THERMOMETRIC TITRATIONS OF SOME CATIONS WITH ETHYLENEDIAMINETETRAACETIC ACID AND WITH CYCLOHEXANEDIAMINETETRAACETIC ACID

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Robert Clark McDonald
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1969

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Thermometric Titrations of Some Cations with Ethylenediaminetetraacetic Acid and with Cyclohexanediaminetetraacetic Acid

by
Robert Clark McDonald

Thermometric titrations of Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Fe^{3+} with ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CyDTA) have been investigated. In addition the following mixtures Ca^{2+}-Mg^{2+}, Fe^{3+}-Co^{2+}, Fe^{3+}-Ni^{2+}, Fe^{3+}-Cu^{2+}, Zn^{2+}-Cu^{2+}, Cd^{2+}-Mg^{2+}, Cd^{2+}-Zn^{2+}, and Pb^{2+}-Cu^{2+}. All mixtures were studied in molar ratios of about 1:1 with the exception of the Fe^{3+}-Co^{2+} mixture in which the effect of varying this ratio was studied. It was found that a molar ratio of about 1:10 was the lowest that could be determined in the procedure used for this work.

It was found that analyses of metal cations could be made in concentrations of about 1 ppm with the use of a thermistor as one leg, in a Wheatstone-bridge set up, and a recording potentiometer as a temperature indicator. All results had an accuracy of better than 50% and a precision of 30% or better.

Although both EDTA and CyDTA were good titrants, CyDTA proved to be the better for more than half of the single ions and mixtures results.

CHAPTER I

INTRODUCTION

Introduction to Chelometric Titrations:

The use of chelons (9) such as ethylenediaminetetraacetic acid (EDTA) as titrants has revolutionized metal ion analysis. This began with the work of Schwarzenbach in 1946 on the volumetric determination of calcium and magnesium, a rapid procedure which was universally adopted for estimation of permanent hardness in water. Since then the EDTA titration has been extended to the determination of about half of the elements listed in the periodic table, and its scope will undoubtedly be broadened even further.

Both EDTA and cyclohexanediaminetetraacetic acid (CyDTA) are hexadentate ligands (see Figure 1) and form chelates with a metal:ligand ratio of 1:1 with most cations (14). This is an advantage in quantitative analysis in that the molecular weight is equal to the equivalent weight of cation.

To simplify the discussion which follows, EDTA and CyDTA will be assigned the formula H_4Y. The compound of EDTA which is most frequently used analytically is the disodium salt, Na_2H_2Y.

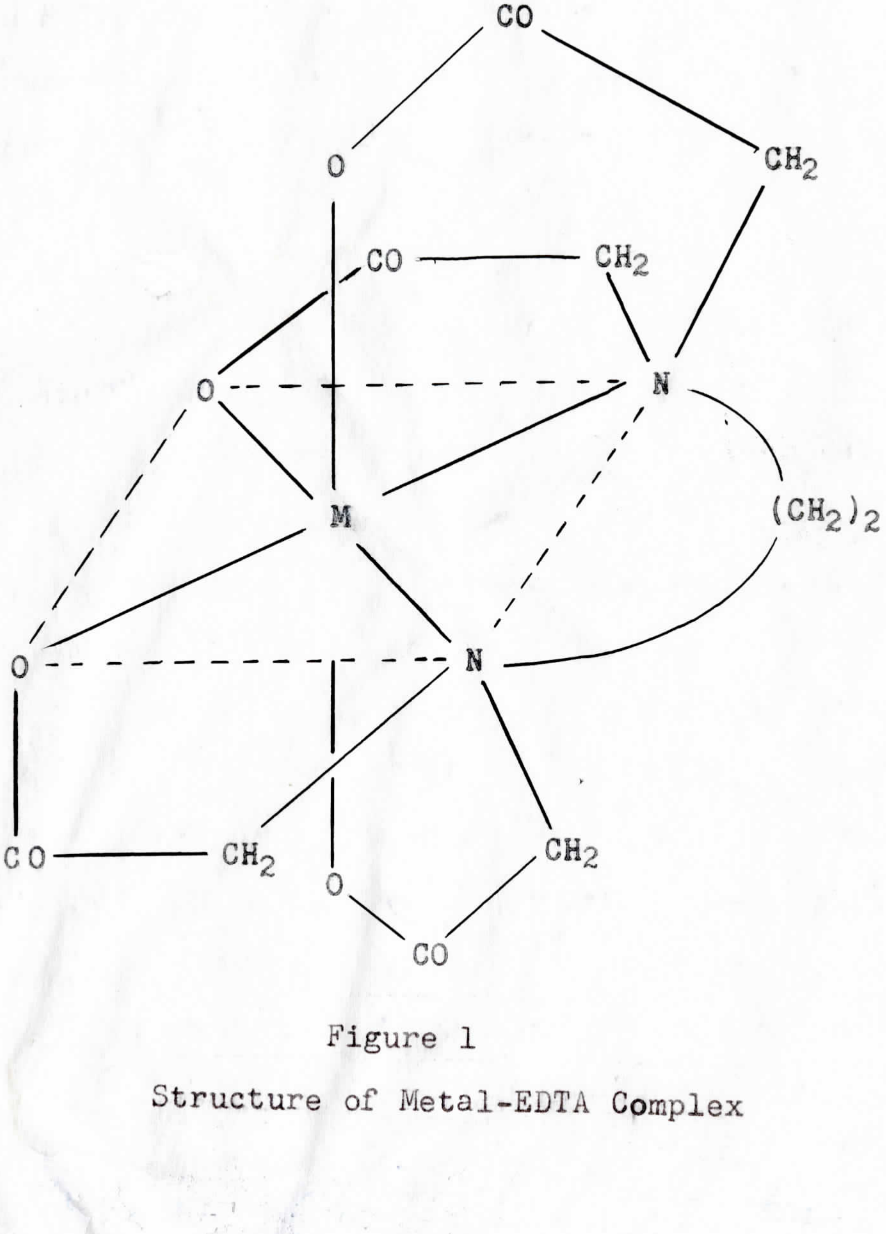


Figure 1

Structure of Metal-EDTA Complex

Cyclohexanediaminetetraacetic acid is obtained in the tetra-acid form, but readily forms the Na_2H_2Y compound in solution when NaOH is added to dissolve the tetra-acid.

The results to be reported in this work are based on the reaction for metal ion chelation shown in the following equation:

$$M^{n+} \quad + \quad Y^{4-} \quad \rightleftharpoons \quad (MY)^{n-4}$$

The equilibrium expression for this reaction is known as the stability constant and is reported in the literature from measurements made under optimum pH conditions. Even though not shown by the equation, there are several equilibria existing in aqueous solution which are dependent on the hydrogen ion concentration. For example: Available protons will react with the Y^{-4} ligand to form HY^{3-} which in turn can accept another proton to form H_2Y^{2-}. Proton addition can continue in highly acidic solutions until each of the four carboxylate groups have been protonated (see Figure 2). Other reactions which are also pH dependent are hydrolysis of the metal ion to form a weak hydroxide and also protonation of the final metal-chelate $[(MY)^{n-4}]$. The solvent (H_2O), a monodentate ligand, offers competition to the chelate ligand (Y^{4-}) for the cation in the formation of the hydrated complex of the metal ion.

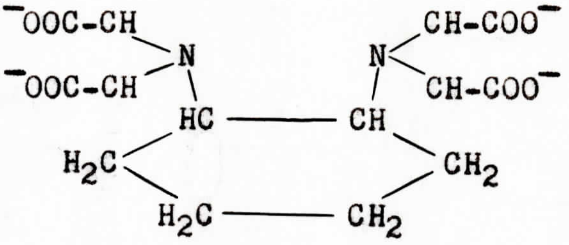
Introduction to Thermometric Titrations:

The basis of thermometric titrations is the heat produced upon the addition of titrant to a solution containing a species

Figure 2

A Comparison of Structures of EDTA and CyDTA

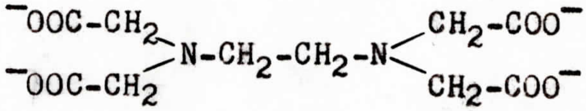
CyDTA



$pk_1 = 12.35$, $pk_2 = 6.12$, $pk_3 = 3.5$, $pk_4 = 2.4$

$T = 20$ C and $\mu = 0.1$

EDTA



$$(^{-}OOC\text{-}CH_2)_2N\text{-}CH_2\text{-}CH_2\text{-}N(CH_2\text{-}COO^{-})_2$$

$pk_1 = 10.26$, $pk_2 = 6.16$, $pk_3 = 2.67$, $pk_4 = 2.00$

$T = 20$ C and $\mu = 0.1$

to be determined. A plot of the temperature change as a function of the volume of the titrant (a thermogram) is made, and the end point is determined from an interpretation of the graph. Usually a change in the slope indicates the end point.

As early as 1921 Dutoit and Grobet (2) had performed thermometric titrations. They and subsequent investigators have applied this method to acid-base, complex-formation, precipitation, and redox reactions. Most of the results were not of sufficient accuracy to be useful until the technique was refined by Mayr and Fisch (8). Although the method now seemed widely applicable, many potential users were discouraged because of the length of time involved. In addition to the reading of a Beckmann thermometer, a long wait after each addition of titrant was necessary to allow the high heat capacity thermometer to come to thermal equilibrium. Even so, the apparatus was simple, consisting of a Beckmann thermometer, a Dewar flask, and cover with insert holes for a buret, and some type of stirrer.

In 1953 there was a major breakthrough in the thermometric titration when Linde, Rogers, and Hume (7) built the first automatic thermometric titrator. They used a thermistor and a recording potentiometer for measurement of temperature, along with a constant flow buret for continuous addition of titrant. This improvement made the method much faster because the low heat capacity thermistor gave almost immediate response.

Also, because smaller temperature changes could be detected, smaller amounts of material could be used. Jordan (5) reported that changes in temperature as low as 10^{-4}°C (approximately tenfold better than can be detected with a Beckmann thermometer) could be measured with such a thermistor-Wheatstone bridge setup. The first commercially manufactured thermometric titration instrument was made available in 1962 by the American Instrument Company (AMINCO), Silver Spring, Maryland (4).

Since thermochemical titrations have begun to play a role in chemical analysis, the following questions arise: How much material is needed for analysis? What is the lower limit of concentration measurable? Which type of temperature measurement is the most precise? Which type of chelometric titrant yields the largest heat change? Can thermometric titrations be made simple enough to be practical? Can more than one cation be analyzed simultaneously?

So far the literature reports no investigations of thermochemical titrations of metal ions in concentrations below 5×10^{-4} M using polyaminocarboxylate titrants. In this paper will be reported the results of the titrations of the following cations: Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Fe^{3+}. Also, the titrations of some selected binary mixtures of the above cations will be reported. The concentration of these metal ions was about 10^{-5} M or approximately one part per million.

The purpose of this investigation was to determine a simple, fast, and practical technique for quantitative analysis of certain metal ions in centrations of about 1 ppm. An extension of this technique to binary mixtures was attempted. Each metal ion and mixture was titrated with both EDTA and CyDTA for the purpose of determining which chelon produced the better titration. No special effort was made to meet optimum conditions for complex formation. This was consistent with the idea of a simple, fast, and practical method of analysis. In this investigation a recording potentiometer was used as part of the temperature measuring system so that in the future an instrument would be available which could easily be automated.

CHAPTER II

EXPERIMENTAL

Materials used:

Standard EDTA uas prepared from reagent grade Na_2H_2EDTA (Fisher Scientific Co.) which had been dried in an oven for one hour at a temperature of 105-110°C, and was used to standardize all cation solutions.

Cyclohexanediaminetetraacetic acid (CyDTA) (J. T. Baker Chemical Co., 96.0% purity) was standardized against a zinc solution. This zinc solution had been previously titrated with standard EDTA solution mentioned above to determine its molarity.

Both standard EDTA and CyDTA solutions were made up to a strength of about 0.1 molar and the EDTA was used at this strength to standardize the cation solutions. Both chelate solutions were diluted to about 0.002 molar for the thermometric titrations of the single ions and mixtures.

All of the metal cation solutions were made from reagent grade chemicals. All cation solutions were made from the hydrated metal nitrate salts with the exceptions of cobalt (II) and calcium, for which the hydrated metal chloride salts were used. All of the solutions were made by dissolving a weighed amount of salt into distilled water. Approximately twenty drops per liter of concentrated nitric acid were added to the zinc, the iron (III), the lead (II) and the mercury (II) solutions to prevent hydrolysis.

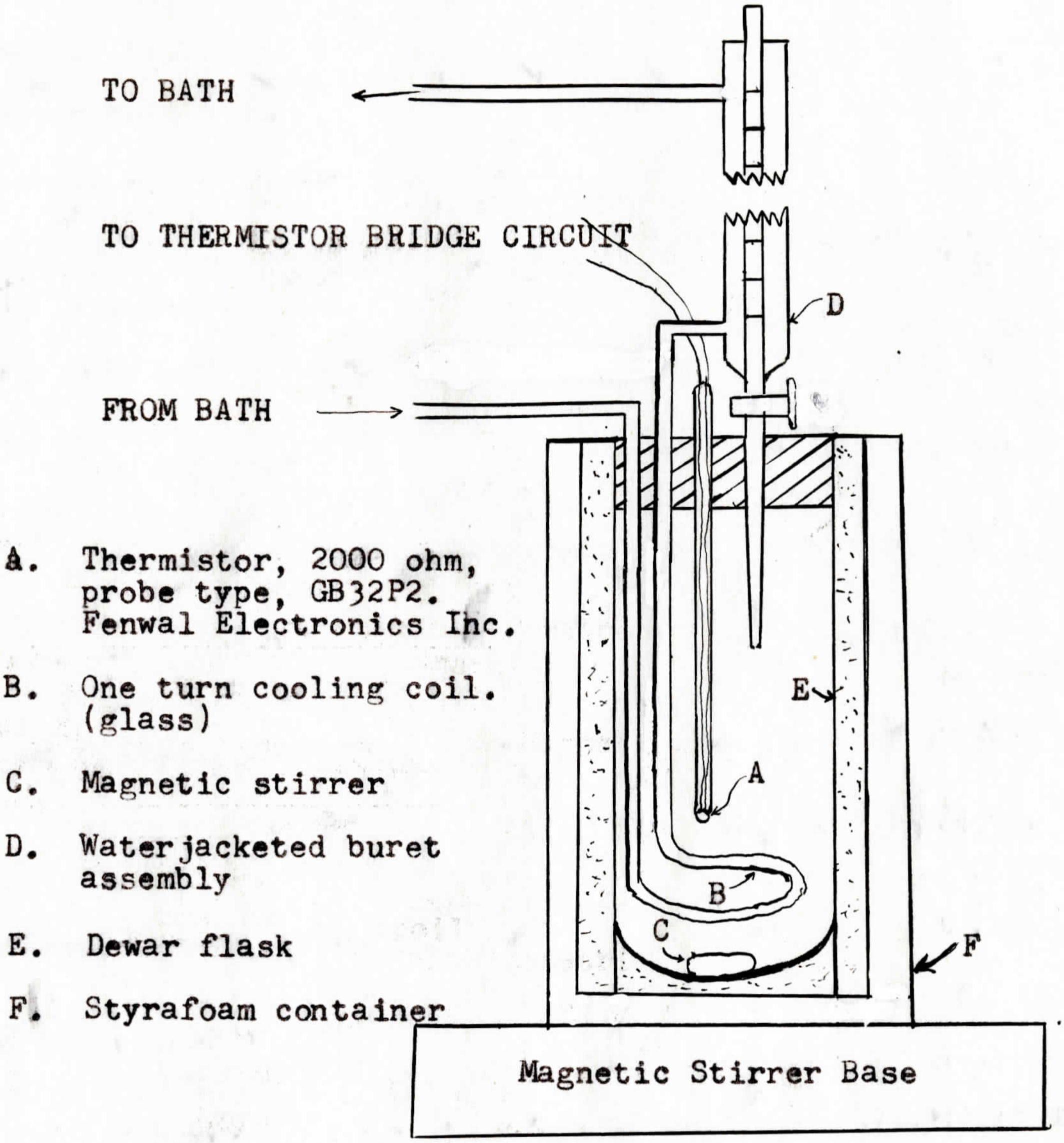
All of the metal ion solutions were standardized with the EDTA standard solution. In the standardizations Eriochrome Black T was used as the indicator along with an appropriate buffer (10) for all cases except calcium and copper (II). For calcium the method of Ross, Aikins, and Reilley (11), in which Acid Alizarin Black SN served as the indicator, was used. Copper (II) was standardized according to a method described by Welcher (14) using murexide indicator.

Thermometric Titration Apparatus:

As illustrated in Figure 3, the calorimeter consisted of a 250 ml Dewar Flask mounted on the inside of a Styrafoam container. Vermiculite insulation was placed between the outside walls of the flask and the inside walls of the container. Stirring during titrations was accomplished by setting the calorimeter on a magnetic stirrer base and inserting a stirring magnet into the solution.

The thermometric titration cell head consisted of a thermistor, a one turn glass coil, and the buret tip. A 10 ml water-jacketed buret was used to deliver titrant to the calorimeter. This was made by placing the buret inside of the outside hull of a glass condenser and sealing with corks. The water was pumped into the bottom of the condenser hull and expelled at the top.

A 25 gallon constant temperature bath complete with a



A. Thermistor, 2000 ohm, probe type, GB32P2. Fenwal Electronics Inc.

B. One turn cooling coil. (glass)

C. Magnetic stirrer

D. Waterjacketed buret assembly

E. Dewar flask

F. Styrafoam container

Figure 3

Thermometric Titration Apparatus

thermoregulator, agitator, and heating and cooling coils was used to bring the titrant and sample to essentially the same temperature prior to titration. This water bath was used also to store distilled water and titrant to be used in the titrations. The cations were added in such small aliquots that they were not kept in the bath. The water in this bath did not vary more than 0.01 degrees while operating and was held at 25°C.

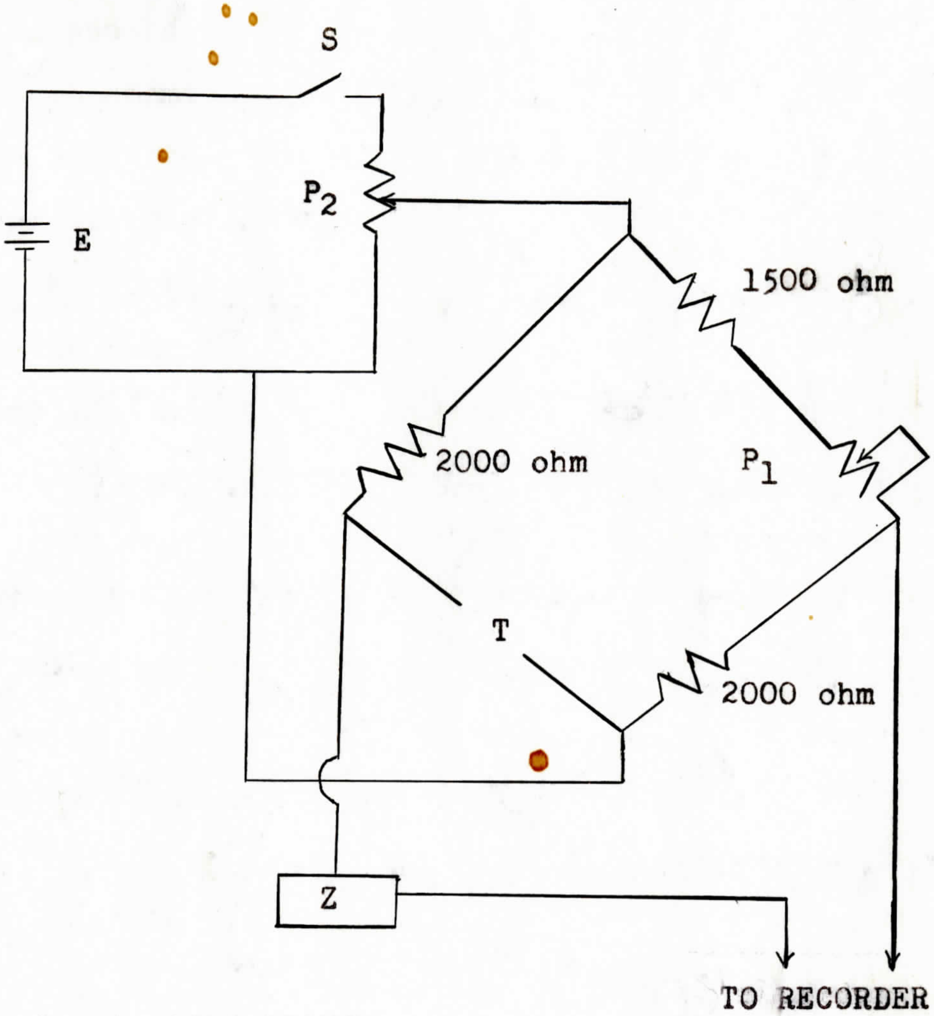
Electrical Measurement of Temperature Change:

A thermistor was mounted inside of a 4 mm glass tube. The leads were insulated from the calorimeter solutions by an epoxy cement seal at each end of the glass tubing, and in such a way as to leave only the thermistor bead exposed to the solution. The leads from this thermistor made up one arm of a Wheatstone bridge circuit (see Figure 4). The Wheatstone bridge circuit used was very similar to the one used by Jordan and Alleman (5).

As the temperature changed in the solution, the resistance of the thermistor also changed inversely and was recorded by means of a recording potentiometer (Heath Co. model EUE-20A).

Thermometric Titration Procedure:

The water-jacketed buret was filled with titrant (about 0.002 M) to the upper level of water in the jacket surrounding it, or a little below. Approximately 235 ml of distilled water was added to the calorimeter. Then an aliquot (1 to 3 ml)



E. 3.0-volt source.

P_1. 1000-ohm fifteen turn potentiometer slidewire.

P_2. 50-ohm ten-turn precision potentiometer-slidewire.

T. 2000-ohm thermistor (Fenwal Electronics Inc.)

S. Toggle switch.

Z. Zero adjust.

Figure 4

Thermistor Bridge Circuit

of standard cation solution was pipetted into the calorimeter. The thermometric titration cell head, with the exception of the buret tip, was then placed on the calorimeter, and the magnetic stirrer speed was adjusted. After the pinch clamp on the tube leading from the glass coil inside the calorimeter to the pump was released, the pump in the constant temperature bath was then turned on and 5 minutes were allowed for thermal equilibrium to be established. The pump was then cut off and the pinch clamp adjusted to prevent any water from circulating. By this time the titrant and the **sample** would be vary close to the same temperature. However, the titrant is usually estimated to be several thousandths of a degree warmer. Next the recorder switch was turned on and the proper sensitivity was set. Then by adjusting the coarse potentiometer, P_1, and the fine potentiometer, P_2, the recorder needle was brought on scale. After one ml of titrant was drained from the buret tip and discarded, the buret was lowered into the titration head so that the tip was below the level of solution in the calorimeter. Increments of titrant (either 0.25 ml or 0.10 ml as needed to give the desired number of points on the thermogram) were added manually every 15 seconds. Just before each addition the chart paper was moved manually to the next division. Titrant was added until it was evident that the reaction was complete. All titrations were **run** in triplicate.

CHAPTER III

DISCUSSION OF RESULTS

The results reported in this thesis are of titrations of Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Fe^{3+} at concentrations in the order of magnitude of 1 ppm. The results are tabulated in Tables I, II, III, and IV. Some selected titration curves may be seen in Figures 5-10.

It was found in this investigation that quantitative analysis of the above cations can be made in concentrations as low as 1 ppm with an error of under 50% and a precision of well below 30% in most cases. These conclusions apply to single ions as well as the binary mixtures. For example, both the % error and average deviation are small in the Cu^{2+} determinations using both titrants. In the CyDTA case both the average deviation and error was 0.0%, whereas in the EDTA case the average deviation was 4.3%, while the error was 11.1%. Although both titrants are entirely satisfactory, CyDTA appears to be slightly superior.

The results of this investigation suggest that EDTA is a better titrant for Mn^{2+}. The EDTA titrations produced an average deviation of 4.3% and an error of 14.3% while the same values for the CyDTA titrations were 32.1% and 31.4% respectively.

From an inspection of Tables I and II it will be found that other examples of cases where one titrant is clearly superior to the other. By using the sum of the Average deviation and the error as a criterion, it was found that CyDTA yielded smaller totals for three-fourths of the single ion determinations, and presumably was the better titrant for these ions. On the other hand, the EDTA titrations were more reproducible for single ion determinations, with the average deviations in all cases less than 10%.

By using the sum of the average deviation and the error for both ions in a mixture as a criterion for the effectiveness of a titrant, it was found that CyDTA was a better titrant in more than one-half of the mixture determinations. The best result with CyDTA was the Zn^{2+}-Cu^{2+} determination, where the average deviation was 4.8% for Zn^{2+} and 3.6% for Cu^{2+}. In both cases the error was 0.0%. In contrast, the least accurate result using CyDTA was obtained in the analysis of the 1:1 molar ratio of Fe^{3+}:Ni^{2+}. The average deviation was 8.4% for Fe^{3+} and 16.7% for Ni^{2+}; the error was 14.3% for Fe^{3+} and 33.3% for Ni^{2+}. However, these results are quite satisfactory for determinations in concentrations of less than 1 ppm.

The best mixture analysis using EDTA as the titrant was obtained with the Fe^{3+}:Ni^{2+} in a molar ratio of 1:2. In this case the average deviation was 0.0% for Fe^{3+} and 7.3%

for Ni^{2+}. The error was 0.0% for both ions. By comparison the least accurate determination using EDTA was the Cd^{2+}:Zn^{2+} mixture in a molar ratio of 2:5. The average deviation was 27.0% for Cd^{2+} and 25.0% for Zn^{2+}, whereas the error was 20.0% for Cd^{2+} and 28.6% for Zn^{2+}. Average deviations and error of such magnitude are considered to be acceptable for determinations in the concentration ranges studied in this thesis.

In most of the mixtures studied the ratio of the molar concentrations of the metal ions was approximately 1:1. To determine the effect of variation in the molar ratio on the shape and interpretation of the thermograms, the Fe^{3+}:Co^{2+} mixture was selected for study as this ratio was varied. Titrations were run on Fe^{3+}:Co^{2+} mixtures at molar rations of about 1:1, 1;5 and 1:10. Actually, the Fe^{3+} concentration was held at 0.7 ppm in each mixture and the Co^{2+} concentration was changed each time to 0.8, 4.1, and 8.3 ppm. For the Fe^{3+}-Co^{2+} mixtures it was found that the thermograms became increasingly difficult to interpret as the ratio approached 1:10. At these low ratios the titration of the species of the smaller concentration is not represented by enough points to be well defined. This problem results from the necessity of using a more concentrated titrant (0.02 M) in order to titrate the more concentrated metal ion. These results are compiled in Table V and the titration curves

TABLE I

Single Metal Ion Titrations with EDTA

Metal Ion	Taken(ppm)	Found(ppm)	% Ave. Dev.	% Error
Mg^{2+}	0.5	0.4	9.1	20.0
Ca^{2+}	0.5	0.6	5.9	20.0
Mn^{2+}	0.7	0.8	4.3	14.3
Fe^{3+}	0.7	0.7	9.5	0.0
Co^{2+}	0.8	0.5	0.0	37.5
Ni^{2+}	0.7	0.9	3.8	28.6
Cu^{2+}	0.9	0.8	4.3	11.1
Zn^{2+}	1.4	1.1	5.5	21.4
Cd^{2+}	1.5	1.8	5.7	20.0
Hg^{2+}	2.4	1.4	1.0	41.7
Pb^{2+}	2.8	3.3	4.4	17.9

TABLE II

Single Metal Ion

Titrations with CyDTA

Metal Ion	Taken(ppm)	Found(ppm)	% Ave. Dev.	% Error
Mg^{2+}	0.5	0.5	0.0	0.0
Ca^{2+}	0.5	0.6	4.2	20.0
Mn^{2+}	0.7	0.5	32.1	31.4
Fe^{3+}	0.7	0.7	4.8	14.3
Co^{2+}	0.8	0.8	12.5	0.0
Ni^{2+}	0.7	0.8	3.1	14.3
Cu^{2+}	0.9	0.9	0.0	0.0
Zn^{2+}	1.4	1.2	19.2	14.3
Cd^{2+}	1.5	1.8	7.2	20.0
Hg^{2+}	2.4	2.6	3.8	8.3
Pb^{2+}	2.8	3.1	6.4	10.7

TABLE III

Metal-EDTA Binary Mixtures

Metal Ion	Molar Ratio	Taken	Found	% Ave. Dev.	% Error
Ca^{2+}	1:2	0.5	0.3	10.0	40.0
Mg^{2+}		0.5	0.4	0.0	20.0
Fe^{3+}	1:1	0.7	0.7	5.0	0.0
Co^{2+}		0.8	0.9	10.7	12.5
Fe^{3+}	2:1	1.4	1.0	16.1	28.6
Ni^{2+}		0.7	0.9	3.6	28.6
Fe^{3+}	1:1	0.7	0.7	4.5	0.0
Ni^{2+}		0.6	0.9	25.0	50.0
Fe^{3+}	1:2	0.7	0.7	0.0	0.0
Ni^{2+}		1.5	1.5	7.3	0.0
Fe^{3+}	1:1	0.7	0.8	8.3	14.3
Cu^{2+}		0.9	0.8	8.3	11.1
Zn^{2+}	3:2	1.4	1.3	7.9	7.2
Cu^{2+}		0.9	1.1	2.9	22.2
Cd^{2+}	1:1	3.1	2.7	9.9	12.9
Mg^{2+}		0.5	0.4	0.0	20.0
Cd^{2+}	1:1	3.1	2.5	16.0	19.3
Zn^{2+}		1.4	1.5	19.5	7.2
Cd^{2+}	1:2	1.5	1.2	5.5	20.0
Zn^{2+}		1.4	1.5	10.9	7.2
Cd^{2+}	2:5	1.5	1.8	27.0	20.0
Zn^{2+}		2.1	1.5	25.0	28.6
Pb^{2+}	1:1	2.8	2.7	1.2	3.6
Cu^{2+}		0.9	1.0	17.3	11.1

TABLE IV

Metal-CyDTA Binary Mixtures

Metal Ion	Molar Ratio	Taken	Found	% Ave. Dev.	% Error
Ca^{2+}	1:2	0.5	0.5	7.2	0.0
Mg^{2+}		0.5	0.4	7.7	20.0
Fe^{3+}	1:1	0.7	0.5	6.3	28.6
Co^{2+}		0.8	0.8	16.7	0.0
Fe^{3+}	2:1	1.4	1.2	2.9	14.3
Ni^{2+}		0.7	0.7	0.0	0.0
Fe^{3+}	1:1	0.7	0.8	8.4	14.3
Ni^{2+}		0.6	0.8	16.7	33.3
Fe^{3+}	1:2	0.7	0.7	4.5	0.0
Ni^{2+}		1.5	1.1	26.4	26.6
Fe^{3+}	1:1	0.7	0.6	15.8	14.3
Cu^{2+}		0.9	0.7	13.6	22.2
Zn^{2+}	3:2	1.4	1.4	4.8	0.0
Cu^{2+}		0.9	0.9	3.6	0.0
Cd^{2+}	1:1	3.1	2.8	8.5	9.7
Mg^{2+}		0.5	0.4	7.7	20.0
Cd^{2+}	1:1	3.1	2.1	7.8	32.3
Zn^{2+}		1.4	1.3	2.5	7.1
Cd^{2+}	1:2	1.5	1.6	1.6	6.7
Zn^{2+}		1.4	1.4	14.3	0.0
Cd^{2+}	2:5	1.5	1.5	13.3	0.0
Zn^{2+}		2.1	1.6	27.7	23.8
Pb^{2+}	1:1	2.8	3.3	10.1	17.9
Cu^{2+}		0.9	1.1	6.1	22.2

TABLE V

Metal-CyDTA Binary Mixtures - Metal:Metal Ratio Varied

Metal Ion	Molar Ratio	Taken	Found	% Ave. Dev.	% Error
Fe^{3+}	1:1	0.7	0.5	6.3	28.6
Co^{2+}		0.8	0.8	16.7	0.0
Fe^{3+}	1:5	0.7	0.9	3.8	28.6
Co^{2+}		4.1	3.8	3.5	14.6
Fe^{3+}	1:10	0.7	0.8	4.3	14.3
Co^{2+}		8.3	8.2	9.8	12.0

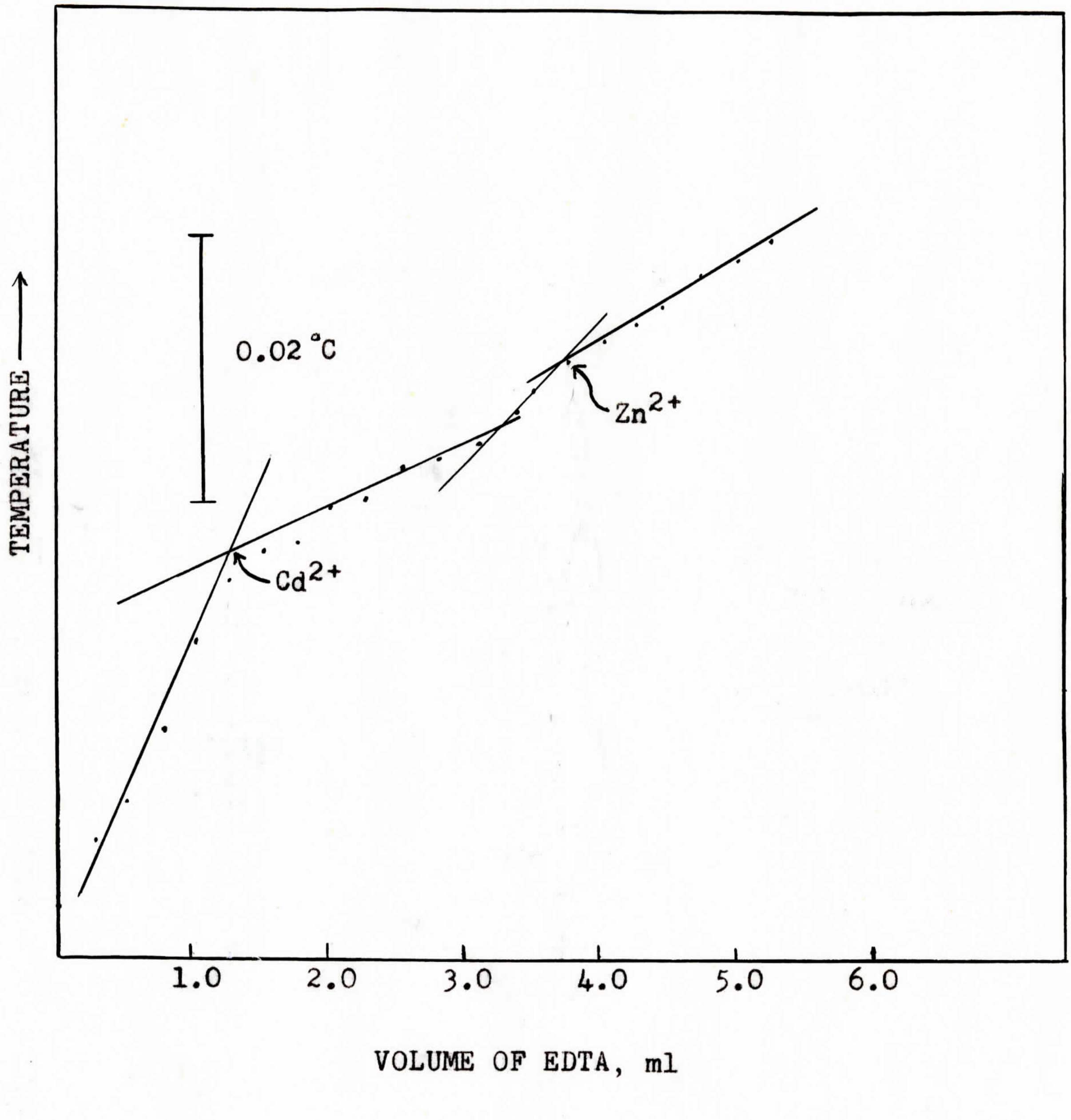


Figure 5

Titration of Cd^{2+}-Zn^{2+} Mixture with EDTA

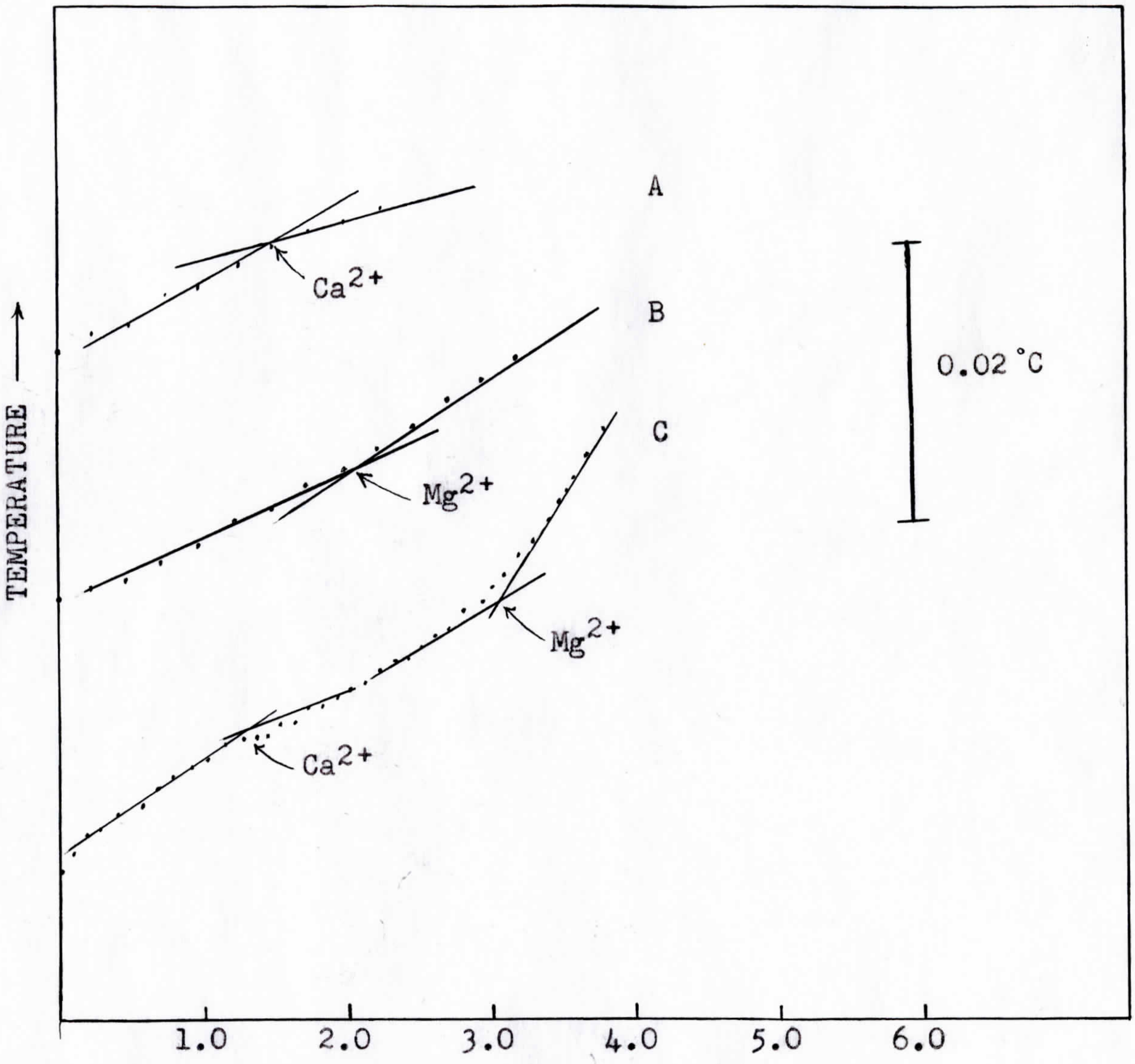


Figure 6

Titrations of Ca^{2+} and Mg^{2+} as Single Ions, and Ca^{2+} and Mg^{2+} as a Binary Mixture

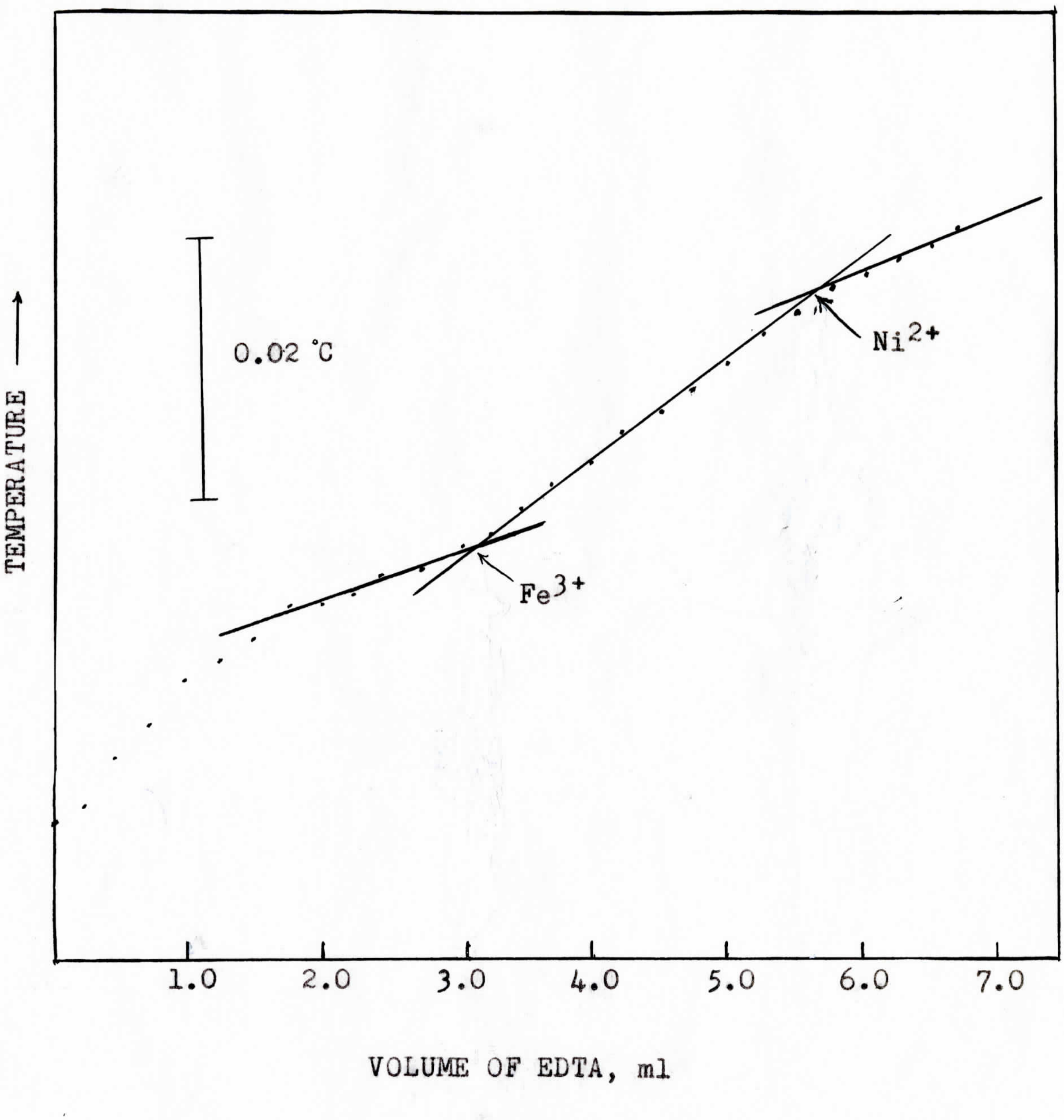


Figure 7

Titration of Fe^{3+}-Ni^{2+} Mixture with EDTA

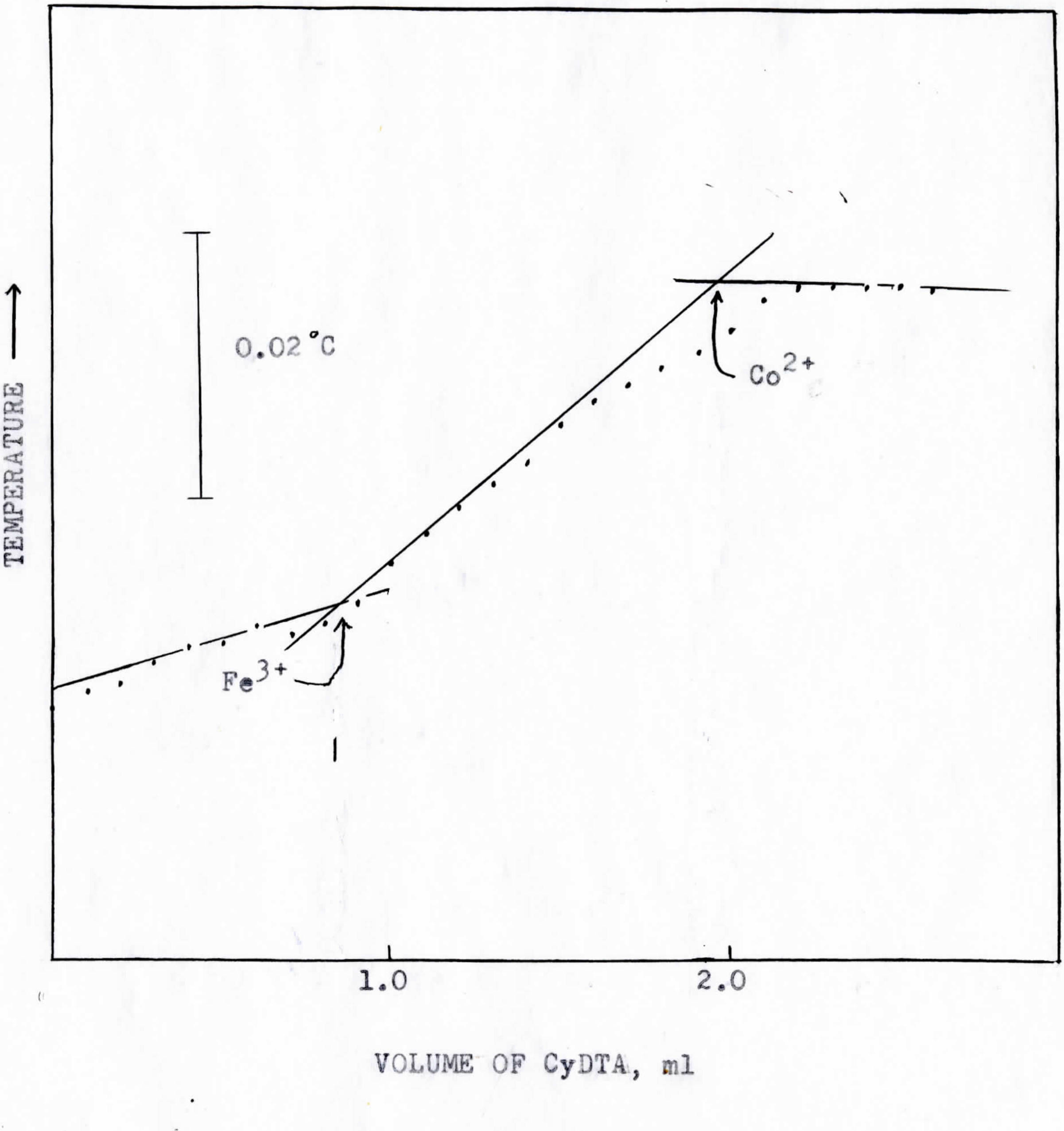


Figure 8
Titration of Fe^{3+}-Co^{2+} Mixture with CyDTA
(1:1 Molar Ratio)

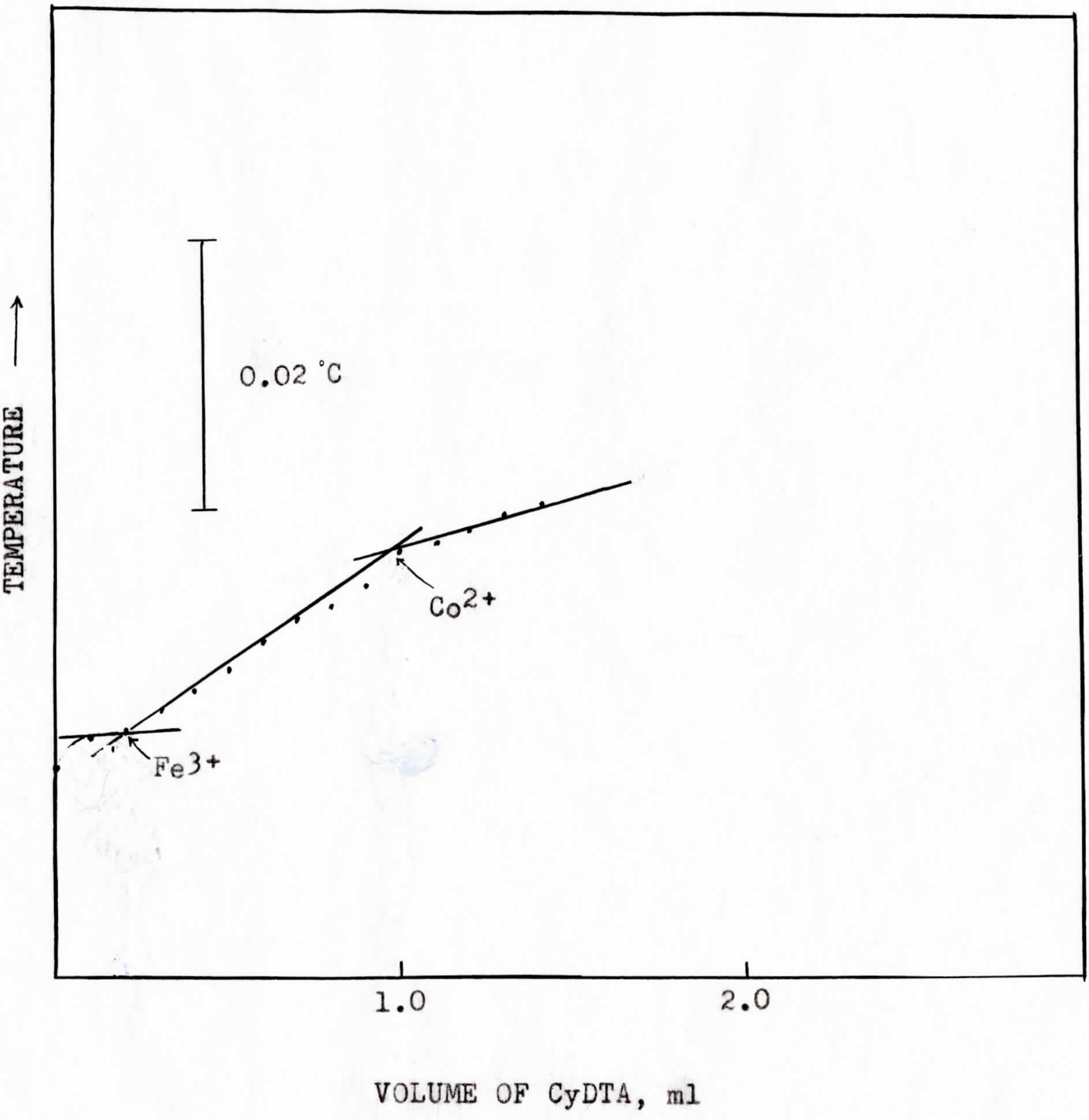


Figure 9

Titration of Fe^{3+}-Co^{2+} Mixture with CyDTA

(1:5 Molar Ratio)

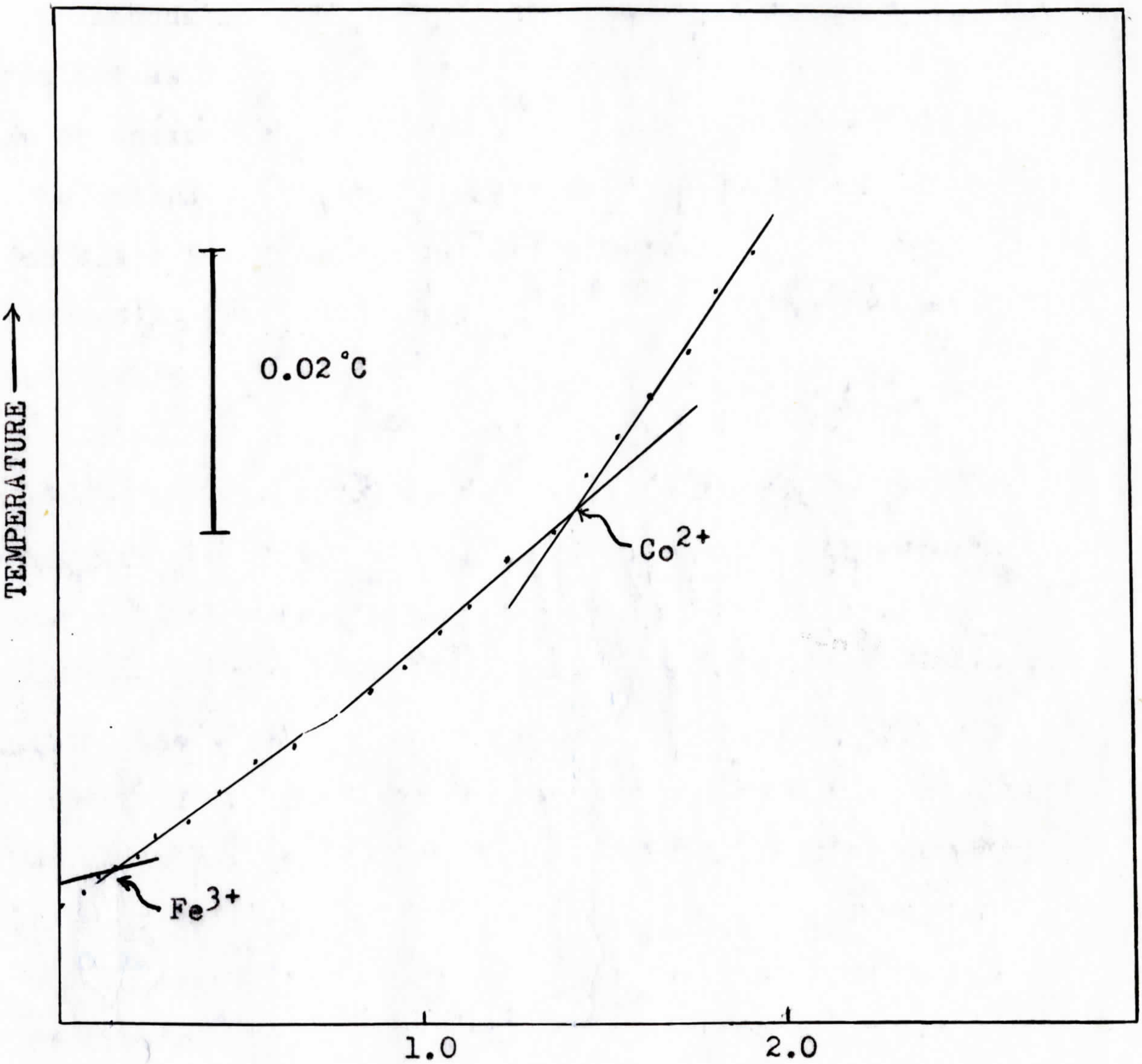


Figure 10

Titration of Fe^{3+}-Co^{2+} Mixture with CyDTA

(1:10 Molar Ratio)

are illustrated by Figures 8, 9, and 10.

Although the average deviations for the binary mixtures were not as small as those for the single ions, this was not an unexpected result because there are two end points to be determined instead of one and the first end point is used again for calculating the volume of titrant needed for the species reacting second, thus introducing the same error twice.

In all of the binary mixtures analyzed, the cation forming the metal-chelate having the higher stability constant was the first to react. However, when the two metal ions being titrated form metal-chelated having nearly the same stability constant, it would be possible for the cation forming the metal-chelate with lower stability constant to react first if its concentration were sufficiently greater than the other cation. A value for the stability constant was not found for iron(III)-CyDTA in the literature, but the thermograms indicated that iron did react before the other cation in the titrations of the Fe^{3+}-Co^{2+} as well as the Fe^{3+}-Ni^{2+} mixtures. To substantiate this further, it was noted in the Fe^{3+}-Co^{2+} mixtures that a color (light green to pink, depending on the relative cobalt concentration) formed after the addition of the first few drops of CyDTA. Cobalt(II) tested singly did not form such a colored solution. Also Fe^{3+} reacted first in all iron(III) mixtures (see Figure 7) when EDTA was used as a titrant. In no case did the order in which the ions were titrated in the same mixture differ as to the titrant used.

The heat of reaction was used to a certain degree in predicting the general shape of the thermograms. This worked best in the case of the Ca^{2+}-Mg^{2+} mixture where Ca^{2+} has an exothermic heat of reaction and Mg^{2+} the opposite. Figure 6 illustrates these points very well, because in the Ca^{2+} single ion titration (A), the slope is greater than for the Mg^{2+} single ion titration (B). This consistent in the mixture titration (C) in which the decrease in slope marks the Ca^{2+} end point. Note that after the second end-point in each thermogram a slope exists that theoretically represents only temperature difference between the titrant and sample solution and the heat of stirring. It follows that if two metal ions yielding exothermic heat of reaction were titrated in a mixture, the most exothermic reaction would produce a greater slope. In this study the cation which yielded the most exothermic reaction always reacted first in the mixture. However, the slope of the first titration was not always the greatest. The following reasons can be given: (1) There was not much difference in the heats of reaction of the two cases and (2) These titrations were carried out at different pH values than those of the heats of reactions in the literature.

The CyDTA reaction studied had more exothermic heats of reactions than the corresponding EDTA reactions in all but four cases. These exceptions were Ni^{2+}, where the EDTA heat of reaction was 0.1 Kcal/mole more exothermic, and Zn^{2+}, Hg^{2+}, and Pb^{2+}, for which the EDTA value was about 0.5 Kcal/mole more. Mg^{2+} was the only cation with an endothermic heat of reaction, and the EDTA value was 1.5 Kcal/mole more endothermic than the CyDTA value. It is believed that the more exothermic heats of reactions contribute to the slight superiority of CyDTA over EDTA as a titrant.

Barrett (1), using a Beckmann Thermometer, was unable to determine mixtures of Cd^{2+} and Zn^{2+}. This mixture determination appeared to be feasible from the heats of reaction. His suggestion that a more sensitive apparatus using a thermistor might work did prove succesful in this investigation (see Figure 5).

A comparison with analyses reported in the literature using colorimetric and polarographic measurements of concentration in the 1 ppm order of magnitude, shows that thermometric titrations are comparable. Koich (6) reported that the lowest concentation detectable by oscillographic square wave polarography (which is more accurate than ordinary d. c. polarography) was about 1 ppm for Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. It is fairly common to find in the literature determinations reported with errors of 100% at these low concentrations.

Generally colorimetric methods are no more accurate than thermometric titrations. There are several exceptions, however, in which colorimetric analysis is much better. A method reported by Vallee (3) for Zn^{2+}, using dithizone as a chromogenic reagent, allows concentrations of 0.1 ppm to be determined with a precision of 2.1%. While this method is better than thermometry, it requires a special solvent, critical pH adjustment, and the use of a 5 cm absorption cell. Also, Snell (12) described several very precise colorimetric methods for iron. In a method using o-Nitroso R Salt, 0.013 ppm of iron can be measured. In the presence of cobalt, however, this reagent cannot be used because of the formation of the wine red complex of cobalt which interferes with the iron determination.

It is the author's opinion that for analysis of binary mixtures, thermometric methods have a definite advantage over colorimetric methods in that small temperature differences can be detected more precisely than small absorbance differences. Also for colorimetric analysis of binary mixtures, quite lengthy procedures and calculations are required.

In the future, analyses of mixtures containing ions with a molar ratio of less than about 1:10, as well as mixtures containing more than two ions, might be achieved by the use of masking agents. Reilley, Schmid, and Sadek (4) have reported many masking and demasking reagents and the conditions of their use in chelometric titrations. For example, at a pH of 10 the cyanide ion will mask Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, as well as Pt^{2+}, Pd^{2+}, Ag^{1+}, and Tl^{2+}; but with the addition of chloral hydrate or formaldehyde, Cd^{2+} and Zn^{2+} are demasked. An application of this information might be carried out in the titration of a mixture of Fe^{3+}, Mg^{2+}, Cu^{2+}, and Zn^{2+}. This could be done thermometrically as follows: (1) Determine the total number of millimoles of all species (only the final end point is needed). At this point some idea as to relative amounts of each ion might be estimated from the thermogram. (2) Next with another sample, adjust the pH to 10 with an ammonia buffer and add KCN (in large excess) and titrate again to determine Fe^{3+} and Mg^{2+}. The Cu^{2+} and Zn^{2+} ions form a very stable complex with CN^- and do not react with the chelon titrant. If, however, the molar ratio of Fe^{3+} to Mg^{2+} is such that simultaneous determination is not possible, then repeat except with the addition of ascorbic acid, which will form a complex with the Fe^{3+} and allow a titration of only Mg^{2+}. In this case the Fe^{3+} is determined by difference. (3) The Cu^{2+} and Zn^{2+} can then be determined by analyzing again with the same buffer and KCN addition, but also with the addition of excess formaldehyde (which demasks the Zn^{2+}). Then the Cu^{2+} and Zn^{2+} in the mixture can be quantitatively determined by difference.

It has been found in this investigation, that with the utilization of a thermistor in a Wheatstone bridge circuit, quantitative analysis of the metal ions studied can be made in concentrations of 1 ppm. Although CyDTA gives, on a statistical basis, better results for most of the cations and mixtures studied, both titrants produced good results for measurements at this low concentration. The thermometric titration has proved to be a simple and rapid method for quantitative analysis, and useful for analysis of cations at very low concentrations.

The author believes that with the addition of a constant flow buret to the apparatus used in this work, an automatic instrument would be available for carrying our titrations with great speed and precision and also could be used for kinetic and enthalpy studies. These studies could be accomplished with greater speed and accuracy than most of the present methods because less material would be needed.

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