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STUDIES IN THE ANALYTICAL CHEMISTRY OF  
IRON-ALUMINUM MIXTURES

- I. HOMOGENEOUS PRECIPITATION OF FERRIC PERIODATE
- II. COMPLEXOMETRIC TITRATIONS OF FERRIC ION WITH  
ETHYLENEDIAMINE TETRAACETIC ACID

A THESIS

Presented to  
the Faculty of the Graduate Division  
by  
William Rich Jacobsen

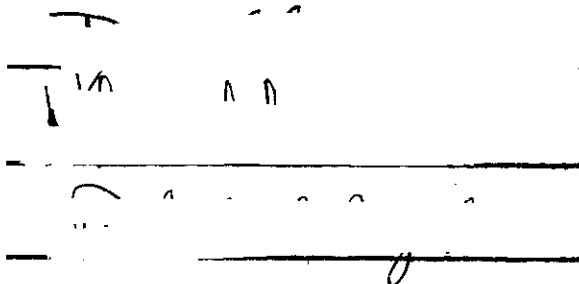
In Partial Fulfillment  
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Master of Science in Chemistry

Georgia Institute of Technology  
June, 1959

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Approved:



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June 3, 1959

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## SUMMARY

The purpose of this research was to devise an analytical procedure for the determination of iron and aluminum in materials containing comparable amounts of each metal. The field of homogeneous precipitation furnished the area for the initial attack on the problem. The use of the periodate ion to oxidize the ferric iron EDTA complex and gradually precipitate ferric periodate was attempted. It was found, however, that the complex was incompletely oxidized by periodate. Moreover, it was apparent that aluminum complexed with EDTA to a measurable extent in the pH range concerned. Thus the initial complexation of iron had to be done in exact molar ratios or subsequent errors in the aluminum determination arose. For these reasons, homogeneous precipitation was abandoned as far as the iron was concerned.

The complexometric titration of iron with EDTA was then investigated. Aluminum had been found by previous workers to cause moderate errors in titrations at pH 2.0-3.0. Calculations of the apparent stability constants of the EDTA complexes of iron and aluminum at pH 1.0 suggested the possibility of the titration of iron at that value without interference from aluminum. A series of experiments was carried out to evaluate this theory. The indicator used was 5-sulfosalicylic acid; the color change at the end point being from the purple



iron-sulfosalicylate complex to yellow iron-EDTA complex. The color change was quite gradual at pH 1.0, so a spectrophotometric technique was employed. The titration was performed in a Beckman DU Spectrophotometer, adapted with a special cell for holding the titration vessel. The absorption maximum of iron-sulfosalicylate at 510 millimicrons was followed and decreasing absorbance plotted versus milliliters of standard EDTA added. The linear portions of the curves obtained were extrapolated to give the end point. Results to within 0.1-0.3 per cent error were obtained in the determination of iron solutions containing 55-60 milligrams of iron in the presence of from 27-204 milligrams of aluminum. The per cent error found in the iron determination was not influenced by the presence of aluminum. Titrations of iron in lower concentrations were less satisfactory.

The procedure devised for iron determinations was shown to be applicable in conjunction with the method of Flaschka and Abdine which was previously used for aluminum alone or the sum of iron plus aluminum.

Some qualitative investigation of the behavior of aluminum in non-aqueous media showed possible areas for further research in aluminum determinations.

PART I

HOMOGENEOUS PRECIPITATION OF FERRIC PERIODATE

## CHAPTER I

### INTRODUCTION

One of the intriguing problems in analytical chemistry is the quantitative determination by wet analysis techniques of iron-aluminum systems containing comparable quantities of each constituent. Trace analysis of either metal is more appropriately assigned to the field of emission spectrography or absorption spectroscopy.

The initial method of attack on the problem was the use of a gravimetric procedure known as homogeneous precipitation. H. H. Willard and N. K. Tang (1) in 1937 first devised a method of homogeneously generating the precipitating agent to combat the phenomenon of coprecipitation which was a great deterrent to accurate gravimetric analyses. Coprecipitation is the carrying-down of impurities from the original solution into the precipitate of the element under analysis. This is caused, in ordinary precipitations, by the localized concentration effects brought about by direct addition of precipitating agent to the solution. Willard and co-workers found that by slowly generating the precipitating agent in solution with the cation under study, coprecipitation could be greatly lessened.

This method is especially applicable in the cases of hydroxide precipitations with ammonia, which invariably lead

to flocculent, hard to handle precipitates. Willard found that urea was an ideal source of homogeneously generated ammonia to study improvements in hydroxide systems. Aluminum precipitations were greatly improved by this technique, coprecipitation being lessened; and when a suitable anion as sulfate or succinate, was present, dense filterable precipitates were formed. These precipitates were then readily ignited to the oxide and weighed.

Further investigations in homogeneous precipitation have been carried out, principally by L. Gordon and various co-workers (2). Many techniques have been devised to slowly generate either cations or anions for analytical procedures and to study the types of coprecipitation.

MacNevin and Dunton (3) reported the homogeneous precipitation of ferric hydroxide by the slow oxidation of the ferric-EDTA complex with hydrogen peroxide. (EDTA is the accepted abbreviation for ethylenediamine tetraacetic acid.) Since ferric iron forms an insoluble periodate, this research was directed toward the use of excess periodate ion as both an oxidizing agent to destroy the ferric-EDTA complex and as a precipitating agent. Given an iron-aluminum mixture in aqueous solution, the iron would be complexed by the addition of EDTA, the aluminum then precipitated by urea hydrolysis or oxine, and finally the iron complex oxidized and ferric periodate precipitated. The respective precipitates could be ignited to their oxides and weighed, or in the case of aluminum oxinate, weighed as such.

This technique proved impractical principally because of the difficulty involved in adding the correct amount of EDTA to complex the iron alone, the aluminum complexing to a small but measurable degree and the failure of periodate to completely oxidize the iron-EDTA complex.

## CHAPTER II

## CHEMICALS AND EQUIPMENT

## Chemicals

Ethylenediamine tetraacetic acid, tetra sodium salt.--Practical grade obtained from Matheson, Coleman and Bell.

Iron wire.--Analytical reagent grade obtained from Mallinkrodt Chemical Works.

Potassium meta-periodate.--Baker C. P. grade.

Potassium persulfate.--Merck C. P. grade.

Calcium carbonate.--Merck reagent grade.

Eriochrome Black T.--Eastman practical grade.

Hydrazine.--Eastman practical grade.

Urea.--Eastman practical grade.

Succinic acid.--Baker C. P. grade.

Aluminum metal.--Baker reagent grade granular metal.

Salicylic acid.--Eastman practical grade.

Potassium dichromate.--Analyzed reagent grade.

## Solutions

Ferric nitrate.--Solutions were prepared by dissolving the required amount of C. P. iron wire in warm dilute reagent grade nitric acid. These solutions were standardized against potassium dichromate standard solution using barium diphenylamine sulfonate as an indicator.

Aluminum Chloride.--Solutions were prepared by dissolving the required amount of C. P. granular aluminum metal in reagent grade hydrochloric acid. These solutions were standardized by the precipitation of aluminum oxinate.

Eriochrome Black T indicator solution.--Solutions were freshly prepared when needed. One-half gram of "Erio-T" was dissolved in 100 milliliters of ethanol.

Buffer solution of pH 10.0.--Seven grams of ammonium chloride dissolved in 57 milliliters of concentrated ammonium hydroxide and diluted to 100 milliliters.

#### Equipment

Muffle furnace.--Electric multiple unit furnace manufactured by the Hevi-Duty Electric Company.

pH Meter.--Beckman "Zeromatic" pH meter.

Porcelain crucibles.--#3001 Sintered disc porcelain crucibles.

## CHAPTER III

## PROCEDURE

Qualitative investigations were carried out to determine whether or not the periodate ion could oxidize the ferric-EDTA complex and effect complete homogeneous precipitation of ferric periodate.

An excess of solid tetra-sodium EDTA was added to 10.0 milliliters of acidic 0.1F ferric ion, resulting in a reddish colored solution. The solution was diluted to about 150 milliliters and all solids dissolved. The pH was then between 6.0 and 7.0. Potassium meta-periodate ( $\text{KIO}_4$ ) was added in excess and the resulting solution heated to 80-90°C on a water bath. A dense, cream-colored precipitate of ferric periodate slowly formed. The solution was allowed to remain at this temperature for three hours, then filtered and more periodate added. Still more precipitate resulted and the solution was still reddish in color, indicating incomplete precipitation of the iron. The supernatant liquid was tested for free ferric ions with potassium ferrocyanide, but no blue precipitate resulted, indicating that the iron left in solution was still complexed.

The experiment was repeated using 0.4 grams of EDTA (slightly more than an amount which would be equivalent to



iron). The pH was adjusted to 7.0 with 1:20 ammonium hydroxide, 1.2 grams  $\text{KIO}_4$  added, and the heating process carried out for two hours. Again, incomplete precipitation of ferric periodate resulted. A ferric ion solution containing 85 milligrams of iron per ten milliliters was used with 0.6 grams EDTA. The pH in this case was adjusted to 3.0 with dilute ammonium hydroxide and nitric acid. At this pH the color of the ferric-EDTA complex is greenish-yellow.  $\text{KIO}_4$  (2.5 grams) was added and the solution heated to  $90^\circ\text{C}$  on a water bath for two hours. A dense cream colored precipitate was formed, but the solution was still greenish-yellow. The pH of the solution rose to five during the heating process. More  $\text{KIO}_4$  was added and more precipitate obtained, but some ferric ion was still left in solution as evidenced by the persistence of the greenish-yellow color.

This procedure was repeated using 2.5 grams of  $\text{KIO}_4$  at pH 5.0, heated to  $95^\circ\text{C}$ ; 5.0 grams  $\text{KIO}_4$  at pH 6.0 heated to  $50^\circ\text{C}$ ; 5.0 grams  $\text{KIO}_4$  at pH 3.0 heated to  $90^\circ\text{C}$ . In all cases, incomplete precipitation of ferric periodate resulted.

The value of addition of potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) was investigated in another series of experiments. Using two to three grams of  $\text{KIO}_4$  with two to three grams  $\text{K}_2\text{S}_2\text{O}_8$ , pH values of 3.0, 4.0 and 8.0, and heating to  $90^\circ\text{C}$  for one to three hours resulted in less colored solutions than previously obtained, but the precipitation of iron was still incomplete. In this case, the pH of the solution was lowered.

The extent of precipitation of ferric periodate was determined. A solution containing 85 milligrams of ferric iron and 0.6 grams EDTA was adjusted to pH 3.0 causing a greenish-yellow color of the complex in solution. Five grams  $\text{KIO}_4$ , and 2.5 grams  $\text{K}_2\text{S}_2\text{O}_8$  were added, the solution diluted and heated at  $90-95^\circ\text{C}$  on a water bath for two hours. The solution was still greenish-yellow in color. The precipitate of ferric periodate was filtered in a sintered disc porcelain crucible, ignited at  $1000^\circ\text{C}$  in a muffle furnace and weighed as  $\text{Fe}_2\text{O}_3$ . Seventy milligrams of iron were found as opposed to 85.0 milligrams taken.

Since the periodate ion obviously did not completely oxidize the ferric-EDTA complex, tests were carried out to determine whether or not it would oxidize the free acid in solution.

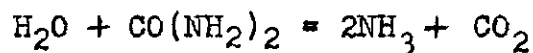
The procedure involved heating the EDTA solution with periodate, adding an aliquot of a standard calcium solution and back titrating with standard EDTA using Eriochrome Black T indicator. The amount of periodate used, pH and temperature conditions were the same as in the previous experiments. It was found necessary to reduce the oxidizing agents with 85 per cent hydrazine to prevent the destruction of the indicator. Ten milliliters of 0.0101F calcium solution were added by pipet, and the solution buffered to pH 10.0 with an ammonium hydroxide-ammonium chloride buffer. A few drops of Eriochrome Black T indicator were added and the calcium

titrated with 0.0098F EDTA. The end point is reached when the red-violet color changes to pale blue. The calculated amount of EDTA necessary was 10.3 milliliters. The results with two separate EDTA solutions with 1.0 and 1.5 grams  $\text{KIO}_4$  were 10.2 and 10.4 milliliters.

It is apparent from these results that the periodate ion will completely oxidize uncomplexed EDTA even though it did not completely destroy the iron complex.

The method of homogeneously precipitating basic aluminum succinate is outlined by Willard (1). This was studied to determine its applicability to this problem.

When urea is hydrolyzed by heating an aqueous solution to boiling, ammonia and carbon dioxide are formed.



The ammonia then furnishes homogeneously generated hydroxide ions throughout the solution.



In the presence of succinate ion, aluminum forms a dense basic succinate when the hydroxide ions are generated by the urea process.

Two 20 milliliter portions of 0.17F aluminum solution were taken and 2.0 grams EDTA added to one. The pH in each was adjusted to between two and three. 4.0 grams urea, 5.0 grams succinic acid and 10.0 grams ammonium chloride were

added, and both were placed on a boiling water bath for one hour. The final pH in both solutions was five. A dense white precipitate was obtained only in the solution without EDTA. No precipitate was noted when EDTA was present. This indicated as expected that aluminum cannot be precipitated from an EDTA complex by urea hydrolysis, even under extreme conditions.

Two samples were then considered. Both contained ten milliliters of ferric solution (85 milligrams of iron). Ten milliliters of aluminum solution (45.6 milligrams) were taken in one case and twice that amount in the other. Both solutions were titrated with 0.1F EDTA to a thiocyanate end point (red to yellow color change) at pH 3.0, thus complexing all the ferric ions. Urea, succinic acid and ammonium nitrate were added in the amounts previously described. The solutions were placed on a boiling water bath for three hours. Dense white precipitates were formed in both solutions. The precipitates were filtered in sintered disc porcelain crucibles and washed with succinic acid solution made neutral with ammonium hydroxide. They were then dried at 110°C and ignited in a muffle furnace. The temperature in the furnace was kept between 900 and 1050°C for one hour. The precipitates were then weighed as  $\text{Al}_2\text{O}_3$ . The calculations showed 44.6 milligrams and 74.0 milligrams aluminum found as compared to 45.6 milligrams and 91.2 milligrams taken.

The filtrates from the aluminum precipitation were treated with  $\text{KIO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$ , and heated for one hour but

incomplete precipitation of ferric periodate again resulted.

The thiocyanate end point in the iron titration was somewhat questionable, so salicylic acid was used as an indicator. When titrated with EDTA, the color change is from the reddish purple color of ferric salicylate to the yellow color of ferric EDTA.

This titration was performed to see if the actual ferric end point was being obtained when aluminum was present. The method outlined by Cheng, Bray and Kurtz (4) was followed. The titration of 10.0 milliliters of 0.1527F ferric iron at pH 2.0-3.0 required 14.53 milliliters of 0.1F EDTA using salicylic acid indicator. The titration of 10.0 milliliters of the ferric solution in the presence of 10.0 and 20.0 milliliters 0.17F aluminum solution required 16.2 and 16.0 milliliters of 0.1F EDTA under the same pH conditions as previously described. Thus it appeared that in the pH range of 2.0-3.0, the aluminum was being partially complexed by the EDTA.

The situation was somewhat bettered when only a slight excess of EDTA was present after the iron titration. Ignition of precipitates from urea hydrolysis resulted in finding 45.0 milligrams against 45.6 milligrams aluminum taken and 89.8 milligrams against 91.2 milligrams taken. However, this procedure required prior knowledge of the volume of EDTA needed to exactly complex the ferric ion.

## CHAPTER IV

### DISCUSSION OF RESULTS AND RECOMMENDATIONS

All homogeneous precipitation techniques are based on the concept of gradual formation of precipitant in solution. Most procedures utilize the formation of anions; the cations being present in solution as "free" metal ions (actually aquo complexes).

Heyn and Schupak (5) utilized the hydrolysis of the peroxydisulfate (persulfate) ion to precipitate barium sulfate from the barium EDTA complex. As the persulfate solution was warmed, the hydrolysis furnished hydrogen ions and sulfate ion. The hydrogen ions caused gradual dissociation of the barium complex since a decrease in pH lowers its apparent stability constant. The barium was then free to precipitate as barium sulfate. This process would not be applicable to metals whose stability constants are relatively high ( $\log K = 16$  or greater) because they would still be complexed sufficiently to prevent precipitation in the pH range of 2.0-3.0 which was the final pH in the Heyn and Schupak (5) method. A discussion of the effect of pH on EDTA complexes is presented in Part II.

The ferric-EDTA complex has a  $\log K$  of 25.1 and the aluminum complex one of 16.13, therefore a hydrogen ion

generating process would not be sufficient to completely dissociate either unless extremely acid conditions were reached.

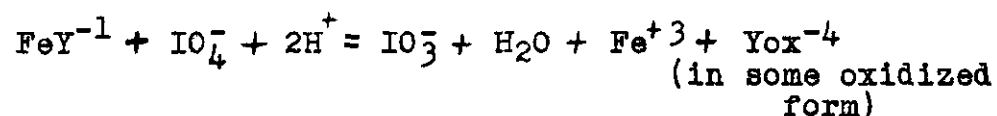
Oxidation of the complex has been accomplished by the use of hydrogen peroxide, resulting in homogeneously precipitated ferric hydroxide (3).

This investigation explored the use of periodate salts since they are known to be good oxidizing agents for organic materials (6). The gradual oxidation of the ferric complex would produce iodate ions, ferric ions, and some oxidized form of EDTA. With an excess of the periodate salt present, homogeneously precipitated ferric periodate would result.

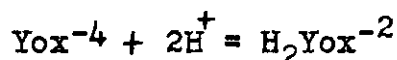
Experimental results showed that the precipitation was incomplete at any temperature, pH, or periodate concentration tried. Moreover, the oxidation process was also incomplete as no positive qualitative test for ferric ion in solution was obtained. The persistence of the colors of the complexes to remain after oxidation also indicate incomplete reaction. It should be noted here that the greenish-yellow color of ferric EDTA complex is observed up to a pH of about six. Above this value, the hydroxo complex ( $\text{FeOHY}^{-2}$ ) is present (7) in amounts increasing with increasing pH. The color of this complex is reddish-brown and was noted in the experiments at pH 7.0.

Several reasons can be postulated for the rise in pH noted during the periodate oxidations. First, the reduction

of periodate to iodate would use up hydrogen ions to form water. Second, the EDTA in a partially oxidized state could be protonated just as the unoxidized form would be. The reaction steps are postulated as follows:



"Y" is the standard abbreviation in chemical equations for EDTA. The equation is not balanced due to lack of knowledge of the EDTA oxidation product.



It is seen that both reactions use up hydrogen ions with resulting rise in pH.

Another possibility arises from the fact that tertiary amines are partially oxidized by  $\text{HIO}_4$  to form ammonia and formaldehyde (6). The presence of ammonia would, of course, cause a rise in pH and the possibility that the precipitate formed could be a mixed hydroxide and periodate. This is not important since ignition to  $\text{Fe}_2\text{O}_3$  followed the precipitation process.

The use of both periodate and persulfate in the same solution was attempted to see if the rate of the oxidation process could be increased by the presence of an oxidizing agent (persulfate) that would not have to serve as precipitating agent as well.



When persulfate is present, the pH of the solution is lowered due to formation of hydrogen ions from hydrolysis as in the barium case described. Since the solution was less colored after this oxidation process than with periodate alone, a set of concentrations of periodate and persulfate may be possible which would effect complete oxidation and precipitation. No further work was undertaken along this line because experiments showed that the iron would have to be titrated with EDTA to be masked for aluminum precipitations since an excess of EDTA caused some aluminum complex to be formed with a resulting error in the aluminum precipitate.

A possible explanation for the fact that the oxidation of EDTA acid by periodate is much faster than the oxidation of the ferric complex may be approached by the Lewis acid-base theory. If the EDTA is considered as a Lewis base or electron pair donor and the iron as an acid or electron pair acceptor, the electron density of the complex is greater around the iron molecule. The points of attack of an oxidation process on EDTA are considered to be the two nitrogen molecules (8). It would seem apparent, then, that an oxidation, or loss of electrons, from the nitrogens would be less readily accomplished when the electron density in those areas has been lowered through complex formation. This problem could no doubt be more clearly explained if the oxidation products of EDTA were definitely known.

The failure of aluminum to be precipitated from its EDTA complex by urea hydrolysis is readily apparent. When the solution is heated, the rate of formation of aluminum EDTA complex is increased and all the aluminum is soon complexed. The generation of hydroxide ions by the urea only serves to enhance the stability of the complex by raising its apparent stability constant.

Since it was found that aluminum complexed with EDTA to a small extent at a pH of 2.0-3.0, the exact titration of iron within this range was prevented. The establishment of a set of conditions at which iron will completely complex and aluminum will not complex at all is then necessary.

The investigation of the field of complexometric titrations was then undertaken and will be discussed in Part II.

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## PART II

### COMPLEXOMETRIC TITRATIONS OF FERRIC ION WITH ETHYLENEDIAMINE TETRA-ACETIC ACID

## CHAPTER I

## INTRODUCTION

The use of complexometric titrations in analytical chemistry has increased rapidly since the introduction of EDTA as a titrant in 1946 by G. Schwarzenbach. A great number of papers giving a wide scope of analytical procedures have been published in the last decade. The books by Schwarzenbach (1), Flaschka (2), and Welcher (3) describe the theory and applications of complexometric techniques with emphasis on the uses of EDTA.

Cheng, Bray and Kurtz (4) devised a procedure for the determination of iron in soils using salicylic acid as an indicator in an EDTA titration. Sweetser and Bricker (5) felt that the visual end point was not good enough and made use of spectrophotometric titration technique to improve it. Their data shows an increasing error in the amount of iron found with increasing amounts of aluminum present. It seemed apparent both from their data and the experiments described in Part I of this thesis that the aluminum was being complexed to a small extent in the pH range of 2.0-3.0 which was used. Other workers have found that the aluminum complex is not completely formed unless the solution is boiled for several minutes (6). The best approach to the problem with which

this research is concerned would be to establish a set of conditions to prevent the formation of the aluminum EDTA complex completely.

This would be accomplished by causing the apparent stability constant of the aluminum complex to become very small while maintaining the iron constant at a value suitable for quantitative determinations. The apparent stability constants for metal complexes can be lowered in two ways. Increasing hydrogen ion concentration lowers them by increasing the amounts of the various protonated species of EDTA present in solution. The presence of another complex forming substance may cause the disruption of an EDTA complex. This is the technique known as masking. The measure of these two effects are known as the alpha and beta factors, respectively. Derivations of expressions for these factors and their application to determining apparent stability constants are included in the appendix.

This research, then, was directed toward the establishment of pH conditions that would permit the titration of ferric ion with EDTA in the presence of aluminum. The application of this method to existing techniques was checked, and finally, the suitability of non-aqueous media for complexometric titrations of aluminum was investigated.

## CHAPTER II

## CHEMICALS AND EQUIPMENT

## Chemicals

5-sulfosalicylic acid.--Eastman white label grade.

Ethylenediamine tetraacetic acid, disodium salt.--Baker Reagent grade.

Bismuth trioxide.--Baker C.P. grade.

Ascorbic acid.--Practical grade.

Thiourea.--Practical grade.

Potassium bitartrate.--Baker reagent grade.

1-(2-Pyridylazo)-2 naphthol (PAN).--Eastman white label grade.

Pontachrome Blue-Black R.--Eastman practical grade.

N,N' dimethyl formamide.--Technical grade.

Dioxane.--Technical grade.

Acetonitrile.--Technical grade.

8-hydroxy quinoline.--Baker reagent grade.

N,N,N',N'-tetrakis (2-hydroxyethyl) ethylenediamine (TKED).--Anhydrous, quaternary-free grade obtained from Arnold, Hoffman and Company.

## Solutions

5-sulfosalicylic acid indicator.--Two per cent solution by weight in distilled water.

Ferric perchlorate solutions.--The required amount of reagent grade iron wire was dissolved in C. P. perchloric acid. After continued warming, no qualitative test for ferrous iron was observed. The solutions were standardized against standard dichromate solution.

Disodium EDTA solution.--The required amount of EDTA was dissolved in distilled water, made up to one liter and kept in polyethylene bottles. The solutions were standardized at pH 1.2-1.4 against a standard bismuth solution using thiourea as an indicator (7). The color change at the end point is from yellow (bismuth-thiourea complex) to colorless (bismuth-EDTA complex). Iron present in the bismuth solution was reduced with ascorbic acid.

Bismuth nitrate solutions.--Eight grams of bismuth trioxide were dissolved in nitric acid and diluted to two liters. The solutions were standardized by the electrodeposition of bismuth on platinum electrodes (8).

Other chemicals and solutions used are described in Part I, Chapter II.

#### Equipment

Beckman model DU spectrophotometer.--The instrument was adapted for titrations by the use of a 3.75 inch by 3.75 inch by 5.5 inch black-painted wooden box which replaced the cell compartment. The buret tip protruded through a hole in the lid and into the solution contained in a 100 milliliter tall-form beaker situated in the light path in the titration



compartment. A magnetic stirrer was placed under the titration cell compartment and afforded good manipulation of the plastic covered stirring bar placed in the solution.

Glassware.--Three ten milliliter pipets and a ten milliliter buret were carefully calibrated and the results incorporated in all volumetric measurements.

## CHAPTER III

## PROCEDURE

Visual titrations of ferric iron versus EDTA using 5-sulfosalicylic acid indicator were performed at pH 2.0-3.0 and pH 1.0. A ten milliliter portion of a standard (0.1F) iron perchlorate solution was taken and dilute (1:20) ammonium hydroxide added until the pH rose to about one. Sodium acetate was then added until the pH reached a value of 2.0-3.0. Eight to ten drops of the two per cent indicator solution then caused a deep violet color in solution. The solution was titrated with standard EDTA. The end point is reached when the last trace of reddish color disappears from the yellow color of the ferric-EDTA complex. The end point for the titration was found to be 14.48 milliliters. When the titration was performed under the same conditions, but in the presence of ten milliliters of 0.2F aluminum, the end point was 16.60 milliliters, further confirming the argument advanced in Part I that the aluminum complexed to a certain extent in this pH range.

The titration was then attempted visually at pH 1.0. The end point with iron alone was about 14.6 milliliters. In the presence of aluminum it was between 14.6 and 14.8 milliliters. The color change was very difficult to observe at this pH, being quite gradual in nature. Even so, it was

apparent that much less aluminum was complexing under these conditions. It was then decided to use the method of Sweetser and Bricker (5) employing the use of spectrophotometer, but at pH 1.0 using 5-sulfosalicylic acid indicator where they used salicylic acid at pH 2.0-3.0.

A series of spectrophotometric titrations was carried out; the results are given in Tables 1-4 and discussed in the following chapter. For these experiments, ferric perchlorate solutions were made up to contain between 55 and 65 milligrams of iron per ten milliliters. Aluminum chloride solutions contained between 27 and 50 milligrams aluminum per ten milliliters. EDTA solutions were 0.1F and standardized against bismuth in the pH range in which the iron titrations were to be carried out. This prevented contaminants in the water from interfering in the standardization. In all cases involving spectrophotometric titrations, the solutions were prepared as follows: portions of the iron and aluminum (if considered) solutions were pipeted into 100 milliliter tall form beakers. Dilute ammonium hydroxide was used to raise the pH to 0.7-0.9, and sodium acetate and dilute perchloric acid employed to adjust it to 1.0-1.1. The solution was diluted to 85-90 milliliters before the final pH adjustment was made. The solutions were titrated with standard EDTA in the Beckman DU spectrophotometer described in the Equipment Section. The absorption maximum of iron sulfosalicylate at 510 millimicrons (9) was followed and decreasing absorption plotted

against milliliters EDTA added. Typical curves obtained are shown in Figs. 1-4. The acidity of the solutions was measured after titrations and changes were never more than 0.1 pH units.

Titration were also carried out using ferric iron solutions in the 0.01-0.025F concentration range.

Flaschka and Abdine (6) devised a procedure for the determination of aluminum alone or the sum of iron plus aluminum by titrating a boiling solution containing the metal ions with EDTA to a copper-PAN end point at a pH of 3.0. When a slight excess of EDTA is present, the copper is displaced from its PAN complex resulting in a color change from red to yellow, signifying the end point. The method for iron determination at pH 1.0 investigated in this research, when applied to the above procedure, would enable both constituents to be titrated. Experiments were performed to test this conclusion. Spectrophotometric titrations at pH 1.0 showed the iron end point to be 9.56 milliliters for the solution used. Ten milliliters of iron solution in the presence of about 50 milligrams of aluminum were taken, the pH adjusted to 1.0, a few drops of sulfosalicylic acid indicator added, and 9.56 milliliters of EDTA added. The pH was adjusted to 3.0 using ammonium acetate solution. The resulting solution was then heated nearly to boiling. A few drops of copper-EDTA solution were added and enough PAN to give a purple color. The hot solution was titrated with standard EDTA to a yellow color. The end points

for two such titrations were 18.64 and 18.70, giving an average value of aluminum found of 52.7 milligrams.

Some qualitative experiments were undertaken using non-aqueous solvents in an attempt to find one suitable for adaptation to aluminum determinations. Dimethyl formamide, acetonitrile and dioxane were investigated. Solid aluminum chloride would not dissolve in dimethyl formamide or dioxane, but formed a white gelatinous precipitate with acetonitrile, probably an addition compound. This precipitate dissolved when either a trace of water, glacial acetic acid or dimethyl formamide was added to the solution. Aluminum solutions were then prepared for investigation by adding enough acetonitrile to some solid aluminum chloride to form the white precipitate. This precipitate was then dissolved in dimethyl formamide.

The addition of Pontachrome Blue Black R to an aqueous aluminum solution causes a bright orange fluorescence to be exhibited when the solution is exposed to ultraviolet light (10). The solution of aluminum in dimethyl formamide also fluoresced when a few drops of Pontachrome Blue Black R in dimethyl formamide were added.

Various substances were tried to see if any could remove the aluminum from the indicator complex with resulting loss of fluorescence. Both disodium EDTA and EDTA acid proved insoluble in the three solvents under consideration. However, 5-sulfosalicylic acid, 8-hydroxy quinoline (oxine) and TKED were all soluble in dimethyl formamide. TKED is a viscous

liquid of similar structure to EDTA with hydroxy groups replacing acid ones.

The addition of an excess of TKED in dimethyl formamide resulted in only a slight loss of orange fluorescence in the aluminum solution. Sulfosalicylic acid in dimethyl formamide caused an immediate change from orange to blue fluorescence and oxine caused an even more dramatic change to yellow-green.

When oxine in dimethyl formamide was added to the aluminum solution without Pontachrome R a green fluorescence was shown, thus possibly doing away with the need for an indicator. The spectra of aluminum, oxine, and aluminum oxinate solutions in dimethyl formamide were taken and are shown in Fig. 5.

## CHAPTER IV

## DISCUSSION OF RESULTS AND RECOMMENDATIONS

When investigating selective titrations in complexometry involving EDTA, careful consideration of changes in apparent stability constants through the alpha and beta factors is necessary. In the following discussion, ionic charges will be omitted for clarity and the symbol "Y" will be used to represent the EDTA anion with a charge of minus four. The absolute stability constants of metal EDTA complexes are defined as:

$$K (\text{absolute}) = \frac{[MY]}{[M] [Y]} \quad (1)$$

These constants have been determined and tabulated in reference works (11). However, in practice, an "apparent" or "conditional" stability constant must be used which reflects actual solution conditions. This apparent constant is related to the absolute constant by the equation:

$$K (\text{apparent}) = \frac{K (\text{absolute})}{\alpha_H \beta_A} \quad (2)$$

The alpha term is a measure of the effect of pH on the completely dissociated form of EDTA. Increasing hydrogen ion concentration causes an increase in the amount of the various protonated species of EDTA present. Beta is the factor

introduced by the presence of other complexing species which compete for the metal ion.

The following equations are derived in the appendix:

$$\alpha = 1 + K_1[\text{H}] + K_1K_2[\text{H}]^2 + K_1K_2K_3[\text{H}]^3 + K_1K_2K_3K_4[\text{H}]^4 \quad (3)$$

where  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  are the acid stability constants for EDTA.

$$\beta = 1 + K_1[\text{A}] + K_1K_2[\text{A}]^2 + \dots K_1K_2\dots K_n[\text{A}]^n \quad (4)$$

where  $K_1$ ,  $K_2$ , and  $K_n$  are the stability constants for the various complexes the metal forms with the added ligand A.

The logarithms of the absolute stability constants for ferric and aluminum EDTA complexes are 25.1 and 16.13, respectively (2). Calculation of the alpha factor at pH 1.0 by use of equation 3 results in a value for log alpha of 17.1. Considering only the alpha factor in equation 2, it is seen that at pH 1.0, the logarithm of the apparent stability constant for the ferric complex is 8.0 while the aluminum complex is almost completely dissociated. While it is true that at low pH values ferric iron forms a protonated complex with EDTA, calculation of the apparent stability constant for this species shows it to have a log K value of 8.0 also, thus causing no difficulty.

The beta factor must be calculated for the iron sulfosalicylate complex. At pH 1.0, ferric iron and sulfosalicylic



acid form a one to one complex, so equation 4 reduces to a simplified form:

$$\beta = 1 + K_1[A]$$

The iron sulfosalicylate stability constant must also be an apparent one, and was calculated from the absolute by use of an alpha factor for 5-sulfosalicylic acid. The calculations are analagous to those for EDTA. By use of the apparent constant, the beta term was calculated to be very close to one and thus not a factor in determining the apparent stability constant of the ferric EDTA complex.

As a general rule, the minimum log K apparent for a satisfactory titration in the presence of an indicator is given by  $6 - \log C$ , where C is the metal ion concentration after dilution. Therefore, since the log K apparent for ferric EDTA at pH one is 8.0, the minimum concentration for effective titration would be  $0.01F$  after dilution.

Above the concentration of  $0.01F$ , the ferric iron in an iron-aluminum mixture could theoretically be titrated with EDTA at pH 1.0 without interference from the aluminum.

When gradual end points are observed as in the visual titrations at pH 1.0, spectrophotometric procedures can often be used to improve them. The linear portions of the curve obtained are extrapolated to determine the end point and data in that region (where the curve is rounded) are not needed. Ferric solutions were made up as perchlorates since the

perchlorate ion does not form complexes. No volume corrections were necessary in the absorption data since the effective part of the curve considered only one milliliter of titrant in 90-100 milliliters of total solution.

Table 1 shows the improvement of iron determinations in the presence of aluminum.

TABLE 1

Comparison of Titrations of Iron with 0.1F EDTA in the Presence of Aluminum at pH 1.0 Spectrophotometrically to Those at pH 2.0-3.0 Visually

<u>pH</u>	<u>mgms. aluminum present</u>	<u>mgms. iron taken</u>	<u>mgms. iron found</u>	<u>per cent error</u>
2.0-3.0 (visual)	51	60.9	65.9	8
2.0-3.0(vis.) (40-50°C)	51	60.9	65.1	7
1.0-1.1	27-204	60.9	60.7 (avg. of 14)	0.3
1.0-1.1	50,100,150	55.87	55.79 (avg. of 3)	0.14

From Table 2, a comparison of methods for iron alone is obtained. The best procedure appears to be spectrophotometric at pH 2.0-3.0, which is unfortunately not usable in the presence of aluminum.

TABLE 2

Comparison of Results of Iron-EDTA Titrations,  
No Aluminum Present.

<u>method</u>	<u>pH</u>	<u>mgms. iron taken</u>	<u>mgms. iron found</u>	<u>per cent error</u>
visual	2.0-3.0 (40-50°C)	55.87	55.92 (avg. of 4)	0.09
visual	2.0-3.0 (40-50°C)	60.9	60.8 (avg. of 4)	0.2
visual	2.0-3.0 (room temp.)	60.9	61.2	0.5
spectro- photometric	2.0-3.0	55.87	55.85	0.03
spectro- photometric	1.0-1.1	60.9	60.7 (avg. of 9)	0.3
spectro- photometric	1.0-1.1	55.87	55.80 (avg. of 2)	0.12

Table 3 is a condensed form of Table 4 found in the appendix. It shows the average values of iron determination with varying amounts of aluminum present at pH 1.0.

TABLE 3

Comparison of Average Results of Iron-EDTA Titrations with No Aluminum Present to Those with Varying Amounts of Aluminum. All Titrations were Spectrophotometric at pH 1.0-1.1

<u>mgms.</u> <u>aluminum</u> <u>present</u>	<u>mgms.</u> <u>iron</u> <u>taken</u>	<u>mgms.</u> <u>iron</u> <u>found</u>	<u>per cent</u> <u>error</u>
none	60.9	60.7	0.3
none	55.87	55.80	0.12
27-204	60.9	60.7	0.3
50-150	55.87	55.79	0.14

It is important to note that the presence of aluminum had almost no effect on the per cent error in the iron determinations. The more carefully standardized solutions showed the same decrease in per cent error both with and without aluminum.

As predicted, the results in the 0.01-0.25F iron concentration range were rather poor. The linear portion of the curve obtained is much shorter and extrapolation errors are easy to make. See Fig. 4 for a typical curve obtained.

The addition of an excess of sulfosalicylic acid at pH 2.0-3.0 for visual titrations resulted in a per cent error of 0.8 in the iron determination. The purpose of this was to attempt to mask the aluminum with the indicator. When too

much indicator was added the end point was hard to detect. The addition of 0.5-1.0 grams of solid sulfosalicylic acid gave the results described. Since the titration at pH 1.0 showed less than 0.8 per cent error, no further work along this line was attempted.

Titanium was found to interfere with the titration at pH 1.0. Thus titanium and all other metals (bismuth and thorium, for example) with stability constants high enough to be complexed even in acid medium will be co-titrated and must be removed or masked in some way. Chromium forms complexes quite slowly and will not interfere if the titration is performed within a reasonable length of time.

From the results shown in Table 4, the iron determination in the presence of aluminum is satisfactory within the limits cited. The aluminum could be determined by precipitation as aluminum oxinate or by homogeneous precipitation of a basic aluminum salt. The applicability of this method to that of Flaschka and Abdine (6) has been shown.

The difficulties encountered with aluminum in complexometric titrations are due to the tendency of the metal ions to readily form unreactive hydroxy complexes in aqueous solution (12). The qualitative work done with non-aqueous media shows definite possibilities for further investigation. Of particular interest is the possible titration of aluminum against oxine in dimethyl formamide. The spectra (see Fig. 5) of the various species show that a spectrophotometric titration at 450-470 millimicrons may be feasible.

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## APPENDIX

Data from the literature used (11).

Absolute stability constants (charges omitted for clarity).

$$K_{\text{FeY}} = \frac{[\text{FeY}]}{[\text{Fe}] [\text{Y}]} = 10^{25.1}$$

$$K_{\text{AlY}} = \frac{[\text{AlY}]}{[\text{Al}] [\text{Y}]} = 10^{16.13}$$

$$K_{\text{Fe sulfosalicylate}} = \frac{[\text{Fe sulfosalicylate}]}{[\text{Fe}] [\text{sulfosalicylate ion}]} = 10^{14.42}$$

$$K_{\text{FeHY}} = \frac{[\text{FeHY}]}{[\text{Fe}] [\text{HY}]} = 10^{16}$$

Acid stability constants:

EDTA.

$$K_1 = \frac{[\text{HY}]}{[\text{H}] [\text{Y}]} = 10^{10.26}$$

$$K_2 = \frac{[\text{H}_2\text{Y}]}{[\text{H}] [\text{HY}]} = 10^{6.16}$$

$$K_3 = \frac{[\text{H}_3\text{Y}]}{[\text{H}] [\text{H}_2\text{Y}]} = 10^{2.67}$$

$$K_4 = \frac{[\text{H}_4\text{Y}]}{[\text{H}] [\text{H}_3\text{Y}]} = 10^{1.99}$$

5-sulfosalicylic acid.

$$K_1 = \frac{[C_6H_3(COO^-)(SO_3^-)(OH)]}{[H][C_6H_3(COO^-)(SO_3^-)(O^-)]} = 10^{11.74}$$

$$K_2 = \frac{[C_6H_3(COOH)(SO_3^-)(OH)]}{[H][C_6H_3(COO^-)(SO_3^-)(OH)]} = 10^{2.67}$$

The sulfonic group is completely dissociated in water.

Derivation of "alpha" equation (2):

The absolute stability constant for a complex MY is defined as:

$$K = \frac{[MY]}{[M][Y]}$$

This expression only considers EDTA in the completely dissociated form Y. However, at pH values less than ten, the uncombined EDTA is present also as HY, H<sub>2</sub>Y, H<sub>3</sub>Y, and H<sub>4</sub>Y. An apparent constant is then defined as:

$$K \text{ apparent} = \frac{[MY]}{[M][Y]^*}$$

[Y]\* equals the total concentration of all dissociated forms and is defined as being equal to [Y] .

$$[Y]^* = [Y] + [HY] + [H_2Y] + [H_3Y] + [H_4Y]$$

By use of the acid stability constants for EDTA, all terms can be expressed in terms of [Y].



$$\text{Then, } [Y]^* = [Y] + K_1 [Y] [H] + K_1 K_2 [Y] [H]^2 + K_1 K_2 K_3 [Y] [H]^3 + K_1 K_2 K_3 K_4 [Y] [H]^4$$

Dividing both sides of the equation by  $[Y]$  leads to equation (3):

$$\frac{[Y]^*}{[Y]} = \alpha = 1 + K_1 [H] + K_1 K_2 [H]^2 + K_1 K_2 K_3 [H]^3 + K_1 K_2 K_3 K_4 [H]^4$$

Derivation of "beta" equation (2):

The apparent stability constant showing dependence on an added ligand "A" is defined as:

$$K_{\text{apparent}} = \frac{[MY]}{[M]^* [Y]}$$

$[M]^*$  equals the total concentration of metal ions not combined with EDTA and is defined as being equal to  $[M] \beta$ .

$$[M]^* = [M] + [MA] + [MA_2] + \dots [MA_n]$$

By use of the stability constants of the complexes that M forms with A, all terms can be expressed in terms of  $[M]$ .

Division by  $[M]$  then leads to equation (4):

$$\frac{[M]^*}{[M]} = \beta = 1 + K_1 [A] + K_1 K_2 [A]^2 + \dots K_1 K_2 \dots K_n [A]^n$$

Combination of both of these expressions gives equation (2):

$$K \text{ apparent} = \frac{K \text{ absolute}}{\alpha \beta}$$

$$\text{or } \log K \text{ apparent} = \log K \text{ absolute} - \log \alpha - \log \beta$$

Sample calculations:

Calculation of  $\alpha$  for EDTA at pH one:

Using constants given on page 38, and equation (3),

$$\begin{aligned} \alpha = & 1 + 10^{10.26} \times 10^{-1} + 10^{10.26} \times 10^{6.16} \times 10^{-2} + 10^{10.26} \times \\ & 10^{6.16} \times 10^{2.67} \times 10^{-3} + 10^{10.26} \times 10^{6.16} \times 10^{2.67} \times \\ & 10^{1.99} \times 10^{-4} \end{aligned}$$

$$\alpha = 1.3 \times 10^{17}$$

$$\log \alpha = 17.1$$

Calculations of  $\beta$  for iron-sulfosalicylate at pH one:

Alpha is calculated from the constants given on page 38.

$$\alpha_{\text{sulfo-salicylic acid at pH one}} = 10^{12.42}$$

$$K \text{ apparent} = \frac{k \text{ absolute}}{\alpha} = \frac{10^{14.42}}{10^{12.42}} = 10^2$$

$$\beta = 1 + K \text{ apparent} [\text{sulfo-salicylic acid}]$$

$$\beta = 1 + 10^2 [5.4 \times 10^{-4}] = 1.05$$

$$K \text{ apparent} = \frac{10^{25.1}}{10^{17.1} \times 1.054} = 10^{8.0}$$

The calculation of the apparent constant for the protonated complex is done in an analagous way, the alpha expression being in terms of  $[HY]$ .

TABLE 4

Comparison of Iron-EDTA Titrations Without Aluminum to Those  
With Varying Amounts of Aluminum.\*

<u>mgms. aluminum present</u>	<u>mgms. iron taken</u>	<u>mgms. iron found</u>	<u>per cent error</u>
none	60.9	60.7	0.3
none	55.87	55.80	0.12
27	60.9	60.7	0.3
50	55.87	55.77	0.2
51	60.9	60.6	0.9
100	55.87	55.83	0.07
102-108	60.9	60.8	0.2
150	55.87	55.77	0.2
153 (only 1)	60.9	60.9	0
204 (only 1)	60.9	61.0	0.2

\* All titrations were spectrophotometric at pH 1.0-1.1.  
Results are averages of several in each case unless noted.

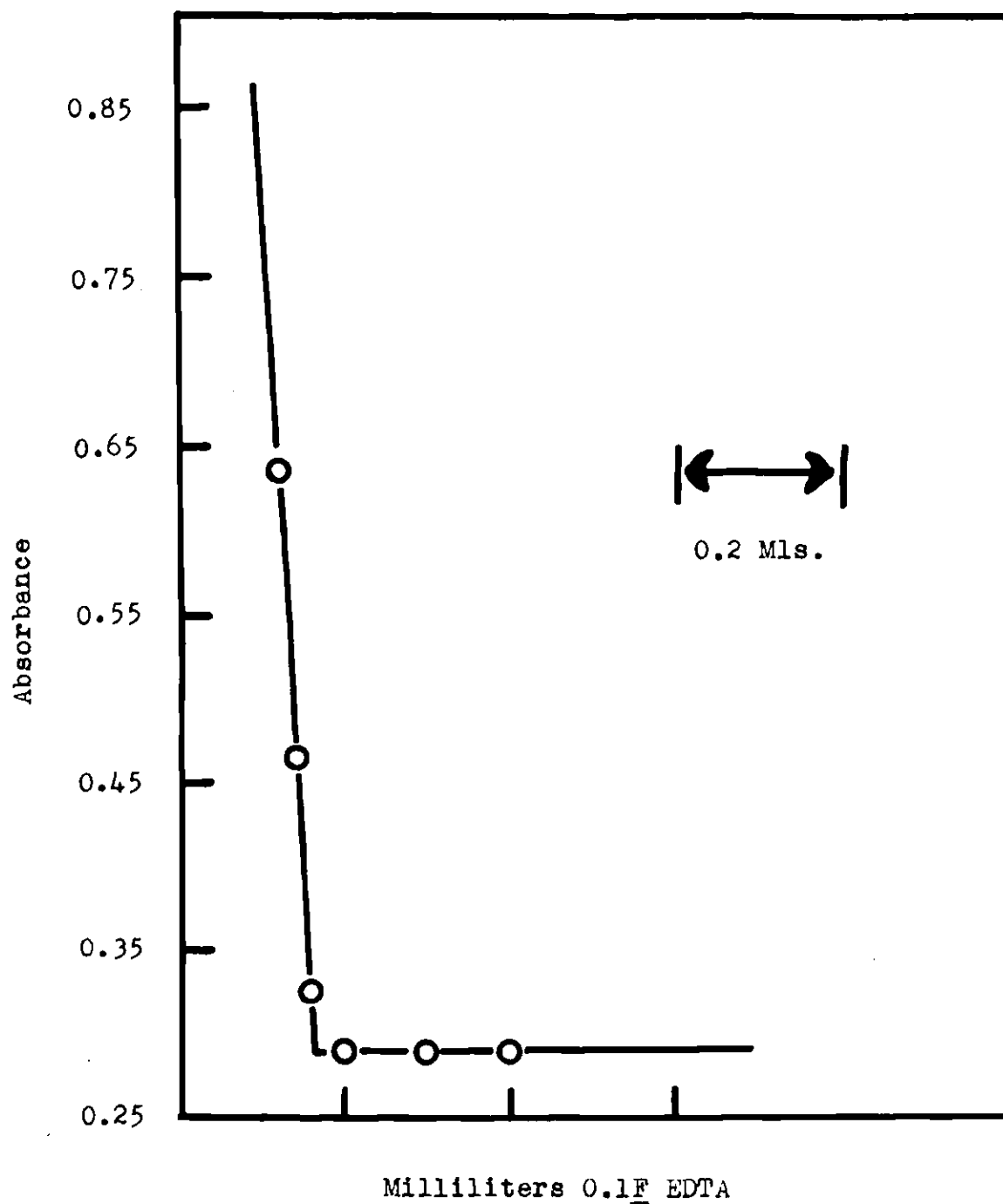


Fig. 1. Spectrophotometric Data for Titration of 0.1F Iron Alone at pH 2.0-3.0

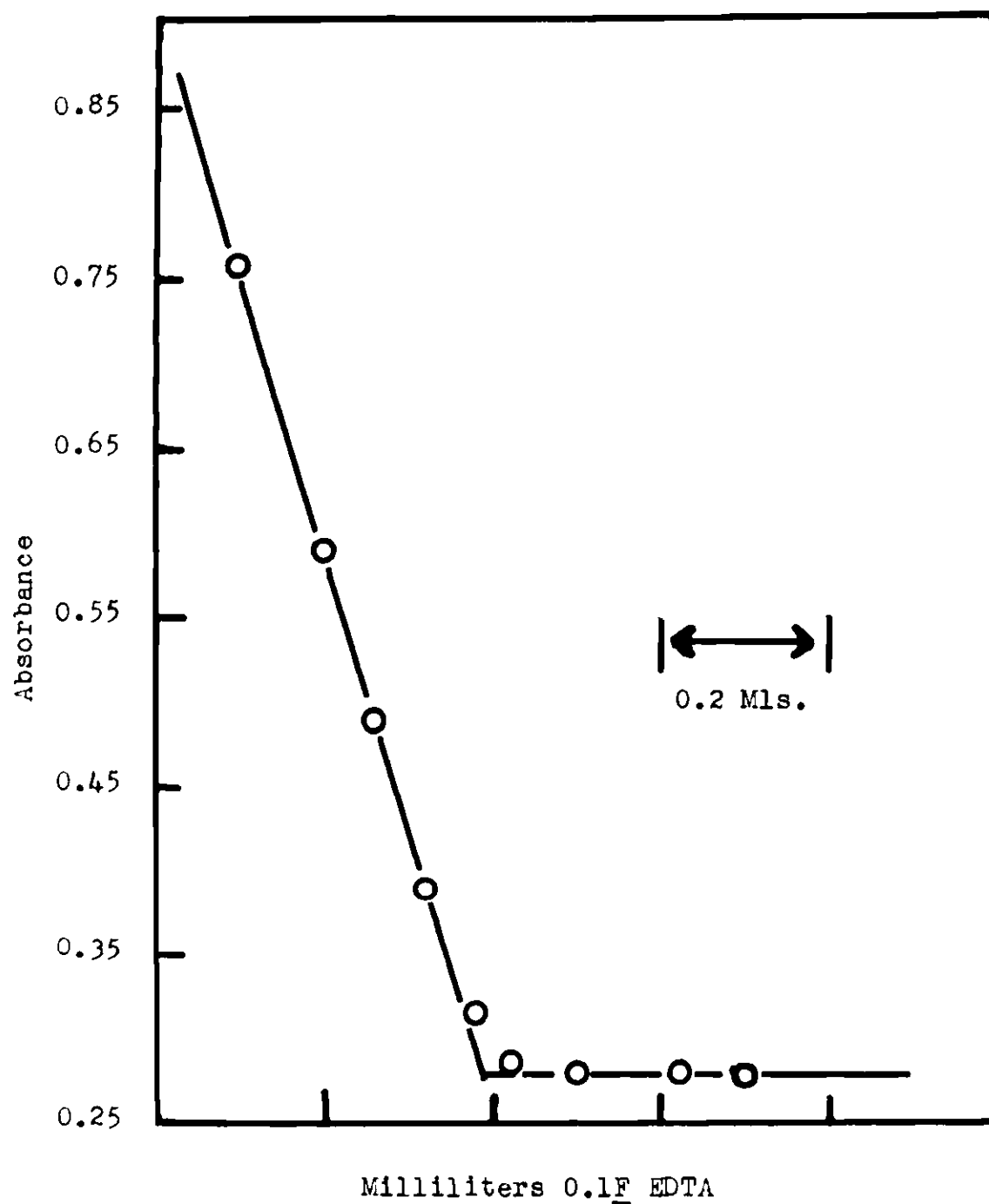


Fig. 2. Spectrophotometric Data for Titration of 0.1F Iron Alone at pH 1.0

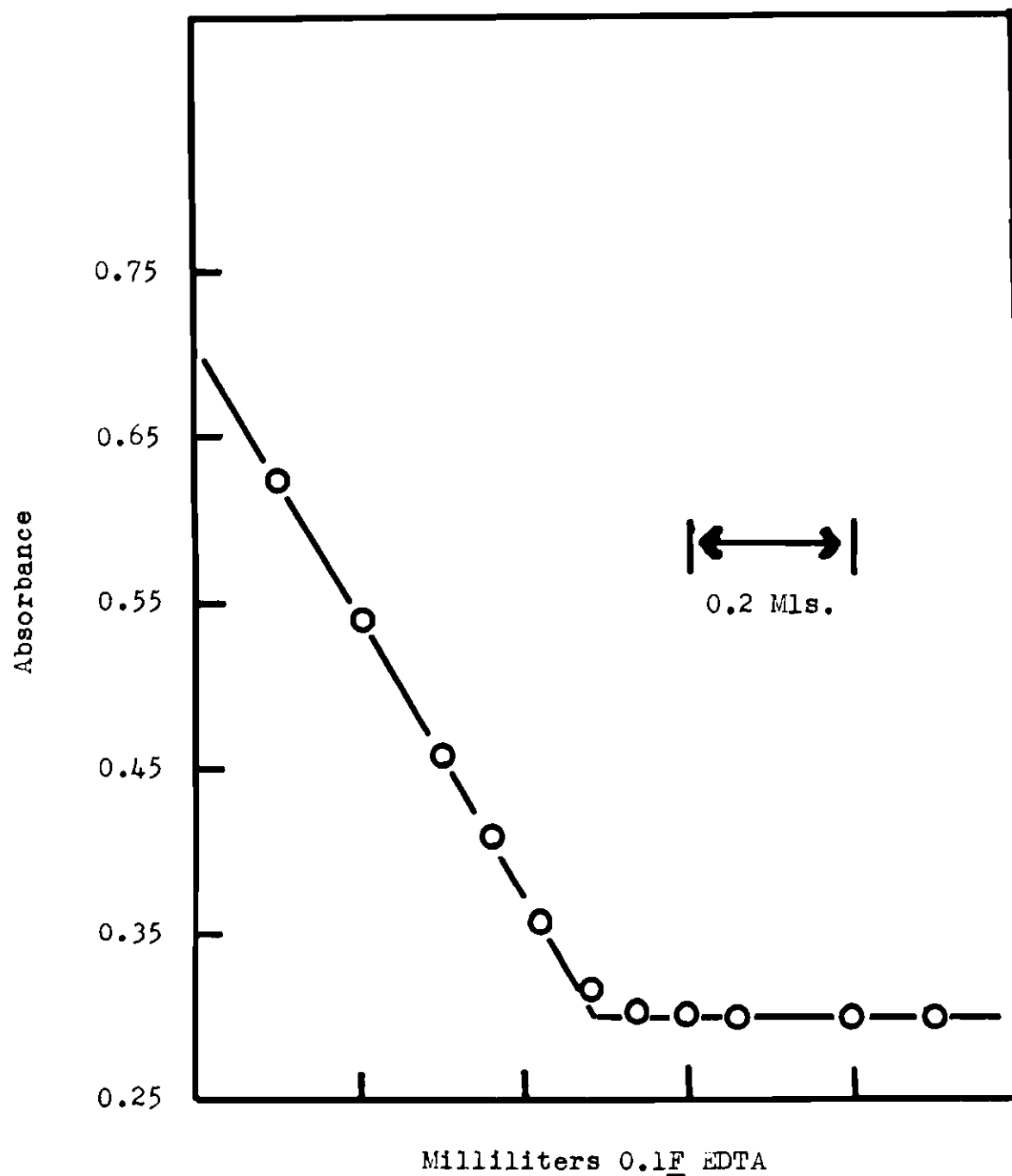


Fig. 3. Spectrophotometric Data for Titration  
of 0.1F Iron in Presence of Aluminum  
at pH 1.0

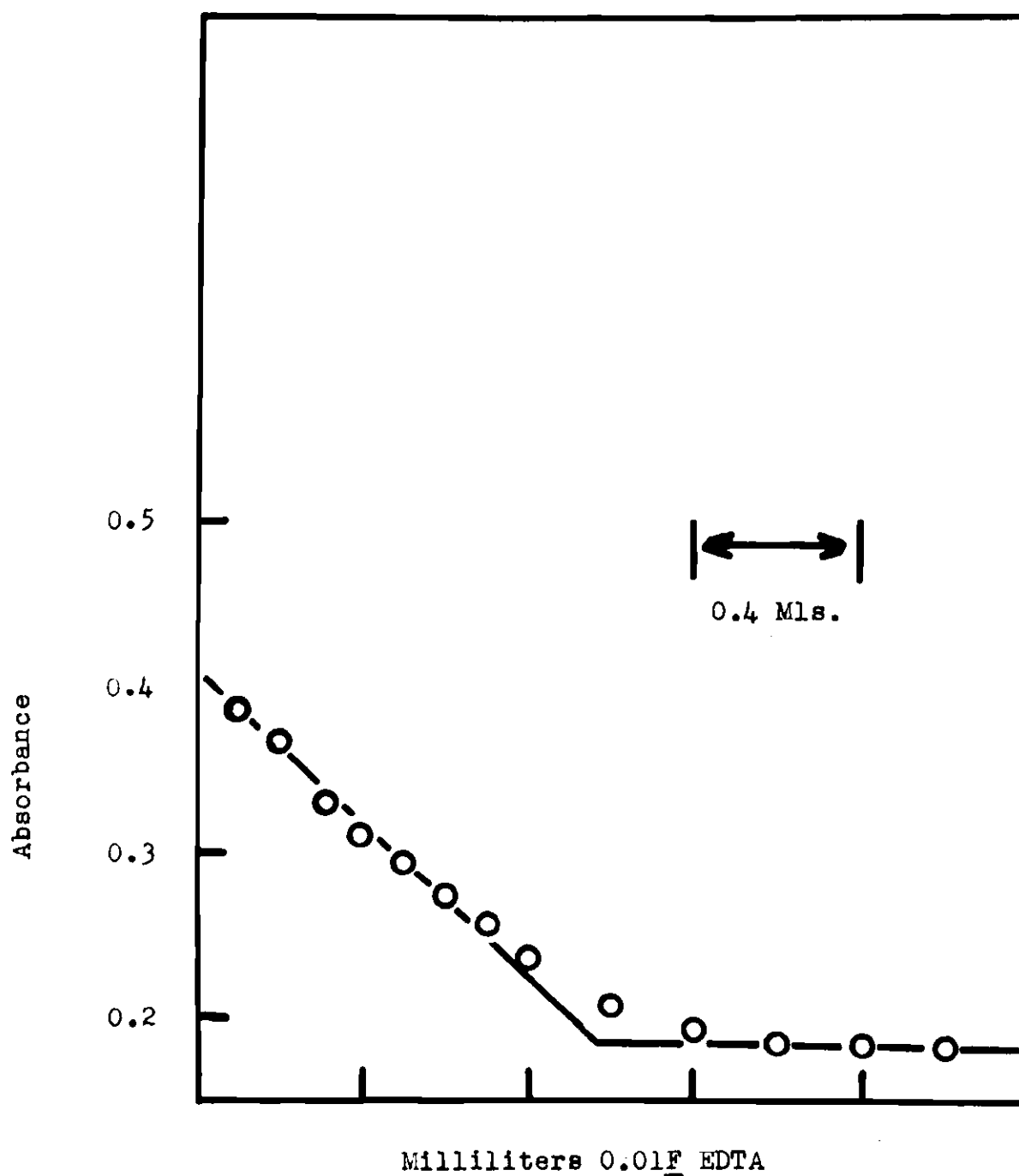


Fig. 4. Spectrophotometric Data for Titration of 0.01F Iron Alone at pH 1.0



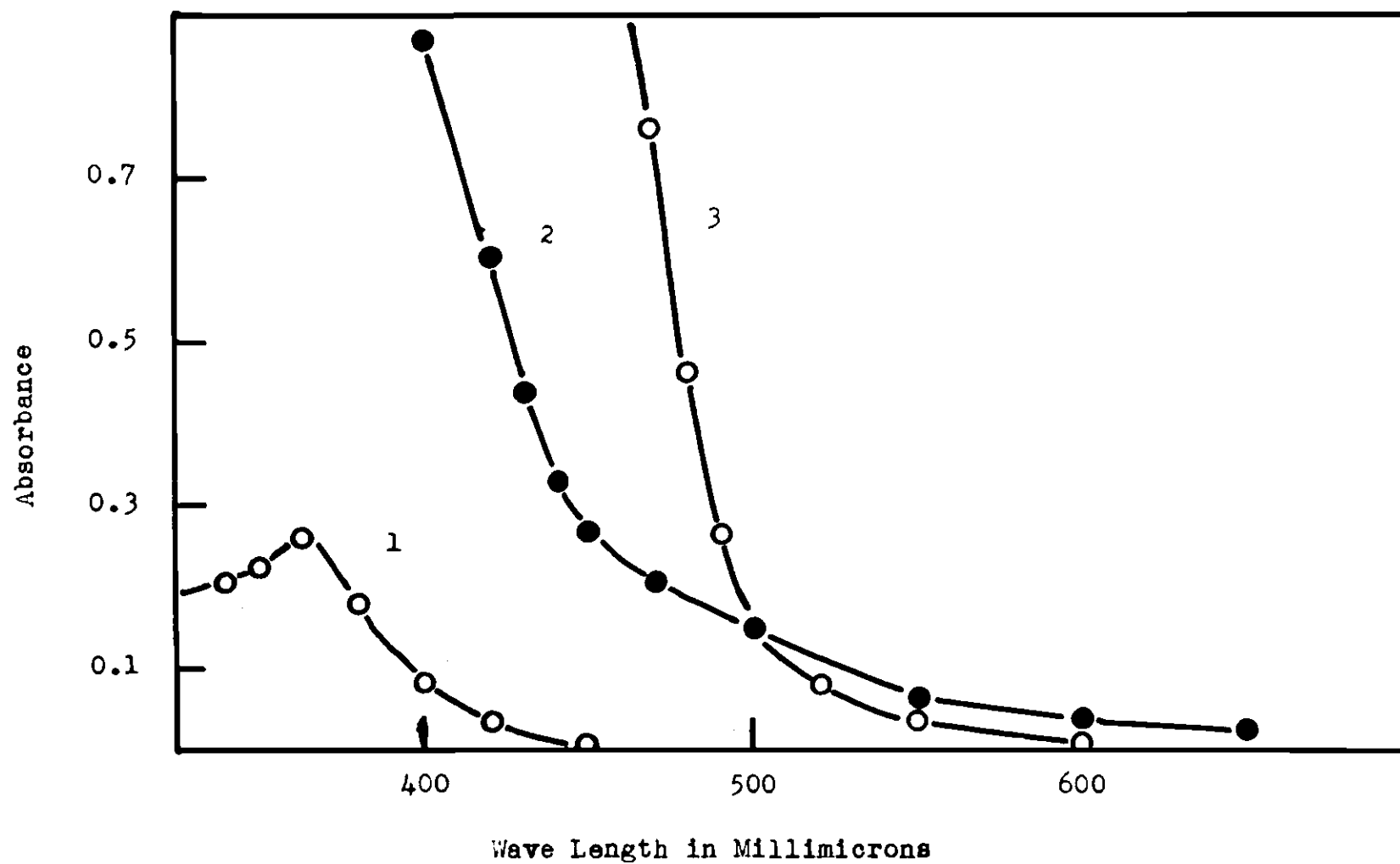


Fig. 5. Absorption Curves for Aluminum Oxinate in Dimethyl Formamide

1. Aluminum 2. Oxine 3. Aluminum Oxinate