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METAL CHELATES OF
CYCLOHEXENEDIAMINETETRAACETIC ACID

by

Thomas Clement Loomis

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I. INTRODUCTION

The compound ethylenediaminetetraacetic acid (EDTA), in the form of its di-, tri-, and tetra- sodium salt, has been in industrial use for a number of years as a sequestering agent in textile processing and dyeing; for the prevention and removal of boiler scale; as a water softening agent in many preparations of soaps, insecticides, germicides, etc.; and for many other applications where metallic ions need to be effectively removed from solution. For these purposes it is sold under various trade names, of which Trilon B, Sequestrene, and Versene are the most common.

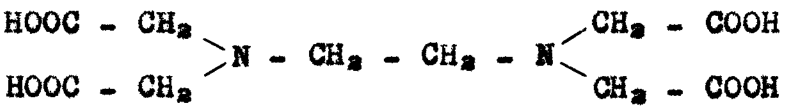
In the last three or four years EDTA has also become an important reagent in analytical chemistry. Wide acceptance has been given to a rapid complexometric titration method for determining the total hardness of water in which the disodium salt of EDTA serves as the titrant. The remarkable ability of EDTA to form very stable complexes with a large number of common metals has resulted in the development of a wide variety of other uses in the field of analytical chemistry for this reagent.

In view of the versatility and growing importance of EDTA as an analytical reagent it seems likely that similar compounds should also prove of interest to the analytical chemist. One such compound, cyclohexenediaminetetraacetic acid (CDTA), has already been shown to form more stable complexes with calcium and magnesium than does EDTA. The present study was made to investigate the stability of complexes of CDTA with other metals and examine its possible use as a reagent in analytical chemistry. The stability constants of complexes of CDTA with a number of bivalent metals were determined, a rapid method for the proximate analysis of brass employing the disodium salt of CDTA as a titrating agent was developed, and some comparisons of CDTA and EDTA as analytical reagents were made.

II. REVIEW OF LITERATURE

A. Nature and Structure of Metal Complexes of Ethylenediaminetetraacetic Acid

The preparation of ethylenediaminetetraacetic acid, which has the structural formula



$$\begin{array}{lcr} \mathrm{HOOC-CH_2} & & \mathrm{CH_2-COOH} \\ & \mathrm{>N-CH_2-CH_2-N<} & \\ \mathrm{HOOC-CH_2} & & \mathrm{CH_2-COOH} \end{array}$$

was first described by Fick and Ulrich [30] in 1936. A mixture of ethylenediamine, hydrogen cyanide, and formaldehyde in aqueous solution was found to react to give a tetranitrile which could be converted to EDTA or its tetra-sodium salt by simple acid or base hydrolysis.

Shortly thereafter the ability of EDTA to form stable, water soluble complexes with metal ions was reported by Ender [28], who described its use as a sequestering (water softening) agent for the textile industry. The preparation and physical properties of the complex compounds and salts of EDTA with the alkaline earth metals and copper have been described by Pfeiffer and co-workers [75, 76, 77]. Similar studies were made by Brintzinger and co-workers [10, 11, 12] for most of the heavy metals, some of the rare earths, lithium, beryllium, uranium, and thorium. Both of these investigators offered some hypotheses regarding the nature of the complexes or salts, based primarily on such physical properties as color, water solubility, and stability towards various precipitating agents.

The first significant attempt to elucidate the nature of these complexes was a study of the magnetic susceptibility of the nickelous complex by Klemm and Raddatz [52]. Their measurements show that since the paramagnetism of the complex is of the same order of magnitude as the free nickel ion, the complex is not of the covalent planar type. The complex is thus presumed to be ionic, but may be either tetrahedral or octahedral. Similar studies by Klemm [51] show that the ferric complex is likewise ionic, but that the cobaltic complex appears to have covalent octahedral bonding. The magnetic properties of the chromic complex were also studied, but no structural information was obtained since covalent and ionic complexes of chromium have the same susceptibility.

Structural diagrams of the metal complexes of EDTA almost always show these compounds as having an octahedral configuration, with the chelating agent occupying all six of the coordination positions of the metal, utilizing both nitrogen atoms and all four carboxyl groups.[1] Actually this picture is not supported by much of the evidence available from the extensive work by Schwarzenbach and co-workers. The calcium and magnesium complexes of EDTA were shown by Schwarzenbach [111] to possess some acidic character, forming hydroxy-complexes in alkaline solution according to the reaction

$$MY^{-2} + OH^{-} \rightleftharpoons MOHY^{-3},$$

where M = calcium or magnesium and H_4Y = EDTA. Since this reaction was found to be almost instantaneous, it seems likely that the hydroxy-complex was actually formed merely by extracting a hydrogen ion from a water molecule already in the coordination sphere of the metal ion. If all the coordination positions had been occupied by the chelating agent, a rearrangement of the molecule would have to take place before a free hydroxy group could enter, probably resulting in a slow reaction. This interpretation then leads to a structure for the normal complex ion in which the EDTA occupies only five positions of the coordination sphere (leaving the EDTA with a free carboxyl group) with the sixth position being occupied by a water molecule.

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[1] For example, see reference [66], p. 146.

The trivalent metal complexes provide still better evidence for this sort of structure. The color reactions of the MnY^-, FeY^-, and CrY^- complexes [12] upon the addition of base can only be attributed to a change within the coordination sphere of the metal ion; thus the reactions

$$FeY^- \text{ (pale brown)} + OH^- \rightleftharpoons FeOHY^{-2} \text{ (dark yellow)}$$
$$MnY^- \text{ (violet)} + OH^- \rightleftharpoons MnOHY^{-2} \text{ (yellow)}$$
$$CrY^- \text{ (violet)} + OH^- \rightleftharpoons CrOHY^{-2} \text{ (blue)}$$

are assumed to be of the same type as those for calcium and magnesium. In this same study numerous examples were cited of the reactions of EDTA-metal complexes with complexing anions such as cyanide, thiocyanate, and bromide. The ease of formation of these hetero-complexes indicates that these anions are simply replacing a water molecule in the complex rather than displacing a carboxyl group. Further, at least in the case of the $CoYBr^{-2}$ complex, the presence of a free carboxyl group can be clearly demonstrated by the production of the cation $CoHYBr^-$ upon acidification. Crystalline sodium, potassium, barium, and tetramethylammonium salts of this cationic complex were prepared and shown to behave as acids with a pK of about 3.

Later work on the ferric complex of EDTA by Schwarzenbach and Heller [119], however, indicates rather clearly that in the case of FeY^- there is no free carboxyl group present to take up a hydrogen ion on acidification. Although FeY^- does take up hydroxyl ions to form $Fe(OH)Y^{-2}$, $Fe(OH)_2Y^{-3}$, and apparently even $Fe(OH)_3Y^{-4}$, the equilibrium constants for these reactions tend to indicate that this process actually represents stepwise decomposition of the complex, with hydroxyl ions replacing the carboxyl groups in the coordination sphere of the metal. In this one case, at least, EDTA appears to serve as a sexadentate group.

Although many speculations have been made regarding the structure of these complexes from consideration of their physical properties and chemical reactions, no direct investigation has yet been reported using the technique of electron or X-ray diffraction. Until such studies are made, the true nature and structure of these complexes will probably remain in dispute.

B. Methods of Determining Stability Constants of EDTA Complexes

The stability of Metal-EDTA complexes toward dissociation in aqueous solution has received much attention in the literature. The first and most extensive work on the determination of the stability constants of EDTA complexes was that of Schwarzenbach in collaboration with a number of coworkers [1, 109, 111, 112, 117, 119, 133]. Most of the constants determined by Schwarzenbach were based on data obtained from pH measurements using a platinum hydrogen electrode and silver-silver chloride electrode potentiometric system or a glass electrode pH meter. Other methods of determining stability constants have been employed by various workers, as will be noted below.

Since EDTA behaves as a tetrabasic acid, a knowledge of the concentration of the various ionic species of EDTA is essential if complex stability constants are to be computed from almost any sort of data. For this purpose the ionization constants determined by Schwarzenbach [111] are usually employed. Schwarzenbach's procedure [120] for measuring these constants was used in the present work to determine the apparent ionization constants of cyclohexenediamine-tetraacetic acid (CDTA), and a complete description of this method will be found in Section III B. Schwarzenbach's values are listed in Table 1 along with results of other investigators using very similar methods.

The methods used for determining the stability constants of EDTA complexes may be divided into five general types: potentiometric (pH), potentiometric (redox), polarographic, radioactive exchange, and spectophotometric. There are, in addition, variations of procedure within these broad types. No attempt will be made here to analyze completely all of these methods, but a brief description of each is given below.

Table 1

Apparent Ionization Constants of EDTA

pK_1	pK_2	pK_3	pK_4	Temp. °C.	Ionic strength	Electrode system	Reference
2.00	2.67	6.16	10.26	20.0	0.1[a]	hydrogen-Ag,AgCl	[111]
2.24	2.95	6.24	10.32	20.0-20.4	0.1[a]	glass-calomel	[15]
2.30	2.86	6.20	9.97	25.0	0.1[a]	glass-calomel	[36]
5.8[b]		6.47	10.1	25.0	0	glass-calomel	[17]

[a] KCl used as the inert electrolyte.

[b] Value of $pK_1 + pK_2$. (Individual constants not determined.)

1. Potentiometric (pH)

a. Method 1(a). In the presence of an excess of a soluble salt of a metal with which it forms a stable complex, the third and fourth hydrogen ions of EDTA are liberated in a more acidic region. This increase in acidity according to the reactions

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

and

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

forms the basis for the method by which Schwarzenbach determined the stability constants for the complexes of EDTA with the alkali and alkaline earth metals [111].

A pH titration curve of EDTA with KOH in the presence of a fifteen-fold excess of a salt of an alkaline earth metal was interpreted in terms of two complex stability constants, K_{k_1} and K_{k_2}, which were defined as the equilibrium constants of the reactions

$$M^{+2} + HY^{-3} \rightleftharpoons MHY^{-}$$

and

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

respectively. A graphical procedure for computing these constants from the total concentration of EDTA, the total concentration of the alkaline earth, and the amount of KOH added was developed by Schwarzenbach, Willi, and Bach [120]. Since this method was used in the present work to determine the cyclohexenediaminetetraacetic acid-alkaline earth metal complexes, the complete derivation of the equations employed will be found in Section III B. The only difference is that in the case of EDTA complexes the ionic species H_4Y and H_3Y^- may be neglected since EDTA is a stronger acid than CDTA.

Schwarzenbach found this procedure to be satisfactory providing the complex formed was of low or intermediate stability. For very strong complexes the equilibrium in equation (b) was found to be too far to the right to permit accurate interpretation of the pH measurements in terms of the various ionic species of EDTA. Use of this procedure was thus limited to the alkali and alkaline earth metal complexes.

b. Method 1(b). A modification of the above procedure was used by Vickery [131] to determine stability constants for rare earth EDTA complexes. The method seems to be based on a pH titration curve of a solution containing EDTA and a rare earth salt in what appears to be a molar ratio of 5:1. Unfortunately the paper contains so many obvious errors (possibly typographic) for which no corrections have as yet appeared that a critical evaluation of the method is not possible at this time. Since the constants reported are of about the right order of magnitude, it seems probable that the method itself is of value even though the described calculation procedure contains much obvious confusion.

c. Method 1(c). A procedure for determining the stability constants of especially stable EDTA complexes has been described by Schwarzenbach and his co-workers [1, 117, 133]. This method is based on the competition between EDTA and a polyamine chelating agent for ions of a heavy metal (M). A second, auxiliary metal (Me) which does not form a stable complex with the polyamine must also be present to compete with M for the EDTA. As the polyamine, Schwarzenbach used triaminotriethylamine (tren) in the form of its trihydrochloride ($H_3trenCl_3$). When such a system is titrated with base, hydrogen ions are liberated according to the equation

$$MY^{-2} + Me^{+\nu} + H_3tren^{+3} \rightleftharpoons M\ tren^{+2} + MY^{\nu-4} + 3H^+$$

where $\nu = 2$ or 3.

All of the quantities on the right-hand side of the equation for the equilibrium constant of this exchange reaction

$$K_{ex} = \frac{[M\ tren^{+2}]\,[MeY^{\nu-4}]\,[H^+]^3}{[H_3tren^{+3}]\,[MY^{-2}]\,[Me^{+\nu}]}$$

may be computed for each point on the titration curve from the initial concentration of the reactants, the amount of base added, and the measured pH.[1]

This equilibrium constant is related to the desired stability constant by the equation

$$K_{ex} = \frac{K_{M\ tren}\ K_{MeY}}{\bar{K}_{H_3tren}\ K_{MY}} ,$$

where $K_{M\ tren}$ is the stability constant of M $tren^{-2}$; K_{MeY} and K_{MY} are the stability constants for MeY^{-4} and MY^{-2}, respectively; and $\bar{K}_{H_3tren}$ is the overall ionization constant of $H_3trenCl_3$. From known values of $K_{M\ tren}$, K_{MeY}, and K_{H_3tren}, the value of K_{MY} was computed from the measured value of K_{ex}.

The procedure was then repeated using the same heavy metal (M) but a different auxiliary metal (Me') for which the stability constant was not known. From the new value measured for K_{ex} and the previously determined value of K_{MY}, the stability constant of the new auxiliary metal, $K_{Me'Y}$ could then be computed. By successive repetition of this procedure the stability constants for a number of metal complexes were determined.

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[1] A detailed explanation of the computations involved, with the complete derivation of all pertinent equations may be found in section III B.

2. Potentiometric (Redox)

a. Method 2. A thorough study of the system iron-EDTA was made by Schwarzenbach and Heller [119] to determine the oxidation-reduction equilibria as well as the stability constants of the various ferric and ferrous complexes. Data were obtained from a series of titrations of ferrous sulfate in the presence of excess EDTA with iodine using a gold electrode to follow the oxidation level of the solutions. Various buffer systems were used to obtain such titrations over a wide pH range. By a complex mathematical analysis of such data these workers were able to ascertain the stability constants for the normal complexes, FeY^{-2} and FeY^{-}, and the equilibrium constants for the reactions by which $FeHY^{-}$ is formed from FeY^{-2} and hydroxy complexes are formed from FeY^{-}.

3. Polarographic

a. Method 3(a). Matyska and Kössler [70] found that the complete polarogram of a solution of EDTA and a mercuric salt contained both an anodic wave and a cathodic wave. The anodic wave was attributed to the process of mercury from the dropping electrode being oxidized to the mercuric-EDTA complex. The step-height of this anodic wave was found to be proportional to the free EDTA concentration. The half-wave potential was shown to be independent of the EDTA concentration but was a function of pH.

From a consideration of the equation defining the stability constant of the complex HgY^{-2},

$$K_{HgY} = \frac{[HgY^{-2}]}{[Hg^{+2}]\,[Y^{-4}]} ,$$

the Ilkovic equation for the diffusion current, and the ionization constants of EDTA, the Nernst equation for the Hg^{+2}, Hg half-cell was transformed to

$$E_m - E_o = \frac{2.303\ RT}{2F}(\log A - \log K_{HgY})$$

where E_m is the measured half-wave potential; E_o is the standard reduction potential for Hg^{+2}, Hg; A is a quantity calculated from the pH of the solution and the ionization constants of EDTA; and R, T, and F have their usual meanings.

By using various buffers a number of polarograms were obtained at different pH values. The values of $E_m - E_o$ from these when plotted as a function of log A gave a straight line for solutions with a pH from 4 to 9. Log K_{HgY} was then determined by extrapolating this line to where $E_m - E_o = 0$, since from the above equation log K_{HgY} must be equal to log A at this point. The departure from linearity for solutions more acid than pH 4 was explained in terms of a hydrogen complex $HgHY^-$ for which the stability constant was also computed. Similarly, the constant for the complex $Hg(OH)Y^-$ was calculated from the non-linear behavior of solutions above pH 9. This method appears to yield very satisfactory results for mercuric complexes, but does not seem to be applicable to the complexes of any other metal.

b. Method 3(b). Blumer and Kolthoff [9] have investigated the polarography of titanium complexes of EDTA. They reported that complexes of both Ti(III) and Ti(IV) form in acidic solutions containing EDTA. These complexes were found to be reduced reversibly at the dropping mercury electrode. From the decrease in the step-height of the cathodic wave as the pH was varied from 0.5 to 2.0, a value for the stability constant of the Ti(IV) complex was estimated. An approximation for the Ti(III) complex was also made. No description of how these values were computed was given, however,

c. Method 3(c). The stability constants of rare earth-EDTA complexes have also been determined using polarographic data [133]. In this method a buffered solution containing the disodium copper salt of EDTA (Na_2CuY) and a salt of a rare earth M in equimolar amounts was allowed to equilibrate. The competition of the rare earth ion for the EDTA in the copper complex produced the reaction

$$CuY^{-2} + M^{+3} \rightleftharpoons Cu^{+2} + MY^{-} .$$

The amount of free copper in the solution at equilibrium was determined polarographically, taking advantage of the fact that the CuY^{-2} complex was reduced only at a much more negative potential than the free copper ion.

From the above equation then,

$$[MY^{-}] = [Cu^{+2}]$$

and since equimolar concentrations of CuY^{-2} and M^{+3} were present at the start,

$$[CuY^{-2}] = [M^{+3}] = C - [Cu^{++}]$$

where C is the initial concentration of both reactants. The equilibrium constant for this reaction may thus be written

$$K_{eq} = \frac{[Cu^{+2}]\,[MY^{-}]}{[CuY^{-2}]\,[M^{+3}]} = \frac{[Cu^{+2}]^{2}}{(C - [Cu^{+2}])^{2}} .$$

Substitution of the polarographically determined value of $[Cu^{+2}]$ and the known initial concentration C in this equation yielded the value of K_{eq}.

Division of the equation defining K_{MY},

$$K_{MY} = \frac{[MY^{-}]}{[M^{+3}]\,[Y^{-4}]} ,$$

by the corresponding equation for K_{CuY},

$$K_{CuY} = \frac{[CuY^{-2}]}{[Cu^{+2}]\,[Y^{-4}]} ,$$

gives

$$\frac{K_{MY}}{K_{CuY}} = \frac{[MY^{-}]\,[Cu^{+2}]}{[M^{+3}]\,[CuY^{-2}]}$$

which is exactly the same as K_{eq}. Hence

$$K_{eq} = \frac{K_{MY}}{K_{CuY}}$$

and

$$\log K_{MY} = \log K_{eq} + \log K_{CuY} .$$

This method was found to give good results for the heavy rare earth complexes, which have stabilities which are approximately the same as or slightly greater than that of the copper complex. The complexes of the lighter rare earths are less stable, however, and the amount of free copper ions produced was comparatively small, resulting in a larger relative error in the measured copper ion concentration. This increased uncertainty in Cu^{+2} made it necessary to assign larger maximum limits of error for the calculated values of

K_{MY} for these elements.

4. Spectrophotometric

a. Method 4(a). The stability of the complex of EDTA with ferric iron was determined by Kolthoff and Auerbach [54] from spectrophotometric measurements at four different wavelengths in the spectral region from 370 to 400 m . For solutions at pH 3 (or higher) containing more EDTA than Fe^{+3}, virtually all of the ferric iron was found to be in the form of the complex. As the acidity of the solution was increased, the complex dissociated because of the lowering of the Y^{-4} concentration due to depression of the ionization of such species as H_4Y and H_3Y^-. By spectrophotometric comparison of a solution containing sufficient perchloric acid to reduce the pH to 1 (or below) with the standard at pH 3, the equilibrium concentration of FeY^- in the more acidic solution was found. Using this measured concentration of FeY^-, the concentration of Fe^{+3} was then easily obtained from the amount of iron initially added to the solution. From the known acidity, Schwarzenbach's data for the ionization constants of EDTA, and the total amount of EDTA present in all ionic forms, the concentration of Y^{-4} was computed. The values of $[FeY^-]$, $[Fe^{+3}]$, and $[Y^{-4}]$ were then merely substituted in the usual equation

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

to obtain a value for the stability constant.

This method of procedure is, of course, limited to metals forming complexes which absorb strongly in the visible or ultra violet. In the case of a complex as stable as FeY^- it was necessary to carry out the measurements in a strongly acid solution so that the concentration of Y^{-4} was kept very low. Otherwise virtually all of the Fe^{+3} or all of the EDTA (depending on their relative concentrations) would have been in the form of the complex. Since both $[Fe^{+3}]$ and $[Y^{-4}]$ were obtained by difference, the relative error in one of them would have been very high in such a case. However, the use of an acidic solution increased the dependence of the measured stability constant on the accuracy of the ionization constants employed, since errors in these would cause a larger relative error in $[Y^{-4}]$ in solutions where the less dissociated ionic species predominate.

<u>b. Method 4(b)</u>. Martell and co-workers [67, 78] used spectrophotometric data to obtain the relative stabilities of various EDTA-metal complexes. The method used was very similar to the polarographic method 3(c) described above except that instead of determining the amount of free metal ions produced, the position of the equilibrium was estab-

lished by spectrophotometric measurement of the decrease in the concentration of a colored complex upon addition of a salt of a second metal. The calculations involved were so analogous that no discussion of them need be mentioned here.

The results of these measurements do not compare well with other values for the same complexes. Part of this discrepancy no doubt results from the use of a high concentration of acetate buffer for the purpose of maintaining constant pH. No correction was made for the probable formation of acetate complexes with some of the metals studied. Some studies were made at higher pH values using carbonate and phosphate buffers. Under these conditions precipitates of the metals employed were found to form. No reasonable values for the stability constants would be expected from such systems since they involve complicated solubility equilibria which were not clearly defined.

5. Radioactive exchange

a. Method 5. Studies by Long and co-workers [20, 49, 60] on the exchange reactions of EDTA complexes with ions of radioactive metals led to the development of a radioactive indicator method for measuring the stability constants of certain complexes. In this method a solution of the metal complex MY^{4-v} was mixed with a solution containing ions of a radioactive isotope of the same metal. The reaction which occurred may be written

$$MY^{4-v} + \overset{*}{M}^{+v} \rightleftharpoons \overset{*}{M}Y^{4-v} + M^{+v}$$

where $\overset{*}{M}$ represents the radioactive isotope. For some metals this exchange was found to be slow enough to permit measurement of the exchange rate. This rate was shown to be a function of pH and (in some cases, at least) also a function of the stability of the complex.

For any system showing measurably slow exchange rates, the radiation data provided a means of computing the stability constant of the complex. After mixing the solutions (as described above), aliquots were taken at measured time intervals; and the free metal ions removed by precipitation with sodium hydroxide or aqueous ammonia. The amount of the radioactive isotope which had entered into the complex due to the exchange reaction as measured by counting the radiation in the filtrate, served as an indication of the fractional exchange which had taken place at that time. The fractional exchange when plotted as a function of time gave approximately a straight line. Extrapolation of this line to zero time yielded the "instantaneous exchange" at the time of mixing. This "instantaneous exchange" was a measure of the free metal ions present in the solution before mixing, just from dissociation of the complex. From the free metal ion concentration as measured in this manner, the known acidity of the solution, the initial concentration of EDTA, and the ionization constants of EDTA (using Schwarzenbach's values), the stability constant of the metal complex was then computed.

The only values obtained by this method which have been reported thus far are those for the ferric and nickelous complexes, using Fe^{59} and Ni^{63}. Exchange studies were reported by the same authors for the ferrous, cobaltous, and cobaltic complexes (using Co^{60}). The exchange rates for these systems were not of the proper magnitude to be useful for determinations of the stability constants by the described procedure. These investigators did report, however, that by varying the pH or introducing other complexing agents such as ammonia they obtained indications that the exchange rates could be suitably altered to permit stability constant determinations. It seems probable that use of this method may thus be extended to other systems which do not show satisfactory exchange rates under the conditions used for nickel and iron.

C. Stability of EDTA Complexes

The values of the stability (formation) constants which have been reported for various metal-EDTA complexes are listed in Table 2. The usual definitions of the stability constants for normal and hydrogen complexes have been used. In the case of calcium, for example, the constant for the normal complex, CaY^{-2}, is defined by

$$K_{CaY} = \frac{[CaY^{-2}]}{[Ca^{+2}]\,[Y^{-4}]}$$

and the constant for the hydrogen complex, CaHY, is defined by

$$K_{CaHY} = \frac{[CaHY^{-}]}{[Ca^{+2}]\,[HY^{-3}]}$$

Some authors reported results in terms of the dissociation constant, K_d. For the sake of uniformity in the table these values were converted to stability constants by taking the reciprocal of K_d. Constants involving solubility equilibria or interactions with other complexing agents which were not taken into account by the original investigators are not included in this tabulation.

The stability constants listed in Table 2 for hydroxy-complexes are actually equilibrium constants for reactions

Table 2

Stability Constants of EDTA Complexes

Metal	Complex	log K	Temp. °C.	Ionic strength	Method[a]	Reference
Li	LiY^{-3}	2.79	20.0	0.1	1(a)	[111]
Na	NaY^{-3}	1.66	20.0	0.1	1(a)	[111]
Mg	$MgHY^{-}$	2.28	20.0	0.1	1(a)	[111]
	MgY^{-2}	8.69	20.0	0.1	1(a)	[111]
Ca	$CaHY^{-}$	3.51	20.0	0.1	1(a)	[111]
		3.62	25.0	0.1	1(a)	[36]
	CaY^{-2}	10.59	20.0	0.1	1(a)	[111]
		10.30	25.0	0.1	1(a)	[36]
		11.1	25.0	0	1(a)	[17]
Sr	$SrHY^{-}$	2.30	20.0	0.1	1(a)	[111]
	SrY^{-2}	8.63	20.0	0.1	1(a)	[111]
Ba	$BaHY^{-}$	2.07	20.0	0.1	1(a)	[111]
	BaY^{-2}	7.76	20.0	0.1	1(a)	[111]
Ti(III)	TiY^{-}	19	b	b	3(b)	[9]
Ti(IV)	TiY	17.7	b	b	3(b)	[9]
Mn(II)	MnY^{-2}	13.47	20.0	0.1	1(c)	[118]
Fe(II)	$FeHY^{-}$	2.75	20.0	0.1	2	[119]
	FeY^{-2}	14.26	20.0	0.1	2	[119]
		14.22	20.0	0.1	1(c)	[118]
		14	25	0.1	1(a)	[49]
	$Fe(OH)Y^{-3}$	4.87	20.0	0.1	2	[119]
	$Fe(OH)_2Y^{-4}$	4.10	20.0	0.1	2	[119]

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[a] Numbers in this column refer to the methods described in the preceding section.

[b] Ionic strength and temperature not specified.

Table 2 (continued)

Metal	Complex	log K	Temp. °C.	Ionic strength	Method	Reference
Fe(III)	FeY^-	25.1	20.0	0.1	2	[119]
		24	25	1.0	5	[49]
		22.3	25	1.0	4	[54]
	$Fe(OH)Y^{-2}$	6.45	20.0	0.1	2	[119]
	$Fe(OH)_2Y^{-3}$	4.53	20.0	0.1	2	[119]
Co(II)	CoY^{-2}	16.10	20.0	0.1	1(c)	[118]
Ni(II)	NiY^{-2}	18.45	20.0	0.1	1(c)	[118]
		19.0	20.0	0.1	5	[20]
Cu(II)	CuY^{-2}	18.38	20.0	0.1	1(c)	[118]
Zn	ZnY^{-2}	16.15	20.0	0.1	1(c)	[118]
Cd	CdY^{-2}	16.48	20.0	0.1	1(c)	[118]
Hg(II)	$HgHY^-$	9.0	20.0	0.1	3(a)	[70]
	HgY^{-2}	15.7	20.0	0.1	3(a)	[70]
	$Hg(OH)Y^{-3}$	6.80	20.0	0.1	3(a)	[70]
Pb(II)	PbY^{-2}	18.2	20.0	0.1	1(c)	[118]
La	LaY^{-2}	14.72	20.0	0.1	1(c)	[133]
		15.30	20.0	0.1	1(b)	[131]
Ce(III)	CeY^-	15.39	20.0	0.1	1(c)	[133]
		15.6	20.0	0.1	3(c)	[133]
		16.05	20.0	0.1	1(b)	[131]
Pr(III)	PrY^-	15.75	20.0	0.1	1(c)	[133]
		15.8	20.0	0.1	3(c)	[133]
		16.55	20.0	0.1	1(b)	[131]
Nd	NdY^-	16.06	20.0	0.1	1(c)	[133]
		16.0	20.0	0.1	3(c)	[133]
		16.75	20.0	0.1	1(b)	[131]
Sm(III)	SmY^-	16.55	20.0	0.1	1(c)	[133]
		16.3	20.0	0.1	3(c)	[133]
		17.2	20.0	0.1	1(b)	[131]

Table 2 (continued)

Metal	Complex	log K	Temp. °C.	Ionic strength	Method	Reference
Eu(III)	EuY^-	16.69	20.0	0.1	1(c)	[133]
		16.5	20.0	0.1	3(c)	[133]
Gd	GdY^-	16.70	20.0	0.1	1(c)	[133]
		16.6	20.0	0.1	3(c)	[133]
		17.2	20.0	0.1	1(b)	[131]
Tb	TbY^-	17.25	20.0	0.1	1(c)	[133]
		17.38	20.0	0.1	3(c)	[133]
Dy	DyY^-	17.57	20.0	0.1	1(c)	[133]
		17.75	20.0	0.1	3(c)	[133]
		17.75	20.0	0.1	1(b)	[131]
Ho	HoY^-	17.67	20.0	0.1	1(c)	[133]
		18.31	20.0	0.1	3(c)	[133]
Er	ErY^-	17.98	20.0	0.1	1(c)	[133]
		18.55	20.0	0.1	3(c)	[133]
		18.15	20.0	0.1	1(b)	[131]
Tm	TmY^-	18.59	20.0	0.1	1(c)	[133]
		19.07	20.0	0.1	3(c)	[133]
Yb	YbY^-	18.68	20.0	0.1	1(c)	[133]
		19.38	20.0	0.1	3(c)	[133]
		18.70	20.0	0.1	1(b)	[131]
Lu	LuY^-	19.06	20.0	0.1	1(c)	[133]
		19.65	20.0	0.1	3(c)	[133]
Y	YY^-	17.38	20.0	0.1	1(c)	[133]
		17.56	20.0	0.1	3(c)	[133]
		18.0	20.0	0.1	1(b)	[131]

of the form

$$M(OH)_iY^{-(\nu+i)} + OH^- \rightleftharpoons M(OH)_{i+1}Y^{-(\nu-i+1)} .$$

Thus the "stability constant" for $Fe(OH)_2Y^{-3}$ is defined by the equation

$$K = \frac{[Fe(OH)_2Y^{-3}]}{[Fe(OH)Y^{-2}]\,[OH^-]} .$$

In addition to the complexes listed above for which quantitative measurements of the stability constants were made, many other complexes are known as a result of qualitative investigations. In some cases, prepared compounds were shown to be complexes rather than simple salts by their failure to give the usual analytical reactions of the corresponding free metal ion. Such was the case with the Co(III), Cr(III), Th(IV), and Bi(III) complexes prepared by Brintzinger [7, 8]. For elements having more than one oxidation state, the relative stability of complexes of the metal in its higher and lower oxidation states was estimated from the change in the standard oxidation or reduction potential on complexation. For example, since the potential for the Co(III)-Co(II) system was lowered from 1.79 volts to about 0.6 volts (depending on the pH) with the addition of EDTA, Pribil [93] concluded that the cobaltic complex was much more stable than the cobaltous.

From consideration of pH measurements, Schwarzenbach [2] found the chromic complex of EDTA to be about as stable as the ferric complex. The aluminum complex was indicated to be less stable than the ferric complex by both Schwarzenbach [114] and Pribil [89]. The formation of a relatively unstable Mn(III) complex upon oxidation of the manganous complex with sodium bismuthate or lead dioxide was also demonstrated by Pribil [81].

In a number of polarographic investigations a shift in the half-wave potential of a metal in the presence of EDTA was taken as evidence of complex formation. In this way, Koryta and Kössler [55] showed the existence of a weak Tl(I) complex, Valenta and Zuman [129] found a weak Ge(IV) complex, Pribil and Matyska [95] showed the Bi and Sb(III) complexes to be very stable, and Dolezal and co-workers [27] found evidence for a silver complex in neutral solution.

Although no stability constants have yet been determined for complexes in which the metal-EDTA ratio is other than 1:1, some evidence for such compounds has been reported. From pH titration curves of thorium in the presence of varying amounts of EDTA, Cabell [15] reported the existence of the complex Th_2Y^{+4} and possibly ThY_2^{-4}. These complexes were believed to be very much less stable than the normal complex ThY. In the same paper Cabell gave some evidence for weak uranyl complexes with the formulas $(UO_2)_2Y$ and UO_2HY^-. As the result of a very complicated mathematical interpretation of polarographic studies on europium solutions containing various amounts of EDTA at varying hydrogen ion concentrations, Onstott [74] apparently found evidence for such complexes as $EuHY^-$, EuY^{-2}, $Eu(HY)_2^{-3}$, EuY_2^{-5}, $EuY(OH)^{-2}$, and possibly $EuY(HY)^{-4}$. However, a thorough study on another rare earth, neodymium, by Moeller and Brantley [72] using spectrophotometric, electrometric (pH) titration, and electrophoretic migration techniques failed to show evidence for anything but a 1:1 complex between EDTA and neodymium.

From the foregoing it may be concluded that EDTA forms stable complexes with almost all divalent and trivalent metal ions. Some tetravalent metals also form stable complexes, and weak complexes are formed even with some monovalent metals. These complexes all contain the metal and EDTA in a 1:1 molar ratio with the exception of those noted above.

D. Analytical Applications of EDTA

The ability of EDTA to form stable, water-soluble complexes with many metal ions has made it an important reagent in analytical chemistry. Despite its lack of specificity, numerous applications of this reagent to problems of separation and analysis of various metals have been worked out.

Indirect determinations of some anions have also been developed.

EDTA was first used as an analytical reagent by Schwarzenbach [116] for the alkalimetric determination of the total hardness of water. When an excess of the disodium salt of EDTA (Na_2H_2Y) was added to a solution containing calcium or magnesium, hydrogen ions were liberated according to the reaction

$$M^{+2} + H_2Y^{-2} \rightleftharpoons MY^{-2} + 2H^+ .$$

By the potentiometric titration of the liberated hydrogen ions, a measure of the total hardness (i.e., $Ca^{+2} + Mg^{+2}$) was obtained. Later, this procedure was extended by Schwarzenbach [114] to include the determination of Cd, Co, Cu, Fe(II), Hg(II), Mn, Ni, Pb, Zn, the rare earths, and possibly Cr and Al. In this same publication a somewhat simpler method for determining the alkaline earth metals, especially calcium and magnesium, was also described. Instead of adding Na_2H_2Y and titrating with a strong base, the solution of calcium or magnesium was simply titrated with Na_4Y. As long as any calcium or magnesium was present, the hydrogen ions liberated as a result of complex formation kept the solution neutral. The first excess of the strongly basic Na_4Y, however, raised the pH sufficiently to cause a color change in a pH indicator such as phenolphthalein. Similar alkalimetric titration methods have been described by Hahn [40] and Krijn [56]. Krijn further pointed out that the hydrogen ions produced could also be determined by a thiosulfate titration of the iodine liberated from an iodate-iodide solution.

The complexometric titration of calcium in water was also described by Schwarzenbach [116]. Advantage was taken of the fact that the red complex formed by calcium with the dye Murexide (ammonium purpurate) was found to be less stable than the calcium-EDTA complex. Thus when an alkaline solution containing calcium and Murexide was titrated with Na_2H_2Y, the free calcium ions were first complexed and, when all these were consumed, the calcium was removed from the Murexide. At this point the color of the solution changed from the red color of the calcium-Murexide complex to the reddish-violet color of the dye itself, thus marking the end point of the titration. Magnesium does not interfere in this titration since it forms a less stable EDTA complex than does calcium, and it gives no color at all with the dye.

Unfortunately, the color change which occurs at the end point is neither sharp nor very pronounced. According to Knight [53], addition of the inert dye Napthol Green B as a background color enhanced the visibility (though not the sharpness) of the end point. Because of its simplicity and speed, however, the Murexide titration for calcium has been widely accepted in cases where highly accurate analyses are not required.

The most successful analytical application of EDTA has been a complexometric titration of total hardness in water which was proposed by Biedermann and Schwarzenbach [8] and further developed by Diehl, Goetz, and Hach [24]. This method is similar to the Murexide titration except that the titration is carried out at pH 10 and the dye used as the indicator produces a color in the presence of magnesium rather than calcium. The indicator used was sodium 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonate. It is sold under a variety of trade names such as Eriochrome-schwartz T, Pontachrome Black T A, Potting Black C, Diamond Blue Black E B S, Omega Chrome Black S, and Solochrome Black. In the "Colour Index" it is listed as number 203, but the designation perhaps used most frequently is F241, which is its number in Schultz' "Farbstofftabellen" [115]. The dye itself has a clear blue color, but with magnesium it forms a wine-red complex which is less stable than the magnesium-EDTA complex. The process which occurs on titration of a solution containing calcium and magnesium with Na_2H_2Y is the complexing of the free calcium ions, then the free magnesium ions, and finally the magnesium is extracted from the dye complex, resulting in a color change from wine-red to blue. This color change is considerably sharper and more distinct than the end point of the Murexide titration described above.

Since the calcium complex of the dye is relatively weak and only faintly colored, pure calcium solutions could be titrated only if magnesium in some form was added. Diehl, Goetz, and Hach recommended the addition of magnesium chloride to the Na_2H_2Y solution before standardization as the most convenient way to insure an adequate amount of magnesium without the need for applying a blank correction. These authors, as well as Biedermann and Schwarzenbach, employed an ammonium chloride-ammonium hydroxide buffer to maintain a constant pH of 10 throughout the titration.

A modification of the method, introduced by Betz and Noll [6], makes use of a sodium hydroxide-sodium sulfide-sodium tetraborate "buffer-inhibitor" in place of the ammoniacal buffer. One disadvantage of this modification is that the "buffer-inhibitor" really has very little actual buffering capacity. For this reason an alkaline solution of EDTA (pH approximately 10) was recommended in place of the usual Na_2H_2Y solution (pH about 5). Although these authors stated in a subsequent publication [7] that all of the reagents used in their method with the exception of the buffer were found to be stable for at least eight months, other investigations [36, 37] have shown that alkaline solutions of EDTA deteriorate very rapidly when stored in soft glass containers. Solutions stored at pH 5, however, were found to be reasonably stable, decreasing in strength by less than 2 percent on standing for twelve months.

The maximum permissible concentration of such common interfering ions as Cu^{+2}, Fe^{+3}, and Al^{+3} were listed by Diehl, Goetz, and Hach [24]. The interference by copper was eliminated by the addition of sodium diethyldithiocarbamate to the indicator, or by the addition of sodium cyanide to the water sample prior to the titration. This latter procedure also increased the concentration of iron which could be tolerated and also eliminated interference by the less commonly encountered cobalt and nickel ions. The difficulty arising from destruction of the indicator by oxidizing agents in some water samples was overcome by the addition of hydroxylamine hydrochloride to the indicator solution. The "buffer-inhibitor" of Betz and Noll [6] also eliminated most interferences, except that the sulfide precipitates obtained with some metals (especially iron) had a tendency to obscure the end point.

This method when combined with the Murexide titration previously described has been shown by many investigators [3, 5, 19, 43, 46, 59, 64, 65, 68, 107, 123, 132] to provide a rapid and reliable means for determining the total hardness and calcium hardness of a wide variety of waters. Some of these investigators introduced minor modifications in the methods, but were primarily concerned with testing their reliability. One disadvantage noted was that these methods could not be applied to boiler waters containing polyphosphates. Removal of the polyphosphates by anion exchange was shown by Brooke and Holbrook [13] to be a satisfactory means for overcoming this objection. The lack of stability of the usual alcoholic solution of the indicator F241 was reported by Porter [79] and Diskant [26]. Porter suggested the use of filter paper strips impregnated with the dye as a stable form of the indicator while Diskant found that triethanolamine and diethanolamine solutions of the dye remained in good condition for at least seven months. These investigators made no mention of the stability of a commercial indicator preparation containing hydroxylamine hydrochloride sold under the trade name "Man Ver". Solutions of this indicator have been reported by the manufacturer[1] to have good stability over a period of several months.

These complexometric titrations using Murexide and F241 have also been adapted for use outside the field of water

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[1] Hach Chemical Co., Ames, Iowa.

analysis. Such applications include the determination of calcium and magnesium in limestone [14, 18], plant tissues [35, 135], and biological fluids [14, 34, 38], the assay of calcium in pharmaceuticals [39, 44, 69], and the determination of magnesium in nickel plating solutions [58]. The use of these methods in micro analysis has also been described [21, 31, 124]. Phosphorus in the form of phosphates has been determined indirectly by precipitating magnesium ammonium phosphate with an excess of standard magnesium solution and titrating the excess with EDTA [22]. An alternate procedure has been described in which the magnesium ammonium phosphate was dissolved in acid, neutralized with ammonia, and the magnesium titrated [47].

Titrimetric methods for a few other metals using F241 as the indicator have been reported. A method for the indirect determination of sodium by titration of the zinc in sodium zinc uranyl acetate has been developed [33]. Flaschka [32] has described a direct microtitration of lead; Kinnunen [50] listed four methods for determination of zinc in zinc concentrates and brass; Manns, _et al_., [63] determined barium in electrolyte solutions used in the manufacture of television tubes; and Landgren [57] used a back-titration with magnesium in the analysis of bismuth solutions. A method for ferrocyanide based on the titration of the excess of a standard zinc solution after precipitation of zinc ferrocyanide was developed by Hol and Leedertse [45]. A similar procedure for the volumetric estimation of sulfate by the determination of excess standard barium solution was discussed by Munger, Nippler, and Ingols [73]. This sulfate procedure was employed by Ueno [128] in a method for the analysis of zinc and sulfate in viscose coagulating liquors. The use of Murexide as an indicator in the titration of nickel in steel with EDTA following the usual dimethylglyoxime separation has been described by Harris and Sweet [42].

A few of the metal complexes of EDTA have proved sufficiently highly colored to permit their use in colorimetric determinations. Oxidation of the cobaltous complex with hydrogen peroxide was shown to produce the rose-colored trivalent cobalt complex by Pribil [81], who suggested its use in a colorimetric procedure. Such a method has been worked out in detail by Jean [48]. Beer's law was found to hold in the range of 0-12 mg. of cobalt (per 100 ml. of solution) using the absorption maximum at 546 mμ and a pH of about 5. Metals commonly associated with cobalt such as Mn, Cu, Ni, Cr, Mo, W, V, Ti, Fe, etc., did not interfere with the described method. Colorimetric procedures using EDTA complexes have also been developed for chromium [90] and trivalent manganese [87]. The chromium complex of EDTA in neutral or dilute acetic acid solution has an absorption maximum at 550 mμ, and was shown to be stable for over ten days. The purple color of this complex was detectable for chromium contents down to 0.1 mg. per 100 ml. of solution. Cobalt, copper, iron, and nickel were found to interfere unless removed by precipitation as hydroxides prior to the determination. The ruby red complex of trivalent manganese, which has an absorption maximum at 475 mμ, was used by Pribil and Hornychova [87] for the determination of manganese in the presence of cobalt and chromium. Very close control of the conditions under which the color developed was found necessary and no advantages over the usual permanganate methods were listed.

EDTA has also been used successfully as a masking agent in colorimetric procedures. Meek and Banks [71] found that the interference by aluminum in the determination of beryllium with sulfosalicylic acid was practically eliminated by complexing most of the aluminum with EDTA. Similar applications include the masking of calcium and magnesium in the determination of nitrate with phenoldisulfonic acid [41] and the elimination of interference by most of the heavy metals in the determination of copper with diethyldithiocarbamate [122], mercury with dithizone [130], and beryllium with Aluminon [61].

A number of gravimetric separations have been made more specific by using EDTA to keep in solution, in the form of soluble complexes, certain ions which would have contaminated the desired precipitate under the usual conditions of separation. Pribil and his co-workers have applied this technique to the determination of molybdenum [92] and tungsten [98] with 8-hydroxyquinoline; the separation of beryllium from aluminum [91]; the separation of titanium from iron and aluminum [97]; the determination of impurities in lead [82]; the separation of zinc from nickel and cobalt [82]; the gravimetric determination of bismuth [84]; the precipitation of mercury with mercaptophenylthiothiodiazolone [121]; the separation of titanium, beryllium, and uranium [103]; and the selective precipitation of calcium oxalate [85], magnesium ammonium phosphate [88], barium sulfate [94], and thallous iodide [106]. A semimicro qualitative analysis scheme based on selective precipitation of various cations in the presence of EDTA through the use of a number of organic and inorganic precipitants and careful pH control was also worked out by Pribil [80].

Souchay and Faucherre [125] first pointed out that EDTA strongly displaces the polarographic reduction potentials of numerous elements. As practical applications of this fact, the authors described a procedure for the polarographic determination of trivalent cobalt in the presence of most other metals and a similar procedure for small amounts of iron in brasses and "pure" metals. A subsequent publication by the same authors [29] described a method for the polarographic determination of iron and copper in bearing metals through separation of the iron, copper, and bismuth waves with EDTA. The polarography of a large number of metals was studied by Pribil and his co-workers. These investigations have resulted in procedures for the polarographic determination of thallium, molybdenum, uranium, zinc, cobalt, and germanium [83, 102, 105, 129], as well as the indirect determination of calcium, barium, and sulfate [102, 107].

Amperometric titrations with EDTA using as the indicator electrode either a rotating platinum electrode or a dropping mercury electrode were also investigated by Pribil. Such titration methods have been applied to the determination of bismuth, iron, nickel, lead, zinc, cadmium, silver, and thallium [27, 95, 106]. Potentiometric titrations involving the use of EDTA were also developed by Pribil for manganese [86, 99], cobalt [101], and such metals as iron, copper, aluminum, cadmium, zinc, nickel, and lead [35]. Other applications of EDTA reported by Pribil include the prevention of interference by copper and iron in the iodometric determination of cerium [100] and the reduction of interference by certain metal ions in the acidimetric determination of boric acid using glycerol or mannitol [104].

A theoretical discussion of chelate complex formation as a basis for titration procedures has been presented by

Schwarzenbach [110]. By treating metals which enter into complex formation as Lewis acids, Schwarzenbach was able to demonstrate that complexometric titrations are completely analogous to ordinary acid-base titrations, and that chelate complexes form useful "metal ion buffers" which are very similar to the usual hydrogen ion buffers so frequently employed in analytical work. An extensive bibliography on the uses of EDTA in many fields, covering the literature to June, 1952, is contained in the technical bulletin, "Sequestrene", published by the Alrose Chemical Company. Many of the more important analytical applications as well as some of the industrial uses of EDTA have been described in some detail in a review of Souchay and Graizon [126].

E. Cyclohexenediaminetetraacetic Acid

A large number of compounds similar to ethylenediaminetetraacetic acid have been tested as chelating agents for metals. Only one such compound, 1,2-cyclohexenediaminetetraacetic acid (CDTA), has been found to possess a complex-forming ability which equals or exceeds that of EDTA. The preparation of CDTA from 1,2-diaminocyclohexane by a procedure similar to that used for EDTA was described in a patent by Schläpfer and Bindler [108]. They also reported that CDTA was found superior to EDTA for the purpose of keep-ing heavy metal ions and the hardness factors of water in solution during textile processing and dyeing, or for redissolving undesirable precipitates already formed.

A brief investigation of CDTA as a chelating reagent was made by Ackermann and Schwarzenbach [113]. Using the method described for EDTA, these investigators found the following ionization constants for CDTA: $pK_1 = 2.43$, $pK_2 = 3.52$, $pK_3 = 6.12$, and $pK_4 = 11.70$ (ionic strength = 0.1, temperature = 25.0°C.). The stability constants of the calcium and magnesium complexes (at this same ionic strength and temperature) were determined by the procedure listed previously for EDTA as "Method 1(a)". These constants were found to be: $\log K_{MgY} = 10.32$ and $\log K_{CaY} = 12.50$. (The corresponding values previously determined for EDTA were $\log K_{MgY} = 8.69$ and $\log K_{CaY} = 10.59$.)

Very recently Pribil [96] reported the study of possible uses of CDTA in polarography. The half-wave potentials of Pb, Cu(II), Bi, Cd, Tl(I), As(III), Sb(III), Sn(II), Mo(IV), Zn, Ni, Co, Mn, Fe(III), Cr, W(IV), Ti(IV), and UO_2 in various solutions containing CDTA were determined. A method employing CDTA in the polarographic determination of copper, bismuth, and thallium in the presence of excess lead without chemical removal of the lead was also presented. A detailed description of this work cannot be given here since only a brief abstract of this paper is presently available.

III. STABILITY CONSTANTS OF CDTA COMPLEXES

A. Materials

1. Cyclohexenediaminetetraacetic acid (CDTA)

The CDTA used in the determination of ionization and stability constants was purified in the following manner. Commercial CDTA (obtained from the Alrose Chemical Company) was dissolved in a slight excess of 1 *N* NaOH, filtered, neutralized to pH 6 with 1 *N* HCl, precipitated as the disodium salt with 95% alcohol, collected on a sintered glass crucible, and washed thoroughly with alcohol. This disodium salt was dissolved in a minimum of water, acidified to pH 2 with 1 *N* HCl to precipitate CDTA, filtered, and washed with water. The precipitated CDTA was then twice recrystallized from water and dried under reduced pressure (1-2 mm. Hg) at 100°C. for at least four hours.

2. Carbonate-free potassium hydroxide solution (0.1 *N*)

A hot solution containing 4.5 g. of sodium hydroxide[1] in 100 ml. of water was slowly added to an equal volume of hot solution containing 18 g. of silver nitrate. The re-

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[1] Except where otherwise specified, all chemicals used were reagent grade.

sulting mixture was kept hot for several minutes to coagulate the precipitate of silver oxide. The silver oxide was filtered on a sintered glass funnel, washed ten times with hot distilled water, and added to about 850 ml. of freshly boiled redistilled water containing approximately 8 g. of potassium chloride. The resulting mixture was allowed to stand (with occasional shaking) for about one day and then filtered by removal of the supernatant liquid with a fritted glass filterstick. The mixing and filtering operations were carried out under nitrogen to prevent absorption of CO_2 by the basic solution.

The resulting potassium hydroxide solution was stored in a Pyrex bottle under a slight pressure of nitrogen and was standardized by comparison with a hydrochloric acid solution which had been standardized gravimetrically. The normality of the hydrochloric acid solution was also checked by comparison with a carbonate-free sodium hydroxide solution that had been standardized with potassium acid phthalate.

3. Carbonate-free sodium hydroxide solution (0.1 N)

A saturated solution of sodium hydroxide was prepared and allowed to stand until the supernatant liquid was clear. Approximately 8 ml. of the clear solution was added to one liter of freshly boiled redistilled water. The resulting solution was stored in the same way as the potassium hydroxide. It was standardized against the same hydrochloric acid and further checked by titration with potassium acid phthalate.

4. Triaminotriethylamine trihydrochloride

This material was prepared from β-bromoethylphthalimide (M.P. 81-83°C.) by the method of Mann and Pope [62]. The crude product was recrystallized twice by solution in the minimum amount of water and precipitated with 95 percent ethanol. The precipitate was filtered each time on a sintered glass crucible and washed several times with absolute ethanol. The doubly recrystallized material was dried for five hours under reduced pressure (1-2 mm. Hg) at 100°C.

5. Solutions of metal ions

All metal ion solutions were prepared from reagent grade salts. The following salts were used without preliminary treatment: $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $Sr(NO_3)_2$, $BaCl_2 \cdot 2H_2O$, and $ZnSO_4 \cdot 7H_2O$. The $Pb(NO_3)_2$ used was recrystallized from water and dried for four hours at 110°C. The following were dehydrated by ignition to constant weight at the temperature indicated: $CuSO_4 \cdot 5H_2O$ (300°C.), $CoSO_4 \cdot 7H_2O$ (600°C.), $CdCl_2 \cdot 2.5H_2O$ (500°C.), $MnCl_2 \cdot 4H_2O$ (250°C.), and $NiSO_4 \cdot 6H_2O$ (300°C.).

6. Potassium perchlorate

In all of the titrations performed, the solutions contained sufficient potassium perchlorate to raise the ionic strength to 0.1. The reagent grade potassium perchlorate used for this purpose was dried at 110°C. for at least five hours.

B. Experimental Procedures

1. Apparent ionization constants of CDTA

The ionization constants of CDTA were determined by the method outlined by Schwarzenbach, Willi, and Bach [120]. In this procedure all four of the desired ionization constants are obtained from a single pH titration of the acid with potassium hydroxide. Two independent values for each constant were obtained by carrying out the titration in duplicate. For this purpose two stock solutions of CDTA were prepared. Solution I contained 0.3487 g. of CDTA and 7.620 g. of potassium perchlorate in sufficient freshly redistilled water to make 500 ml. of solution. Solution II was identical except for the CDTA content which was 0.3944 g.

a. Titration procedure. The titration was carried out on a 50-ml. portion of one of the above solutions diluted with an equal volume of 0.0900 M potassium perchlorate solution. The resulting mixture was 0.1000 molar in $KClO_4$ and approximately 0.001 molar in CDTA.

The titration cell employed was a 150-ml. beaker (without pouring spout) sealed into a glass outer jacket through which water was circulated from a constant temperature bath maintained at 25.00 ± 0.02°C. (The bath thermometer was checked with a thermometer certified by the Bureau of Standards.) A rubber stopper provided with holes for the electrodes, buret tip, and nitrogen gas inlet and outlet tubes sealed the top of the titration cell. The potassium hydroxide solution was added by means of a self-filling 5-ml. Pyrex buret[1] graduated to 0.01 ml. The finely drawn tip of the buret fit tightly into the rubber stopper and extended below the surface of the solution being titrated. After each addition of base, the solution was mixed by means of a small Pyrex-covered Alnico bar magnet activated by a conventional magnetic stirrer located under the titration cell. Carbon dioxide was excluded from the system by bubbling CO_2-free nitrogen (saturated with water vapor at 25.0°C.) through the solution during the titration.

A Beckman Model G pH meter was used to measure the hydrogen ion concentration. To minimize errors in pH readings

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[1] Recalibrated at 0.5 ml. intervals for delivery of 0.1 N base by weighing the amount of 0.1 N NaOH actually delivered.

the meter was standardized three times for each titration: at the start (with Beckman pH 4.00 buffer), during the first break (with pH 7.00 buffer), and during the second break (with pH 10.00 buffer). For measurements below pH 9 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 meter and were treated with Desicote to prevent loss of solution when they were removed from the titration cell for restandardization. For measurements above pH 9, these were replaced with a system consisting of a similar calomel electrode and a "Type E" glass electrode designed especially for use in alkaline solutions. No Desicote was used on these electrodes since Desicote-treated electrodes were found to give erratic response in alkaline solutions (above pH 10).

b. Procedure for calculation of K_1 and K_2. An examination of such a titration curve for CDTA (curve A, Figure 1) shows that the first break in the curve occurs at $\underline{a} = 2$, where $\underline{a}$ = moles of KOH added per mole of CDTA. This means that the first two ionization constants, K_1 and K_2, of CDTA are of approximately the same magnitude. The quantities which are known in this system are the total concentration of CDTA (C_A), the measured hydrogen ion concentration (pH = $-\log [H^+]$), and the fraction of CDTA titrated ($\underline{a}$). The unknown quantities in the system are K_1, K_2, and the concentrations of the various ionic species of CDTA ($[H_4Y]$, $[H_3Y^-]$, $[H_2Y^{-2}]$, $[HY^{-3}]$, and $[Y^{-4}]$). The last two of these, $[HY^{-3}]$ and $[Y^{-4}]$, are negligible in the acidic pH region where K_1 and K_2 are calculated. This leaves five unknowns to be computed. Since only four equations are available for each point on the neutralization curve, at least two sets of values of C_A, *a*, and pH are required to specify the five unknowns.

The equations available are:[1]

$$K_1 = \frac{[H]\,[H_3Y]}{[H_4Y]} \qquad (a)$$

$$K_2 = \frac{[H]\,[H_2Y]}{[H_3Y]} \qquad (b)$$

$$C_A = [H_4Y] + [H_3Y] + [H_2Y] \qquad (c)$$

$$[H] = [H_3Y] + 2[H_2Y] - \underline{a}C_A \;. \qquad (d)$$

Equations (a) and (b) define the desired constants while equation (c) merely defines C_A. Equation (d) arises from

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[1] To simplify the writing of equations the usual indication of the sign and magnitude of the charge on ions has been omitted.

the fact that for each H_3Y^- ion present in the solution one hydrogen ion has been liberated; for each H_2Y^{-2} ion two hydrogen ions have been liberated; and for each molecule of potassium hydroxide added, one hydrogen ion has been consumed. Thus, at any stage of the titration between $\underline{a} = 0$ and $\underline{a} = 2$,[1] the hydrogen ion concentration is equal to the concentration of H_3Y^- plus twice the concentration of H_2Y^{-2} minus the amount of KOH added. This is expressed mathematically in equation (d), which is also the equation for the balance of electrical charges.

A general equation containing K_1 and K_2 as the only unknowns may be derived from the above four equations by the elimination of $[H_4Y]$, $[H_3Y]$, and $[H_2Y]$. To accomplish this, $[H_4Y]$ and $[H_3Y]$ are first expressed in terms of K_1, K_2, $[H]$, and $[H_2Y]$ by combining and rearranging equations (a) and (b) to obtain

$$[H_3Y] = \frac{[H]}{K_2}[H_2Y] \quad \text{and} \quad [H_4Y] = \frac{[H]^2}{K_1K_2}[H_2Y] \quad .$$

Substitution of these expressions for $[H_4Y]$ and $[H_3Y]$ in equation (c) and (d) gives

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[1] Actually $\underline{a}$ must be slightly lower than 2 to avoid the necessity of considering the ionic species HY^{-3} which begins to appear as $\underline{a}$ approaches 2.

$$C_A = \frac{[H]^2}{K_1K_2}[H_2Y] + \frac{[H]}{K_2}[H_2Y] + [H_2Y]$$

and

$$\frac{[H]}{K_2}[H_2Y] + 2[H_2Y] - \underline{a}C_A = [H] \; .$$

Rearrangement of these leads to the expressions

$$C_A = [H_2Y]\left(\frac{[H]^2}{K_1K_2} + \frac{[H]}{K_2} + 1\right) \qquad \text{(e)}$$

and

$$[H_2Y]\left(\frac{[H]}{K_2} + 2\right) = [H] + \underline{a}C_A \; . \qquad \text{(f)}$$

Multiplication of equation (e) by (f) yields

$$[H_2Y]\left(\frac{[H]}{K_2} + 2\right)C_A = \left([H] + \underline{a}C_A\right)\left(\frac{[H]^2}{K_1K_2} + \frac{[H]}{K_2} + 1\right)[H_2Y]$$

which may be simplified by dividing both sides of the equation by $[H_2Y]$ and multiplying through by K_2,

$$\left([H] + 2K_2\right)C_A = \left([H] + \underline{a}C_A\right)\left(\frac{[H]^2}{K_1} + [H] + K_2\right), \quad ✓$$

performing the multiplications indicated by parentheses,

$$[H]C_A + 2K_2C_A = \left([H] + \underline{a}C_A\right)\frac{[H]^2}{K_1} + \left([H] + \underline{a}C_A\right)[H] + K_2\left([H] + \underline{a}C_A\right)$$

and combining like terms to give

$$K_2\left(2C_A - [H] - \underline{a}C_A\right) - \frac{1}{K_1}\left([H]^2\right)\left([H] + \underline{a}C_A\right) = [H]\left([H] + \underline{a}C_A - C_A\right)$$

which reduces to

$$K_2\left((2 - \underline{a})C_A - [H]\right) - \frac{1}{K_1}[H]^2\left([H] + \underline{a}C_A\right) = [H]\left((\underline{a} - 1)C_A + [H]\right) . \qquad (f)$$

Equation (f) is a linear equation of the form ax + by = c, where $x = K_2$ and $y = \frac{1}{K_1}$. The intercepts of the line represented by such an equation are $\frac{c}{a}$ on the x axis and $\frac{c}{b}$ on the y axis. For equation (f) these intercepts are:

$$\text{on the x axis,}\quad a = \frac{[H]\left((\underline{a} - 1)C_A + [H]\right)}{(2 - \underline{a})C_A - [H]}$$

on the y axis, $$B = -\frac{[H]\left((\underline{a} - 1)C_A + [H]\right)}{[H]^2 \quad [H] + \underline{a}C_A} = -\frac{(\underline{a} - 1)C_A + [H]}{[H]\left([H] + \underline{a}C_A\right)} .$$

To construct the line represented by equation (f), it is merely necessary to plot the calculated intercepts A and B on a set of coordinate axes and connect these points by a straight line.

For each point on the titration curve between $\underline{a} = 0$ and $\underline{a} = 2$, there is an equation of the form of equation (f). These form a series of simultaneous linear equations in $1/K_1$ and K_2. Since there must be a single pair of values for $1/K_1$ and K_2 which satisfy all the equations, there must be a single point which is common to all the lines representing these equations. The coordinates of this point are, of course, $1/K_1$ and K_2.

Therefore to find K_1 and K_2, the value of the intercepts A and B are computed for a number of experimental points ($\underline{a}$ values) on the titration curve. These intercepts are then plotted on coordinate axes and from the intercepts the straight lines representing equation (f) for each value of $\underline{a}$ are drawn. Within the limits of experimental error all these lines should have a common point of intersection. The coordinates A_0 and B_0 of this point of intersection represent K_2 and $1/K_1$ respectively.

c. Procedure for calculation of K_3. Of the four ionization constants of CDTA the third one (K_3) is the simplest to determine. Curve A, Figure 1, exhibits distinct breaks at $\underline{a} = 2$ and $\underline{a} = 3$. This means that the concentration of H_3Y^- diminishes very rapidly in the vicinity of $\underline{a} = 2$ and the concentration of Y^{-4} is not appreciable until $\underline{a} = 3$ is almost reached. In the vicinity of $\underline{a} = 2.5$, therefore, only the species H_2Y^{-2} and HY^{-3} need be considered.

In this region the problem of determining K_3 is very similar to the problem of determining K_A for a simple monobasic weak acid. Thus

$$K_3 = \frac{[H]\,[HY]}{[H_2Y]} = \frac{[H]\text{ (fraction titrated)}}{\text{(fraction untitrated)}}$$

In the discussion of the determination of K_1 and K_2 the fraction titrated was designated as $\underline{a}$. In the present case, however, two equivalents of KOH per mole of CDTA have already been neutralized at $\underline{a} = 2$; the fraction titrated therefore becomes $(\underline{a} - 2)$. The neutralization of H_2Y^{-2} ends at $\underline{a} = 3$, hence the fraction untitrated is $(3 - \underline{a})$. Substitution of these quantities in the above equation gives

$$K_3 = \frac{[H]\,(\underline{a} - 2)}{(3 - \underline{a})} .$$

Upon converting to logarithms,

$$\log K_3 = \log [H^+] + \log \frac{(\underline{a} - 2)}{(3 - \underline{a})}$$

from which

$$-\log K_3 = -\log [H^+] + \log \frac{(3 - \underline{a})}{(\underline{a} - 2)}$$

or, more simply,

$$pK_3 = pH + \log \frac{(3 - \underline{a})}{(\underline{a} - 2)} .$$

This last equation permits a simple computation of pK_3 from all sets of values of $\underline{a}$ and pH in the range of $\underline{a} = 2.5$.

d. Procedure for calculation of K_4. The problem of determining K_4 is complicated somewhat by the ionic species Y^{-4} being only a very weak acid. This ion, which is produced by the reaction

$$HY^{-3} + KOH \rightleftharpoons Y^{-4} + K^+ + H_2O$$

hydrolyzes to a large extent according to the reverse reaction

$$Y^{-4} + H_2O \rightleftharpoons OH^- + HY^{-3} .$$

This is shown by the fact that in curve A, Figure 1, no indication of a break at $\underline{a} = 4$ is found.

If no hydrolysis occurred, the concentration of Y^{-4} could be calculated simply by subtracting the amount of KOH added. Since three molecules of KOH are needed to produce one HY^{-3} ion, the concentration of Y^{-4} would be given by

$$[Y] = (\underline{a} - 3)C_A .$$

Since in the hydrolysis reaction one Y^{-4} ion is consumed for each OH^- produced, the concentration of Y^{-4} actually is

$$[Y] = (\underline{a} - 3)C_A - [OH] . \qquad (a)$$

The only ionic species of CDTA present in this alkaline region between $\underline{a} = 3$ and $\underline{a} = 4$ are HY^{-3} and Y^{-4}, hence

$$C_A = [HY] + [Y] . \qquad (b)$$

By substituting the value found for [Y] given by equation (a) into equation (b) it is found that

$$[HY] = C_A - (\underline{a} - 3)C_A - [OH]$$

or

$$[HY] = (4 - \underline{a})C_A + [OH] .$$

Upon substitution of the expressions for [HY] and [Y], the equation defining K_4 becomes

$$K_4 = \frac{[H]\,[Y]}{[HY]} = \frac{[H]\,\big((\underline{a} - 3)C_A - [OH]\big)}{(4 - \underline{a})C_A + [OH]}. \qquad (c)$$

Equation (c) permits the calculation of K_4 from sets of experimental values of C_A, pH, and a for all points on the titration curve beyond a = 3.

2. Stability of lead and alkaline earth metal complexes of CDTA

The stability constants of the lead and alkaline earth metal complexes were determined by the procedure outlined in principle by Schwarzenbach, Willi, and Bach [120] and described briefly in the Review of Literature of this thesis [Section II A, Method 1(a)]. Since CDTA is a weaker acid than EDTA, the method of calculation was modified to include consideration of the species H_4Y and H_3Y^- which the above authors found to be negligible with EDTA. Also, the graphical method of computation used by these authors was found to be satisfactory only in the case of the barium and strontium complexes, as will be explained later.

a. Titration procedure. The titration procedure used was the same as that previously described for the titration of CDTA alone, with the following exceptions: (1) the 0.0900 M potassium perchlorate solution was replaced by 50 ml. of a 0.0300 M solution of a salt of the metal being investigated and (2) the pH meter was standardized only at the start of the titration[1] (using Beckman pH 4.00 buffer solution), but was checked (with the same buffer solution) at the conclusion of the titration. The same CDTA solutions (I and II) were employed. The mixing of 50 ml. of one of these solutions with 50 ml. of 0.0300 M metal salt produced a solution which was 0.0150 molar in the metal ion, 0.0550 molar in potassium perchlorate, and approximately 0.001 molar in CDTA. Such a solution had an ionic strength of 0.100.

b. Procedure for the calculation of K_{MHY} and K_{MY}. The curves in Figure 1 show that in the presence of excess metal ions CDTA behaves as a much stronger acid, especially during the last half of the titration. This apparent increase in acidity results from the displacement of hydrogen ions by the metal according to the following reactions:

$$H_2Y^{-2} + M^{++} \rightleftharpoons MHY^- + H^+$$

$$HY^{-3} + M^{++} = MY^{-2} + H^+ .$$

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[1] The pH readings in the alkaline portion of the titration curves were used only for the purpose of locating the end-point. The relatively small error in these readings resulting from non-linearity of the pH meter was not significant.

Accordingly, two new apparent ionization constants for the third and fourth ionization stages of CDTA may be introduced. These new constants are defined as follows:[1]

$$K_3' = \frac{[H]\left([MHY] + [HY]\right)}{[H_2Y]} \qquad (a)$$

and

$$K_4' = \frac{[H]\left([MY] + [Y]\right)}{[MHY] + [HY]} . \qquad (b)$$

The concentration of the metal [M] does not enter into the above expressions because it is kept essentially constant during the titration through the use of a fifteenfold excess of metal salt and, hence, is part of K_3' and K_4'.

It can be seen from Figure 1 that in all of the cases investigated no distinct break in the curve is found at $a = 3$. This implies that K_3' and K_4' are of about the same order of magnitude and indicates that they must be calculated in a manner similar to that previously employed in finding K_1 and K_2. The equations used in the case of K_1 and K_2 can be suitably modified to serve for the derivation of a linear

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[1] As in previous derivations, the indication of the charge on ions will be omitted in this discussion.

equation with K_3' and K_4' as the only unknowns.

In addition to the above expressions for K_3' and K_4', the equations available for this derivation are those defining the first two ionization constants of CDTA

$$K_1 = \frac{[H]\,[H_3Y]}{[H_4Y]} \qquad (c)$$

$$K_2 = \frac{[H]\,[H_2Y]}{[H_3Y]} \qquad (d)$$

and expressions for C_A and [H] similar to those in the previous derivation. Upon inclusion of all the ionic species which may be present in the solution, these equations become

$$C_A = [H_4Y] + [H_3Y] + [H_2Y] + \Big([MHY] + [HY]\Big) + \Big([MY] + [Y]\Big) \qquad (e)$$

$$[H] = [H_3Y] + 2[H_2Y] + 3\Big([MHY] + [HY]\Big) + 4\Big([MY] + [Y]\Big) - \underline{a}C_A \qquad (f)$$

Following the procedure used in the derivation of the equation for K_1 and K_2 equations (a), (b), (c), and (d) are rearranged and combined so that all ionic species are expressed in terms of $[H_2Y]$, [H], and their respective ionization constants:

$$[H_4Y] = \frac{[H]^2}{K_1K_2}[H_2Y] \qquad [H_3Y] = \frac{[H]}{K_2}[H_2Y]$$

$$[MHY] + [HY] = \frac{K_3'}{[H]}[H_2Y] \qquad [MY] + [Y] = \frac{K_3'K_4'}{[H]^2}[H_2Y] .$$

Upon substitution of these expressions in (e) and (f), the latter equations become

$$C_A = \left(\frac{[H]^2}{K_1K_2} + \frac{[H]}{K_2} + 1 + \frac{K_3'}{[H]} + \frac{K_3'K_4'}{[H]^2}\right)[H_2Y] \tag{g}$$

and

$$\left(\frac{[H]}{K_2} + 2 + 3\,\frac{K_3'}{[H]} + 4\,\frac{K_3'K_4'}{[H]^2}\right)[H_2Y] = [H] + \underline{a}C_A . \tag{h}$$

Multiplication of equation (g) by equation (h) gives

$$C_A\left(\frac{[H]}{K_2} + 2 + 3\,\frac{K_3'}{[H]} + 4\,\frac{K_3'K_4'}{[H]^2}\right)[H_2Y] =$$

$$[H] + \underline{a}C_A \left(\frac{[H]^2}{K_1K_2} + \frac{[H]}{K_2} + 1 + \frac{K_3}{[H]} + \frac{K_3'K_4'}{[H]^2}\right)[H_2Y]$$

which may be simplified by dividing both sides by $[H_2Y]$, carrying out the multiplication indicated by the parentheses, and collecting like terms:

$$C_A \frac{[H]}{K_2} + 2C_A + 3C_A \frac{K_3'}{[H]} + 4C_A \frac{K_3'K_4'}{[H]^2} =$$

$$\left([H] + \underline{a}C_A\right) \frac{[H]^2}{K_1K_2} + \left([H] + \underline{a}C_A\right) \frac{[H]}{K_2} + \left([H] + \underline{a}C_A\right) +$$

$$\left([H] + \underline{a}C_A\right) \frac{K_3'}{[H]} + \left([H] + \underline{a}C_A\right) \frac{K_3'K_4'}{[H]^2}$$

$$\left(4C_A - [H] - \underline{a}C_A\right) \frac{K_3'K_4'}{[H]^2} - \left([H] + \underline{a}C_A\right) \frac{[H]^2}{K_1K_2} +$$

$$\left(C_A - [H] - \underline{a}C_A\right) \frac{[H]}{K_2} + 2C_A - [H] - \underline{a}C_A =$$

$$\left([H] + \underline{a}C_A - 3C_A\right) \frac{K_3'}{[H]} \quad .$$

This equation may be further simplified by the introduction of a new term defined as

$$b = (\underline{a} - 2)C_A + [H] \quad .$$

Introduction of this expression converts the equation into

$$(2C_A - b)\,\frac{K_3'K_4'}{[H]^2} - (2C_A + b)\,\frac{[H]^2}{K_1K_2} - (C_A + b)\,\frac{[H]}{K_2} - b \;=\; (b - C_A)\,\frac{K_3'}{[H]} \;. \qquad \text{(i)}$$

Multiplication of this by $\frac{[H]^2}{K_3'}$ gives

$$(2C_A - b)\,K_4' - [H]^2\left((2C_A + b)\,\frac{[H]^2}{K_1K_2} + (C_A + b)\,\frac{[H]}{K_2} + b\right)\frac{1}{K_3'} \;=\; (b - C_A)\,[H] \qquad \text{(j)}$$

which is the desired linear equation in K_4' and $1/K_3'$.

As in the previously described case for K_1 and K_2, each pair of experimental values for a and pH leads to one such equation. This permits the calculation of a series of simultaneius linear equations in K_4' and K_3' which may be solved graphically as described earlier. In the present case the intercepts A and B are computed from the following expressions:

$$A = \frac{(b - C_A)\,[H]}{2C_A - b}$$

$$B = -\frac{(b - C_A)}{[H]\left((2C_A + b)\dfrac{[H]^2}{K_1K_2} + (C_A + b)\dfrac{[H]}{K_2} + b\right)}$$

The coordinates A_0 and B_0 of the intersection of the lines drawn through these intercepts represent K_4' and $1/K_2'$ respectively.

This method of computation will be shown to give satisfactory results in the case of barium and strontium, but it leads to unsatisfactory results for lead, calcium, and magnesium. The difficulty in the case of these stronger complexes arises from the fact that the straight lines must be extended too far before they intersect. Thus a small error in A or B (or in drawing the lines) results in a much larger error in the intersection. This is most easily seen by comparing the graphs for strontium (Figures 4 and 5) with those for barium (Figures 6 and 7) which forms a much weaker CDTA complex.

In the case of the stronger complexes a method of successive approximation may be employed. To simplify the discussion and reduce confusion, K_2' and K_4' are replaced by new constants K_{k_1}' and K_{k_2}' according to the following relations:

$$K_{k_1}' = K_2' = \frac{[H]\left([MHY] + [HY]\right)}{[H_2Y]} \qquad (k)$$

and

$$K'_{k_2} = K'_3K'_4 = \frac{[H]^2\,([MY] + [Y])}{[H_2Y]} \quad . \qquad (1)$$

When these values are introduced, equation (1) above becomes

$$(2C_A - b)\frac{K'_{k_2}}{[H]^2} - (2C_A + b)\frac{[H]^2}{K_1K_2} - (C_A + b)\frac{[H]}{K_2} - b =$$

$$(b - C_A)\frac{K'_{k_1}}{[H]} \quad .$$

Multiplication of this equation by $\frac{[H]^2}{2C_A - b}$ gives

$$K'_{k_2} - \frac{[H]^2\left((2C_A + b)\frac{[H]^2}{K_1K_2} + (C_A + b)\frac{[H]}{K_2} + b\right)}{2C_A - b} =$$

$$\frac{[H]\,(b - C_A)}{2C_A - b}\,K'_{k_1}$$

which may be rearranged to

$$K'_{k_2} = \frac{[H]^2\left((2C_A - b)\frac{[H]^2}{K_1K_2} + (C_A + b)\frac{[H]}{K_2} + b\right)}{2C_A - b} + \frac{[H]\,(b - C_A)}{2C_A - b}\,K'_{k_1} \;.$$

Upon introducing the symbol Δ for the complex term on the right-hand side of the equation and σ for the coefficient of K'_{k_1}, this equation reduces to

$$K'_{k_2} = \Delta + \sigma K'_{k_1} \;. \qquad (m)$$

A set of values for Δ and σ may be computed for each experimental value of a and pH. When these are tabulated, it is found that Δ is always positive, but decreases as a increases. On the other hand, as a increases, σ likewise increases, going from negative values to positive. There is thus a region where the magnitude of σ is small compared to Δ, and in this region K'_{k_2} is very nearly equal to Δ. The average value of Δ in this region may be taken as a first approximation for K'_{k_2}.

Equation (m), upon rearrangement, gives

$$K'_{k_1} = \frac{K'_{k_2} - \Delta}{\sigma} \qquad (n)$$

from which K'_{k_1} may be calculated for each pair of Δ and σ values[1] using the first approximation for K'_{k_2}. Using the average of these K'_{k_1} values as a first approximation, K'_{k_2} may be computed for each pair of values of σ and Δ according to equation (m). The average of these new K'_{k_2} values is then used to recalculate K'_{k_1}. This process may be repeated until it fails to result in a significant change in the average value for K'_{k_1} and K'_{k_2}.

The desired stability constants, K_{MHY} and K_{MY}, defined by the equations

$$K_{MHY} = \frac{[MHY]}{[M]\,[HY]} \qquad \text{and} \qquad K_{MY} = \frac{[MY]}{[M]\,[Y]}$$

may easily be obtained from the ionization constants K'_{k_1} and K'_{k_2} (or K'_3 and K'_4). Equation (k), which defines K'_{k_1}, may be rearranged to

$$K'_{k_1} = \frac{[H]\,[MHY]}{[H_2Y]} + \frac{[H]\,[HY]}{[H_2Y]}$$

---

[1] It should be noted that where $(K'_{k_2} - \Delta)$ and σ are both small, no significant value for K'_{k_1} may be calculated due to the error always encountered in taking the difference of two relatively large numbers.

or

$$\frac{[H]\,[MHY]}{[H_2Y]} = K'_{k_1} - \frac{[H]\,[HY]}{[H_2Y]} .$$

Dividing this equation by the equation which defines K_2,

$$\frac{[H]\,[HY]}{[H_2Y]} = K_2 ,$$

gives

$$\frac{[H_2Y]}{[H]\,[HY]} \times \frac{[H]\,[MHY]}{[H_2Y]} = \frac{K'_{k_1}}{K_2} - 1$$

or

$$\frac{[MHY]}{[MY]} = \frac{K'_{k_1} - K_2}{K_2} .$$

This last equation when divided by [M] gives

$$\frac{[MHY]}{[M]\,[HY]} = K_{MHY} = \frac{K'_{k_1} - K_2}{[M]\,K_2} .$$

Since the metal (M) is present in great excess and $K'_{k_1} = K'_2$,

$$K_{MHY} = \frac{K'_{k_1} - K_2}{C_M K_2} = \frac{K'_2 - K_2}{C_M K_2} . \qquad (1)$$

where C_M is the initial concentration of the metal. By a similar procedure it is found that

$$K_{MY} = \frac{K'_{K_2} - K_3K_4}{C_MK_3K_4} = \frac{K'_3K'_4 - K_3K_4}{C_MK_3K_4} . \qquad (m)$$

3. Stability of heavy metal complexes of CDTA

The method of determining stability constants described in the preceding section does not give satisfactory results for complexes more stable than the lead complex. Even in the case of lead the corrections for the ionic species H_4Y and H_3Y^- are too large for the method to be very reliable. For more stable complexes these corrections would become even larger and, in addition, throughout nearly all of the titration the solution would be so acidic that complexes such as H_2MY might be of importance. The complex competition method developed by Schwarzenbach and co-workers [1, 118] for the determination of especially stable complexes of EDTA was found to give fairly satisfactory results for the complexes of CDTA with heavy metals. The basis for this method was previously discussed in Section II A, Method 1(c). Inasmuch as the ionization constants of triaminotriethylamine trihydrochloride and the stability constants of its heavy metal complexes were determined by Schwarzenbach only at 20°C., it was necessary in this work to redetermine these values at 25°C.

a. Ionization constants of triaminotriethylamine trihydrochloride. A stock solution approximately 0.004 M in triaminotriethylamine trihydrochloride ($H_3trenCl_3$) was prepared by dissolving 0.2554 g. of $H_3trenCl_3$ in sufficient 0.1000 M $KClO_4$ solution to make a total volume of exactly 500 ml. To obtain the data necessary for calculating the ionization constants, 25 ml. of the stock solution was diluted with 75 ml. of 0.1000 M $KClO_4$ and titrated with 0.1217 N NaOH using the apparatus and procedure previously described for the titration of CDTA. The pH meter was standardized with Beckman pH 10.00 buffer.

Since no breaks are found in the titration curve (Curve A, Figure 8), the three ionization constants must be of about the same order of magnitude. A method of determining all three of these constants simultaneously from a single titration curve has been developed by Ackermann and Schwarzenbach [1].

In the treatment of this problem the symbol a is again allowed to represent the apparent degree of neutralization (i.e., moles of NaOH added per mole of $H_3trenCl_3$). The equations which apply to this system include those which define the desired ionization constants,

$$K_1 = \frac{[H]\,[H_2tren]}{[H_3tren]} , \qquad (a)$$

$$K_2 = \frac{[H]\,[H\ tren]}{[H_2tren]} , \qquad (b)$$

and

$$K_3 = \frac{[H]\,[tren]}{[H\ tren]} ; \qquad (c)$$

and an expression for the total concentration of $H_3trenCl_3$,

$$C_T = [H_3tren] + [H_2tren] + [H\ tren] + [tren] . \qquad (d)$$

In addition to these equations an expression for the hydrogen ion concentration similar to the one used in deriving K_1 and K_2 for CDTA may be written. In the present case, however, all of the ionic species of $H_3trenCl_3$ are such weak acids that hydrolysis must be taken into account. Perhaps the simplest way of doing this is to consider the free hydroxyl ions in the solution to have resulted from failure of all of the NaOH added to react with $H_3trenCl_3$. The NaOH added therefore reduces the hydrogen ion concentration by ($\underline{a}C_T$ - [OH]) rather than $\underline{a}C_T$. The equation for hydrogen ion concentration is thus given by:

$$[H] = [H_2tren] + 2[H\ tren] + 3[tren] - (\underline{a}C_T - [OH]) .$$

Upon rearrangement this becomes

$$\underline{a}C_T + [H] - [OH] = [H_2tren] + 2[H\ tren] + 3[tren] . \qquad (e)$$

Equation (e) when divided by equation (d) yields

$$\underline{a} + \frac{[H] - [OH]}{C_T} = \frac{[H_2tren] + 2[H\ tren] + 3[tren]}{[H_3tren] + [H_2tren] + [H\ tren] + [tren]} .$$

To simplify the writing of subsequent equations, the left side of the above equation is replaced by the symbol $\underline{g}$, so that

$$\underline{g} = \underline{a} + \frac{[H] - [OH]}{C_T} = \frac{[H_2tren] + 2[H\ tren] + 3[tren]}{[H_3tren] + [H_2tren] + [H\ tren] + [tren]} . \qquad (f)$$

From equations (a), (b), and (c) the concentration of the ionic species H_2tren^{++}, $H\ tren^{+}$, and tren may easily be obtained in terms of $[H_3tren]$, $[H]$, K_1, K_2, and K_3. The results of this process are:

$$[H_2tren] = \frac{K_1}{[H]}[H_3tren]$$

$$[H\ tren] = \frac{K_1K_2}{[H]^2}[H_3tren]$$

$$[tren] = \frac{K_1K_2K_3}{[H]^3}[H_3tren] \ .$$

Upon substitution of these expressions, equation (f) becomes

$$\underline{g} = \frac{\left(\frac{K_1}{[H]} + 2\frac{K_1K_2}{[H]^2} + 3\frac{K_1K_2K_3}{[H]^3}\right)[H_3tren]}{\left(1 + \frac{K_1}{[H]} + \frac{K_1K_2}{[H]^2} + \frac{K_1K_2K_3}{[H]^3}\right)[H_3tren]}$$

from which [H$_3$tren] of course cancels out.

To simplify this equation both sides are multiplied by the denominator of the right side

$$\underline{g} + \frac{K_1}{[H]}\underline{g} + \frac{K_1K_2}{[H]^2}\underline{g} + \frac{K_1K_2K_3}{[H]^3}\underline{g} = \frac{K_1}{[H]} + 2\frac{K_1K_2}{[H]^2} + 3\frac{K_1K_2K_3}{[H]^3}$$

and like terms collected,

$$\underline{g} + (\underline{g} - 1)\frac{K_1}{[H]} + (\underline{g} - 2)\frac{K_1K_2}{[H]^2} + (\underline{g} - 3)\frac{K_1K_2K_3}{[H]^3} = 0 \ . \qquad (g)$$

K_1, K_2, and K_3 may be determined by computing *g* for three sets of experimental values of *a*, pH, and C_T to obtain three simultaneous linear equations in the three unknowns (K_1, K_1K_2, and $K_1K_2K_3$) and then solving these equations by means of determinants. Additional values for K_1, K_2, and K_3 may be obtained by repeating this process for other sets of three values of *a*, pH, and C_T. This method is very laborious, however, and may advantageously be replaced by a method of successive approximations.

In this method a first approximation for K_1 is obtained by neglecting all ionic species except $[H_3tren]$ and $[H_2tren]$. If hydrolysis of these species is likewise neglected, $[H_3tren]$ will be equal to $[H_2tren]$ when *a* is 0.5 . At this point then

$$K_1 = \frac{[H]\,[H_2tren]}{[H_3tren]} = [H] \qquad (h)$$

with sufficient accuracy to serve as a first approximation.

Using this approximate value of K_1, the values of K_2 and K_3 may be estimated by a graphical method similar to that employed for the first two ionization constants of CDTA. For this purpose equation (g) is rearranged to:

$$\underline{g} + (\underline{g} - 1)\frac{K_1}{[H]} + (\underline{g} - 3)\frac{K_1K_2K_3}{[H]^3} = -(\underline{g} - 2)\frac{K_1K_2}{[H]^2}$$

and both sides divided by K_2 to give

$$\left(\underline{g} + (\underline{g} - 1)\frac{K_1}{[H]}\right)\frac{1}{K_2} + \frac{(\underline{g} - 3)\ K_1}{[H]^3}\ K_3 = -(\underline{g} - 1)\frac{K_1}{[H]^2}\ . \qquad (1)$$

The intercepts A and B to be plotted for equation (1) are:

$$A = -\frac{(\underline{g} - 2)\frac{K_1}{[H]^2}}{\underline{g} - (\underline{g} - 1)\frac{K_1}{[H]}} = -\frac{(\underline{g} - 2)\ K_1}{[H]\ \left(\underline{g}[H] + (\underline{g} - 1)\ K_1\right)}$$

and

$$B = -\frac{(\underline{g} - 2)\frac{K_1}{[H]}}{(\underline{g} - 3)\frac{K_1}{[H]^3}} = -\frac{[H]\ (\underline{g} - 2)}{(\underline{g} - 3)}\ .$$

Using the approximate value for K_1 and experimental values of $\underline{a}$, pH, and C_T for a number of points between $\underline{a} = 1$ and $\underline{a} = 3$ on the titration curve, the values of the intercepts A and B for these titration points may be computed. The family of lines having these intercepts on the x and y axis, respectively, may thus be constructed. The coordinates A_0 and B_0 of the common intersection of these lines have the following relationships to K_2 and K_3:

$$K_2 = 1/A_0 \qquad \text{and} \qquad K_3 = B_0 \ .$$

These values of K_2 and K_3 may be substituted in equation (g) and a second approximation of K_1 calculated for several points on the titration curve between $\underline{a} = 0$ and $\underline{a} = 1$. Using this new value of K_1 and the graphical value of K_3, a better value for K_2 may be obtained using points on the curve from $\underline{a} = 1$ to $\underline{a} = 2$. With the aid of the new values for K_1 and K_2, K_3 may then be recalculated using points on the curve between $\underline{a} = 2$ and $\underline{a} = 3$. This entire process may again be repeated for all three constants until consistent values are obtained.

b. Stability of heavy metal complexes of triaminotriethylamine trihydrochloride. A solution which was 0.001 molar in H_3trenCl$_3$, 0.001 molar in a salt of the heavy metal, and 0.1000 molar in $KClO_4$ was titrated with 0.1 $\underline{N}$ NaOH using the same apparatus and procedure previously described. The total volume of the solution at the start was 100 ml. The pH meter was standardized with pH 7.00 buffer except in the case of the copper complex for which pH 4.00 buffer was used.

Such titration curves for several metals are shown in

Figure 8. It can be seen from these curves that in the presence of a complex-forming metal the hydrogen ions of H_3tren^{+3} are all liberated in a more acidic region. This apparent increase in the acidity is due to the reaction

$$H_3tren^{+3} \; + \; M^{++} \rightleftharpoons M\,tren^{+2} \; + \; 3H^{+} \quad .$$

The ionic species of tren which may be present during such a titration include all the ionization stages of tren, plus the metal complex. This gives rise to the equation

$$C_T \; = \; [H_3tren] + [H_2tren] + [H\,tren] + [tren] + [M\,tren] \; . \qquad (a)$$

The equation for the hydrogen ion concentration described in the previous section becomes

$$[H] \; = \; [H_2tren] + 2[H\,tren] + 3[tren] + 3[M\,tren] - (\underline{g}C_T - [OH]) \quad .$$

Substitution of the term $\underline{g}$ (as defined in the previous section) reduces this to

$$\underline{g}C_T \; = \; \underline{a}C_T + [H] - [OH] \; = \; [H_2tren] + 2[H\,tren] + 3[tren] + 3[M\,tren] \; . \qquad (b)$$

The ionic species H_2tren^{+2}, H $tren^{+}$, and tren are again eliminated by means of the equations defining the ionization constants of the acid:

$$[H_2tren] = \frac{K_1}{[H]}[H_3tren]$$

$$[H\ tren] = \frac{K_1K_2}{[H]^2}[H_3tren]$$

$$[tren] = \frac{K_1K_2K_3}{[H]^3}[H_3tren] \quad . \tag{c}$$

Substitution of these in equations (a) and (b) gives

$$C_T = \left(1 - \frac{K_1}{[H]} + \frac{K_1K_2}{[H]^2} + \frac{K_1K_2K_3}{[H]^3}\right)[H_3tren] + [M\ tren]$$

and

$$\underline{g}C_T = \left(\frac{K_1}{[H]} + 2\frac{K_1K_2}{[H]^2} + 3\frac{K_1K_2K_3}{[H]^3}\right)[H_3tren] + 3[M\ tren]$$

or

$$C_T = \alpha[H_3tren] + [M\ tren] \tag{d}$$

and

$$\underline{g}C_T = \beta\,[H_3tren] + 3[M\ tren] \tag{e}$$

where

$$\alpha = 1 + \frac{K_1}{[H]} + \frac{K_1K_2}{[H]^2} + \frac{K_1K_2K_3}{[H]^3}$$

and

$$\beta = \frac{K_1}{[H]} + 2\frac{K_1K_2}{[H]^2} + 3\frac{K_1K_2K_3}{[H]^3} .$$

The desired stability constant is the equilibrium constant for the reaction

$$K_{M\ \mathrm{tren}} = \frac{[M\ \mathrm{tren}]}{[M]\ [\mathrm{tren}]} . \qquad (f)$$

As will be shown below, all of the quantities on the right side of this equation can be expressed in terms of known or measured quantities through equations (c), (d), and (e) and the expression for the total metal concentration

$$C_M = [M] + [M\ \mathrm{tren}] .$$

This last equation may also be written

$$C_T = [M] + [M\ \mathrm{tren}] \qquad (g)$$

since equimolar amounts of $H_3trenCl_3$ and the metal were used in the titration.

Equations (d) and (e) may be solved for $[H_3 tren]$ and $[M\ tren]$ in terms of the known quantities C_T, α, β, and $\underline{g}$. This process yields

$$[H_3 tren] = \frac{C_T (3 - \underline{g})}{3\alpha - \beta} \qquad (h)$$

and

$$[M\ tren] = \frac{C_T (\alpha \underline{g} - \beta)}{3\alpha - \beta} . \qquad (i)$$

The concentration of M^{++} may be found by substituting this value for $[M\ tren]$ in equation (g):

$$C_T = [M] + \frac{C_T (\alpha \underline{g} - \beta)}{3\alpha - \beta}$$

$$[M] = C_T - \frac{C_T (\alpha \underline{g} - \beta)}{3\alpha - \beta} = \frac{C_T (3 - \underline{g})\alpha}{3\alpha - \beta} \qquad (j)$$

Equation (f) may be converted to

$$K_M\ tren = \frac{[M\ tren]\ [H]^3}{[M]\ [H_3 tren]\ K_1 K_2 K_3} \qquad (k)$$

when the relation between $[H_3 tren]$ and $[tren]$ shown in equation (c) is introduced. The values of the quantities $[H_3 tren]$, $[M\ tren]$, and $[M]$ from equations (h), (i), and (j) may be substituted into equation (k) to give

$$K_{M\ \text{tren}} = \frac{\left(\dfrac{C_T\ (\alpha \underline{g} - \beta\ )}{3\alpha - \beta}\right)[H]^2}{\left(\dfrac{C_T\ (3 - \underline{g})\,\alpha}{3\alpha\ - \beta}\right)\left(\dfrac{C_T\ (3 - \underline{g})}{3\alpha\ - \beta}\right) K_1K_2K_3} \cdot$$

This may be simplified to

$$K_{M\ \text{tren}} = \frac{C_T\ (\alpha \underline{g} - \beta\ )\ [H]^2}{\dfrac{C_T^2\ \alpha\,(3 - \underline{g})^2\ K_1K_2K_3}{3\alpha\ - \beta}}$$

which further reduces to

$$K_{M\ \text{tren}} = \frac{(3\alpha\ - \beta\ )\ (\ \alpha \underline{g} - \beta\ )\ [H]^2}{C_T\ \alpha\,(3 - \underline{g})^2\ K_1K_2K_3} \qquad (1)$$

from which $K_{M\ \text{tren}}$ may be calculated for all sets of experimental values of $\underline{a}$, pH, and C_T.

c. Exchange reaction equilibrium constants. As was explained previously, the method used to determine the stability constants of the alkaline earth complexes of CDTA will not suffice for the determination of the more stable complexes formed by CDTA with most other bivalent metals. The complex competition method employed by Schwarzenbach and Freitag [11] for the determination of the constants for the heavy metal complexes of EDTA also gives satisfactory results with CDTA.

In this method, a solution that is approximately 0.001 molar in CDTA, $H_3trenCl_3$, and M^{++} (where M is the heavy metal) and 0.01 molar in Ca^{+2} is titrated with NaOH. The solution is acidic in the region from $\underline{a} = 0$ to $\underline{a} = 4$, the hydrogens of the CDTA being liberated during this period. A pH rise occurs at $\underline{a} = 4$ and beyond this point the hydrogen ions are produced according to the exchange reaction

$$MY^{-2} + H_3tren^{+3} + Ca^{+2} \rightleftharpoons$$

$$CaY^{-2} + M\,tren^{+2} + 3H^+ .$$

Because of the high stability of the heavy metal complexes of CDTA no exchange with tren would take place unless another metal were present to take up the Y^{-4} ions as they are released from the heavy metal complex. Calcium serves very well in this capacity since of the metals which form no complex with tren calcium forms the most stable CDTA complex.

For each point on the titration curve from $\underline{a} = 4$ to $\underline{a} = 7$ a value for the equilibrium constant of this reaction

$$K_{ex} = \frac{[H]^3\,[M\,tren]\,[CaY]}{[Ca]\,[H_3tren]\,[MY]} \qquad (a)$$

may be computed from the experimental values of $\underline{a}$, pH, and the total concentrations of the various substances added. For this purpose the following relationships are employed:

Total concentration of metal =

$$C_M = [M\ \mathrm{tren}] + [MY] + [M] \tag{a}$$

Total concentration of calcium =

$$C' = [CaY] + [Ca] \tag{b}$$

Total concentration of CDTA =

$$C_Y = [CaY] + [MY] + \sum_{i=0}^{4} [H_iY] \tag{c}$$

Total concentration of tren =

$$C_T = [M\ \mathrm{tren}] + \sum_{i=0}^{3} [H_i\mathrm{tren}] \tag{d}$$

and

$$[H] = 3[M\ \mathrm{tren}] + \sum_{i=0}^{2} (3-i)[H_i\mathrm{tren}] + \sum_{i=0}^{3} (4-i)[H_iY] + 4[MY] + 4[CaY] - (\underline{a}C-[OH])\ . \tag{e}$$

In all cases studied equation (a) may be simplified by neglecting [M] in comparison with [M tren] and [MY]. In the presence of a tenfold excess of calcium in neutral or alkaline solution virtually all the CDTA not in the form of MY^{-2} will have formed a complex with calcium, hence the terms involving H_iY may be neglected in equations (c) and (e). As in the preceding section on the metal complexes of tren,

$$\sum_{i=0}^{3} [H_i\text{tren}] = \alpha [H_3\text{tren}]$$

and

$$\sum_{i=0}^{2} (3-i)[H_i\text{tren}] = \beta [H_3\text{tren}]$$

where and have the definitions given in that section. The complexity of the system was reduced materially by preparing the solutions so that C_M, C_Y, and C_T were identical.

With these simplifications introduced the above equations become:

$$C_M = C = [M\ \text{tren}] + [MY] \qquad (a')$$

$$C' = [CaY] + [Ca] \qquad (b')$$

$$C_Y = C = [CaY] + [MY] \qquad (c')$$

$$C_T = C = [M\ \text{tren}] + \alpha [H_3\text{tren}] \qquad (d')$$

and

$$[H] + \underline{a}C - [OH] =$$

$$3[M\ tren] + \beta[H_3tren] + 4[MY] + 4[CaY] \quad . \qquad (e')$$

Substitution of equation (c') in equation (e') converts the latter to

$$\underline{a}C + [H] - [OH] =$$

$$3[M\ tren] + \beta[H_3tren] + 4C$$

or

$$(\underline{a} - 4)C + [H] - [OH] =$$

$$3[M\ tren] + \beta[H_3tren] \quad . \qquad (f)$$

From equation (d')

$$[M\ tren] = C - \alpha[H_3tren] ,$$

which may be substituted into equation (f) to obtain

$$(\underline{a} - 4)C + [H] - [OH] =$$

$$3C - 3\alpha[H_3tren] + \beta[H_3tren]$$

from which

$$[H_3tren] = \frac{(7 - \underline{a})C - [H] + [OH]}{3\alpha - \beta} \qquad (g)$$

For convenience, let

$$\underline{g}' = (7 - \underline{a})C - [H] + [OH] , \qquad (h)$$

then

$$[H_3\text{tren}] = \frac{\underline{g}'}{3\alpha - \beta} . \qquad (i)$$

Combining this equation with equation (d') gives

$$[M\ \text{tren}] = C - \frac{\alpha\underline{g}'}{3\alpha - \beta} . \qquad (j)$$

This may in turn be placed in equation (a') to obtain

$$[MY] = C - \left(C - \frac{\alpha\underline{g}'}{3\alpha - \beta}\right) = \frac{\alpha\underline{g}'}{3\alpha - \beta} . \qquad (k)$$

Equation (k) in conjunction with equation (c') yields

$$[CaY] = C - \frac{\alpha\underline{g}'}{3\alpha - \beta} \qquad (l)$$

which with equation (b') permits the evaluation of the last unknown

$$[Ca] = C' - C + \frac{\alpha\underline{g}'}{3\alpha - \beta} . \qquad (m)$$

An expression for calculating K_{ex} results from the substitution of equations (i), (j), (k), (l), and (m) in equation (a) so that

$$K_{ex} = \frac{[H]^3 \left(C - \frac{\alpha \underline{g}'}{3\alpha - \beta} \right) \left(C - \frac{\alpha \underline{g}'}{3\alpha - \beta} \right)}{\left(C' - C + \frac{\alpha \underline{g}'}{3\alpha - \beta} \right) \left(\frac{\underline{g}'}{3\alpha - \beta} \right) \left(\frac{\alpha \underline{g}'}{3\alpha - \beta} \right)}$$

or

$$K_{ex} = \frac{[H]^3 \left(C - \frac{\alpha \underline{g}'}{3\alpha - \beta} \right)^2}{\left(C' - C + \frac{\alpha \underline{g}'}{3\alpha - \beta} \right) \left(\frac{\underline{g}}{3\alpha - \beta} \right)^2 \alpha} \tag{n}$$

Using equation (n), K_{ex} could be calculated for each experimental point between $\underline{a} = 4$ and $\underline{a} = 7$ on a titration curve of a solution containing equimolar concentrations of CDTA, H_3tren Cl_3, and a salt of the metal under investigation, plus a tenfold excess of a calcium salt.

Schwarzenbach and Freitag found, however, that the reaction between tren and a metal complex of EDTA was too slow to permit a normal titration to be carried out. To overcome this difficulty the mixture to be titrated was placed in five individual flasks and different amounts of NaOH added to each of these aliquots. These solutions were then allowed to equilibrate for 24 hours before the pH was measured. In the present work this kinetic factor was found to be somewhat more serious with CDTA complexes (perhaps because of their higher stability), hence the time allowed for equilibration was increased to two days. This time proved adequate except for the nickel complex which required seven days.

The individual solutions upon which the pH measurements were made consisted of the following: (a) 5.00 ml. of 0.01 M $H_3trenCl_3$, (b) 25.00 ml. of 0.01 M CDTA, (c) 5.00 ml. of a 0.01 M solution of a salt of the heavy metal, (d) 5.00 ml. of 0.1 M $CaCl_2$, (e) 1.8-2.6 ml. of 0.1217 N NaOH, and (f) sufficient 0.0600 M $KClO_4$ to make a 50.0 ml. solution. The $H_3trenCl_3$, CDTA, heavy metal salt, and $CaCl_2$ solutions were all 0.0600 molar in $KClO_4$. The five individual solutions prepared in this way for each heavy metal were thus 0.001 molar in CDTA, $H_3trenCl_3$, and M^{+2}; 0.01 molar in Ca^{+2}; and had an ionic strength of 0.1. After being thoroughly mixed, these solutions (in 50-ml. glass-stoppered volumetric flasks) were maintained at 25.00°C. in a constant temperature water bath. After two days (seven days in the case of nickel), a portion of each solution was transferred to a glass-stoppered weighing bottle also maintained at 25.00°C., and the pH of each solution measured using the same pH meter and electrode system previously described. The pH meter was standardized with pH 10.00 buffer in the case of the manganese, nickel, and cobalt complexes and with pH 7.00 buffer in the case of the copper, zinc, and cadmium complexes. The value of K_{ex} for each individual solution was then computed according to equation (n) from the measured pH, the initial concentration of the various reactants, and the amount of NaOH added.

d. Stability constants of heavy metal complexes of CDTA. An equation relating such a measured equilibrium constant, K_{ex}, to the desired stability constant may be derived in the following manner. By combining the equations which define the ionization constants of $H_3trenCl_3$, the expression for the overall dissociation of this acid is found to be

$$K_1K_2K_3 = \frac{[H]^3\,[tren]}{[H_3tren]} .$$

Multiplication of this equation by the equations which define $K_{M\ tren}$ and K_{CaY} gives

$$K_1K_2K_3\ K_{M\ tren}\ K_{CaY} =$$

$$\frac{[H]^3\,[tren]}{[H_3tren]} \times \frac{[M\ tren]}{[M]\,[tren]} \times \frac{[CaY]}{[Ca]\,[Y]}$$

which reduces to

$$K_1K_2K_3\ K_{M\ tren}\ K_{CaY} = \frac{[H]^3\ [M\ tren]\ [CaY]}{[H_3tren]\ [M]\ [Ca]\ [Y]}\ . \qquad (o)$$

Division of the equation which defines K_{ex} [see equation (a) above] by equation (o) yields

$$\frac{K_{ex}}{K_1K_2K_3\ K_{M\ tren}\ K_{CaY}} =$$

$$\frac{[H]^3\ [M\ tren]\ [CaY]}{[Ca]\ [H_3tren]\ [MY]} \times \frac{[H_3tren]\ [M]\ [Ca]\ [Y]}{[H]^3\ [M\ tren]\ [CaY]}$$

which may be simplified to

$$\frac{K_{ex}}{K_1K_2K_3\ K_{M\ tren}\ K_{CaY}} = \frac{[M]\ [Y]}{[MY]}\ .$$

The right-hand side of this expression is simply the reciprocal of K_{MY}; hence,

$$K_{MY} = \frac{K_1K_2K_3\ K_{M\ tren}\ K_{CaY}}{K_{ex}}\ . \qquad (p)$$

For ease of computation, equation (p) may be converted to logarithms, giving

$$\log K_{MY} = \log K_{M\,\mathrm{tren}} + \log K_{CaY} - \log K_{ex} - (pK_1 + pK_2 + pK_3) \qquad (q)$$

which was the expression employed in the present work for computing the stability constants of the various heavy metal complexes of CDTA.

C. Experimental Results

Using the procedures described in Section III B, paragraphs 1 and 2, pH titrations were carried out on (1) CDTA alone and (2) CDTA in the presence of a fifteenfold excess of barium, strontium, magnesium, calcium, and lead. These titrations were performed in duplicate using both stock solutions of CDTA (see Section III B, paragraph 1) except in case of lead, for which only solution II was used. The data obtained in these titrations are shown in Tables 3, 4, 5, 6, 7, and 8. The titration curves drawn from these data for solution I titrations are shown in Figure 1. In order that the curve for the titration of CDTA solution II in the presence of excess lead could also be included for comparison, these curves show the measured pH plotted as a function of a (*i.e.*, moles of KOH per mole of CDTA) rather than as a function of the volume of KOH added. When put on this basis,

Table 3

Titration of CDTA with Potassium Hydroxide[a]

Run I. CDTA Solution I

pH meter standardized at 4.00			pH meter standardized at 7.00			pH meter standardized at 10.00		
Ml. KOH	a	pH	Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.09	1.656	2.115	5.46	2.432	3.106	9.47
0.201	0.257	3.18	1.701	2.172	5.63	2.452	3.131	9.65
0.401	0.512	3.28	1.751	2.236	5.77	2.502	3.195	9.90
0.600	0.766	3.41	1.801	2.300	5.90	2.553	3.260	10.07
0.800	1.022	3.56	1.901	2.428	6.13	2.603	3.324	10.19
1.002	1.280	3.74	1.922	2.454	6.18	2.653	3.388	10.28
1.200	1.532	3.97	1.942	2.480	6.22	2.703	3.452	10.36
1.300	1.660	4.14	1.961	2.504	6.26	2.754	3.517	10.43
1.400	1.788	4.36	1.983	2.532	6.31	2.803	3.581	10.49
1.450	1.852	4.50	2.001	2.555	6.36	2.853	3.645	10.53
1.500	1.916	4.69	2.100	2.682	6.59	2.907	3.712	10.57
1.551	1.981	4.93	2.200	2.809	6.98	2.957	3.776	10.61
1.601	2.044	5.17	2.251	2.875	7.10	3.005	3.837	10.65
			2.282	2.914	7.29	3.054	3.900	10.69
			2.302	2.940	7.46	3.106	3.866	10.72
			2.312	2.952	7.60	3.156	4.030	10.75
			2.322	2.965	7.75	3.207	4.095	10.78
			2.332	2.978	7.93			
			2.342	2.991	8.19			
			2.352	3.004	8.47			
			2.363	3.018	8.73			
			2.372	3.029	8.90			
			2.382	3.042	9.05			
			2.392	3.055	9.18			
			2.402	3.067	9.28			

[a] C_A = 0.001 M; N_{KOH} = 0.1215.

Table 3 (continued)

Run II. CDTA Solution II

pH meter standardized at 4.00			pH meter standardized at 7.00			pH meter standardized at 10.00		
Ml. KOH	a	pH	Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.06	1.955	2.207	5.71	2.752	3.107	9.56
0.200	0.226	3.14	2.002	2.260	5.82	2.803	3.165	9.85
0.400	0.452	3.24	2.051	2.316	5.93	2.853	3.221	10.03
0.600	0.677	3.34	2.101	2.372	6.03	2.903	3.277	10.16
0.800	0.903	3.47	2.151	2.428	6.13	2.954	3.335	10.25
0.999	1.128	3.61	2.201	2.485	6.22	3.004	3.392	10.33
1.199	1.354	3.79	2.251	2.541	6.32	3.054	3.448	10.40
1.299	1.467	3.90	2.302	2.599	6.42	3.104	3.504	10.46
1.399	1.579	4.02	2.352	2.655	6.53	3.155	3.562	10.51
1.500	1.694	4.19	2.402	2.712	6.64	3.205	3.618	10.56
1.601	1.808	4.40	2.452	2.768	6.77	3.255	3.675	10.60
1.651	1.864	4.54	2.502	2.825	6.92	3.305	3.731	10.63
1.681	1.898	4.63	2.552	2.881	7.11	3.355	3.788	10.67
1.701	1.920	4.71	2.582	2.915	7.28	3.406	3.845	10.71
1.721	1.943	4.79	2.602	2.938	7.43	3.456	3.902	10.74
1.741	1.966	4.87	2.612	2.949	7.52	3.506	3.958	10.77
1.761	1.988	4.96	2.622	2.960	7.63	3.556	4.015	10.79
1.781	2.011	5.04	2.633	2.973	7.78			
1.801	2.033	5.16	2.643	2.984	8.00			
1.821	2.056	5.24	2.653	2.995	8.24			
1.851	2.090	5.36	2.663	3.007	8.59			
1.871	2.112	5.43	2.673	3.018	8.83			
1.901	2.146	5.54	2.686	3.032	9.08			
1.951	2.203	5.68	2.703	3.052	9.28			
			2.713	3.063	9.37			
			2.733	3.086	9.51			

Table 4

Titration of CDTA in the Presence of Excess Barium[a]

Run I. CDTA Solution I

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.03	2.602	3.323	6.61
0.20	0.26	3.10	2.702	3.450	6.82
0.40	0.51	3.18	2.803	3.579	7.03
0.60	0.77	3.28	2.905	3.710	7.27
0.70	0.89	3.33	2.954	3.772	7.42
0.80	1.02	3.39	3.004	3.836	7.61
0.90	1.15	3.47	3.054	3.900	7.85
1.00	1.28	3.55	3.084	3.938	8.08
1.10	1.40	3.64	3.104	3.964	8.31
1.20	1.53	3.74	3.115	3.978	8.45
1.30	1.66	3.87	3.124	3.989	8.60
1.40	1.79	4.03	3.135	4.003	8.77
1.50	1.92	4.20	3.145	4.016	8.93
1.600	2.043	4.41	3.155	4.029	9.09
1.701	2.172	4.61	3.165	4.042	9.22
1.801	2.300	4.81	3.175	4.054	9.33
1.901	2.428	4.98	3.185	4.067	9.42
2.001	2.555	5.18	3.205	4.093	9.57
2.101	2.683	5.39	3.225	4.118	9.69
2.201	2.811	5.61	3.255	4.157	9.84
2.302	2.940	5.86	3.305	4.220	10.03
2.402	3.067	6.13	3.406	4.349	10.27
2.502	3.195	6.38			

[a] C_A = 0.001 $\underline{M}$; C_{Ba} = 0.0150 $\underline{M}$; N_{KOH} = 0.1215.

Table 4 (continued)

Run II. CDTA Solution II

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.00	2.800	3.161	6.32
0.20	0.23	3.06	2.900	3.274	6.52
0.40	0.45	3.13	3.001	3.388	6.71
0.60	0.68	3.22	3.101	3.501	6.90
0.70	0.79	3.27	3.202	3.615	7.09
0.80	0.90	3.32	3.305	3.731	7.31
0.90	1.02	3.37	3.352	3.784	7.44
1.00	1.13	3.43	3.403	3.842	7.61
1.10	1.24	3.50	3.453	3.898	7.82
1.20	1.35	3.58	3.483	3.932	8.00
1.30	1.47	3.66	3.503	3.955	8.18
1.40	1.58	3.76	3.513	3.966	8.28
1.50	1.69	3.89	3.523	3.977	8.40
1.60	1.81	4.03	3.533	3.989	8.55
1.70	1.92	4.18	3.543	4.000	8.72
1.798	2.030	4.37	3.553	4.011	8.90
1.899	2.144	4.57	3.563	4.023	9.06
1.998	2.256	4.74	3.573	4.034	9.20
2.098	2.369	4.91	3.583	4.045	9.31
2.197	2.480	5.08	3.593	4.056	9.41
2.298	2.594	5.25	3.603	4.068	9.50
2.399	2.708	5.43	3.624	4.091	9.64
2.498	2.820	5.63	3.654	4.125	9.81
2.598	2.933	5.85	3.704	4.182	10.02
2.699	3.047	6.08	3.804	4.295	10.26

Table 5

Titration of CDTA in the Presence of Excess Strontium[a]

Run I. CDTA Solution I

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.04	2.702	3.450	5.23
0.20	0.26	3.12	2.802	3.578	5.34
0.40	0.51	3.21	2.875	3.671	5.44
0.60	0.77	3.31	2.925	3.735	5.52
0.81	1.03	3.44	2.975	3.799	5.63
0.90	1.15	3.52	3.025	3.863	5.78
1.00	1.28	3.59	3.055	3.901	5.93
1.10	1.40	3.68	3.075	3.927	6.07
1.20	1.53	3.78	3.085	3.940	6.14
1.30	1.66	3.90	3.095	3.952	6.26
1.40	1.79	4.02	3.106	3.966	6.43
1.50	1.92	4.15	3.116	3.979	6.69
1.601	2.044	4.28	3.122	3.987	6.97
1.700	2.171	4.40	3.126	3.992	7.35
1.800	2.299	4.51	3.131	3.998	7.91
1.901	2.428	4.60	3.136	4.005	8.27
2.000	2.554	4.68	3.146	4.017	8.71
2.100	2.682	4.76	3.156	4.030	8.92
2.201	2.811	4.83	3.176	4.056	9.22
2.301	2.938	4.91	3.196	4.081	9.41
2.401	3.066	4.98	3.226	4.120	9.64
2.501	3.194	5.06	3.276	4.183	9.90
2.600	3.320	5.13	3.377	4.312	10.18

[a] C_A = 0.001 M; C_{Sr} = 0.0150 M; N_{KOH} = 0.1215.

Table 5 (continued)

Run II. CDTA Solution II

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.00	3.004	3.392	5.20
0.20	0.23	3.07	3.102	3.502	5.28
0.40	0.45	3.15	3.206	3.620	5.38
0.60	0.68	3.24	3.305	3.731	5.52
0.80	0.90	3.35	3.355	3.788	5.61
0.90	1.02	3.41	3.386	3.823	5.68
1.00	1.13	3.47	3.406	3.845	5.73
1.10	1.24	3.55	3.426	3.868	5.79
1.20	1.35	3.62	3.446	3.891	5.88
1.30	1.47	3.71	3.466	3.913	5.99
1.40	1.58	3.80	3.486	3.936	6.13
1.50	1.69	3.91	3.506	3.958	6.33
1.60	1.81	4.02	3.515	3.968	6.49
1.701	1.920	4.14	3.526	3.981	6.81
1.801	2.033	4.26	3.536	3.992	7.40
1.901	2.146	4.37	3.546	4.003	8.39
2.001	2.259	4.48	3.556	4.015	8.82
2.101	2.372	4.56	3.567	4.027	9.03
2.201	2.485	4.64	3.576	4.037	9.16
2.301	2.598	4.71	3.586	4.049	9.28
2.402	2.712	4.78	3.606	4.071	9.48
2.502	2.825	4.85	3.626	4.094	9.63
2.600	2.935	4.91	3.657	4.129	9.80
2.701	3.049	4.97	3.707	4.185	10.00
2.802	3.163	5.04	3.808	4.299	10.24
2.904	3.279	5.12			

Table 6

Titration of CDTA in the Presence of Excess Magnesium[a]

Run I. CDTA Solution I

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.08	2.803	3.579	4.53
0.40	0.51	3.26	2.904	3.708	4.63
0.60	0.77	3.37	3.004	3.836	4.79
0.80	1.02	3.48	3.054	3.900	4.93
1.00	1.28	3.61	3.084	3.938	5.08
1.20	1.53	3.74	3.105	3.965	5.30
1.40	1.79	3.85	3.114	3.977	5.47
1.606	2.051	3.94	3.124	3.989	5.88
1.700	2.171	3.98	3.136	4.005	7.60
1.803	2.302	4.03	3.146	4.017	8.37
1.903	2.430	4.07	3.155	4.029	8.66
2.001	2.555	4.11	3.165	4.042	8.87
2.103	2.686	4.15	3.175	4.054	9.03
2.201	2.811	4.19	3.195	4.080	9.23
2.302	2.940	4.23	3.225	4.118	9.46
2.402	3.067	4.28	3.225	4.157	9.62
2.502	3.195	4.33	3.335	4.259	9.81
2.602	3.323	4.39	3.41	4.35	10.07
2.703	3.452	4.46	3.51	4.48	10.21

[a] $C_A = 0.001\ \underline{M}$; $C_{Mg} = 0.0150\ \underline{M}$; $N_{KOH} = 0.1215$.

Table 6 (continued)

Run II. CDTA Solution I

Ml. KOH	a	pH
0.000	0.000	3.05
0.20	0.23	3.12
0.40	0.45	3.20
0.60	0.68	3.30
0.80	0.90	3.41
1.00	1.13	3.53
1.20	1.35	3.64
1.40	1.58	3.75
1.60	1.81	3.85
1.802	2.034	3.94
1.902	2.147	3.98
2.001	2.259	4.02
2.101	2.372	4.06
2.201	2.485	4.10
2.302	2.599	4.13
2.403	2.713	4.17
2.502	2.825	4.20
2.611	2.948	4.24
2.703	3.052	4.28
2.803	3.165	4.32
2.904	3.279	4.37
3.004	3.392	4.43
3.104	3.504	4.49
3.205	3.618	4.56
3.305	3.731	4.65
3.407	3.846	4.80
3.456	3.902	4.93
3.486	3.936	5.05
3.506	3.958	5.21
3.516	3.970	5.32
3.526	3.981	5.54
3.536	3.992	6.09
3.546	4.003	7.51
3.556	4.015	8.43
3.566	4.026	8.75
3.586	4.049	9.08
3.606	4.071	9.31
3.657	4.129	9.62
3.707	4.185	9.81
3.81	4.30	10.07
3.91	4.41	10.21

Table 7

Titration of CDTA in the Presence of Excess Calcium[a]

Run I. CDTA Solution I

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	3.02	2.704	3.453	4.08
0.20	0.25	3.09	2.803	3.579	4.16
0.40	0.51	3.15	2.907	3.712	4.30
0.60	0.76	3.22	3.003	3.835	4.51
0.80	1.02	3.30	3.055	3.901	4.72
1.00	1.28	3.38	3.087	3.942	5.00
1.20	1.53	3.45	3.098	3.956	5.17
1.40	1.78	3.52	3.107	3.968	5.35
1.601	2.044	3.59	3.118	3.982	5.80
1.704	2.176	3.63	3.129	3.996	6.76
1.802	2.301	3.66	3.138	4.007	8.07
1.900	2.426	3.69	3.150	4.023	8.61
2.001	2.555	3.73	3.158	4.033	8.81
2.100	2.682	3.77	3.168	4.046	9.01
2.201	2.811	3.81	3.188	4.071	9.24
2.301	2.938	3.85	3.208	4.097	9.42
2.400	3.065	3.90	3.239	4.136	9.66
2.506	3.200	3.95	3.289	4.200	9.90
2.602	3.323	4.01	3.389	4.328	10.18

[a] C_A = 0.001 M; C_{Ca} = 0.0150 M; N_{KOH} = 0.1215.

Table 7 (continued)

Run II. CDTA Solution II

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	2.99	3.202	3.615	4.19
0.20	0.22	3.06	3.303	3.729	4.31
0.40	0.45	3.12	3.353	3.786	4.40
0.60	0.68	3.18	3.404	3.843	4.52
0.80	0.90	3.25	3.424	3.866	4.58
1.00	1.13	3.32	3.444	3.888	4.66
1.20	1.35	3.39	3.464	3.911	4.75
1.40	1.58	3.45	3.484	3.933	4.90
1.599	1.805	3.52	3.494	3.945	5.01
1.799	2.031	3.58	3.504	3.956	5.14
1.901	2.146	3.61	3.514	3.967	5.32
2.001	2.259	3.64	3.526	3.981	5.83
2.099	2.370	3.67	3.532	3.987	6.26
2.199	2.483	3.71	3.536	3.992	7.27
2.300	2.597	3.74	3.543	4.000	8.22
2.402	2.712	3.77	3.554	4.012	8.71
2.500	2.822	3.80	3.564	4.024	8.96
2.600	2.935	3.84	3.584	4.046	9.25
2.701	3.049	3.89	3.604	4.069	9.46
2.801	3.162	3.94	3.625	4.092	9.60
2.902	3.276	3.99	3.655	4.126	9.78
3.001	3.388	4.04	3.705	4.183	9.98
3.102	3.502	4.11	3.806	4.297	10.22

Table 8

Titration of CDTA in the Presence of Excess Lead[a]

CDTA Solution II

Ml. KOH	a	pH	Ml. KOH	a	pH
0.000	0.000	2.56	2.703	3.052	3.18
0.200	0.226	2.57	2.803	3.165	3.24
0.400	0.452	2.60	2.904	3.279	3.31
0.600	0.677	2.63	3.004	3.392	3.40
0.800	0.903	2.66	3.105	3.506	3.50
1.000	1.129	2.69	3.205	3.618	3.62
1.200	1.355	2.72	3.305	3.731	3.81
1.400	1.581	2.76	3.354	3.787	3.94
1.601	1.807	2.80	3.406	3.845	4.14
1.801	2.033	2.85	3.456	3.902	4.47
1.901	2.146	2.88	3.486	3.936	4.83
2.001	2.259	2.91	3.506	3.958	5.09
2.101	2.372	2.94	3.516	3.970	5.21
2.201	2.485	2.97	3.526	3.981	5.30
2.304	2.601	3.01	3.546	4.003	5.49
2.402	2.712	3.05	3.612	4.078	5.75
2.502	2.825	3.09	3.709	4.187	5.92
2.602	2.938	3.13			

[a] C_A = 0.001 M; C_{Pb} = 0.0150 M; N_{KOH} = 0.1215.

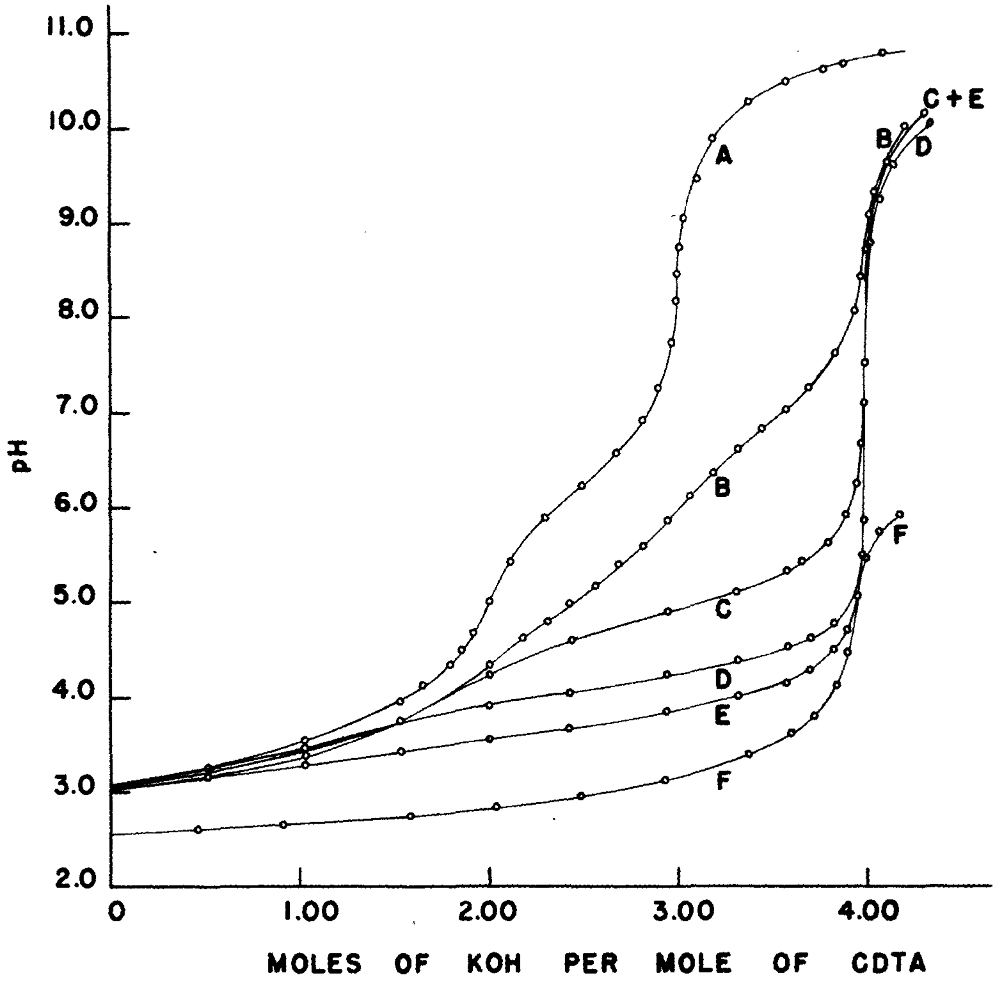

Figure 1. Titration Curves of CDTA

Curve A. CDTA Solution I
Curve B. CDTA Solution I + Barium
Curve C. CDTA Solution I + Strontium
Curve D. CDTA Solution I + Magnesium
Curve E. CDTA Solution I + Calcium
Curve F. CDTA Solution II + Lead

the curves for other solution II titrations were found to be virtually identical with the curves for the corresponding solution I titrations.

The concentration of CDTA (C_A) in the solutions titrated was determined graphically. For this purpose, the portion of each curve corresponding to the sharpest pH rise for that curve was expanded and the "end-point" of the titration estimated visually. This "end-point" was taken as the point at which $\underline{a} = 3$ in the case of the titration of the acid alone, but for the titrations in the presence of excess metal ions the "end-point" occurred at $\underline{a} = 4$. The initial concentration of CDTA was then computed from the milliliters of KOH added at the "end-point", the value of $\underline{a}$ at the "end-point", and the initial volume of the solution (100 ml.). The results of this procedure are shown in Table 9. The average values for C_A in Table 9 were employed in all subsequent calculations on data obtained from titrations involving CDTA solutions I and II. The small decrease in C_A caused by the increase in the total volume of the solution from addition of KOH was found to be negligible in all cases.

Table 9

Determination of C_A

	Metal	"End-point" KOH added (ml.)	a		$C_A x10^3$ (moles/liter)
Solution I					
	None	2.350	3		0.951
	Ba	3.132	4		0.951
	Sr	3.128	4		0.950
	Mg	3.133	4		0.951
	Ca	3.130	4		0.951
				Av.	0.951
Solution II					
	None	2.657	3		1.076
	Ba	3.546	4		1.076
	Sr	3.539	4		1.075
	Mg	3.543	4		1.076
	Ca	3.535	4		1.074
	Pb	*	-		-
				Av.	1.075

*Satisfactory end-point was not obtained due to formation of lead hydroxide.

1. Ionization constants of CDTA

a. Calculation of K_1 and K_2. Using the equations derived in Section III B, paragraph 1, the values of the intercepts (A and B) of the linear equation (f) in K_1 and K_2 were computed for each point on the titration curves from $\underline{a} = 0$ to $\underline{a} = 1.7$. The results of these computations are listed in Table 10. The values of C_A used in these calculations were the average values of this quantity given in Table 9. The value of $\underline{a}$ for each point was determined from

$$\underline{a} = \frac{\text{ml. KOH x } N_{KOH}}{C_A x 10^{\cancel{3}\,2}} .$$

The graphical solutions of equation (f) for the titrations involving CDTA solutions I and II are shown in Figures 2 and 3. The coordinates of the points of intersection (A_O and B_O) of the lines in these graphs are listed in Table 11 together with the corresponding values of pK_1 and pK_2 computed from

$$pK_1 = -\log 1/B_O \qquad \text{and} \qquad pK_2 = -\log A_O .$$

Table 10

Apparent Ionization Constants of CDTA Calculation of A and B[a]

Run I. CDTA Solution I

a	pH	$A \times 10^{4}$	$B \times 10^{-2}$
0.000	3.09	-1.03	2.09
0.257	3.18	-0.30	0.77
0.512	3.28	0.36	-1.15
0.766	3.41	0.82	-3.82
1.022	3.56	1.24	-8.63
1.280	3.74	1.62	-17.6
1.532	3.97	1.94	-36.7
1.660	4.14	2.02	-58.3

Run II. CDTA Solution II

a	pH	$A \times 10^{4}$	$B \times 10^{-2}$
0.000	3.06	-1.39	2.69
0.226	3.14	-0.66	1.54
0.452	3.24	-0.07	0.23
0.677	3.34	0.52	-2.03
0.903	3.47	0.95	-5.29
1.128	3.61	1.37	-10.7
1.354	3.79	1.66	-20.7
1.467	3.90	1.77	-29.2
1.579	4.02	1.91	-42.8
1.694	4.19	1.98	-66.5

[a] From data listed in Table 3.

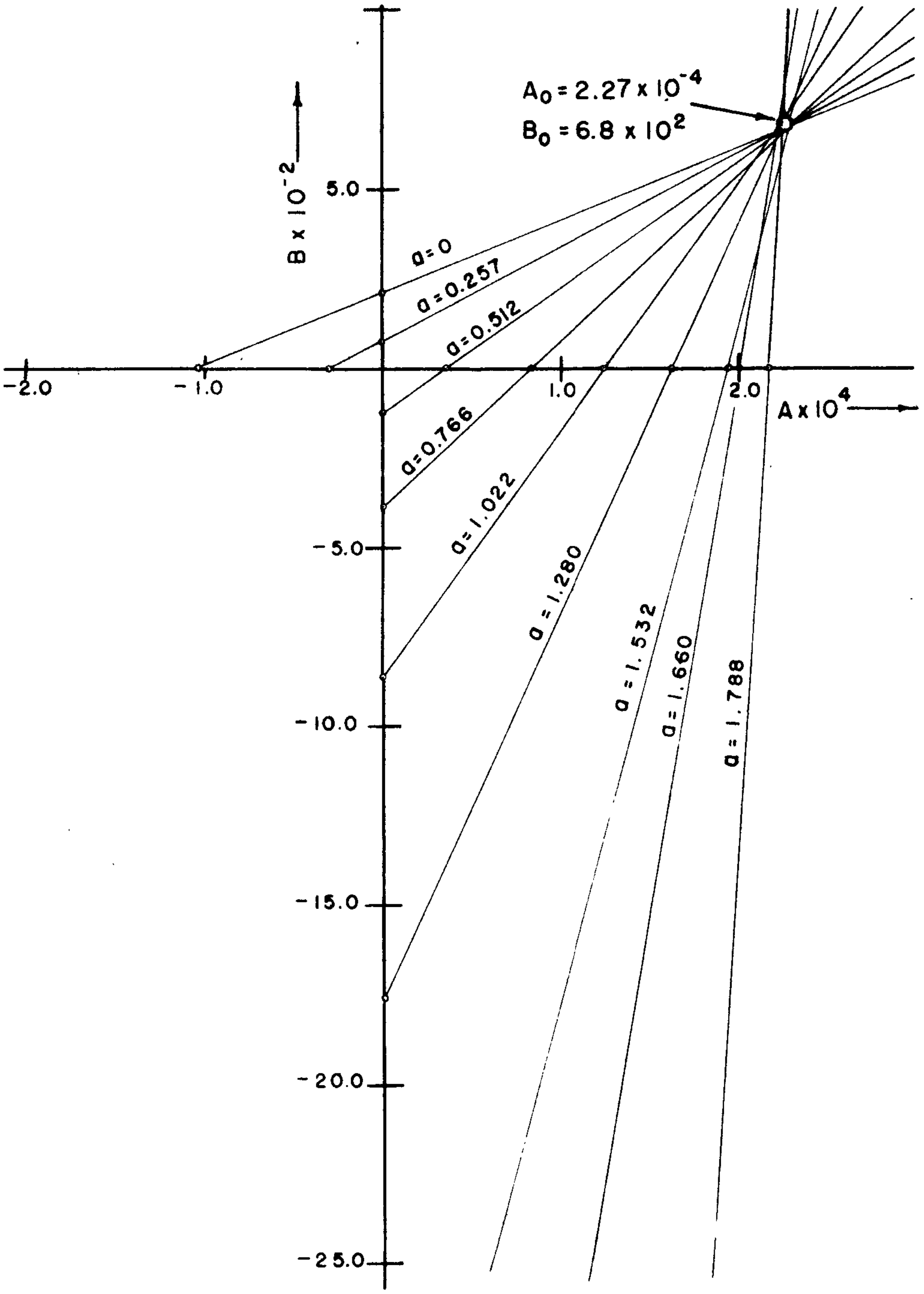

Figure 2. Apparent Ionization Constants of CDTA Determination of K_1 and K_2 (Run I)

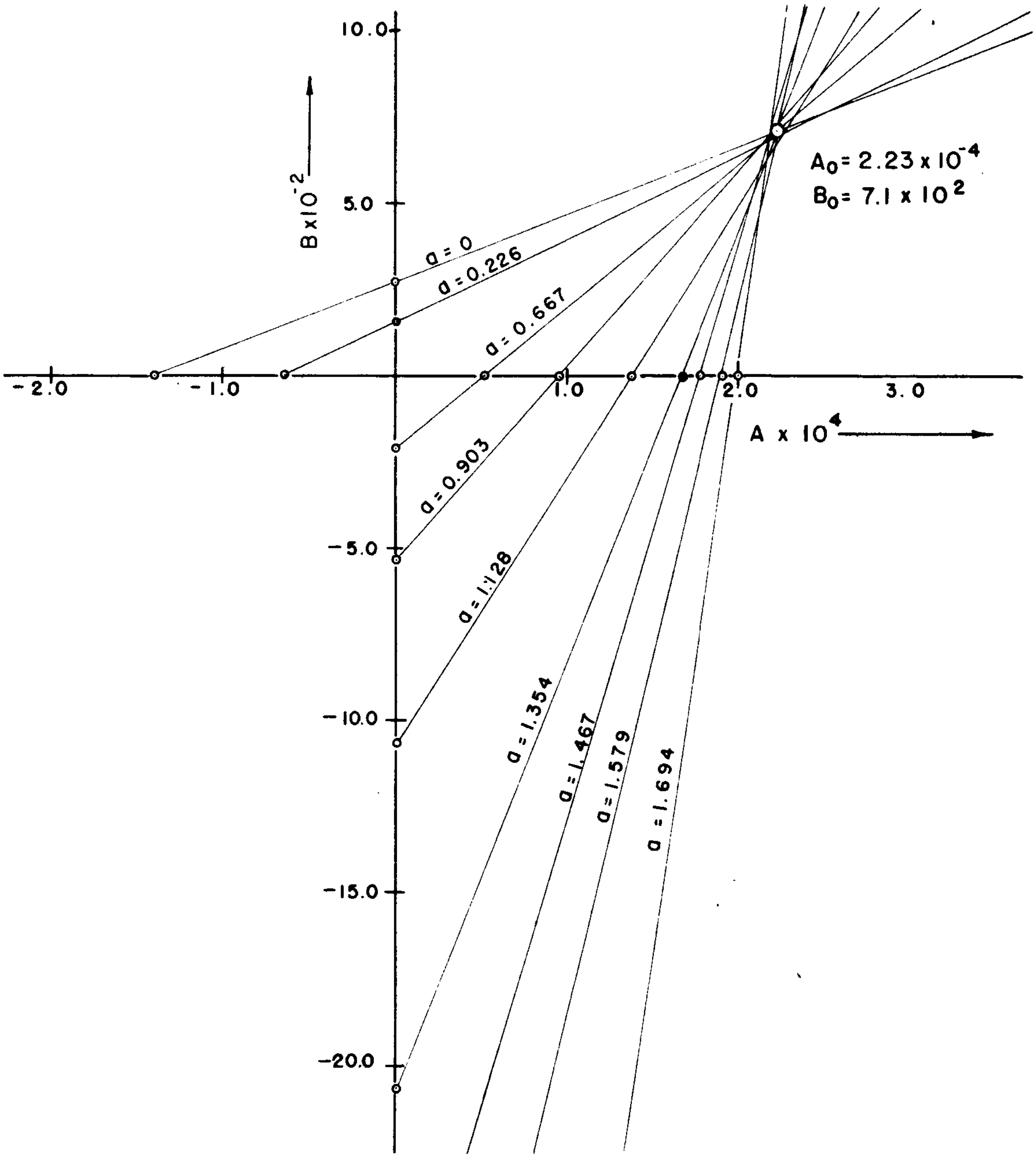

Figure 5. Apparent Ionization Constants of CDTA

Determination of K_1 and K_2 (Run II)

Table 11

Apparent Ionization Constants of CDTA[a]
Determination of K_1 and K_2

	$A_o x10^4$	$B_o x10^{-2}$	pK_1	pK_2
Run I	2.27	6.8	2.83	3.64
Run II	2.23	7.1	2.85	3.65
Av.	2.25	7.0	2.84	3.65

[a] Ionic strength = 0.1; temperature = 25.0°C.

<u>b. Determination of K_3</u>. Values of pK_3 were computed according to the equation given in Section III B, paragraph 1, for all points on the titration curves from <u>a</u> = 2.25 to <u>a</u> = 2.75. The results of these computations are shown in Table 12. For both runs, it was found that

$$pK_3 = 6.26 \; .$$

Table 12

Apparent Ionization Constants of CDTA[a]
Calculation of K_3[b]

Run I. CDTA Solution I

<u>a</u>	pH	pK_3
2.300	5.90	6.27
2.428	6.13	6.26
2.454	6.18	6.26
2.480	6.22	6.25
2.504	6.26	6.25
2.530	6.31	6.26
2.555	6.36	6.26
2.682	6.59	6.26
	Av.	6.26

Run II. CDTA Solution II

<u>a</u>	pH	pK_3
2.260	5.82	6.27
2.316	5.93	6.26
2.372	6.03	6.26
2.428	6.13	6.26
2.484	6.22	6.26
2.541	6.32	6.25
2.599	6.42	6.25
2.655	6.53	6.25
2.712	6.64	6.25
	Av.	6.26

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] From data listed in Table 3.

c. Determination of K_4. Using the equation derived in Section III B, paragraph 1, values of pK_4 were calculated for all points on the titration curves from $a = 3.25$ to $a = 4.00$. The results of these computations, given in Table 13, lead to the following (average) value for pK_4:

$$pK_4 = 10.93 .$$

Table 13

Apparent Ionization Constants of CDTA[a]
Calculation of K_4[b]

Run I. CDTA Solution I

a	pH	pK_4
3.260	10.07	10.87
3.324	10.19	10.91
3.388	10.28	10.91
3.452	10.36	10.93
3.517	10.43	10.94
3.581	10.49	10.95
3.645	10.53	10.92
3.712	10.57	10.92
3.776	10.61	10.88
3.837	10.65	10.89
3.900	10.69	10.89
3.966	10.72	10.87
	Av.	10.91

Run II. CDTA Solution II

a	pH	pK_4
3.277	10.16	10.94
3.335	10.25	10.94
3.392	10.33	10.95
3.448	10.40	10.96
3.504	10.46	10.97
3.562	10.51	10.96
3.618	10.56	10.97
3.675	10.60	10.96
3.731	10.63	10.93
3.788	10.67	10.93
3.845	10.71	10.94
3.902	10.74	10.93
3.958	10.77	10.93
	Av.	10.95

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] From data listed in Table 3.

2. Stability of lead and alkaline earth metal complexes of CDTA

a. Barium. The stability constants of the complexes formed between CDTA and barium were calculated from the data in Table 4, using the graphical procedure outlined in Section III B, paragraph 2. Values of the intercepts A and B computed for points on the titration curve from $a = 2.5$ to $a = 3.5$ are listed in Table 14. For any point outside this range of a values, the magnitude of the intercept A was too great to permit convenient plotting. Figures 4 and 5 show the graphs constructed from the intercepts listed in Table 14. The values of pK_3' and pK_4' ($-\log 1/B_0$ and $-\log A_0$, respectively) computed from the coordinates A_0 and B_0 of the intersections of the lines in these graphs are shown in Table 15. Also listed in Table 15 are the values of log K_{BaHY} and log K_{BaY} calculated from

$$K_{BaHY} = \frac{K_3' - K_3}{C_{Ba}K_3}$$

and

$$K_{BaY} = \frac{K_3'K_4' - K_3K_4}{C_{Ba}K_3K_4} .$$

Table 14

Stability Constants of CDTA-Barium Complexes Calculation of A and B[a]

Run I. CDTA Solution I

a	pH	$Ax10^7$	$Bx10^{-5}$
2.428	4.98	-37.8	1.22
2.555	5.18	-20.1	1.18
2.683	5.39	-9.69	1.12
2.811	5.61	-3.88	0.94
2.940	5.86	-0.76	0.45
3.067	6.13	0.54	-0.86
3.195	6.38	1.01	-3.90
3.323	6.61	1.17	-9.94
3.450	6.82	1.24	-20.6

Run II. CDTA Solution II

a	pH	$Ax10^6$	$Bx10^{-5}$
2.594	5.25	-16.1	1.19
2.708	5.43	-8.35	1.10
2.820	5.63	-3.53	0.92
2.933	5.85	-0.87	0.50
3.047	6.08	0.42	-0.55
3.161	6.32	0.92	-2.89
3.274	6.52	1.14	-7.13
3.388	6.71	1.24	-14.3
3.501	6.90	1.27	-26.6

[a] From data listed in Table 4.

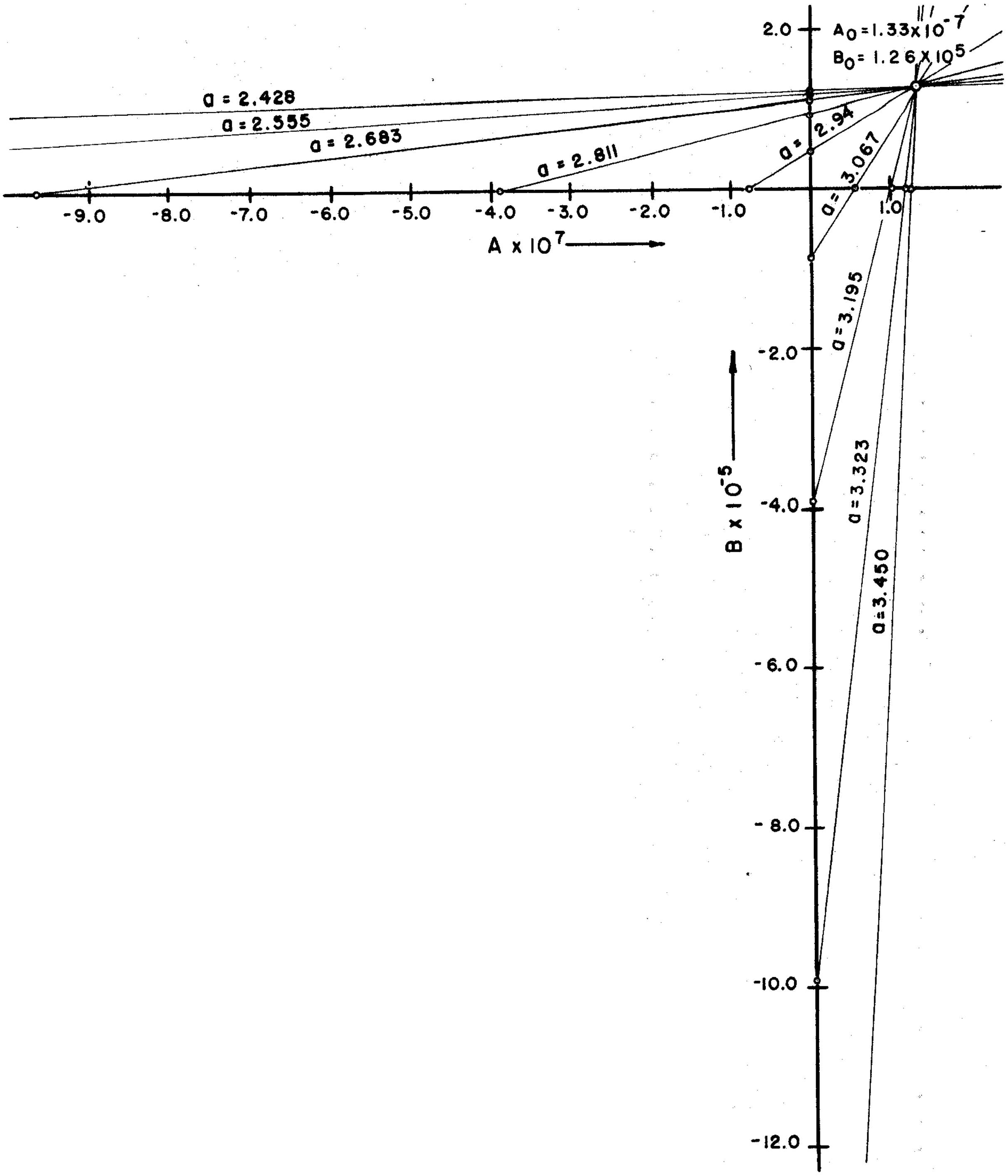

Figure 4. Stability Constants of CDTA-Barium Complexes

Determination of K_3' and K_4' (Run I)

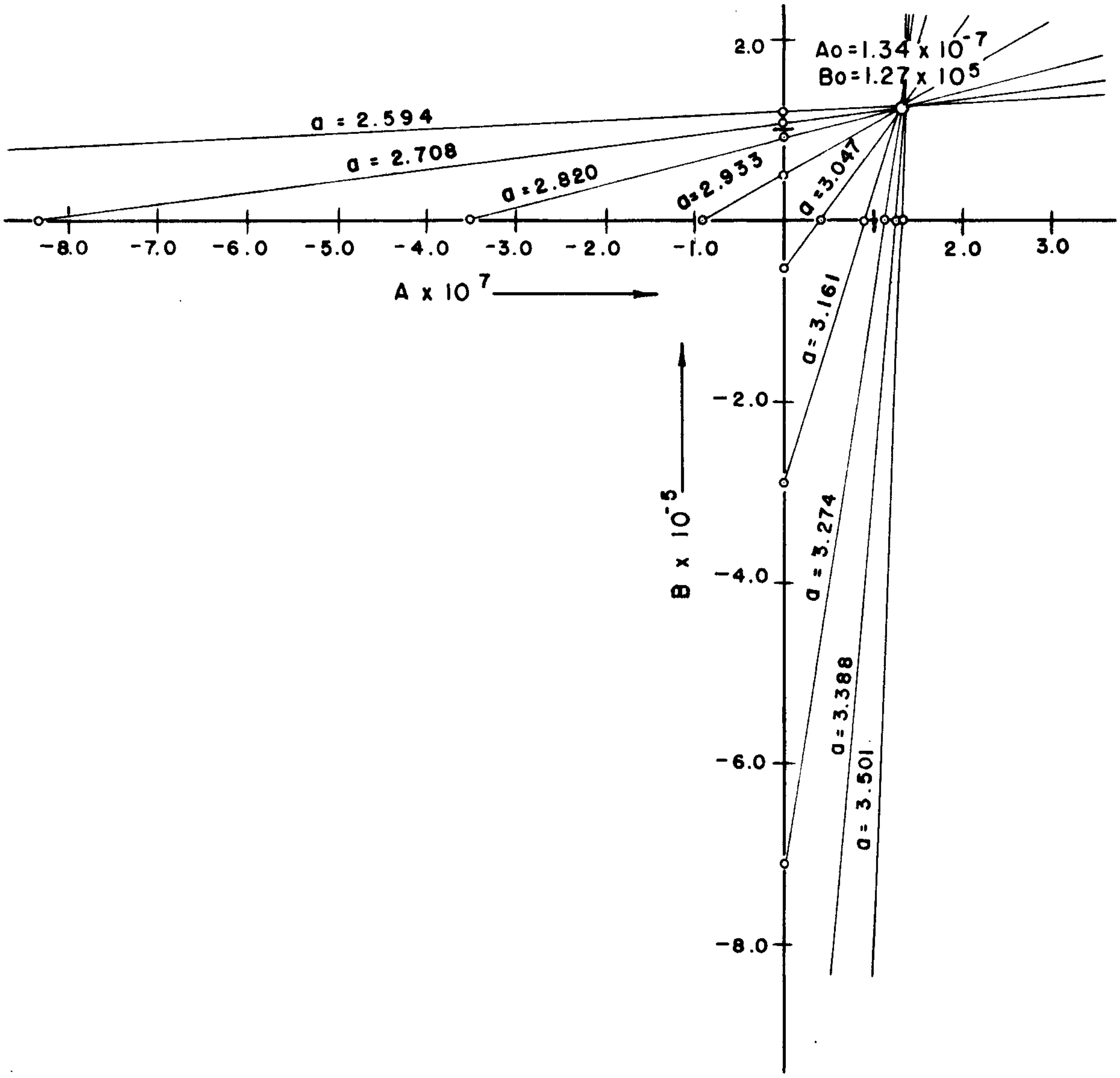

Figure 5. Stability Constants of CDTA-Barium Complexes

Determination of K_3' and K_4' (Run II)

Table 15

Stability Constants of CDTA-Barium Complexes[a]

	$K'_3 x10^6$	$K'_4 x10^7$	log K_{BaHY}	log K_{BaY}
Run I	7.9	1.33	2.94	7.02
Run II	7.9	1.34	2.94	7.02
Av.	7.9	1.34	2.94	7.02

[a] Ionic strength = 0.1; temperature = 25.0°C.

<u>b. Strontium</u>. The graphical procedure also was used for the determination of the stability constants of CDTA-strontium complexes from data in Table 5. Values of A and B computed for points on the titration curves from <u>a</u> = 2.3 to <u>a</u> = 3.6 are listed in Table 16. Figures 6 and 7 show the graphical determination of A_0 and B_0 (and, hence, K'_3 and K'_4). The corresponding values of K'_3, K'_4, log K_{SrHY}, and log K_{SrY} are listed in Table 17.

Table 16

Stability Constants of CDTA-Strontium Complexes
Calculation of A and B[a]

Run I. CDTA Solution I

a	pH	$Ax10^{5}$	$Bx10^{-4}$
2.428	4.60	-0.88	3.53
2.554	4.68	-0.62	2.83
2.682	4.76	-0.40	2.07
2.811	4.83	-0.22	1.24
2.938	4.91	-0.06*	0.38*
3.066	4.98	0.07*	-0.54*
3.194	5.06	0.22	-1.81
3.320	5.13	0.36	-3.15
3.450	5.23	0.50	-5.08
3.578	5.34	0.64	-7.81
3.671	5.44	0.75	-10.8

Run II. CDTA Solution II

a	pH	$Ax10^{5}$	$Bx10^{-4}$
2.372	4.56	-1.03	3.87
2.485	4.64	-0.76	3.27
2.598	4.71	-0.54	2.60
2.712	4.78	-0.36	1.92
2.825	4.85	-0.20	1.20
2.935	4.91	-0.06*	0.41*
3.049	4.97	0.07*	-0.48*
3.163	5.04	0.19	-1.49
3.279	5.12	0.31	-2.77
3.392	5.20	0.42	-4.31
3.502	5.28	0.54	-6.21

[a] From data listed in Table 5.

*Not shown on graph. "A" is too small to permit accurate location of line.

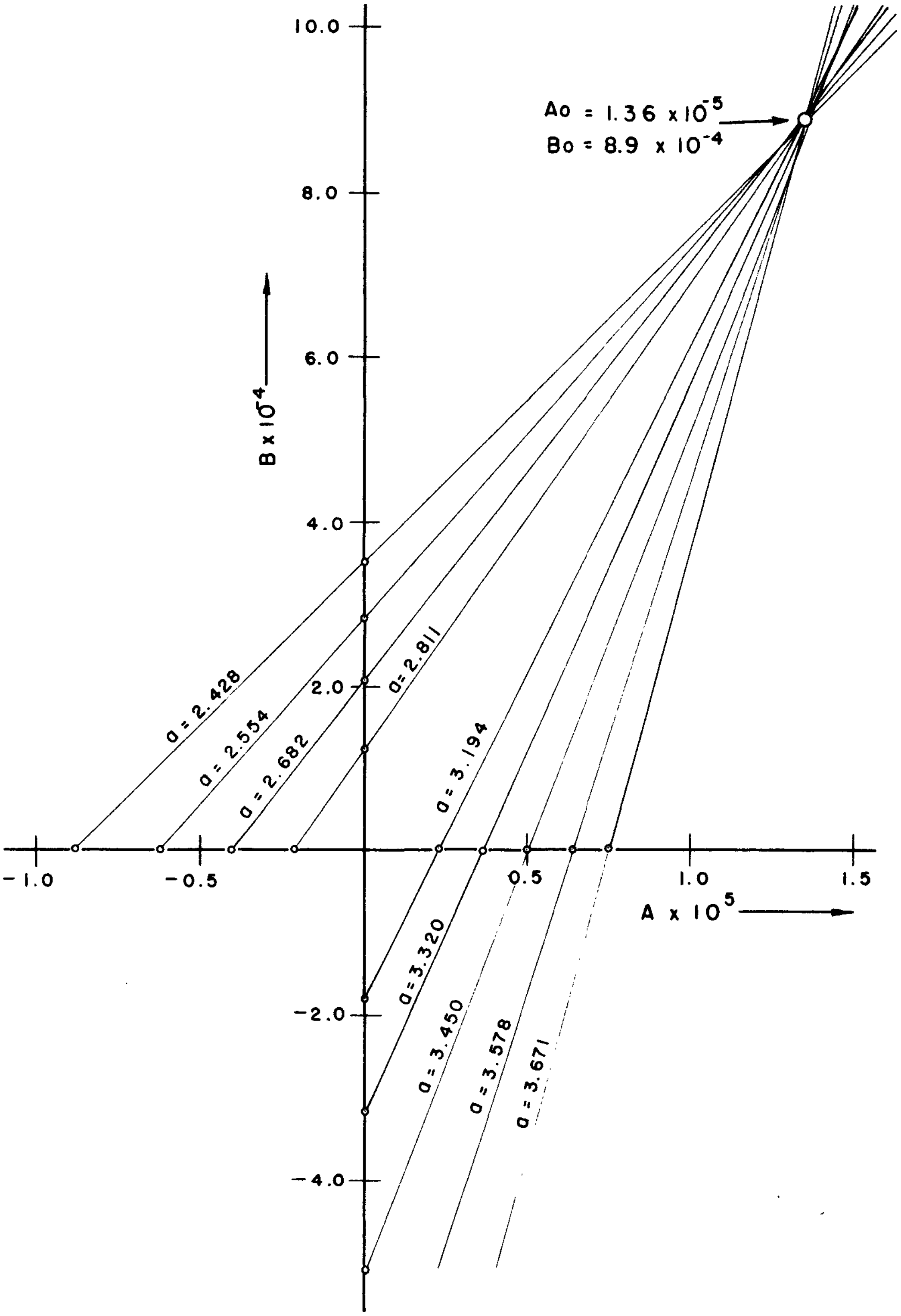

Figure 6. Stability Constants of CDTA-Strontium Complexes Determination of K_3' and K_4' (Run I)

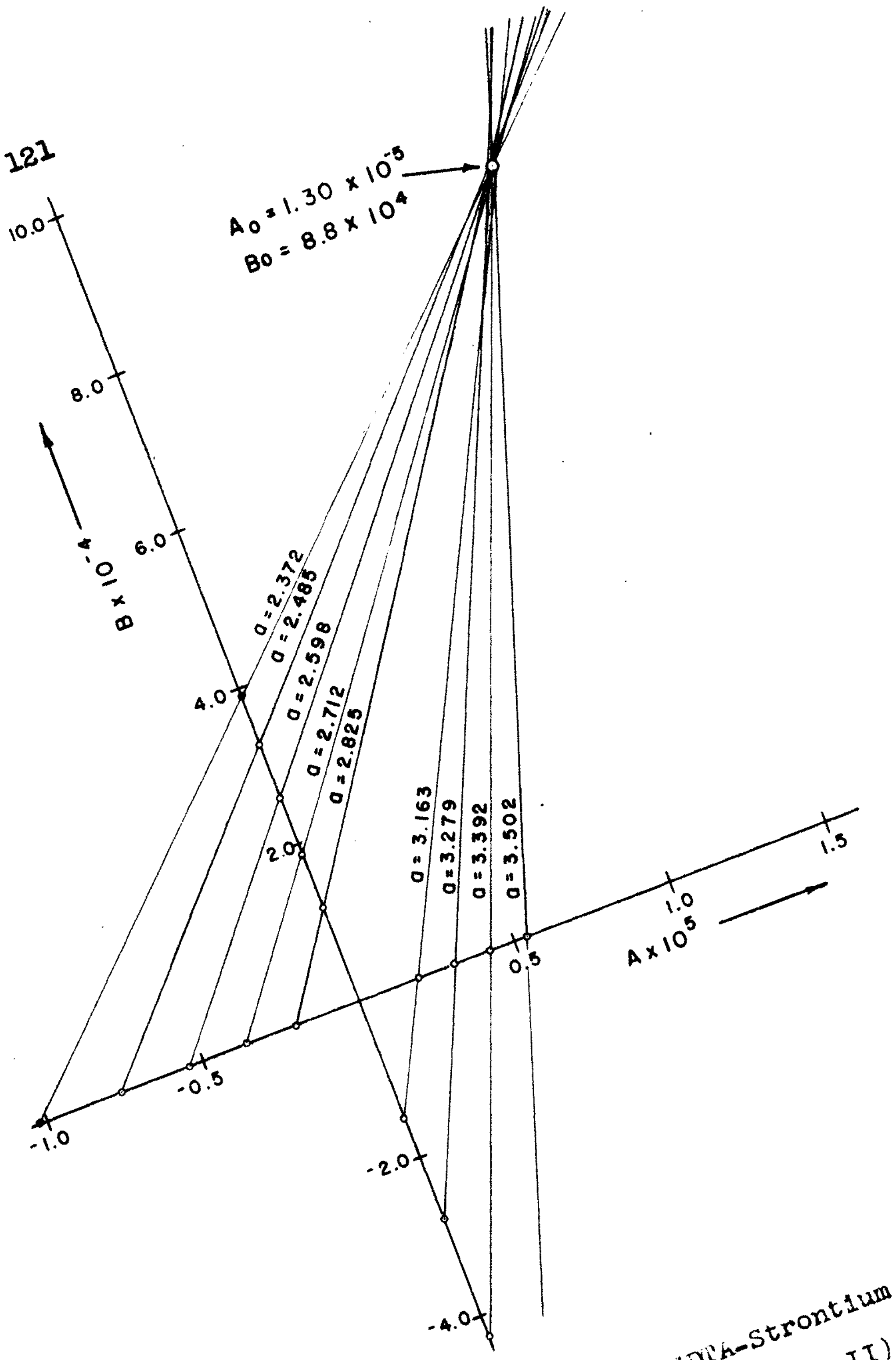

Figure 7. Stability Constants of CDTA-Strontium Complexes

Determination of K_3' and K_4' (Run II)

Table 17

Stability Constants of CDTA-Strontium Complexes[a]
Graphical Determination

	$K_3' \times 10^5$	$K_4' \times 10^5$	$\log K_{SrHY}$	$\log K_{SrY}$
Run I	1.12	1.36	3.10	9.18
Run II	1.14	1.30	3.11	9.17
Av.	1.13	1.33	3.10	9.18

[a] Ionic strength = 0.1; temperature = 25.0°C.

As an extra check, K_{SrHY} and K_{SrY} were also determined by the method of successive approximations discussed in Section III B, paragraph 2. The values obtained for K'_{k_1} and and K'_{k_2} are given in Table 18. The values of these constants (the average values of the last two columns of Table 18) are shown in Table 19 along with the corresponding values of K_{SrHY} and K_{SrY} computed from

$$K_{SrHY} = \frac{K'_{k_1} - K_3}{C_{Sr}K_3} \quad \text{and} \quad K_{SrY} = \frac{K'_{k_2} - K_3K_4}{C_{Sr}K_3K_4}.$$

Comparison of Table 19 with Table 17 shows that the two methods of calculation lead to essentially the same results.

Table 18

Stability Constants of CDTA-Strontium Complexes
Calculation of K'_{k_1} and K'_{k_2}[a]

Run I. CDTA Solution I[b]

a	pH	$\Delta x10^{10}$	$\sigma x10^5$	(1) $K'_{k_2}x10^{10}$	(2) $K'_{k_1}x10^5$	(3) $K'_{k_2}x10^{10}$	(4) $K'_{k_1}x10^5$
2.299	4.51	2.96	-1.24	-	1.19	1.58	1.16
2.428	4.60	2.52	-0.88	-	1.18	1.54	1.14
2.554	4.68	2.21	-0.62	-	1.18	1.52	1.11
2.682	4.76	1.95	-0.40	-	1.18	1.51	1.08
2.811	4.83	1.77	-0.22	1.77	1.31	1.53	1.14
2.938	4.91	1.53	-0.06	1.53	**	1.46	**
3.066	4.98	1.37	0.07	1.37	**	1.45	**
3.194	5.06	1.23	0.22	1.23	1.14	1.47	**
3.320	5.13	1.14	0.36	-	0.94	1.54	1.06
3.450	5.23	0.98	0.50	-	1.00	1.54	1.08
3.578	5.34	0.82	0.64	-	1.03	1.53	1.09
3.671	5.44	0.70	0.75	-	1.04	1.53	1.09
3.799	5.63	0.51	0.94	-	1.03	1.55	1.07
3.901	5.93	0.27	1.09	-	1.11	1.48	1.15
			Av.	1.48	1.11	1.52	1.11

[a] Data listed in Table 5.

[b] For Run I K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 1.48x10^{-10}$, (3) $K'_{k_1} = 1.11x10^{-5}$, (4) $K'_{k_2} = 1.52x10^{-10}$.

**No significant value for K'_{k_1} may be calculated.

Table 18 (continued)

Run II. CDTA Solution II[c]

<u>a</u>	pH	$\Delta x10^{10}$	$\sigma x10^{5}$	(1) $K'_{k_2}x10^{10}$	(2) $K'_{k_1}x10^{5}$	(3) $K'_{k_2}x10^{10}$	(4) $K'_{k_1}x10^{5}$	(5) $K'_{k_2}x10^{10}$
2.259	4.48	3.17	-1.38	-	1.24	1.67*	1.22	1.65*
2.372	4.56	2.69	-1.03	-	1.19	1.57	1.17	1.56
2.485	4.64	2.31	-0.76	-	1.12	1.48	1.09	1.47
2.598	4.71	2.09	-0.54	-	1.17	1.50	1.13	1.50
2.712	4.78	1.86	-0.36	-	1.11	1.47	1.05	1.46
2.825	4.85	1.65	-0.20	1.65	1.0*	1.43	0.8*	1.43
2.935	4.91	1.53	-0.06	1.53	**	1.46	**	1.46
3.049	4.97	1.41	0.07	1.41	**	1.49	**	1.49
3.163	5.04	1.27	0.19	1.27	1.0*	1.48	1.1*	1.48
3.279	5.12	1.11	0.31	-	1.13	1.45	1.19	1.45
3.392	5.20	0.97	0.42	-	1.17	1.43	1.21	1.43
3.502	5.28	0.87	0.54	-	1.09	1.46	1.13	1.46
3.620	5.38	0.78	0.69	-	0.99	1.53	1.01	1.54
3.731	5.52	0.61	0.83	-	0.90	1.51	0.93	1.52
3.845	5.73	0.42	1.02	-	1.02	1.53	1.04	1.54
			Av.	1.46	1.09	1.48	1.10	1.48

[c] For Run II K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 1.46x10^{-10}$, (3) $K'_{k_1} = 1.09x10^{-5}$, (4) $K'_{k_2} = 1.48x10^{-10}$, (5) $K'_{k_1} = 1.10x10^{-10}$.

*Neglected in computing average.

**No significant value for K'_{k_1} may be calculated.

Table 19

Stability Constants of CDTA-Strontium Complexes[a]
Method of Successive Approximations

	$K'_{k_1} \times 10^5$	$K'_{k_2} \times 10^{10}$	log K_{SrHY}	log K_{SrY}
Run I	1.11	1.52	3.10	9.18
Run II	1.10	1.48	3.09	9.17
Av.	1.10	1.50	3.09	9.18

[a] Ionic strength = 0.1; temperature = 25.0°C.

c. Magnesium. The calculation of K'_{k_1} and K'_{k_2} for the magnesium complexes by the method of successive approximations is shown in Table 20. Points on the titration curves (data in Table 6) between a = 2.0 and a = 3.9 were used. Table 21 gives the average values of K'_{k_1} and K'_{k_2} and the corresponding values of log K_{MgHY} and log K_{MgY} computed by the procedure described in the preceding paragraph for the strontium complexes. The graphical method of calculation used in the case of the barium and strontium complexes was not found to be satisfactory because the intersection of the lines lay too far from the origin. This difficulty was previously pointed out in Section III B, paragraph 2.

Table 20

Stability Constants of CDTA-Magnesium Complexes
Calculation of K'_{k_1} and K'_{k_2}[a]

Run I. CDTA Solution I[b]

$\underline{a}$	pH	$\Delta x10^9$	$\sigma x10^5$	(1) $K'_{k_2}x10^9$	(2) $K'_{k_1}x10^5$	(3) $K'_{k_2}x10^9$	(4) $K'_{k_1}x10^5$
2.051	3.94	6.18	-5.21	-	1.7	5.29	1.8
2.171	3.98	6.13	-4.41	-	1.9	5.39	2.0
2.302	4.03	5.69	-3.39	-	1.2	5.01	1.4
2.430	4.07	5.64	-2.76	-	1.2	5.19	1.5
2.555	4.11	5.52	-2.08	-	1.1	5.17	1.4
2.686	4.15	5.50	-1.36	5.50	1.5	5.27	2.0
2.811	4.19	5.41	-0.69	5.41	1.6	5.29	**
2.940	4.23	5.42	0.01	5.42	**	5.42	**
3.067	4.28	5.15	0.73	5.15	**	5.27	**
3.195	4.33	5.02	1.52	5.02	1.8	5.28	1.4
3.323	4.39	4.74	2.35	-	2.4	5.14	2.1
3.452	4.46	4.42	3.31	-	2.7	4.98	2.4*
3.579	4.53	4.39	4.62	-	2.0	5.18	1.8
3.708	4.63	4.15	6.39	-	1.8	5.24	1.7
3.836	4.79	3.69	9.4	-	1.7	5.29	1.6
3.900	4.93	3.27	12.2	-	1.7	5.34	1.6
			Av.	5.30	1.7	5.23	1.7

[a] From data listed in Table 6.

[b] For Run I K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 5.30x10^{-9}$, (3) $K'_{k_1} = 1.70x10^{-5}$, (4) $K'_{k_2} = 5.23x10^{-9}$.

*Neglected in computing average.

**No significant value for K'_{k_1} may be calculated.

Table 20 (continued)

Run II. CDTA Solution II[c]

$\underline{a}$	pH	$\Delta x10^9$	$\sigma x10^5$	$K'^{(1)}_{k_2}x10^9$	$K'^{(2)}_{k_1}x10^5$	$K'^{(3)}_{k_2}x10^9$	$K'^{(4)}_{k_1}x10^5$
2.034	3.94	5.78	-5.31	-	1.4	5.04	1.5
2.147	3.98	5.65	-4.40	-	1.4	5.03	1.5
2.259	4.02	5.50	-3.80	-	1.2	4.97	1.4
2.372	4.06	5.27	-3.08	-	0.7	4.84	0.9
2.485	4.10	5.08	-2.43	-	**	4.74	0.4*
2.599	4.13	5.23	-1.84	-	1.1	4.97	1.4
2.713	4.17	5.04	-1.23	5.04	**	4.87	**
2.825	4.20	5.17	-0.65	5.17	1.8	5.08	**
2.948	4.24	5.13	0.02	5.13	**	5.13	**
3.052	4.28	4.96	0.59	4.96	1.5	5.04	**
3.165	4.32	4.96	1.27	4.96	0.7	5.14	**
3.279	4.37	4.76	2.01	-	1.4	5.04	1.1
3.392	4.43	4.46	2.78	-	2.1	4.85	1.9
3.504	4.49	4.32	3.72	-	2.0	4.84	1.8
3.618	4.56	4.22	5.00	-	1.7	4.92	1.5
3.731	4.65	4.12	6.8	-	1.4	5.07	1.3
3.846	4.80	3.71	9.7	-	1.4	5.07	1.3
			Av.	5.05	1.4	4.98	1.4

[a] For Run II K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 5.05x10^{-9}$, (3) $K'_{k_1} = 1.40x10^{-5}$, (4) $K'_{k_2} = 4.98x10^{-9}$.

*Neglected in computing average.

**No significant value for K'_{k_1} may be calculated.

Table 21

Stability Constants of CDTA-Magnesium Complexes[a]

	$K'_{k_1} \times 10^5$	$K'_{k_2} \times 10^9$	log K_{MgHY}	log K_{MgY}
Run I	1.7	5.23	3.29	10.72
Run II	1.4	4.98	3.20	10.70
Av.	1.6	5.1	3.2	10.71

[a] Ionic strength = 0.1; temperature = 25.0°C.

d. Calcium. Table 22 shows the results of the calculation of K'_{k_1} and K'_{k_2} for calcium complexes of CDTA using the method of successive approximations. Data from Table 7 were used to compute these constants for points on the titration curves between *a* = 2.0 and *a* = 3.9. The results for K'_{k_1} and K'_{k_2} are summarized in Table 23, which also lists the corresponding values of log K_{CaHY} and K_{CaY} calculated from K'_{k_1} and K'_{k_2}. The graphical method of calculation was not used for the reason stated in the preceding paragraph in connection with the magnesium complexes.

Table 22

Stability Constants of CDTA-Calcium Complexes Calculation of K'_{k_1} and K'_{k_2}[a]

Run I. CDTA Solution I[b]

$\underline{a}$	pH	$\Delta x10^8$	$\sigma x10^5$	(1) $K'_{k_2}x10^8$	(2) $K'_{k_1}x10^4$	(3) $K'_{k_2}x10^8$	(4) $K'_{k_1}x10^4$
2.044	3.59	9.03	-10.5	-	3.1	6.51	2.7
2.301	3.66	7.85	-6.99	-	2.9	6.17	2.4
2.426	3.69	7.58	-5.40	-	3.3	6.28	2.6
2.555	3.73	6.95	-3.71	-	3.1	6.06	2.0
2.682	3.77	6.41	-2.07	6.41	2.9	5.91	**
2.811	3.81	5.97	-0.40	5.97	4.0*	5.87	**
2.938	3.85	5.66	1.33	5.66	1.1*	5.98	**
3.065	3.90	5.20	3.11	5.20	2.0	5.95	**
3.200	3.95	4.79	5.15	-	2.0	6.03	2.7
3.323	4.01	4.29	7.26	-	2.1	6.03	2.6
3.453	4.08	3.84	9.79	-	2.0	6.19	2.4
3.579	4.16	3.47	13.0	-	1.8	6.59	2.1
3.712	4.30	2.57	16.2	-	2.0	6.46	2.2
3.835	4.51	1.63	20.2	-	2.1	6.48	2.3
3.901	4.72	1.00	22.1	-	2.2	6.30	2.3
			Av.	5.81	2.4	6.19	2.4

[a] From data listed in Table 7.

[b] For Run I K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 5.81x10^{-8}$, (3) $K'_{k_1} = 2.40x10^{-4}$, (4) $K'_{k_2} = 6.19x10^{-8}$.

*Neglected in computing average.

**No significant value for K'_{k_1} may be calculated.

Table 22 (continued)

Run II. CDTA Solution II[c]

$\underline{a}$	pH	$\Delta x10^8$	$\sigma x10^5$	$K'^{(1)}_{k_2}x10^8$	$K'^{(2)}_{k_1}x10^4$	$K'^{(3)}_{k_2}x10^8$	$K'^{(4)}_{k_1}x10^4$
2.031	3.58	9.10	-11.1	-	2.6	6.32	2.8
2.145	3.61	8.59	-9.50	-	2.5	6.21	2.7
2.259	3.64	8.18	-7.91	-	2.5	6.20	2.7
2.370	3.67	7.61	-6.34	-	2.2	6.02	2.5
2.483	3.71	6.91	-4.90	-	1.4	5.69	1.8
2.597	3.74	6.67	-3.45	-	1.4	5.81	1.9
2.712	3.77	6.49	-1.96	6.49	1.5	6.00	2.4
2.822	3.80	6.30	-0.47	6.30	2.1	6.18	**
2.935	3.84	5.82	1.07	5.82	3.6	6.09	**
3.049	3.89	5.15	2.63	-	4.0	5.81	3.3
3.162	3.94	4.62	4.22	-	3.7	5.68	3.3
3.276	3.99	4.28	6.02	-	3.2	5.78	2.9
3.388	4.04	4.06	8.17	-	2.6	6.10	2.4
3.502	4.11	3.59	10.5	-	2.5	6.21	2.3
3.615	4.19	3.21	13.4	-	2.2	6.56*	2.1
3.729	4.31	2.57	16.9	-	2.1	6.79*	2.0
3.843	4.52	1.60	20.4	-	2.3	6.70*	2.2
3.888	4.66	1.15	21.8	-	2.3	6.60*	2.2
			Av.	6.20	2.5	6.01	2.5

[c]For Run II K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 6.20x10^{-8}$, (3) $K'_{k_1} = 2.50x10^{-4}$, (4) $K'_{k_2} = 6.01x10^{-8}$.

*Neglected in computing average.

**No significant value for K'_{k_1} may be calculated.

Table 23

Stability Constants of CDTA-Calcium Complexes[a]

	$K'_{k_1}\times10^{4}$	$K'_{k_2}\times10^{8}$	log K_{CaHY}	log K_{CaY}
Run I	2.4	6.2	3.45	11.79
Run II	2.5	6.0	3.47	11.78
Av.	2.4	6.1	3.5	11.79

[a] Ionic strength = 0.1; temperature = 25.0°C.

e. Lead. The calculation of K'_{k_1} and K'_{k_2} for the lead complexes of CDTA by the method of successive approximations from data in Table 8 is shown in Table 24. Because of the magnitude of these constants it was necessary to use points on the titration curve having smaller a values than those employed in the computation of the constants for the strontium, magnesium, and calcium complexes. Points used in the case of lead had a values between 0.4 and 3.6. The average values of K'_{k_1} and K'_{k_2} resulting from these calculations are 2.0×10^{-1} and 2.6×10^{-4}, respectively. The values of K_{PbHY} and K_{PbY} computed from K'_{k_1} and K'_{k_2} are the following:

$$\log K_{PbHY} = 7.4 \quad \text{and} \quad \log K_{PbY} = 15.6 \; .$$

Table 24

Stability Constants of CDTA-Lead Complexes[a]
Calculation of K'_{k_1} and K'_{k_2}[b]

<u>a</u>	pH	$\Delta x10^4$	$\sigma x10^4$	(1) $K'_{k_2}x10^4$	(2) K_{k_1}	(3) $K'_{k_2}x10^4$	(4) K_{k_1}
0.452	2.60	4.07	-4.5	-	0.30*	3.2*	0.32*
0.677	2.63	3.31	-3.0	3.31	0.20	2.7	0.22
0.903	2.66	2.88	-1.3	2.88	0.14	2.6	0.18
1.129	2.69	2.51	0.4	2.51	0.48*	2.6	0.32*
1.355	2.72	2.29	2.7	2.29	0.15	2.8	0.13*
1.581	2.76	1.86	4.3	-	0.20	2.7	0.18
1.807	2.80	1.51	5.9	-	0.20	2.7	0.19
2.033	2.85	1.12	7.4	-	0.21	2.6	0.21
2.259	2.91	0.78	8.3	-	0.23	2.5	0.22
2.485	2.97	0.58	9.8	-	0.22	2.6	0.21
2.712	3.05	0.36	1.05	-	0.22	2.5	0.22
2.938	3.13	0.25	1.24	-	0.20	2.8	0.19
3.165	3.24	0.14	1.34	-	0.19	2.8	0.19
3.392	3.40	0.06	1.27	-	0.21	2.6	0.20
3.618	3.62	0.02	1.27	-	0.21	2.5	0.21
			Av.	2.7	0.20	2.64	0.20

[a] From data listed in Table 8.

[b] K'_{k_1} and K'_{k_2} were computed assuming: (1) $K'_{k_1}\sigma = 0$, (2) $K'_{k_2} = 2.70x10^{-4}$, (3) $K'_{k_1} = 2.0x10^{-1}$, (4) $K'_{k_2} = 2.64x10^{-4}$.

*Neglected in computing average.

**No significant value for K'_{k_1} may be calculated.

3. Stability of heavy metal complexes of CDTA

a. Ionization constants of triaminotriethylamine trihydrochloride. The data obtained from the titration of 100 ml. of 0.001 M triaminotriethylamine trihydrochloride ($H_3trenCl_3$) with 0.1217 N NaOH is shown in Table 25. The titration curve resulting from plotting the measured pH as a function of a is shown in Figure 8 (Curve A). The procedure for calculating the ionization constants of $H_3trenCl_3$ from such a titration curve was described in Section III B, paragraph 3a.

As a first approximation, pK_1 is equal to the pH at the point where $a = 0.5$. From Figure 8, this value is estimated to be

$$pK_1 = 8.40$$

or

$$K_1 = 4.0 \times 10^{-9} .$$

First approximations of K_2 and K_3 were obtained by the graphical solution of equation (1) (Section III B, paragraph 3a). The values computed for the intercepts A and B (from data in Table 25) are listed in Table 26, and the graphical estimation of K_2 and K_3 is shown in Figure 9. From the average point of intersection of the lines in Figure 9, the

Table 25

Titration of Triaminotriethylamine Trihydrochloride[a]

Ml. NaOH	*a*	pH	Ml. NaOH	*a*	pH
0.000	0.000	5.33	1.200	1.460	9.42
0.050	0.061	7.07	1.300	1.582	9.52
0.100	0.122	7.53	1.400	1.704	9.62
0.200	0.243	7.94	1.500	1.826	9.71
0.300	0.365	8.20	1.601	1.948	9.80
0.400	0.487	8.38	1.701	2.069	9.89
0.500	0.608	8.55	1.801	2.191	9.98
0.600	0.730	8.70	1.901	2.312	10.07
0.700	0.852	8.84	2.001	2.434	10.15
0.800	0.974	8.97	2.101	2.556	10.23
0.900	1.095	9.09	2.201	2.678	10.31
1.000	1.217	9.21	2.302	2.801	10.38
1.100	1.339	9.32	2.402	2.923	10.45

[a] C_T = 1.00×10^{-3}; N_{NaOH} = 0.1217.

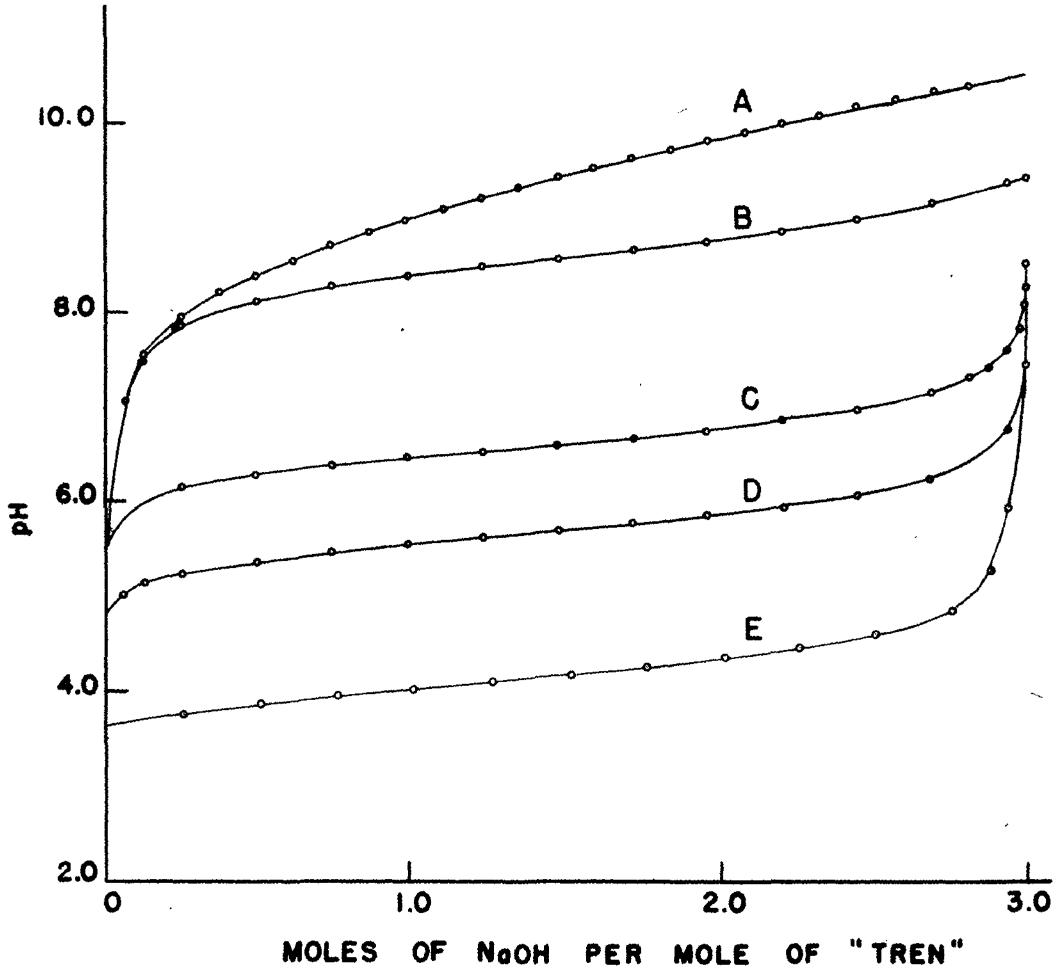

Figure 8. Titration Curves of Triaminotriethylamine Trihydrochloride ($H_3trenCl_3$)

Curve A. $H_3trenCl_3$ alone
Curve B. $H_3trenCl_3$ + Manganese (II)
Curve C. $H_3trenCl_3$ + Cadmium
Curve D. $H_3trenCl_3$ + Zinc
Curve E. $H_3trenCl_3$ + Copper (II)

Table 26

Apparent Ionization Constants of Triaminotriethylamine Trihydrochloride Graphical Estimation of K_2 and K_3[a]

a	pH	g	$A\times10^{9}$	$B\times10^{-10}$
1.217	9.21	1.201	3.39	-2.69
1.460	9.42	1.434	2.57	-1.38
1.704	9.62	1.662	1.86	-0.60
1.948	9.80	1.884	0.76	-0.16
2.191	9.98	2.095	-0.55	0.11
2.434	10.15	2.293	-3.09	0.30
2.678	10.31	2.473	-6.47	0.54

[a] Assuming $K_1 = 4.0\times10^{-9}$.

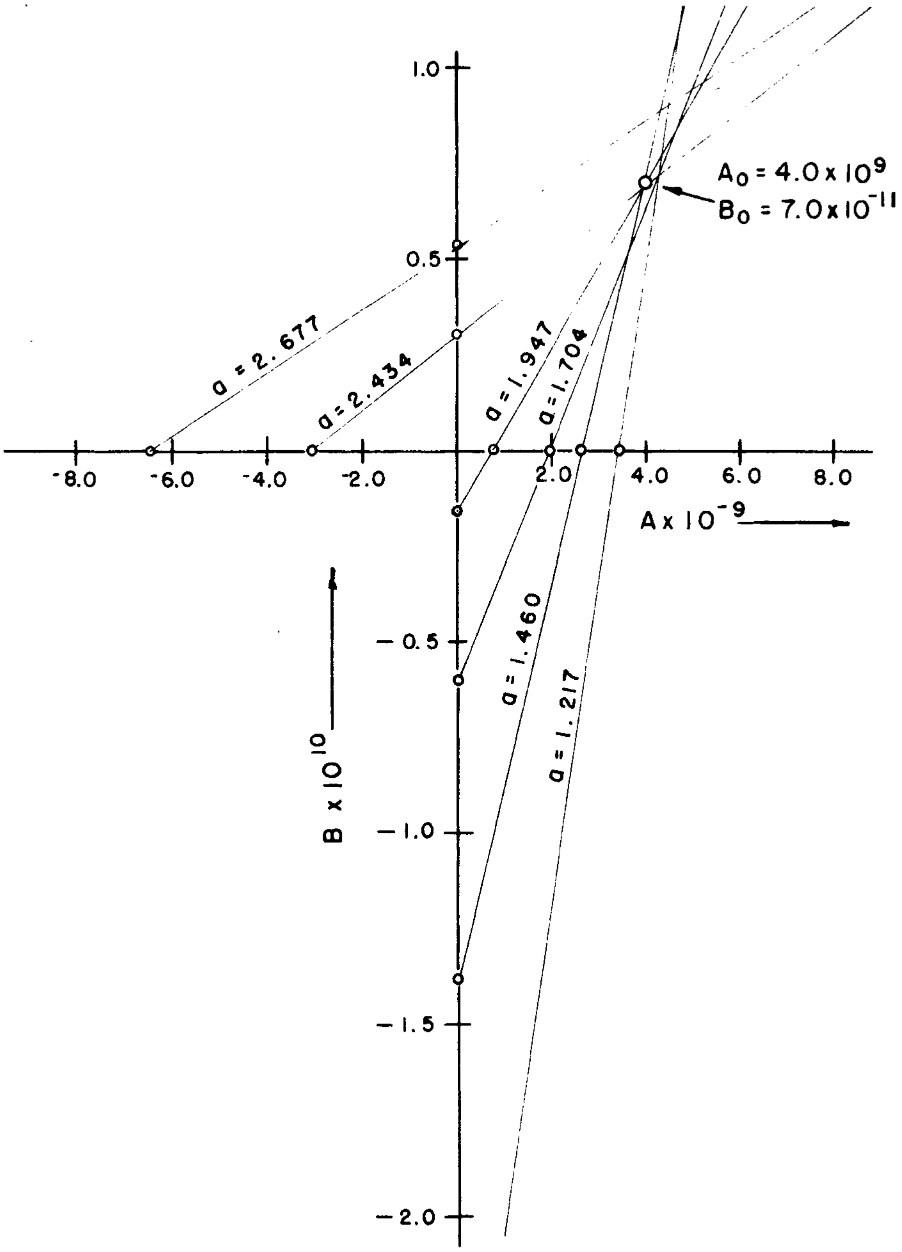

Figure 9. Apparent Ionization Constants of Triaminotriethylamine Trihydrochloride

Graphical Estimation of K_2 and K_3

first approximations of K_2 and K_3 were found to be

$$K_2 = 1/A_0 = \frac{1}{4.0\text{x}10^9} = 2.5\text{x}10^{-10}$$

and

$$K_3 = B_0 = 7.0\text{x}10^{-11} ,$$

or

$$pK_2 = 9.60 \qquad \text{and} \qquad pK_3 = 10.15 .$$

Better values for K_1, K_2, and K_3 were obtained by the method of successive approximations outlined in Section III B, paragraph 3a. The results of this process are shown in Table 27. The final values obtained for these constants (at 25.0°C. and ionic strength of 0.1) are

$$pK_1 = 8.48 ,$$

$$pK_2 = 9.57 ,$$

and

$$pK_3 = 10.19 .$$

These agree very well with the values

$$pK_1 = 8.56 ,$$

Table 27

Apparent Ionization Constants of Triaminotriethylamine Trihydrochloride[a]

a	pH	g	pK_1[b]	pK_2[c]	pK_3[d]	pK_1[e]	pK_2[f]	pK_3[g]
0.243	7.94	0.242	8.46			8.46		
0.365	8.20	0.363	8.48			8.48		
0.487	8.38	0.485	8.47			8.48		
0.608	8.55	0.604	8.49			8.49		
0.730	8.70	0.725	8.49			8.50		
0.852	8.84	0.847	8.48			8.48		
1.217	9.21	1.201		9.58			9.58	
1.339	9.32	1.318		9.59			9.58	
1.460	9.42	1.434		9.57			9.56	
1.582	9.52	1.549		9.58			9.56	
1.704	9.62	1.662		9.60			9.58	
1.826	9.71	1.775		9.59			9.57	
2.191	9.98	2.095			10.19			10.19
2.312	10.07	2.194			10.20			10.21
2.434	10.15	2.293			10.18			10.19
2.556	10.23	2.386			10.17			10.18
2.678	10.31	2.473			10.15			10.16
2.801	10.38	2.559			10.11*			10.11*
		Av.	8.48	9.58	10.18	8.48	9.57	10.19

[a] Ionic strength = 0.1, temperature = 25.0°C.

[b] Assuming $pK_2 = 9.60$ and $pK_3 = 10.15$.

[c] Assuming $pK_1 = 8.48$ and $pK_3 = 10.15$.

[d] Assuming $pK_1 = 8.48$ and $pK_2 = 9.58$.

[e] Assuming $pK_2 = 9.58$ and $pK_3 = 10.18$.

[f] Assuming $pK_1 = 8.48$ and $pK_3 = 10.18$

[g] Assuming $pK_1 = 8.48$ and $pK_2 = 9.57$.

*Neglected in computing average.

$$pK_2 = 9.59 ,$$

and

$$pK_3 = 10.29 .$$

reported by Ackermann and Schwarzenbach [1] for these same constants (at 20.0°C. and ionic strength of 0.1).

b. Stability of heavy metal complexes of triaminotriethylamine. Following the procedure outlined in Section III B, paragraph 3b, solutions of triaminotriethylamine trihydrochloride and salts of various heavy metals in equimolar concentrations were titrated with 0.1 N NaOH. The data obtained from these titrations for Mn(II), Ca(II), Ni(II), Zn, Cd, and Cu(II) are listed in Tables 28, 29, 30, 31, 32, and 33. Also listed in these same tables are the values of log $K_{M\ tren}$ calculated by means of equation (1) (Section III B, paragraph 3b). Representative titration curves obtained by plotting the measured pH as a function of a are shown in Figure 8. Table 34 gives the average values of the constants determined and also lists for comparison the constants reported by Schwarzenbach [110] for these same complexes at 20.0°C.

Table 28

Stability Constant of Complex of Triaminotriethylamine with Manganese (II)[a]

Ml. NaOH	pH	$\underline{a}$[b]	log $K_{Mn\ tren}$
0.000	5.51	0.000	-
0.100	7.52	0.122	-
0.200	7.85	0.243	6.01*
0.400	8.13	0.487	5.85
0.600	8.27	0.730	5.85
0.800	8.39	0.974	5.80
1.000	8.48	1.217	5.82
1.200	8.57	1.460	5.81
1.300	8.62	1.582	5.81
1.400	8.66	1.704	5.82
1.500	8.70	1.826	5.84
1.600	8.74	1.947	5.88
1.700	8.79	2.069	5.90
1.800	8.84	2.191	5.92
1.900	8.90	2.312	5.95
2.000	8.97	2.434	5.97
2.100	9.04	2.556	-
2.200	9.13	2.677	-
2.300	9.23	2.799	-
2.350	9.28	2.860	-
2.400	9.35	2.921	-
2.450	9.38	2.979	-
2.500	9.44	3.042	-
		Av.	5.86

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Computed using $C = 1.000 \times 10^{-3}$ $\underline{M}$ and $N_{NaOH} = 0.1217$.

*Neglected in computing average.

Table 29

Stability Constant of Complex of Triaminotriethylamine with Cobalt (II)[a]

Ml. NaOH	pH	a[b]	log $K_{Co\ tren}$
0.000	5.16	0.000	-
0.200	5.47**	0.243	-
0.400	5.56**	0.487	-
0.600	5.67**	0.730	-
0.800	5.83**	0.974	-
1.000	6.05**	1.217	-
1.200	6.19	1.460	12.84*
1.400	6.29	1.704	12.76
1.500	6.33	1.826	12.76
1.600	6.38	1.947	12.73
1.700	6.43	2.069	12.72
1.800	6.48	2.191	12.71
1.900	6.54	2.312	12.70
2.000	6.60	2.434	12.71
2.100	6.67	2.556	12.73
2.200	6.76	2.677	12.76
2.300	6.86	2.799	-
2.350	6.93	2.860	-
2.400	7.03	2.921	-
2.440	7.12	2.969	-
2.500	7.38	3.042	-
		Av.	12.73

---

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Computed using $C = 1.000 \times 10^{-3}$ M and $N_{NaOH} = 0.1217$.

*Neglected in computing average.

**Equilibrium reached very slowly. pH readings drifted from alkaline to acid for 30 to 45 minutes before becoming constant.

Table 30

Stability Constant of Complex of Triaminotriethylamine with Nickel (II)[a]

Ml. NaOH	pH	$\underline{a}$[b]	log $K_{Ni\ tren}$
0.000	4.76	0.000	-
0.197	5.18**	0.240	-
0.400	5.33**	0.487	14.62*
0.600	5.44**	0.730	14.55
0.800	5.51**	0.974	14.57
1.000	5.58**	1.217	14.56
1.200	5.65**	1.460	14.55
1.400	5.73**	1.704	14.54
1.600	5.82**	1.947	14.51
1.800	5.92**	2.191	14.49
2.000	6.04**	2.434	14.48
2.204	6.27**	2.682	14.30*
2.300	6.47***	2.799	-
2.351	6.68***	2.861	-
2.401	7.70***	2.922	-
		Av.	14.53

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Computed using $C = 1.000 \times 10^{-3}$ $\underline{M}$ and $N_{NaOH} = 0.1217$.

*Neglected in computing average.

**Equilibrium reached very slowly. Constant pH readings obtained only after 15 to 20 minutes standing following addition of each increment of NaOH.

***pH had not become constant after 30 minutes standing.

Table 31

Stability Constant of Complex of Triaminotriethylamine with Zinc[a]

Ml. NaOH	pH	$\underline{a}$[b]	log $K_{Zn\ tren}$
0.000	4.86	0.000	-
0.040	5.03	0.049	-
0.101	5.15	0.124	-
0.202	5.26	0.248	14.46
0.400	5.38	0.491	14.47
0.601	5.47	0.737	14.47
0.800	5.55	0.982	14.45
1.000	5.62	1.227	14.45
1.202	5.69	1.475	14.45
1.401	5.76	1.720	14.45
1.600	5.84	1.963	14.46
1.801	5.93	2.210	14.47
2.001	6.06	2.455	14.46
2.201	6.24	2.701	14.47
2.403	6.73	2.948	-
2.422	6.88	2.972	-
2.442	7.70	2.996	-
2.452	8.27	3.009	-
2.462	8.50	3.021	-
2.482	8.76	3.045	-
		Av.	14.46

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Computed using $C = 9.92 \times 10^{-4}$ $\underline{M}$ and $N_{NaOH} = 0.1217$.

Table 32

Stability Constant of Complex of Triaminotriethylamine with Cadmium[a]

Ml. NaOH	pH	a[b]	log $K_{Cd\ tren}$
0.000	5.39	0.000	-
0.200	6.14	0.245	-
0.400	6.28	0.491	11.76
0.600	6.37	0.736	11.76
0.800	6.44	0.982	11.78
1.000	6.52	1.227	11.75
1.200	6.59	1.472	11.75
1.400	6.66	1.718	11.76
1.600	6.74	1.963	11.76
1.800	6.84	2.209	11.74
2.000	6.96	2.454	11.75
2.200	7.13	2.699	11.79
2.300	7.29	2.822	-
2.351	7.41	2.885	-
2.380	7.50	2.920	-
2.400	7.58	2.945	-
2.420	7.70	2.969	-
2.440	8.06	2.994	-
2.450	8.51	3.006	-
2.460	8.80	3.018	-
2.480	9.13	3.043	-
2.500	9.32	3.068	-
		Av.	11.76

---

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Computed using $C = 9.92 \times 10^{-4}$ *M* and $N_{NaOH} = 0.1217$.

Table 33

Stability Constant of Complex of Triaminotriethylamine with Copper (II)[a]

Ml. NaOH	pH	*a*[b]	$\log K_{Cu\ tren}$
0.000	3.66	0.000	-
0.200	3.75	0.249	-
0.400	3.84	0.498	19.24*
0.600	3.93	0.747	19.20
0.800	4.01	0.996	19.17
1.000	4.08	1.245	19.15
1.100	4.12	1.370	19.14
1.200	4.15	1.494	19.15
1.300	4.19	1.618	19.13
1.400	4.23	1.743	19.12
1.500	4.28	1.868	19.09
1.600	4.32	1.992	19.09
1.700	4.37	2.116	19.09
1.800	4.43	2.241	19.07
2.000	4.58	2.490	19.02*
2.200	4.81	2.739	-
2.300	5.25	2.863	-
2.350	5.89	2.925	-
2.400	6.90	2.988	-
2.450	7.45	3.050	-
		Av.	19.13

---

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Computed using $C = 1.000 \times 10^{-3}$ *M* and $N_{NaOH} = 0.1245$.

*Neglected in computing average.

Table 34

Stability Constants of Heavy Metal Complexes of Triaminotriethylamine

Metal	$\log K_M$ tren	
	Experimental[a]	Literature[b]
Manganese (II)	5.9	5.8
Cadmium	11.76	11.7
Cobalt (II)	12.73	12.8
Zinc	14.46	14.8
Nickel (II)	14.53	14.6
Copper (II)	19.1	18.8

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Reference [110]. Ionic strength = 0.1; temperature = 20.0°C.

c. Equilibrium constants of exchange reactions. Using the procedure discussed in Section III B, paragraph 3c, the equilibrium constants of the reactions involving competition between CDTA and triaminotriethylamine for the ions of a heavy metal were measured. This process was carried out for manganese (II), cobalt (II), nickel (II), copper (II), cadmium, and zinc. Table 35 summarizes the results obtained and lists the values computed for the various exchange (equilibrium) constants by means of equation (n) derived in Section III B, paragraph 3c.

d. Stability constants of heavy metal complexes of CDTA. Using the values for the ionization constants of H_3-trenCl_3, the stability constants of tren complexes, and the exchange reaction equilibrium constants listed in the three preceding paragraphs, the stability constants of CDTA complexes of the previously listed heavy metals were computed. The method of calculation was described in Section III B, paragraph 3d. The results of these computations are listed in Table 36.

Table 35

Equilibrium Constants for Metal Exchange Reactions between CDTA and Triaminotriethylamine[a]

Manganese (II)						Av.
Ml. NaOH	1.917	2.076	2.239	2.402	2.565	
a	4.70	5.10	5.50	5.90	6.30	
pH	8.41	8.72	8.99	9.31	9.58	
log K_{ex}	-25.12	-25.16	-25.20	-25.25	-25.36*	-25.18
Cobalt (II)						
Ml. NaOH	1.917	2.076	2.239	2.402	2.565	
a	4.70	5.10	5.50	5.90	6.30	
pH	8.51	8.88	9.19	9.50	9.81	
log K_{ex}	-25.76*	-26.00	-26.04	-26.17	-26.24	-26.11
Nickel (II)						
Ml. NaOH	1.917	2.076	2.239	2.402	2.565	
a	4.70	5.10	5.50	5.90	6.30	
pH	8.53	8.90	9.23	9.53	9.86	
log K_{ex}	-26.00	-26.12	-26.24	-26.26	-26.44*	-26.16
Copper (II)						
Ml. NaOH	1.917	2.076	2.239	2.402	2.565	
a	4.70	5.10	5.50	5.90	6.30	
pH	7.30	7.49	7.67	7.80	8.00	
log K_{ex}	-20.98	-20.97	-21.01	-20.90	-20.90	-20.95
Zinc						
Ml. NaOH	1.832	2.035	2.238	2.441	2.643	
a	4.50	5.00	5.50	5.99	6.49	
pH	6.84	7.12	7.30	7.51	7.73	
log K_{ex}	-19.90	-19.97	-19.89	-19.91	-19.76*	-19.92
Cadmium						
Ml. NaOH	1.832	2.035	2.238	2.441	2.643	
a	4.50	5.00	5.50	5.99	6.49	
pH	7.73	8.03	8.26	8.47	8.71	
log K_{ex}	-22.83	-22.84	-22.88	-22.79	-22.55*	-22.84

[a] Ionic strength = 0.1; temperature = 25.0°C.
$C = 9.92\text{x}10^{-4}\underline{M}$; $C' = 1.00\text{x}10^{-2}\underline{M}$; $N_{NaOH} = 0.1217$.

*Neglected in computing average.

Table 36

Stability Constants of Heavy Metal Complexes of CDTA[a]

Metal	log K_{MY}
Manganese (II)	14.6
Zinc	17.9
Cadmium	18.2
Cobalt (II)	22.4
Copper (II)	23.6
Nickel (II)	24.2

[a] Ionic strength = 0.1; temperature = 25.0°C.

D. Discussion

1. Ionization constants of CDTA

The ionization constants found for CDTA in the present work are summarized in Table 37. The only values to be found in the literature for comparison are those reported by Schwarzenbach and Ackermann [113]. These constants, determined at 20.0°C. rather than 25.0°C., are also listed in Table 37.

Table 37

Apparent Ionization Constants of CDTA

	Experimental[a]			Literature[b]
	Run I	Run II	Av.	
pK_1	2.83	2.85	2.84	2.43
pK_2	3.64	3.65	3.65	3.52
pK_3	6.26	6.26	6.26	6.12
pK_4	10.91	10.95	10.93	11.70

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] Reference [113]. Ionic strength = 0.1; temperature = 20.0°C.

Table 37 shows that reasonably good agreement was obtained with the constants determined by Schwarzenbach except for pK_4. The apparent increase in dissociation of the fourth hydrogen ion with only a five degree increase in temperature is somewhat larger than might be expected. This same trend is shown, however, by EDTA. The values of pK_4 determined at 25°C. and ionic strength of 0.1 were 9.8[1] by Carini and Martell [17] and 9.97 by Goetz and Loomis [36] while the values at 20°C. were 10.26 by Schwarzenbach and Ackermann [111] and 10.32 by Cabell [15]. Apparently, a decrease of about 0.4 in pK_4 of EDTA results from a temperature increase of five degrees. Thus, the difference of 0.8 in the values shown for pK_4 of CDTA in Table 37 is probably not entirely due to experimental error.

2. Stability constants of CDTA complexes

The only values of stability constants of CDTA available in the literature for direct comparison with the constants determined in this work are those for the calcium and magnesium reported by Schwarzenbach and Ackermann [113]. The values they obtained at 20.0°C.,

$$\log K_{MgY} = 10.32 \quad \text{and} \quad \log K_{CaY} = 12.50 \ ,$$

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[1] Estimated from curve showing pK_4 as a function of ionic strength.

do not agree very well with the corresponding values,

$$\log K_{MgY} = 10.71 \quad \text{and} \quad \log K_{CaY} = 11.79 \ ,$$

determined in the present work at 25.0°C.[1] The method of calculation employed by Schwarzenbach and Ackermann was not given in detail, but was implied to be the same as that used in preceding work on EDTA and other similar chelating agents. This indicates that the ionic species H_4Y and H_3Y^- were neglected in their computations. Inasmuch as the flat portion of the titration curve of CDTA in the presence of excess calcium (Curve E, Figure 1) lies entirely below pH 4, neglect of these species could produce a rather large error in the calculated value of the stability constant.

It is also of some interest to compare the constants for CDTA complexes with those for the corresponding EDTA complexes. Table 38 shows such a comparison, summarizing the values obtained for CDTA complexes in the present work and repeating from Table 2 the values of corresponding EDTA complexes determined by Schwarzenbach.

The constants shown in Table 36 for heavy metal complexes of CDTA must be regarded as only approximate. Be-

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[1] It should be noted that the orders of magnitude of these sets of constants do correspond, however. This agreement is satisfactory for most purposes.

Table 38

Comparison of Stability of CDTA and EDTA Complexes

		log K	
Metal	Complex	CDTA[a]	EDTA[b]
Ba	$BaHY^-$	2.94	2.07
	BaY^{-2}	7.02	7.76
Sr	$SrHY^-$	3.09	2.30
	SrY^{-2}	9.18	8.63
Mg	$MgHY^-$	3.2	2.28
	MgY^{-2}	10.71	8.69
Ca	$CaHY^-$	3.5	3.51
	CaY^{-2}	11.79	10.59
Mn(II)	MnY^{-2}	14.6	13.5
Pb(II)	$PbHY^-$	7.4	-
	PbY^{-2}	15.6	18.2
Zn	ZnY^{-2}	17.9	16.15
Cd	CdY^{-2}	18.2	16.48
Co(II)	CoY^{-2}	22.4	16.10
Cu(II)	CuY^{-2}	23.6	18.38
Ni(II)	NiY^{-2}	24.2	18.45

[a] Ionic strength = 0.1; temperature = 25.0°C.

[b] References [11, 17]. Ionic strength = 0.1; temperature = 20.0°C.

cause of the high stability of the CDTA complexes relative to the tren complexes, the reaction

$$MY^{-2} + H_3tren^{+3} + Ca^{+2} \rightleftharpoons M\ tren^{+2} + CaY^{-2} + 3H^{+}$$

does not proceed very far to the right. The concentrations of $M\ tren^{+2}$ and CaY^{-2} at equilibrium are thus rather small and the computed values of these quantities must naturally be assigned larger limits of possible relative error. For this reason the values of log K_{MY} were reported to an accuracy of only ± 0.1. Use of an auxiliary metal which forms a stronger complex with CDTA than does calcium would shift the position of the equilibrium to the right and lead to more accurate values of the measured constants. The use of one of the rare earth metals in this capacity should probably be investigated in future work.

E. Summary and Conclusions

1. The ionization (dissociation) constants of 1,2-cyclohexenediaminetetraacetic acid (CDTA) at 25.0°C. and an ionic strength of 0.1 were determined from pH titration curves of the acid.

2. The stability (association) constants of the lead

and alkaline earth metal complexes of CDTA (at the same temperature and ionic strength) were determined from similar titration curves of CDTA in the presence of a fifteenfold excess of a salt of the metal being investigated.

3. The stability constants of the complexes formed by CDTA with some heavy metals were determined from measurements of the equilibrium constants of reactions involving competition between CDTA and a polyamine chelating agent, triaminotriethylamine, for ions of the heavy metals. The position of the equilibria in these reactions was determined from pH measurements at 25.0°C. on solutions having an ionic strength of 0.1. To permit evaluation of these equilibrium constants, the ionization constants of triaminotriethylamine trihydrochloride as well as the stability constants of heavy metal complexes of triaminotriethylamine were also determined at 25.0°C. and an ionic strength of 0.1 from pH measurements.

4. A comparison of the measured stability constants of CDTA complexes with those reported in the literature for ethylenediaminetetraacetic acid (EDTA) shows that CDTA forms more stable complexes with nearly all of the metals investigated. The complexing action of CDTA does not appear to be significantly more specific than that of EDTA, however.

5. No evidence was found of CDTA complexes with other than 1:1 ratio of CDTA to metal having sufficiently high

stability to cause systematic error in the measurements of the stability constants of the normal 1:1 complex. This is to be expected from the similarity of CDTA to EDTA (for which little evidence of such complexes has been reported).

IV. COMPLEXOMETRIC TITRATIONS WITH CDTA

A. Materials

1. Preparation of 0.02 N CDTA solution

Commercially available CDTA (obtained from the Alrose Chemical Company) was used without further purification. Eighteen grams of this material were treated with 10 ml. of 35% sodium hydroxide and about 25 ml. of water[1] and allowed to stand until all the CDTA had dissolved (20-30 minutes). The solution was then diluted with water to about 500 ml. and neutralized to pH 5 with 5 N hydrochloric acid. Final dilution with water to five liters gave a CDTA solution approximately 0.02 N (0.01 M).

2. Preparation of 0.02 N magnesium chloride solution

Ten grams of reagent grade $MgCl_2 \cdot 6H_2O$ were dissolved in five liters of water to obtain a 0.02 N (0.01 M) solution of magnesium.

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[1] All water employed in the work discussed in this chapter was ordinary singly distilled water.

3. Indicators

a. F241. The commercially available[1] indicator preparation "Man Ver", consisting of 0.5 g. of analytical reagent grade Eriochrome Black T and 4.5 g. of hydroxylammonium chloride dissolved in 100 ml. of methanol, was used throughout this work.

b. Murexide. The diluted dry powder indicator available[2] under the name "Cal Ver" was used. This mixture consists of 1 part Murexide (ammonium purpurate) in 100 parts of finely powdered potassium sulfate.

4. Buffer (pH 10)

The pH 10 buffer solution used was prepared by adding 67.5 g. of ammonium chloride to 570 ml. of concentrated ammonium hydroxide and diluting the resulting mixture to one liter with water.

5. Primary standards

The primary standards used for standardization of CDTA solutions were calcium carbonate and pure copper wire. The calcium carbonate employed was the special analytical re-

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[1] From the Hach Chemical Company, Ames, Iowa.

[2] From the Hach Chemical Company, Ames, Iowa.

agent "Low Alkali" grade sold for use in the J. Lawerence Smith method. This material was dried for at least two hours at 110°C. before use. The copper wire was cleaned by immersion in dilute nitric acid followed by thorough rinsing with water and then acetone. The cleaned wire was dried at 110°C. for 15 minutes.

6. Miscellaneous

Unless otherwise specified, all other chemicals used in this work were reagent grade (meeting A.C.S. specifications).

B. Experimental Procedures

1. General titration procedures

a. Titrations using Murexide. About 50 ml. of solution containing 0.4 to 0.8 m.e. of copper dissolved in nitric or perchloric acid was neutralized with 5 N NaOH to the appearance of a precipitate of $Cu(OH)_2$, 1 ml. of concentrated ammonium hydroxide and about 0.1 g. of diluted Murexide were added, and the solution was titrated with 0.02 N CDTA. At the start the solution had the deep blue color of the cupric-ammonia complex. This changed gradually during the titration to a deep green color. At the end-point the color of the solution changed very sharply to the deep blue color of the copper-CDTA complex, passing through an intermediate gray color which was taken as the end-point. Nickel was titrated by following the procedure described for copper, except that an excess of CDTA was added and the mixture was back-titrated with standard copper solution. The end-point in this titration was marked by a change in the color of the solution from purple to yellow-brown.

b. Direct titrations using F241. Direct titrations of magnesium or zinc solutions with CDTA were carried out by simply adding 1 ml. of pH 10 buffer solution and 5-6 drops of Man Ver indicator and titrating with CDTA to the disappearance of any red color in the solution. The color change at the end-point is from wine-red to blue.

c. Indirect titrations using F241. Titrations of several other metals with CDTA were carried out as follows: an excess of standard CDTA solution was added to an acid solution of the metal, the mixture was neutralized to the thymolphthalein end-point with 5 N NaOH, 1 ml. of pH 10 buffer solution and 5-6 drops of Man Ver were added, and the solution was titrated with standard magnesium solution to the appearance of a red tint in the blue solution.

2. Standardization of CDTA and magnesium chloride solutions with calcium carbonate

A comparison of the magnesium chloride and CDTA solution was made by titrating 25.00 ml. of the CDTA solution with the standard magnesium using 1 ml. of pH 10 buffer and

5-6 drops of Man Ver indicator. A standard calcium solution was prepared by dissolving an accurately weighed amount (0.35 to 0.4 g.) of primary standard calcium carbonate in 50 ml. of water containing 5 ml. of 5 N hydrochloric acid. The solution was boiled briefly to expel CO_2, cooled, and diluted to volume in a 250-ml. volumetric flask. A 25 ml. aliquot was back-titrated with the magnesium solution following the addition of 50 ml. of CDTA, using the procedure described in paragraph 1c.

From the first titration (CDTA with $MgCl_2$), the number of milliliters of magnesium chloride (P) equivalent to 25 ml. of CDTA was obtained. Subtraction of the number of milliliters of magnesium solution (Q) used in the second titration from the number of milliliters of magnesium solution equivalent to 50 ml. of CDTA gives the number of milliliters of magnesium solution equivalent to the calcium present. The normality of the magnesium solution was thus found from

$$N_{Mg} = \frac{N_{Ca} \times 25.00}{2P - Q}$$

where

$$N_{Ca} = \frac{\text{grams of } CaCO_3}{\text{equivalent weight* of } CaCO_3} \times \frac{1000}{250} .$$

The normality of the CDTA solution was then obtained from

$$N_{CDTA} = N_{Mg} \times \frac{P}{25.00} .$$

For convenience in computing the results of titrations involving these solutions, the strength of the magnesium solution was actually expressed in terms of its titer (T) for various metals. This was accomplished simply by multiplying N_{Mg} by the equivalent weight of the metal involved. (Since the reaction of any metal with CDTA occurs in a 1:1 ratio, the equivalent weight of any metal was always taken as the atomic weight divided by two, regardless of the oxidation state of the metal.) The results for the determination of a metal (M) by indirect titration could be calculated from

$$\%M = \frac{(P' - Q')\,(T_M)\,(100)}{(\text{milligrams of sample})}$$

where P' was the number of milliliters of magnesium equiva-

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*For complexometric titrations the equivalent weight of calcium carbonate is one-half the molecular weight.

lent to the CDTA added, Q' was the number of milliliters of magnesium solution added in the back-titration, and T_M was the titer of the magnesium solution for M expressed in milligrams per milliliter.

3. Standardization of CDTA solutions with copper

Using the Murexide titration procedure described in paragraph 1a, solutions containing 0.6 to 0.8 m.e. of copper were titrated directly with CDTA. The copper solutions were either 20-mg. samples of pure copper wire (weighed on a semimicro balance) dissolved in 5 ml. concentrated nitric acid or 25-ml. aliquots of a solution prepared by dissolving 0.2 g. of copper in 10 ml. of concentrated nitric acid and diluting to 250 ml. In either case the calculations were straightforward.

4. Determination of lead and copper by simultaneous electrodeposition

Synthetic sample solutions of lead and copper were prepared by dissolving 0.6 to 0.8 g. of cleaned copper wire in 5 ml. of concentrated nitric acid in a 300-ml. tall form beaker, and adding from 5 to 50 ml. of a solution containing 3.313 g. of lead nitrate in sufficient water to make exactly one liter of solution. The samples were then diluted with water to 50 ml. and neutralized with concentrated ammonium hydroxide to the appearance of a precipitate. The precipitate was just dissolved by the dropwise addition of 70-72% perchloric acid, then a 5 ml. excess of the acid was added and the sample diluted to 100-125 ml. with water. About 0.5 g. of ammonium persulfate was added and the sample electrolyzed at 2.5 amperes for about one hour using a weighed stationary platinum gauze cathode[1] and a rotating platinum gauze anode.[2] Without interrupting the current, the electrodes were rinsed down with a fine stream of water as the sample beaker was lowered. The cathode was then removed from the electrolysis apparatus, rinsed with acetone, dried at 110°C. for about 15 minutes, cooled, and weighed to obtain the weight of the copper deposit. The anode was placed in a 250-ml. Erlenmeyer flask containing 25 ml. of water to which 0.5 ml. concentrated nitric acid and 0.25 g. of hydroxylammonium chloride had been added. The flask was tipped and rolled until all the lead dioxide deposit had been dissolved off the electrode. The electrode was then retrieved (with the aid of a pair of rubber-tipped forceps), rinsed down with water, and removed from the flask. The lead content was then determined using the indirect titration with F241 described above.

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[1] The cathodes used were in the form of cylinders with a diameter of 1 5/8 inches and a height of 2 inches.

[2] Similar to the cathodes except 1/2 inch in diameter.

5. Analysis of brass

The procedure used for separating the various constituents of a normal brass consisted of a modification of the usual gravimetric analysis scheme found in standard elementary quantitative analysis texts.[1] The procedure given below is described in detail only in those sections dealing with separations where standard methods have been modified. The CDTA solutions used were standardized with calcium carbonate.

a. Determination of tin. A one-gram sample of the finely divided brass sample was weighed into a 150-ml. beaker and covered with 5 ml. of water. The sample was dissolved by the addition of 10 ml. of concentrated nitric acid and the resulting solution was allowed to evaporate (for about one hour) to a volume of 5 ml. Filter paper pulp was then added, the sample was diluted to 50 ml. with water, and the precipitate of metastannic acid was allowed to digest for about 30 minutes on a steam plate. The tin precipitate was then filtered using close-textured paper (Whatman 42), washed with dilute (1:100) nitric acid, ignited, and weighed in the usual manner. The ignited stannic oxide was then

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[1] For example, see reference [134] p. 434, or reference [25] p. 427.

corrected for impurities by the volatization of stannic iodide using the method of Caley and Burford [16]. The residue from the tin purification (which consisted primarily of ferric oxide with possibly some silica and copper and lead oxides) was dissolved in the crucible by gentle heating with about 2 ml. of concentrated hydrochloric acid. The hydrochloric acid was removed by evaporating the solution almost to dryness on a hot plate following the addition of 2 ml. of 70-72% perchloric acid. The resulting metal perchlorates were dissolved in a small amount of water and rinsed into the main body of solution consisting of the filtrate and washings from the tin separation.

b. Determination of lead and copper. Lead and copper were determined on the solution resulting from the addition of the dissolved oxide residues from the tin purification to the filtrate and washings from the tin separation. The method employed was the simultaneous electrodeposition procedure described in paragraph 3 above. The volume of solution obtained from the tin determination was about 100-125 ml., hence no further dilution was required.

c. Determination of iron. The solution remaining from the copper and lead determination was evaporated to a volume of about 100 ml., neutralized with concentrated ammonium hydroxide to methyl red, and a 5 ml. excess added to the hot solution. The mixture was kept hot for 30 minutes before the hydrous ferric oxide precipitate was filtered and washed with 1:100 ammonium hydroxide in the usual manner. If more than a trace of iron was found, the hydrous oxide was dissolved by pouring 25 ml. of hot 1:5 hydrochloric acid through the filter, washing the filter with 1:100 hydrochloric acid, reprecipitating the iron with ammonia, filtering through the same paper, and washing the precipitate as before. The reprecipitated hydrous ferric oxide was again dissolved in the same manner and the iron content in this new solution (including the washings) was determined by the indirect titration procedure of paragraph 1c (above).

d. Nickel. The nickel in the filtrate from the iron determination was precipitated by the usual dimethylglyoxime procedure [23], filtered through Whatman 41 paper, and washed with water. The precipitate was dissolved by pouring 10 ml. of hot 1:3 nitric acid through the filter and rinsed through with several small portions of water. About 0.25 g. of hydroxylammonium chloride was added to the solution and the nickel content determined by the indirect titration (with magnesium) described in paragraph 1c.

e. Zinc. The filtrate (and washings) from the nickel determination was diluted to exactly 500 ml. with water. A suitable aliquot (50 or 100 ml.) was titrated for zinc using the indirect procedure described in paragraph 1c.

C. Experimental Results

1. CDTA titrations using Murexide

Attempts were made to utilize Murexide as an indicator in the direct titration of various metals with CDTA. The titration of copper with CDTA using Murexide has been described above as a method for standardizing CDTA solutions. The end-point of this titration was found to be extremely sharp. Using a 0.1 N CDTA solution on correspondingly larger amounts of copper gave titrations in which the transition from green to blue was so sharp that the intermediate gray color could be obtained only by adding the titrant in increments of less than one-third of a drop near the end-point. Despite this sharp end-point, the method does not show promise as a method for the determination of copper since all of the metals commonly associated with copper--iron, zinc, nickel, cobalt, etc.--also are titrated. As a means of standardizing CDTA solutions, however, the titration of samples of pure copper gave values for the normality of CDTA solutions which agreed to within one or two parts per thousand with those obtained using calcium carbonate.

The direct titration of nickel with CDTA using Murexide was not found to be satisfactory. Although the greenish-yellow to purple end-point was fairly sharp, the titration had to be carried out very slowly near the end-point. Heating the solution did not increase the rate of reaction sufficiently to permit a practical determination. The addition of excess CDTA followed by a back-titration with standard copper solution gave an end-point which was sufficiently rapid for a normal titration. This method was not believed to be as accurate or convenient as the method to be described later using F241 as the indicator and involving a back-titration with magnesium.

No method was found for the titration of calcium with CDTA using Murexide which could be considered an improvement over the titration with EDTA. The end-point was just as broad and indistinct with CDTA as with EDTA. An attempt was made to utilize a procedure involving a back-titration with standard copper solution. This resulted in an end-point very much like that found for calcium alone and, in addition, any magnesium present was partially titrated.

2. CDTA titrations using F241

a. Direct titrations. The only metals found to give satisfactory direct titrations with CDTA using F241 as the indicator were magnesium and zinc. In both cases the end-points were found to be very sharp. About two drops (0.1 ml.) of 0.02 N CDTA at the end-point caused the complete color change from red to blue. (Four or five drops of 0.02 N EDTA would be required to produce the same change.)

The use of CDTA to replace EDTA in the water hardness titration appears to be of doubtful value. Providing the magnesium-calcium ratio was at least 1:10, a very sharp end-point was obtained on synthetic water samples. Titrations of pure calcium solutions were unsatisfactory, however, even using CDTA solutions containing magnesium. Premature end-points always occurred unless the calcium solutions were hot and the titration carried out extremely slowly near the end-point. Satisfactory standardizations of CDTA solutions with calcium carbonate were obtained only by the addition of excess CDTA followed by back-titration with standard magnesium solution.

b. Indirect titrations. The indirect titration procedure described in Section IV B, paragraph 1c, was found to yield excellent end-points with calcium, strontium, lead, zinc, manganese (II), iron (II), iron (III), cadmium, cobalt (II), and nickel (II). Quantitative investigations of the stoichiometry of these titrations were carried out for calcium, lead, iron, and nickel. Titrations (using CDTA solutions standardized against calcium carbonate) of lead and nickel solutions gave results agreeing to within two or three parts per thousand with those obtained by the standard gravimetric procedures. Discrepancies of from one to three percent were observed in the titration of solutions of iron prepared from electrolytic iron. Also, the maximum amount of iron which could be determined appeared to be about 10 mg. These difficulties limit the use of the iron titration to such small amounts of iron as are found in brass and other copper-base alloys.

Two metals, barium and copper, failed to give satisfactory titrations. In the case of barium the end-point was broad and indistinct, probably due to the low stability of the barium-CDTA complex. The copper titration failed because of the irreversibility of the reaction of copper with F241. The premature end-points caused by this led to errors of as much as ten to fifteen percent of total copper present. It should perhaps be pointed out, however, that small amounts of copper in the presence of large amounts of other titrable substance merely titrated along with other ions but did not interfere with the end-point.

3. Determination of lead and copper by simultaneous electrodeposition

The lead nitrate solution employed was analyzed for lead by the standard gravimetric sulfate procedure.[1] Table 39 gives the results obtained on 50-ml. samples. The purity of the copper wire used was checked by the electrodeposition

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[1] For example, see reference [134] p. 441.

of 1-g. samples from the usual nitrate-sulfate solution [134]. The results of this analysis are shown in Table 40. Table 41 shows results obtained on synthetic samples of lead and copper using the simultaneous electrodeposition procedure described in Section IV B, paragraph 4. The CDTA and magnesium solutions used were standardized with calcium carbonate.

4. Analysis of brass

Results obtained for the analysis of a typical brass using the procedure described in Section IV B, paragraph 5, are given by part A of Table 42. Part B of this table shows the results of a procedure which was the same except that the tin purification step was omitted. Analyses of two National Bureau of Standards copper-base alloy samples are shown in Table 43. The tin precipitate was corrected for impurities in both of these analyses.

Table 39

Gravimetric Analysis of Lead Nitrate Solution

No.	Vol. of sample ml.	Wt. of $PbSO_4$ g.	Pb. content mg./ml.	Dev. mg./ml.
1	50.00	0.1517	2.073	+0.001
2	50.00	0.1515	2.070	-0.002
3	50.00	0.1517	2.073	+0.001
4	50.00	0.1518	2.074	+0.002
		Av.	2.072	±0.002

Table 40

Assay of Copper Wire by Electrodeposition from Nitrate-sulfate Solution

No.	Wt. of sample g.	Cu found g.	Cu %	Dev. %
1	0.8784	0.8777	99.92	0.00
2	0.8712	0.8706	99.93	+0.01
3	0.9384	0.9376	99.92	0.00
4	1.0397	1.0388	99.91	-0.01
		Av.	99.92	±0.01

Table 41

Simultaneous Electrodeposition of Copper and Lead

No.	Pb taken mg.	Pb found mg.	Error mg.	Cu taken[a] g.	Cu found g.	Cu %	Dev. from av. %
1	10.4	10.4	0.0	0.7522	0.7518	99.95	+0.03
2	20.7	20.7	0.0	0.6747	0.6741	99.91	-0.01
3	31.2	31.1	-0.1	0.6882	0.6876	99.92	0.00
4	41.4	41.5	+0.1	0.7233	0.7228	99.93	+0.01
5	51.8	51.8	+0.0	0.7062	0.7056	99.92	0.00
6	62.3	62.4	+0.1	0.6502	0.6496	99.91	-0.01
7	82.9	82.6	-0.3	0.7094	0.7089	99.93	+0.01
8	103.6	103.7	+0.1	0.7243	0.7238	99.93	+0.01
		Av.	±0.1			99.92	±0.01

[a] Figures in this column refer to actual weights of copper wire taken. They are not corrected for the lack of purity of the wire shown in Table 40.

Table 42

Analysis of Brass: Hach Chemical Company Sample 67

Sample no.	Tin %	Lead %	Copper %	Iron %	Nickel %	Zinc %	Total %
Grav. anal.[a]	3.08	4.22	78.32	0.22	0.58	13.56	99.98
A. Tin volatilized with ammonium iodide. Residue added to the sample solution prior to the determination of lead and copper.							
1	3.06	4.20	78.34	0.18	0.586	13.57	99.94
2	3.07	4.27	78.32	0.14	0.576	13.57	99.95
3	3.10	4.24	78.35	0.14	0.577	13.60	100.01
4	3.07	4.28	78.36	0.17	0.584	13.56	100.02
Av.	3.08	4.25	78.34	0.16	0.581	13.58	99.98
Error	0.00	+0.03	+0.02	-0.06	0.00	+0.02	
B. Tin precipitate not corrected for impurities.							
1	3.28	4.25	78.31	0.08	0.579	13.55	100.05
2	3.25	4.26	78.37	0.08	0.577	13.54	100.08
3	3.30	4.18	78.34	0.08	0.576	13.55	100.03
4	3.29	4.20	78.39	0.06	0.577	13.56	100.07
Av.	3.28	4.22	78.35	0.08	0.577	13.55	100.06
Error	+0.20	0.00	+0.03	-0.14	0.00	-0.01	

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[a] Analysis supplied by Hach Chemical Company, Ames, Iowa.

Table 43

Analysis of National Bureau of Standards Copper-base Alloys

No.	Tin %	Lead %	Copper %	Iron %	Nickel %	Zinc %	Total %
<u>NBS Sheet Brass No. 37</u>							
NBS[a]	1.01	0.99	70.29	0.29	0.52	26.89	99.99
1	1.00	0.99	70.30	0.25	0.523	26.85	99.91
2	1.00	0.99	70.24	0.27	0.519	26.84	99.86
3	0.97	0.98	70.26	0.27	0.521	26.88	99.88
4	1.01	0.99	70.22	0.28	0.524	26.83	99.89
Av.	1.00	0.99	70.25	0.27	0.522	26.85	99.88
Error	-0.01	0.00	-0.04	-0.02	0.00	-0.04	
<u>NBS Cast Bronze No. 52b</u>							
NBS[a]	8.00	0.011	88.25	0.032	0.72	2.96	99.98
1	8.02	0.02	88.26	0.032	0.724	2.97	100.02
2	8.02	0.02	88.24	0.041	0.722	2.99	100.03
3	8.02	0.03	88.23	0.032	0.724	2.97	100.00
4	8.04	0.02	88.24	0.038	0.724	2.99	100.05
Av.	8.02	0.02	88.24	0.04	0.724	2.98	100.02
Error	+0.02	+0.01	-0.01	+0.01	0.00	+0.02	

[a] Certificate values.

5. Stability of CDTA solutions

No experiments were set up specifically for checking the stability of CDTA solutions. An indication of their stability was provided, however, by the results of the standardizations performed during the course of other work. Three different CDTA solutions were standardized according to the procedure given in Section IV B, paragraph 2, at various time intervals. These solutions were stored in a 6-liter Pyrex glass flask fitted with a siphon tube outlet. The air inlet tube on the flask was kept closed by a pinch-clamp when the CDTA was not in use. No other precautions were taken. The data available concerning the stability of these solutions are summarized in Table 44. Incidental to these studies, it was found that the 0.02 N magnesium solutions did not undergo any appreciable change upon storage for periods of at least three months.

Table 44

Stability of CDTA Solutions

Days stored	Normality[a]	Loss in strength %
Solution No. 1 - pH 6.0		
0	0.01955	--
11	0.01948	0.35
37	0.01946	0.45
Solution No. 2 - pH 5.8		
0	0.01977	--
7	0.01971	0.3
21	0.01971	0.3
34	0.01971	0.3
Solution No. 3 - pH 5.0		
0	0.02060	--
11	0.02054	0.3
21	0.02052	0.4
72	0.02050	0.5

[a] Each figure in this column represents the average of four standardizations.

D. Discussion

1. Effect of pH on titration of magnesium

One of the disadvantages of EDTA titrations is that close control of the pH of the sample solutions is essential for results to be reproducible. This is especially true of the magnesium titration. The superiority of CDTA over EDTA in this regard is demonstrated in Table 45 and Figure 10. The data shown in Table 45 for EDTA were obtained by titrating a 0.02 N solution of EDTA (buffered at pH 10.5 with ammonium chloride and ammonium hydroxide) with 0.02 N magnesium solution to the F241 end-point. Then 1.0 N hydrochloric acid was added to reduce the pH to 10.3 (as measured with a pH meter) and sufficient magnesium added to restore the end-point. This process was continued until the titration failed to give a reasonably sharp end-point. The difference in amount of magnesium solution added at any pH from that added at pH 10 was taken as the "error" introduced by the variation in pH. The entire procedure was repeated for CDTA except that the starting pH was 11.1. The smaller errors found for the CDTA titration indicate that CDTA is to be preferred for titrations of metals in highly buffered solutions where accurate pH control cannot be established by the simple addition of the proper buffer mixture. Such a case is the determination of zinc in the brass analysis

Table 45

Effect of Variation of pH on the titration of EDTA and CDTA with Magnesium Chloride

pH	Error ml. of $MgCl_2$	
	EDTA	CDTA
9.00	+0.43*	+0.34*
9.10	+0.33*	+0.25*
9.30	+0.25	+0.14
9.50	+0.18	+0.07
9.70	+0.11	+0.03
9.90	+0.04	+0.01
10.00	±0.00	±0.00
10.10	-0.05	-0.01
10.30	-0.13	-0.03
10.50	-0.22*	-0.05
10.70	--	-0.07
10.90	--	-0.10
11.10	--	-0.15*

*Indicates poor end-point.

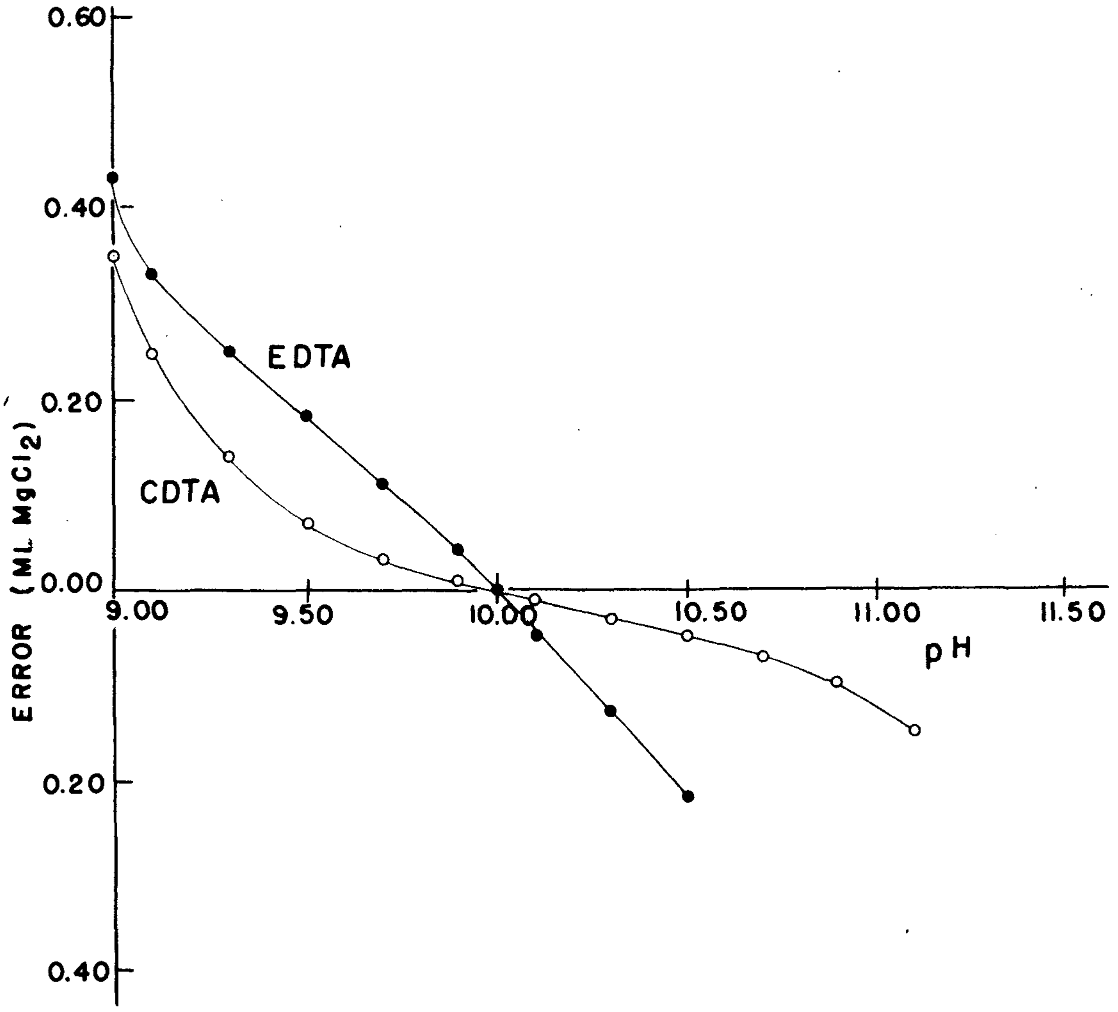

Figure 10. Effect of Variation of pH on the Titration of EDTA and CDTA with Magnesium Chloride

scheme described above. Because of the large amounts of ammonium salts in the sample solution at that point, the addition of a fairly large amount of 5 N sodium hydroxide is required to produce a pH of 10. Inasmuch as pH adjustment of this sort is only approximate, precise results could not be obtained if large errors in the titration were produced by small errors in the pH.

2. Determination of lead and copper

The method described in Section IV B, paragraph 4, was developed after difficulties were encountered with the simultaneous electrodeposition of lead and copper from the three percent nitric acid solution ordinarily employed. This latter procedure gave satisfactory results on brass samples containing only one or two percent lead, but for samples having higher lead content the acidity apparently was insufficient to keep lead from depositing on the cathode with the copper. Increasing the nitric acid concentration sufficiently to prevent the deposition of metallic lead also seriously retarded the deposition of copper. Perchloric acid was then tried as a means of increasing the acidity without increasing the nitrate ion concentration, but satisfactory results were not obtained until ammonium persulfate was added to supply the oxidizing power necessary to cause the lead to deposit satisfactorily on the anode.

3. Analysis of brass

Tables 42 and 43 show that the rapid method for the analysis of brass compares favorably with the more tedious gravimetric procedures from the standpoint of accuracy. The effect of neglecting the purification of the tin precipitate is demonstrated in Table 42. Although this leads to appreciable error in the results for tin and iron, it is doubtful that the extra time and effort required are justified for most routine analyses.

As in most conventional procedures, the iron determination is really an "R_2O_3" determination. Since the amount of iron in brass is almost always small, this causes little difficulty. If the determination of the individual constituents of the "R_2O_3" precipitate is desired, standard methods for this purpose are available in the literature.

4. Stability of CDTA solutions

The data given in Table 44 indicate that CDTA solutions stored at a pH of 5 to 6 show an initial deterioration of about 0.3% during the first week or so following preparation. After this initial loss of strength, however, such solutions appear to be fully as stable as EDTA solutions stored under the same conditions [36, 37].

E. Summary and Conclusions

1. The complexometric titration of a variety of common metals with CDTA has been studied. Direct titrations of copper in ammoniacal solution using Murexide as the indicator, and of zinc and magnesium using F241 indicator were found to yield very sharp end-points. These titrations were not at all specific, however. Calcium, strontium, lead, zinc, cadmium, manganese, iron, cobalt, and nickel were all titrated by the addition of an excess of CDTA followed by titration of the excess CDTA with standard magnesium solution. Again, due to lack of specificity, these titrations are of practical use only if the metal to be titrated has been isolated by a suitable separation procedure.

2. A method was developed for the separation of lead and copper from complex mixtures by simultaneous electrodeposition from a nitrate-perchlorate-persulfate solution. The copper was then determined gravimetrically and the lead was determined by indirect CDTA titration.

3. A scheme was devised for the rapid analysis of brass and other copper-base alloys. The procedure makes use of the above copper and lead determination and conventional separations concluded by indirect CDTA titrations. The method described is faster and more convenient than the usual gravimetric procedures, but does not result in any loss

of accuracy.

4. A study of the storage qualities of standard CDTA solutions shows that after an initial rapid decline in strength during the first few days after preparation, such solutions do not seriously deteriorate on standing for periods exceeding two months.

5. End-points obtained in CDTA titrations were found to be sharper than those encountered in similar EDTA titrations. The titration of magnesium with EDTA was shown to be influenced much more by variations in the pH of the sample solution than was the corresponding titration with CDTA. In both these respects CDTA appears to be the superior reagent for complexometric titrations.

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