progressively farther apart as the elution is carried out. The overlapping of one band into another is considerable unless the adsorbed band travels many times its original length.

This method is very satisfactory for separating tracer quantities because the originally adsorbed band may be only a few millimeters long. Such a short band can very easily be eluted many band lengths, and a continually growing band is desirable, if not absolutely necessary, for fractionating the separated ions as they elute off the bottom of the column. The very factors which make the method desirable for tracer-scale separations make it ineffective for separating macro quantities. In such separations, the originally absorbed band may be several meters long. Because of this, and the band's coninual growth, it is extremely impractical to elute the band enough lengths to effect a good separation. The research described in this thesis is primarily concerned with the separation of rare earths on a macroscopic scale. Therefore, no further attempt is made to review the numerious papers found in the literature describing elutions with 5% citric acid.

Elution with 0.1% citric acid at high pH. It became evident to Spedding and his co-workers at Ames that elution with 5% citric acid at a low pH is impractical for the separation of macroscopic quantities of pure rare earths. Spectroscopic evidence (50) was obtained which indicated that four separate distinct complexes are formed between rare earth ions and citric acid; each one becoming important as the pH and citric acid concentration are changed. Previous experiments had shown that the resin bed over which a rare earth band had been eluted was completely saturated with ammonium ions. This indicated that a desirable process might be one in which the rare earth band was eluted with a solution of low citric acid concentration--to conserve expense--and a high ammonium ion concentration--to ensure a rapid displacement of the rare earth band.

In this method, a rare earth band is eluted down the resin bed with a 0.1% citric acid solution, adjusted to a pH between 5.0 and 8.0 with ammonium hydroxide (51,52,53,54,55,56). The only important rare earth complex in this pH range was found to be the $Mcit_2^{\equiv}$ ion. Under these conditions, the rare earth band spreads out initially as it moves down a resin bed, until it reaches an equilibrium value. The equilibrium band length depends upon the eluant pH, but is approximately double the length of the originally adsorbed band at pH 8.0. At lower pH values, the equilibrium length becomes greater and approaches an infinite length in the region of pH 5. The equilibrium band has very sharp front and rear edges. The elution curve is rectangular in shape rather than bell-shaped. Under these conditions, the concentrations of the total rare earth, the ammonium ion, and the hydrogen ion in contact with any part of this band are constant and the ratios of these constant values are the same in the eluate solution as on the resin phase in contact with the solution. Since the ammonium ion does not overrun the rare earth band, only pure hydrogen-cycle resin is found ahead of the adsorbed band and pure ammonium-cycle resin behind the rare earth band. If several individual rare earth species are present in the originally adsorbed band, they tend to separate into individual bands which follow one another head to tail as the total band is eluted down the column. The boundaries between the individual species are very sharp once an equilibrium state has been reached, but they do not pull apart from each other. The sharpness of the individual rare earth band fronts is a result of the equilibria set up between the various rare earth species and the slight differences in $cit^{\equiv}$ concentration found for each of the individual rare earth bands.

The sharp front and rear edges of the rare earth band and the rectangular shaped elution curve are a result of the constraining reactions which take place at the front and rear edges of the band once equilibrium conditions have been established. When the ammonium citrate eluant reaches the rear edges of the rare earth band, the ammonium ions are exchanged for rare earth ions; the ammonium ions being adsorbed on the resin, and the rare earth ions being chelated by the citrate anions. The equilibrium constant for this reaction is quite large so the reaction goes to completion. As the rare earth citrate complex passes through the rare earth resin bed, a continual exchange takes place. The citrate anions compete with the resin for possession of the rare earth ions. Separation is achieved by this exchange since each time an exchange takes place, a separation coefficient is applied to the system. When the rare earth citrate complex reaches the front edge of the band, the rare earth is readsorbed on the resin in place of hydrogen and citric acid (which then flows on out the bottom of the column) is formed. Once again the equilibrium constant is very large and the reaction goes to completion. The reactions at both ends of the rare earth band are driven further to completion because the reaction products are removed from the reaction zones.

This method has been successfully used on a pilot plant scale (70). Killogram quantities of all of the rare earths have been separated with a purity of 99.99% or better.

Spedding and Powell (71,72) have proposed a theory which explains the formation of the sharp bands and the rectangular elution curves. There are twelve important unknown variables in this system, but it is possible to write twelve independent equations involving only material balances, electrical neutrality, stability constants of the various complexes formed, and the equilibrium conditions. The authors found that, knowing the composition of the eluant, the capacity of the resin bed, and the total amount of rare earth adsorbed on the resin, they could solve the twelve equations and calculate the concentrations of all ionic species in the eluate and on the resin to better than 1% accuracy. The theory also enabled them to calculate the equilibrium lengths of the adsorbed bands on the resin bed.

Ion-exchange separations using amino-polyacetic acids

Several amino-polyacetic acid chelating agents have been used in attempting to separate the rare earths by ion exchange. Holleck and Hartinger (73) performed a series of experiments in which they adsorbed a mixture of light rare earths on a bed of Nalcite HCR resin and selectively removed them from the column by pouring successive quantities of a chelating agent through the column. The rare earths were initially adsorbed onto various types of resin beds; namely beds in the hydrogen, sodium, potassium or ammonium cycle. The authors compared the effectiveness of ethylenediaminetetraacetic acid, o-diaminocyclohexane tetraacetic acid, bis(2-aminoethyl)ether tetraacetic acid and ethylene glycol bis(2-aminoethyl)ether tetraacetic acid. They report that the best enrichments were obtained with the last named chelating agent at pH 6.75. However, they did not obtain any pure rare earths.

Several investigators have recognized the potential advantage of using EDTA as an eluant for ion-exchange separations, but evidently they have not found the proper conditions for separating the rare earths by this means (74,75,76,77). In all of the work thus far conducted, except that to be described later in this chapter, a rare earth mixture was adsorbed on either a hydrogen or an ammonium cycle resin bed prior to elution. When a rare earth band is eluted onto hydrogen cycle resin with ammonia-buffered EDTA, the sparingly soluble free acid of the chelating agent crystallizes out of solution at the rare earth-hydrogen boundary.

This results from the great increase in the hydrogen-ion concentration at the boundary as the rare earth band is eluted down the resin bed. In most cases, the acid precipitate blocks the column and prevents further elution. Vickery (74) and Freiling and Myer (75) performed some separations using such a low eluant concentration that no precipitate could be observed. Such conditions are not at all practical for macroscopic separations. Taylor (76) performed some experiments with an ammonium bed ahead of the rare earth band. He reported that the ethylenediaminetetraacetate complexes of the rare earths and thorium are so strong that little, if any, exchange occurs between the complex and the resin bed. Taylor concluded that EDTA is suited only for stripping the exchanger of adsorbed ions.

Nitrilotriacetic acid was used by Iya and Loriers (77) to separate scandium from the rare earths. The eluant consisted of 20 grams of nitrilotriacetic per liter adjusted to pH 4 with ammonium hydroxide. The ions to be separated were adsorbed in a band at the top of a column of Dowex-50 in the hydrogen cycle. Then, before pouring the eluant through the column, a solution of ammonium chloride was passed through the column to convert the hydrogen resin to ammonium resin. With such a system, true elution probably did not occur. The scandium and rare earth nitrilotriacetate complexes are so stable that little or no readsorption could have taken place. The ions were merely selectively removed from the resin bed, scandium being removed first. Fitch and Russell (78,79) used a comparable method for selectively removing some light rare earths from a bed of Amberlite IR-120 resin with nitrilotriacetic acid. In this case, 25 grams of crude didymium oxide were dissolved in HCl and adsorbed on a bed of ammonium cycle resin from a solution of pH 2. A 0.5% solution of nitrilotriacetic acid adjusted to pH 5.0 with ammonium hydroxide was used to selectively remove the rare earths from the column. A fair degree of concentration was achieved, but no pure rare earths were obtained.

Use of EDTA as an Eluant

The stability constants of the rare earth-EDTA complexes vary from $10^{15.14}$ for lanthanium to $10^{20.07}$ for lutetium. The difference corresponds to a factor of $10^{4.93}$ across the series or a mean of 2.38 from one rare earth to the next. The rare earth-citrate complexes have not been measured, but since EDTA is a possible hexadentate chelating agent while the two citrate anions associated with each rare earth ion are tridentate, the rare earth-EDTA constants should be much more sensitive to ionic size, and the differences between them should be larger than the differences between those of the rare earth-citrate complexes. This section is devoted to describing the methods which were developed for utilizing the greater selectivity of EDTA to separate the rare earth elements by ion exchange.

Ion-exchange resin used as a differential filter

Discussion of problem. The citric acid method for separating the rare earths, as developed in the Ames Laboratory, depends upon the adsorption of a band of rare earths on a cation-exchange resin and the subsequent elution of this band down the resin bed. However, a much more rapid process could be effected if the ion-exchange columns could be used to adsorb differentially one rare earth or group of rare earths from a mixture and allow the others to pass through without being appreciably adsorbed. This technique has been tried by Fitch and Russell (78,79) and Iya and Loriers (77) using nitrilotriacetic acid.

The process consists essentially of complexing part of the rare earths in a mixture with EDTA, then separating the complexed rare earth ions from the uncomplexed ions by passing the solution through an ion-exchange resin bed in the ammonium cycle. The complexed ions pass through the column while the uncomplexed ions are adsorbed on the resin. A resin bed of sufficient capacity to adsorb all of the uncomplexed ions must, of course, be used. EDTA is particularly useful in this type of separation because of the stability of the complexes that are formed and the selectivity of the chelating agent.

Materials, apparatus, and experimental procedures. Two separate experiments were devised to show the utility of this method. The first experiment involved the separation of a multigram sample of crude rare earths, extracted from gadolinite, into five enriched fractions. The second experiment, involving the separation of neodymium from praseodymium, was carried out in order to determine the amount of time necessary for the reaction

$$NdY^{-} + Er^{+3} \rightleftharpoons ErY^{-} + Nd^{+3}$$

to reach equilibrium conditions.

Fractionation of ore sample. A neutral solution containing 312 grams of mixed rare earths, weighed as oxide, was obtained by dissolving a known larger amount of the rare earth material in a limited amount of hydrochloric acid and recovering the undissolved rare earth. A previously prepared solution of diammonium dihydrogen ethylenediamine tetraacetate, containing the theoretical amount of EDTA required to complex the heavy rare earths in the mixture (75 grams), and adjusted to a pH of 10, was added to the rare earth solution, and the mixture diluted to 90 liters. After equilibration for 24 hours, the pH of the solution was adjusted from about 6 to 4.5 by the addition of 5 ml of concentrated hydrochloric acid. Following a second 24-hour equilibration period, this solution was passed rapidly through a 4-inch diameter glass column containing a 4-foot bed of Dowex-50 resin, and the column washed free of complexed rare earths with pure water. The rare earths remaining on the resin were fractionally removed by pouring four successive predetermined amounts of EDTA solution, which had been adjusted to a pH of 9.5 with ammonium hydroxide, through the column at a slow flow rate. Twenty four hours were allowed for each fraction, so as to let the liquid remain in contact with the resin long enough to approach equilibrium conditions. The five samples were recovered and the concentration of the individual rare earths determined by spectrophotometric analysis. The results are presented in Table 13.

Separation of neodymium from erbium. A solution of the neodymium-EDTA complex was prepared by dissolving 16.000 grams of Nd_2O_3 in hydrochloric acid, adding 29.64 grams of diammonium dihydrogen ethylenediaminetetraacetate (not quite enough to complex all of the neodymium),

Table 13

Grams of Rare Earth Oxide Recovered from One Run on Gadolinite Ore

Elements	Sample I	Sample II	Sample III	Sample IV	Sample V	Total
Lu	1.67					1.67
Yb	14.02	1.69				15.71
Tm	1.55	1.22				2.77
Er	5.58	9.83				15.41
Ho	1.04	3.57	0.25			4.86
Dy	2.15	11.17	9.04	0.30		22.66
Tb	0.06	0.13	0.10	0.75	0.69	1.73
Gd				7.37	5.80	13.17
Sm				3.87	5.42	9.29
Nd				3.75	7.45	11.20
Pr				0.37	0.68	1.05
Ce				0.81	2.27	3.08
La				0.81	2.27	3.08
Y	13.81	65.17	72.80	25.80	13.22	190.80
Totals	39.88	92.78	82.19	43.83	37.80	296.48

and adjusting the pH to 4.08 with ammonium hydroxide. The uncomplexed neodymium was separated from the complexed neodymium by passing the solution through a short column containing Dowex-50 resin in the ammonium cycle. Then two drops of 1:1 HCl were added to adjust the pH to 4.55 and the solution was diluted to exactly 2 liters. A 100-ml aliquot was removed from the solution and the rare earth recovered from the aliquot sample and weighed as Nd_2O_3. This analysis indicated that the solution contained 7.473 grams of rare earth, weighed as oxide, per liter. This concentration was checked by recovering the neodymium which had been adsorbed onto the resin and subtracting it from 16.000 grams. This second analysis gave a value of 7.474 grams of rare earth, weighed as oxide, per liter of solution. An erbium chloride solution, having an exactly equivalent molar concentration, was prepared by dissolving 16.983 grams of Er_2O_3 in HCl, adjusting the solution to pH 4.5 with ammonium hydroxide, and diluting the solution to 2 liters.

The experiment was performed by mixing 100 ml of the neodymium solution with 100 ml of the erbium solution and pouring the combined mixture quickly through a column containing enough Dowex-50 resin in the ammonium cycle to adsorb all of the uncomplexed rare earth ions present in solution. The column was carefully flushed with pure water to remove all complexed rare earth. Both the rare earth fraction which passed through the resin bed and that which was adsorbed were recovered and the composition determined by spectrophotometric analysis. A second experiment was performed in exactly the same manner except that the mixture was allowed to equilibrate for 10 minutes before being passed through the ion-exchange column. The results are presented in Table 14.

Table 14

Separation of Neodymium from Erbium

Sample No.	Equilibration time (min)	Grams of R_2O_3 in mixture	Grams of R_2O_3 recovered	% Er_2O_3	% Nd_2O_3
1-A	0.0	1.596	0.841	94.8	6.4
1-B	0.0		0.699	5.1	94.8
2-A	10	1.596	0.830	94.8	6.3
2-B	10		0.705	5.9	93.5

Results and conclusions. The results given in Table 13 and Table 14 show that this method can be used to separate rapidly the heavy rare earths from the light rare earths (80). Such a "rough cut" would be very advantageous prior to separating the heavy rare earths from each other in high purity by other elution methods. It is known that the crude rare earths extracted from gadolinite contain, by occlusion, small amounts of beryllium, thorium, iron, and other impurities. Most of these impurities would not be recovered with the rare earths by the oxalate precipitation following the ion-exchange separation. This accounts for most of the differences between the 312 grams of R_2O_3 in the original solution and the 296.5 grams of R_2O_3 recovered at the completion of the experiment. A very small part of the discrepancy may be due to the small solubility losses which occur in this type of experiment because of the large quantities of solution involved.

This method is very satisfactory for separating rare earths or groups of rare earths which are a considerable distance apart in the rare earth series, i.e., lanthanum from lutetium or lanthanum and cerium from ytterbium and lutetium. The method is not satisfactory for isolating pure rare earths from a naturally occuring mixture--which always contains adjacent rare earths--because the separation coefficients between the individual adjacent rare earths are not large enough to give a complete separation by the single application achieved in this type of separation.

Elutions with iron III as a retaining ion

Discussion of problem. It soon became evident that some mechanism had to be found that would allow the rare earths to be continually readsorbed onto the resin from the rare earth-EDTA complex as the rare earth band moves down the column if the rare earths were to be separated from each other in pure form with EDTA. In citric acid systems, this mechanism is provided by the acid-form resin ahead of the rare earth band. Acid-cycle resin cannot be used with EDTA because, unlike citric acid, the acid form of the chelating agent is quite insoluble. The stability constant of the iron III-EDTA complex has been found to be $10^{25.1}$ (36), much larger than any of the rare earth constants. An iron III bed ahead of the rare earth band should serve much the same function as a hydrogen bed for citric acid elutions. When the tightly held rare earth complex comes into contact with the iron-phase resin, an exchange should take place and the rare earth be readsorbed; the soluble iron complex being swept out the bottom of the column. These suppositions were tested by experimental separations and found to be true in part.

Materials, apparatus, and experimental procedures. Two successful experiments were conducted using an iron III ion barrier. In the first experiment, 5.00 grams of Nd_2O_3 were mixed with 5.00 grams of Pr_6O_{11}, dissolved in hydrochloric acid, and the solution adjusted to a pH of 5.2 with ammonium hydroxide. A bed of 30 to 40 mesh Dowex-50, 16 cm long and 22 mm in diameter was completely saturated with rare earth ions (required 5.790 grams, weighed as oxide) by passing the above solution through the bed, followed by a wash of pure water to remove all unadsorbed ions. A second bed, 20 cm long and 22 mm in diameter, of 30 to 40 mesh Dowex-50 was completely saturated with iron III ions by passing a solution of reagent grade iron III nitrate through the bed, followed by pure water. The bottom of the rare earth-cycle column was then connected to the top of the iron-cycle column and the rare earths were eluted down the iron-cycle bed at 200 ml per hour with an eluant of 10 grams of diammonium dihydrogen ethylenediaminetetraacetate per liter, adjusted to a pH of 7.95 with ammonium hydroxide. The eluate was fractionated into 200-ml samples. The composition of the individual rare earth samples, recovered from the eluate by oxalate precipitation, was determined by spectrophotometric analysis. The results are shown in Table 15.

The second successful elution was carried out with the same equipment and in exactly the same manner as the first experiment except that a flow rate of 50 ml per hour was used rather than 200 ml per hour. The rare earth column contained 5.9012 grams of rare earth weighed as oxide. The eluate was again collected in 200 ml fractions. The results from the second elution are shown in Table 16.

Results and conclusions. A fair degree of separation was attained in these two experiments (81), but iron trailed quite badly into the rare earth band. In these preliminary experiments, only short resin beds were used. Subsequent experiments with longer resin beds indicated that iron III is not the most desirable retaining ion. It was found that the pH range of the eluant was very limited with the iron III system. If the eluant is too acidic, the acid H_4Y tends to precipitate in the interstices of the resin bed and, if it is too basic, hydrous ferric oxide clogs the bed. Some ion having a more soluble hydroxide than iron

Table 15

Separation of Neodymium from Praseodymium (Run I)

Sample No.	Grams of R_2O_3	% Nd_2O_3	% Pr_6O_{11}
1	0.0798	97.4	0.9
2	0.4747	97.2	1.6
3	0.7028	96.7	3.2
4	0.7455	87.7	13.1
5	0.7927	63.6	37.2
6	0.8064	34.4	66.6
7	0.8101	14.4	84.8
8	0.8326	5.3	93.5
9	0.5163	2.1	96.5
10	0.0026		
	Total = 5.7635		

Table 16

Separation of Neodymium from Praseodymium (Run II)

Sample No.	Grams of R_2O_3	% Nd_2O_3	% Pr_6O_{11}
1	0.1200	100	- - -
2	0.6710	100	- - -
3	0.8886	97.8	1.5
4	0.8652	93.3	5.7
5	0.8468	46.6	52.5
6	0.8457	3.3	96.7
7	0.8434	- - -	100
8	0.8174	- - -	100
9	0.0108		
Total =	5.9089		

III would be a more desirable choice for the retaining ion in this type of elution.

Elutions with copper II as a retaining ion

Discussion of problem. Consideration of the stability constants for the EDTA complexes with the rare earths and other metal ions (37) shows that copper II, nickel II, and lead II should serve to retain a number of the rare earth ions. In solutions having an ionic strength of 0.1, the stability constants of the EDTA complexes with these ions lie between the erbium and dysprosium constants. However, the relative stabilities of the EDTA complexes are not the only factors which determine the order of elution of ions from ion-exchange beds; particularly ions of different charges. The general rule for the order of affinity of ions for cation exchange resins is $M^{+4} > M^{+3} > M^{+2} > M^{+}$. This means that, while copper II is complexed less strongly than erbium by EDTA, the rare earths are, in general, more firmly attached to the resin. The two effects are complimentary and copper II can be eluted ahead of all of the rare earths under carefully controlled conditions. The following sections illustrate the conditions that are necessary and the results that can be achieved.

Materials, apparatus, and experimental procedures. A 40 to 50 mesh bed of Dowex-50, 25 cm long and 22 mm in diameter, was completely saturated with an approximately equal molar mixture of neodymium and praseodymium ions. The column was loaded from a solution prepared by dissolving 9.00 grams of Nd_2O_3 and 9.21 grams of Pr_6O_{11} in hydrochloric acid and adjusting the pH to 5.0 with ammonium hydroxide. The loaded column was flushed with pure water to remove all unadsorbed ions and the excess rare earth was recovered. A second bed of 40 to 50 mesh resin, 67 cm long and 22 mm in diameter, was saturated with copper II ions from a solution of reagent grade copper II sulfate and washed clear of all unadsorbed ions with pure water. The two columns were then connected in series and eluted with a solution containing 10 grams of diammonium dihydrogen ethylenediaminetetraacetate per liter, adjusted to pH 7.46 with ammonium hydroxide. The flow rate was maintained at a constant value of 0.3 cm per minute and the eluate was collected in 200-ml fractions. Under these conditions, the rare earth-copper boundary was very sharp. Only the intermixing due to the tilting of the band front could be detected. The rare earth samples recovered from the eluate fractions were analyzed both spectrophotometrically and spectrographically. The results of this experiment are presented in Table 18. Two similar separations were carried out using eluant pH values of 7.97 and 8.47. The important column loading data for all three experiments is presented in Table 17. The analytical results for the second and third separation are given in Table 19 and Table 20 respectively.

Results and conclusions. The results depicted in Tables 18, 19 and 20 indicate very clearly the enormous advantage that can be gained by using the copper-EDTA system in preference to any other known method for separating adjacent rare earths. It should be noted that the concentrations of the rare earths in the EDTA solution are about ten times as great as

Table 17

Column Loading and Elution Data for Neodymium-Praseodymium Separations

	Run I	Run II	Run III
Grams of oxide adsorbed on primary column	11.8458	11.6194	11.6017
pH at which rare earth was loaded	5.00	4.90	5.18
pH of solution from which copper II ions were loaded on secondary column	3.96	3.96	3.96
pH of eluant	7.46	7.97	8.47
Volume of elution fractions	200 ml	250 ml	250 ml
Grams of oxide recovered from eluate	11.2667*	11.3730	10.0598*

*Some eluate solution was lost due to failure of electronic bottle changing apparatus.

Table 18

Separation of Adjacent Rare Earth (Run I)

Sample No.	Grams of R_2O_3 recovered	% Pr_6O_{11}	% Nd_2O_3
1	0.1136	< 0.08	> 99.9
2	0.5830	< 0.08	> 99.9
3	0.7228	< 0.08	> 99.9
4	0.7153	< 0.08	> 99.9
5	0.7252	< 0.08	> 99.9
6	0.7230	< 0.08	> 99.9
7	0.7240	< 0.08	> 99.9
8	0.7214	3	95
9	0.7005	28	67
10	0.7056	75	22
11	0.7023	98	2
12	0.6817	99.9	0.2
13	0.6890	> 99.9	< 0.06
14	0.6894	> 99.9	< 0.06
15	0.6886	> 99.9	< 0.06
16	0.6926	> 99.9	< 0.06
17	0.6887	> 99.9	< 0.06

Table 19

Separation of Adjacent Rare Earths (Run II)

Sample No.	Grams of R_2O_3 recovered	% Pr_6O_{11}	% Nd_2O_3
1	0.4126	< 0.08	> 99.9
2	0.9584	< 0.08	> 99.9
3	0.9519	< 0.08	> 99.9
4	0.9867	< 0.08	> 99.9
5	0.9575	< 0.08	> 99.9
6	0.9453	11	88
7	0.9400	64	34
8	0.9283	96	4
9	0.9213	99.9	0.1
10	0.9156	> 99.9	< 0.06
11	0.9122	> 99.9	< 0.06
12	0.9167	> 99.9	< 0.06
13	0.6265	> 99.9	< 0.06

Table 20

Separation of Adjacent Rare Earths (Run III)

Sample No.	Grams of R_2O_3 recovered	% Pr_6O_{11}	% Nd_2O_3
1	0.2634	< 0.08	> 99.9
2	1.0084	< 0.08	> 99.9
3	1.0837	< 0.08	> 99.9
4	1.0816	< 0.08	> 99.9
5	1.0983	19	79
6	1.0496	95	6
7	1.0307	98	4
8	1.0434	> 99.9	< 0.06
9	1.0437	> 99.9	< 0.06
10	1.0390	> 99.9	< 0.06
11	0.3180	> 99.9	< 0.06

was found expedient in the citrate elutions. This increases the elution rate and decreases the amount of pure water needed.

In the separation of rare earths by the various citric acid methods (56,67), there are certain groups of elements which are very difficult to separate. These groups are lutetium-ytterbium, dysprosium-yttrium-terbium, and gadolinium-europium-samarium. Powell (82) has applied the copper-EDTA method to each of these three troublesome groups with excellent success. Powell's separations were carried out using an eluant solution of approximately 2% dihydrogen diammonium ethylenediaminetetraacetate adjusted to a pH of 8.5 and a linear flow rate of 0.5 cm per minute. Later production separations have indicated that the best results can be obtained with an eluant of 5 grams of the diammonium salt of EDTA per liter adjusted to a pH between 8.0 and 8.2.

The operating conditions for the copper II-EDTA method must be carefully controlled, but the pH range is considerably broader than the pH range for the iron III-EDTA method. Again, if the eluant pH is too low, the acid H_4Y will precipitate in the resin bed and hamper the operation of the column. If the eluant pH is too high, a copper complex, Cu_2Y, precipitates and causes trouble. At a concentration of 5 grams of the diammonium salt of EDTA per liter, the eluant pH must not be above 8.2 or some of the heavy rare earths from erbium to lutetium may pass through the copper barrier and be lost.

Separations Using HEDTA as an Eluant

Discussion of problem

Two important facts can be observed from Table 6 and Figure 2. First of all, there is no significant variation in the magnitude of the stability of the rare earth-HEDTA constants from samarium to erbium. This means that little or no separation of these elements from one another could be obtained by an ion-exchange elution when HEDTA is used as the eluting agent. The second important fact to observe is the very dramatic shift of the yttrium stability constant from its usual holmium-dysprosium region to the neodymium-praseodymium region. Since the R_2O_3 leached from gadolinite ore contains 60% yttrium, 25% light rare earths and only 15% heavy rare earths, this shift presents the possibility of a very fast and economical removal of yttrium from the more desirable heavy rare earth fraction of the ore. HEDTA has the advantage of being quite soluble in acid solutions, so it can be used to elute rare earth bands directly onto resin in the hydrogen cycle without any precipitation trouble.

Materials, apparatus, and experimental procedure

Four 4-inch Pyrex glass columns 5 feet long, filled to a depth of 4.5 feet with 100 to 200 mesh Dowex-50 x 12 cation exchange resin, were used for the experiment. The resin in each column was carefully backwashed several times to insure a uniformly packed resin bed. The resin bedc were next reconditioned by pouring several hundred liters of 5% ammonium citrate solution, whose pH was about 8, through the columns. The citrate solution was followed with 100 liters of one normal hydrochloric acid. Such a reconditioning removes all unwanted cations and leaves the resin in the hydrogen cycle. Of course, all excess acid was removed by washing with pure water.

A 1500 gram sample of crude ore (R_2O_3) was reprecipitated to remove non rare earth impurities, and 1400 grams (as R_2O_3) were dissolved in HCl and the solution diluted to 20 liters. The first of the four columns was disconnected and the resin placed in the rare earth cycle by passing the 20 liter solution of mixed rare earth through it, followed by pure water to remove any excess rare earth ions. The rare earth in the effluent was recovered, converted to oxide, and found to weigh 177 grams. Thus 1223 grams (as R_2O_3) were adsorbed on the ion-exchange resin.

The rare earth saturated column was then reconnected to the other three columns and the four column system was eluted at a rate of 120 ml per minute with a solution containing 5 grams of HEDTA per liter, buffered to a pH of 8.68 with ammonium hydroxide. It required about 720 liters of such an eluant to displace the rare earth band one band length down the system. As the eluate flowed from the bottom of the fourth column, it was fractionated into 20-liter fractions. The rare earth in each fraction was recovered and converted to the oxide. The content of the individual rare earths in each fraction was determined by spectrophotometric and spectrographic analysis. The analytical results are presented in Table 21.

Table 21

Separation of an Ore Sample with HEDTA

Sample No.	% Yb	% Tm	% Er	% Ho	% Dy	% Tb	% Gd	% Sm	% Nd	% Pr	% Lu, Y,* Ce, La
1	39	8	16	2	10	2	7	4			13
2	13	4	30	6	29	2	10	6			5
3	5	2	19	7	37	2	23	10			1
4	4	1	10	6	37	2	26	15			1
5	2	1	7	5	34	2	29	20			2
6	2	1	4	4	28	2	27	25			12
7	2	1	3	3	20	2	27	25			20
8	2	1	2	2	12	2	20	21			39
9	2	1	2	1	5	2	14	13			61
10	2	1	2	1	4	0.8	8	8			74
11	2	1	2	0.5	2	0.4	4	4			85
12	2	1	2	0.5	2	0.3	3	3			88
13	1	1	2	0.4	2	0.3	3	3			89
14	1	1	1	0.3	2	0.1	3	2	0.2		90
15	1	1	1	0.3	2	0.3	3	2	0.2		90
16	1	1	1	0.2	2	0.2	2	1	0.4		92
17	M**	1	1	0.2	1	0.2	1	1	0.5		95
18	M	0.6	0.4	0.1	0.1	0.2	1	0.7	0.4		97
19	M	0.5	0.4	0.1	0.1	0.1	1	0.7	1.1		96
20	M	0.5	0.4	0.1	0.1	0.1	0.7	0.6	0.8		97

---

*Determined as difference. The lutetium is concentrated in samples 1,2 and 3. Almost all of the difference from sample 4 to sample 34 is due to yttrium. The cerium and lanthanum are concentrated in samples 35, 36, and 37.

**Indicates measurable content of less than 1%.

Table 21 (continued)

Sample No.	% Yb	% Tm	% Er	% Ho	% Dy	% Tb	% Gd	% Sm	% Nd	% Pr	% Lu, Y Ce, La
21									1		99
22									2		98
23									3		97
24									4		96
25									5		95
26									7		93
27									9		91
28									10		90
29									12		88
30									15		85
31									20	0.3	80
32									24	0.7	75
33									30	3	67
34									34	17	49
35									20	13	67
36									6	6	88
37									3	4	93

Results and conclusions

The results, as indicated in Table 21, show too much trailing of the heavy rare earths into the yttrium region and no separation of any of the rare earths from samarium to lutetium. This separation is inferior to that which can be obtained by the copper-EDTA method. The results do show that the yttrium is concentrated between samarium and neodymium; thus giving support to the correctness of the yttrium-HEDTA stability constant.

It would be helpful if a chelating agent, such as HEDTA, could be found which would shift the elution position of yttrium even farther into the light rare earth series than does HEDTA. The elution of the crude rare earths, as extracted from gadolinite, by such a chelating agent would make possible the isolation of the samarium to lutetium rare earths away from yttrium and the light rare earths. The heavy rare earth fraction could then be eluted by the copper II-EDTA method. This would greatly reduce the amount of labor and expense necessary to separate the samarium to lutetium rare earths away from each other in a high state of purity. It would be relatively simple to separate the light rare earths away from each other and from yttrium by the copper II-EDTA method.

Summary and Conclusions

1. A rapid method for separating rare earths into enriched fractions has been developed. The process consists of complexing part of the rare earths in a mixture—those rare earths which form the more stable complexes—with EDTA and separating the complexed rare earth ions from

the uncomplexed rare earth ions by passing the mixture through an ion-exchange column in the ammonium cycle. The complexed ions pass through the resin bed, but the uncomplexed ions are adsorbed.

2. A method has been found for separating pure rare earths in multigram quantities from rare earth mixtures. The method consists of eluting a band of mixed rare earths, adsorbed on a cation-exchange resin, through a second cation-exchange resin bed in the copper II or iron III state. Copper was found to be far superior to iron. The eluant consists of an ammonia-buffered solution of ethylenediaminetetraacetic acid.

3. The elution of a mixture of all of the rare earths down an ion-exchange bed with an ammonia buffered solution of HEDTA indicated that this chelating agent is not as effective for separating the heavy rare earths as the EDTA-copper II system under the conditions tested.

LITERATURE CITED

1. Morgan, G. T., and Drew, H. D. K., J. Chem. Soc., 117, 1456 (1920).

2. Fick, R., and Ulrich, G., Ger. Patent 638,071 (1936). [Original not seen; cited in C. A., 31, 1043 (1937).]

3. Chaberek, S. Jr., and Bersworth, F. C., Science, 118, 280 (1953).

4. Brintzinger, H., Thiele, H., and Müller, U., Z. anorg. u. allgem. Chem., 251, 285 (1943).

5. Moeller, T., and Brantley, J. C., J. Am. Chem. Soc., 72, 5447 (1950).

6. Martell, A. E., and Calvin, M., "Chemistry of the Metal Chelate Compounds", New York, Prentice-Hall, 1952.

7. Pfeiffer, P., and Simons, H., Ber. deut. chem. Ges., 76, 847 (1943).

8. Pfeiffer, P., and Offerman, W., ibid., 75 B, 1 (1942).

9. Pfeiffer, P., and Schmitz, E., Z. anorg. Chem., 258, 247 (1949).

10. Brintzinger, H., and Munkelt, S., ibid., 256, 65 (1948).

11. Brintzinger, H., and Hesse, G., Z. anorg. u. allgem. Chem., 249, 113 (1942).

12. Busch, D. H., and Bailor, J. C. Jr., J. Am. Chem. Soc., 75, 4574 (1953).

13. Schwarzenbach, G., Helv. Chim. Acta, 32, 839 (1949).

14. Klemm, W., and Raddatz, K. H., Z. anorg. u. allgem. Chem., 250, 204 (1942).

15. Klemm, W., Z. anorg. Chem., 252, 225 (1944).

16. Jones, S. S., and Long, F. A., J. Phys. Chem., 56, 25 (1952).

17. Schwarzenbach, G., and Heller, J., Helv. Chim. Acta, 34, 576 (1951).

18. Schwarzenbach, G., and Biederman, W., ibid., 31, 459 (1948).

19. Schwarzenbach, G., Willi, A., and Bach, R. O., ibid., 30, 1303 (1947).

20. Schwarzenbach, G., and Ackerman, H., ibid., 30, 1798 (1947).

21. Wheelwright, E. J., Spedding, F. H., and Schwarzenbach, G., *J. Am. Chem. Soc.*, *75*, 4196 (1953).

22. Vickery, R. C., *J. Chem. Soc.*, London *1952*, 1895.

23. Loomis, T. C., "Metal Chelates of Cyclohexedenediaminetetraacetic Acid". Unpublished Ph. D. Thesis, Iowa State College Library, Ames, Iowa. 1953.

24. Ackerman, H., and Schwarzenbach, G., *Helv. Chim. Acta*, *32*, 1543 (1949).

25. Schwarzenbach, G., and Freitag, E., *ibid.*, *34*, 1492 (1951).

26. Schwarzenbach, G., and Freitag, E., *ibid.*, p. 1503.

27. Carini, F. F., and Martell, A. E., *J. Am. Chem. Soc.*, *74*, 5745 (1952).

28. Carini, F. F., and Martell, A. E., *ibid.*, *75*, 4810 (1953).

29. Carini, F. F., and Martell, A. E., *ibid.*, *76*, 2153 (1954).

30. Koryta, J., and Kössler, Jr., *Collection Czechoslov. Chem. Comms.*, *15*, 241 (1950).

31. Matyska, B., and Kössler, I., *ibid.*, *16*, 221 (1951).

32. Ackerman, H., and Schwarzenbach, G., *Helv. Chim. Acta*, *35*, 485 (1952).

33. Blumer, M., and Kolthoff, I. M., *Experientia*, *8*, 138 (1951).

34. Pecsok, R. L., and Maverick, E. F., *J. Am. Chem. Soc.*, *76*, 358 (1954).

35. Bril, K., and Krumholz, P., *J. Phys. Chem.*, *57*, 874 (1953).

36. Schwarzenbach, G., and Sandera, J., *Helv. Chim. Acta*, *36*, 1089 (1953).

37. Schwarzenbach, G., Gut, R., and Anderegg, G., *ibid.*, *37*, 937 (1954).

38. Kolthoff, I. M., and Auerbach, C., *J. Am. Chem. Soc.*, *74*, 1452 (1952).

39. Plumb, R. C., Martell, A. E., and Bersworth, F. C., J. Phys. and Colloid Chem., 54, 1208 (1950).

40. Martell, A. E., and Plumb, R. C., J. Phys. Chem., 56, 993 (1952).

41. Cook, C. M., and Long, F. A., J. Am. Chem. Soc., 73, 4119 (1951).

42. Jones, S. S., and Long, F. A., J. Phys. Chem., 56, 25 (1952).

43. Fulda, M. O., and Fritz, J. S., unpublished data, Ames Laboratory, 1955.

44. Prue, J. E., and Schwarzenbach, G., Helv. Chim. Acta, 33, 963 (1950).

45. Schwarzenbach, G., and Ackerman, H., Helv. Chim. Acta, 30, 1798 (1947).

46. Chaberek, S., and Martell, A. E., J. Am. Chem. Soc., 77, 1477 (1955).

47. Spedding, F. H., Voigt, A. F., Gladrow, E. M., and Sleight, N. R., J. Am. Chem. Soc., 69, 2777 (1947).

48. Spedding, F. H., Voigt, A. F., Gladrow, E. M., Sleight, N. R., Powell, J. E., Wright, J. M., Butler, T. E., and Wright, J. M., ibid., 69, 2786 (1947).

49 Spedding, F. H., Fulmer, E. I., Butler, T. A., Gladrow, E. M., Gobush, M., Porter, P. E., Powell, J. E., and Wright, J. M., ibid., 69, 2812 (1948).

50. Spedding, F. H., Fulmer, E. I., Ayers, B. O., Butler, T. A., Powell, J. E., Tevebaugh, A. D., and Thompson, R. Q., ibid., 70, 1671 (1948).

51. Spedding, F. H., Fulmer, E. I., Butler, T. A., and Powell, J. E., ibid., 72, 2349 (1950).

52. Spedding, F. H., Fulmer, E. I., Butler, T. A., and Powell, J. E., ibid., 72, 2354 (1950).

53. Spedding, F. H., Discussions Faraday Soc., No. 7, 214 (1949).

54. Spedding, F. H., and Powell, J. E., J. Am. Chem. Soc., 74, 856 (1952).

55. Spedding, F. H., and Powell, J. E., ibid., 74, 857 (1952).

56. Spedding, F. H., Fulmer, E. I., Powell, J. E., Butler, T. A., and Yaffe, I. S., ibid., 73, 4840 (1951).

57. Spedding, F. H., and Dye, J. L., *ibid.*, *72*, 5350 (1950).

58. Lange, E., and Nagel, K., *Z. Elektrochem.*, *42*, 210 (1936). [Original not seen; cited in *C. A.*, *30*, 4425 (1936).]

59. Erätmetsä, O., Sahama, G., and Kamula, V., *Ann. Acad. Sci. Fennicae*, *A57*, 5 (1941).

60. Erätmetsä, O., *Bull. comm. geol. Finlande*, *14*, 36 (1941). [Original not seen; cited in *C. A.*, *37*, 3316 (1943).]

61. Croatto, U., *Ricera sci.*, *12*, 157 (1941). [Original not seen; cited in *C. A.*, *37*, 2680 (1943.]

62. Russell, R. G., and Pearce, D. W., *J. Am. Chem. Soc.*, *65*, 595 (1943).

63. Johnson, W. C., Quill, L. L., and Daniels, F., *Chem. Eng. News*, *25*, 2494 (1947).

64. Tompkins, E. R., Khym, J. X., and Cohn, W. E., *J. Am. Chem. Soc.*, *69*, 2769 (1947).

65. Marinsky, J. A., Glendenin, L. E., and Voryell, C. D., *ibid.*, p. 2781.

66. Harris, D. H., and Tompkins, E. R., *ibid.*, p. 2792.

67. Ketelle, B. H., and Boyd, G. E., *ibid.*, p. 2800.

68. Tompkins, E. R., and Mayer, S. W., *ibid.*, p. 2859.

69. Mayer, S. W., and Tompkins, E. R., *ibid.*, p. 2866.

70. Spedding, F. H., and Powell, J. E., *Chemical Engineering Progress Symposium Series*, *50 No. 14*, 7 (1954).

71. Spedding, F. H., and Powell, J. E., *J. Am. Chem. Soc.*, *76*, 2545 (1954).

72. Spedding, F. H., and Powell, J. E., *ibid.*, p. 2550.

73. Holleck, L., and Hartinger, L., *Angew Chem.*, *66*, 586 (1954). [Original not seen; cited in *C. A.*, *49*, 690 (1955).]

74. Vickery, R. C., *J. Chem. Soc.*, *1952*, 4357.

75. Freiling, E. C., and Mayer, S. W., *J. Am. Chem. Soc.*, *75*, 5647 (1953).

76. Taylor, A. E., United States Atomic Energy Commission, Report NP-1434, February 1, 1950.

77. Iya, V. K., and Loriers, J., Compt. rend., 237, 1413 (1953).

78. Fitch, F. T., and Russell, D. S., Can. J. Chem., 29, 363 (1951).

79. Fitch, F. T., and Russell, D. S., Anal. Chem., 23, 1469 (1951).

80. Wheelwright, E. J., and Spedding, F. H., J. Am. Chem. Soc., 75, 2529 (1953).

81. Spedding, F. H., Powell, J. E., and Wheelwright, E. J., J. Am. Chem. Soc., 76, 612 (1954).

82. Spedding, F. H., Powell, J. E., and Wheelwright, E. J., ibid., p. 2557.

76 612

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks and appreciation to Dr. F. H. Spedding for his encouragement and helpful advice during the course of these investigations and in the preparation of this thesis. The author also desires to thank Dr. J. E. Powell for reading the first draft of this manuscript and offering several suggestions. In addition, he would like to thank his wife, Rayola, for her assistance in preparing the manuscript.