

- I. INVESTIGATIONS INTO THE DETERMINATION OF  
TRACE LEVELS OF IRON.
- II. A FIELD METHOD FOR THE DETERMINATION OF  
EDTA IN NATURAL WATER

A THESIS

Presented to

The Faculty of the Division of Graduate  
Studies and Research

by

John Joseph Tice IV

In Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy  
In the School of Chemistry

Georgia Institute of Technology

February, 1978

- I. INVESTIGATIONS INTO THE DETERMINATION OF  
TRACE LEVELS OF IRON.
- II. A FIELD METHOD FOR THE DETERMINATION OF  
EDTA IN NATURAL WATER.

1 /  
Approved: \_\_\_\_\_

\_\_\_\_\_  
H.A. Flaschka, Chairman

\_\_\_\_\_  
P.E. Sturrock

\_\_\_\_\_  
R.F. Browner

Date approved by Chairman Feb. 23. 78.

## ACKNOWLEDGEMENTS

It is a pleasure to acknowledge my indebtedness to Dr. H.A. Flaschka, my Professor and friend, for his willingness to share his wide experience, vast knowledge, and keen insight. His guidance and inspiration have made an invaluable contribution to the accomplishment of this work. His influence on me since 1970 has been profound.

Dr. Peter E. Sturrock and Dr. Richard F. Browner provided generous assistance in the preparation of the manuscript and this aid is gratefully acknowledged.

In addition, the other members of the research group provided helpful advice and continual encouragement.

This work was supported by a Graduate Teaching Assistantship from the School of Chemistry. I wish to express my thanks for this assistance to the Director, Dr. Joseph A. Bertrand.

I am especially grateful to my wife Betty for her cheerful support during the course of this work. Her willingness to sacrifice much and to lend a sympathetic ear is most appreciated. Her economic support and assistance in the preparation of the manuscript are gratefully acknowledged.

## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	v
LIST OF ILLUSTRATIONS	vi
SUMMARY	vii
PART I	
Chapter	
I. GENERAL BACKGROUND	2
Development of an Analytical Method	
The Extracting Solvent: Basic Considerations	
Distribution Equilibria	
Classification of Extraction Systems	
Extraction of Iron	
II. COMPLEXING AGENTS FOR IRON(II)	28
Introduction	
1,10-Phenanthroline	
1,10-Phenanthroline Derivatives	
Triazine Derivatives	
III. BACKGROUND TO THE EXPERIMENTS	38
IV. TITRATIONS IN MEDIATED MIBK	47
Titration of Iron(II)	
Titration of Iron(III)	
V. THE DETERMINATION OF IRON AFTER REEXTRACTION	56
Introduction	
The Reextraction	
The Prereduction of Iron(III)	
The Titration with Cerium(IV)	
The Determination of Large Amounts of Iron	
The Dust Problem	
The Determination of Small Amounts of Iron	

## TABLE OF CONTENTS (concluded)

	Page
Chapter	
VI. A NOVEL APPLICATION OF FERROCENE	78
Introduction	
The Reduction	
Ferrocene Method for the Photometric Determination of Iron	
Ferrocene as a Prereductor	
VII. EQUIPMENT AND CHEMICALS	86
Laboratory Equipment	
Chemicals	
BIBLIOGRAPHY	90
PART II	
Chapter	
I. A SURVEY OF EDTA METHODS	94
Introduction	
Existing Methods	
Abbreviations Used in Table 8	
II. THE DETERMINATION OF EDTA	103
Introduction	
The Formation and Separation of Iron(III)	
The Iron Determination	
Interference Study	
The Determination of EDTA in the Absence of Cr and Ni	
The Chromium and Nickel Interference	
The Determination of EDTA in the Presence of Chromium and/or Nickel	
III. EQUIPMENT AND CHEMICALS	118
Laboratory Equipment	
Chemicals	
BIBLIOGRAPHY	120
VITA	123

## LIST OF TABLES

Table	Page
1. Extraction of Various Ions from 6 <u>F</u> Hydrochloric Acid into Diethyl Ether	17
2. Extraction of Metal Ions into Methyl Isobutyl Ketone	24
3. Results of Wickbold in the Form Shown by Tinsley	25
4. Compounds Investigated as Oxidizing Titrants	50
5. Typical Results Using the Prereduction Method	61
6. Determination of Large Amounts of Iron	73
7. Determination of Small Amounts of Iron	76
8. Survey of Methods for EDTA and Related Compounds	96
9. Recovery of 0.4 $\mu$ moles of EDTA in the Presence of Certain Metals	107
10. Representative Results Obtained from Procedure I	110
11. Determination of EDTA in the Presence of Nickel	116
12. Determination of EDTA in the Presence of Chromium	117

## LIST OF ILLUSTRATIONS

Figure		Page
1.	Extraction of Iron(III) from Hydrochloric Acid Solutions into Various Solvents	19
2.	Volume Change on Equilibrating Equal Volumes of Ether and HCl	20
3.	Final Formality at Equilibrium as a Function of Initial Formality	21
4.	Absorbance Curves of Iron(II) Complexes (Same Iron Concentration)	36
5.	Dissociation of Iron(II) Complexes in 1 $\underline{F}$ $\text{HClO}_4$	37
6.	Time Necessary for the Complete Reduction of Iron(III) by Ferrocene	53
7.	Curve for the Photometric Titration of Iron(III) with Ferrocene	54
8.	pH Dependence of In Situ Reduction and Complexation	59
9.	Calibration Curve Using the Prereduction Method	63
10.	Typical Curve for the Titration of Iron(II)-Fz with Cerium(IV)	65
11.	Effect of Copper Upon the Titration	68
12.	Calibration Curve Using Procedure I	70
13.	Influence of Shaking Time on Complete Reduction	81
14.	Calibration Curve for the Ferrocene Method	84
15.	The Small Walden Reductor (Drawn to Size)	87
16.	Time Required for Complete Color Development with 1,10-Phenanthroline	106
17.	Calibration Curve for Procedure I	111
18.	Dissociation of Cr(III)-EDTA as a Function of Acidity	113

## SUMMARY

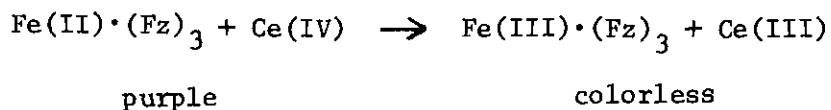
The investigations reported in this thesis concern two areas of study: 1) the determination of small amounts of iron, and 2) the determination of small amounts of EDTA. While it might appear that these two areas are unrelated, in fact, both are concerned with the determination of iron on the trace level.

## Part I

A number of approaches are investigated for the determination of iron after its extraction from 6 F hydrochloric acid into MIBK. Because of the nature of the metals which are coextracted with the iron, a number of new redox titrations of iron are explored.

The redox titration of iron in the mediated MIBK is studied. Of particular moment in these investigations was the development of a new application of the Walden Reductor for the in situ reduction and complexation of iron(III) in the mediated MIBK.

The determination of iron after its reextraction from MIBK into water is reported. The in situ prereduction and complexation of the iron(III) in aqueous solutions using the Walden Reductor is described. The determination of the iron is based upon the photometric titration of iron(II)·FerroZine with cerium(IV) according to the reaction





The MIBK present in the aqueous phase after the reextraction interferes with the method. Two ways for eliminating this interference are given. The effect of various metal ions upon the determination, and studies of the stability of dilute solutions of cerium(IV) are described. Two procedures are given: one for the determination of more than 10  $\mu\text{g}$  of iron, and the other for the determination of less than 10  $\mu\text{g}$  of iron.

A novel application of ferrocene to the reduction of iron(III) is presented. The aqueous iron(III) solution is shaken with a  $10^{-2}$   $\text{F}$  ferrocene solution in benzene and the iron(II) determined photometrically as the FerroZine complex.

## Part II

A literature survey of the recent methods for the determination of EDTA and related compounds in aqueous solutions is presented in tabular form.

A method for the determination of EDTA on the trace level in the presence of ten metal ions is presented. The procedure employed is as follows. An excess of iron is added to the solution containing the EDTA. The solution is then passed through a cation-exchange resin where the uncomplexed iron is retained and the complexed iron is passed. The amount of EDTA is determined by photometrically determining the amount of iron present in the eluate. Chromium and nickel interfere and a modified procedure is presented for determining the EDTA in the presence of either or both of these metals.

PART I

INVESTIGATIONS INTO THE DETERMINATION  
OF TRACE LEVELS OF IRON

## CHAPTER I

### GENERAL BACKGROUND

Iron is the second most abundant naturally occurring metallic element and is distributed in various forms in most ores and rocks (1). The metal has been known for thousands of years; artifacts have been found that reportedly were prepared prior to 3100 B.C. (2). Iron is rarely used as the pure metal; rather its chief use is in the preparation of steel and various types of ferrous alloys. Within the past century, iron at the trace level has become important. In certain cases such as biological systems, trace amounts of iron may be essential, while in other cases such as certain electrochemical cells or semiconductor material, trace amounts of iron may be detrimental (3). Therefore, methods for the determination of iron at both the macro level as well as at the trace level are important. While there are literally hundreds of methods available for the determination of iron in specific types of samples (2), few methods are available which are applicable to a broad variety of samples. Thus the development of such a method is a noteworthy goal.

#### Development of an Analytical Method

In developing any analytical procedure there are many parameters to be considered; however, the two principal ones are the sample matrix and the method of determination.

### Sample Matrix

In inorganic analysis, the sample is usually a solid or a liquid. Methods such as x-ray fluorescence spectroscopy and emission spectrography can easily accommodate solid samples with little or no treatment; however these techniques are beyond the scope of this discussion. Only analytical methods, which require dissolution of the sample in aqueous media, will be considered. The dissolution of the sample is accomplished after the attack on the sample and the procedure followed depends upon the composition of the matrix. The matrix consists of the chemical components which accompany the sought for substance in the sample material. These matrix components are organic or inorganic in nature.

The dissolution of the sample is often the most troublesome step of the analytical process. In a few instances, the sought for substance is readily soluble in water, and dissolution is quite easy. However, the usual case is that the sample is not readily dissolved and a more vigorous form of attack is required. For example, alloys are usually attacked by hot mineral acids, ores and rocks by fluxes, and organic material by ashing. In dry ashing, high temperatures (800 - 1100°C) are employed and the organic material is destroyed. In wet ashing, strong oxidants such as nitric acid or perchloric acid are employed to accomplish the destruction of the organic material. Consequently, after ashing and dissolution, the organic components of the matrix are not present in the analytical solution. Inorganic components are rarely removed during sample attack (Hg, As, or ammonia compounds are a few of the exceptions) and therefore the inorganic matrix components must be considered as possible interferences.

### Selective Versus Specific Method

When choosing a particular analytical method, it is important to distinguish whether the method is specific or selective. A method is specific if the measured response, i.e. the signal, is due only to one substance. A method is selective if two or more substances give the same signal. Care must be taken in the use of the terms specific and selective. The term specific should be used without qualification: a method is either specific or it is not specific. The term selective, on the other hand, permits qualification. A highly selective method is one in which only very few substances give the same signal; a non-selective method is one in which many substances give the same signal. It should be kept in mind that alien entities, while not giving the same signal as the sought for substance and therefore not affecting the qualification of selectivity, may very well have pronounced influence on the size of the signal and thus still are interferences.

The fact that an analytical method is highly selective for a particular substance is not the sole reason to choose it for the determination of that substance. The time required for the analysis, the cost factors, the required level of training of the analyst, and other parameters need consideration, too. Realistically, most organizations are not willing to underwrite an expensive method of determination if it is to be used only for relatively unimportant materials and low numbers of analyses. Many inexperienced analytical chemists have difficulty appreciating this point.

### Interferences

Three approaches are possible for dealing with the interfering species: 1) determination of the compound of interest in the presence of the interfering species by adjusting the solution conditions so that the effects of these species are minimized or eliminated; 2) determination of the compound of interest after removing the interfering species from the solution; 3) determination of the compound of interest after isolating it from the interfering species.

Many methods have been developed for the determination of a compound in various types of materials using the first approach. Elimination of the effects of the interfering species without separation is performed via masking. Masking is accomplished by one or more of the following operations: 1) complexation; 2) pH adjustment; 3) oxidation or reduction; 4) precipitation. While masking is an effective way to minimize the influence of interfering species in a particular sample solution, it is impossible to devise a masking scheme that would be applicable to all types of samples. The use of masking requires a knowledge of the types and concentrations of the interfering species and their behavior. When these parameters are not known, rather lengthy investigations are normally required to establish them.

The second approach, namely the separation of the interfering species prior to the determination of the compound of interest, suffers from the same limitations as those mentioned for the first approach. While many schemes can be devised for separating the interfering species, again a detailed knowledge concerning the components of the matrix is

necessary. For trace applications, it is difficult to devise a scheme for the clean removal of large amounts of interfering species from the trace compound of interest. Quite often a portion of the sought for substance is also removed, or enough of the interfering species may remain to cause trouble.

The third approach, isolating the compound of interest from the interfering species, offers the best possibility for dealing with trace substances. This isolation of the compound of interest can be accomplished by several techniques: 1) precipitation; 2) distillation; 3) chromatography; 4) extraction.

Precipitation methods were once in widespread use, but the technique has lost much of its popularity because of the development of better separations. The drawbacks to precipitation include complications due to the carrying down of unwanted substances. When dealing with trace analysis, the situation is especially aggravating because the amount of sought for substance present in the solution may be too small to allow formation of a precipitate.

Distillation is applicable to only a few elements which form volatile compounds. Consequently the technique has limited use, particularly at the trace level. A notable example (4) is the removal of arsenic (III), antimony (III), and tin (IV) from aqueous solution by distillation of their respective halides.

Chromatography is a broad field encompassing such techniques as ion exchange chromatography, paper chromatography, thin layer chromatography, and gas chromatography. Ion exchange chromatography is very

useful for separating ionic substances, especially of inorganic nature. One of the most significant separations ever achieved, namely that of the rare earths, was accomplished using this technique (5). Considerable knowledge of the constituents of the sample is necessary to employ ion exchange chromatography, and the method is fairly slow. The introduction of high speed liquid chromatographs has shortened the development times for ion exchange chromatography, as well as others, but with considerable sacrifice in the sample size.

Thin layer and paper chromatography are both fast techniques for the separation of complex mixtures. Although both techniques have been employed extensively for organic mixtures, they have not received as much attention for the separation of inorganic mixtures. The sample size, which is in the micrograms range, is a further restriction.

Gas chromatography suffers from the same limitations as distillation methods in that few metals are easily converted into volatile compounds.

These evaluations are made predominately with trace analysis in mind. There, it is commonly necessary to start with a rather large amount of sample material but the restrictions in sample size, virtues for other types of analyses, exclude these techniques from serious consideration.

Extraction is one of the oldest methods of chemical separation. A familiar example of "extraction" is the high temperature aqueous leaching of ground coffee beans to produce the morning life saver. In analytical chemistry, however, the term extraction refers to a



liquid-liquid system. In this sense, the first extraction of an inorganic compound was reported by E. Peligot in 1842, who extracted uranyl nitrate from a solution of pitch-blend into diethyl ether (5). Since that time extraction as a means of chemical separation has been used widely for many applications including the purification of organic and inorganic compounds, the separation of rare earths, and the chemical enrichment of trace elements.

Solvent extraction as a means of separation has great appeal for use in an analytical method because it is fast and easy to perform. Chemical enrichment of the material of interest can be achieved by using a volume of the extracting solvent that is small in comparison to that of the sample solution. When such a favorable ratio of the volumes cannot be employed, enrichment is still possible by ready volatilization of the commonly low-boiling extractants. Information about the behavior of compounds, which in a particular extraction are coextracted with the substance of interest, is often available; if not, the required parameters are in most cases easily determined.

In extraction procedures, "coextraction" occurs only to the extent that substances that are extracted together with the sought for substance would also be extracted in its absence. This is in contrast to precipitation where "coprecipitation" also causes the carrying down of substances that would otherwise remain in solution. After separation of the substance of interest from the sample solution by extraction, chemical operations such as masking can be employed to minimize the effects of the few interfering species that accompany the substance to

be determined. Extraction is an important step in the analytical method developed in this study and it is therefore warranted to give a survey of the theoretical and practical aspects of it.

#### The Extracting Solvent: Basic Considerations

In selecting a solvent for extraction, several requirements should be kept in mind. The requirements as suggested by Dilts (5) are summarized below:

- 1) The extracting solvent should have a higher solubility for the solute than does water.
- 2) The solvent and water should have low mutual miscibility.
- 3) The solvent should have a density which is different from that of water.
- 4) The solvent should have a low viscosity.
- 5) The solvent should not form stable emulsions with water.
- 6) The solvent should have a low vapor pressure.
- 7) The solvent should be inexpensive, readily available, and in adequate purity.
- 8) The solvent should be neither toxic nor highly flammable.

A few comments are in order concerning these requirements. These remarks will be presented by numbered reference to the above.

1) A greater solubility of the solute in the extracting solvent is desirable so that a high distribution constant is achieved. This ensures that only a few extraction steps are required to completely isolate the solute. The distribution constant will be discussed in some detail in the next section.

2) A low mutual miscibility is not always necessary. For example, solvents such as diethyl ether, ethyl acetate, and n-butyl alcohol, which are frequently used for the extraction of inorganic solutes, have relatively high aqueous solubilities (6.90, 7.94 and 7.80 g/100 g, respectively).

3) A high density difference permits rapid establishment of a clean-cut phase boundary between the two phases and facilitates the separation of the two liquids after extraction. For the separation of organic solvents whose density is quite close to that of water, centrifugation may be necessary.

4) A low solvent viscosity is desirable so that adequate contact between the solvent and water is readily obtained when shaking. In the case where a highly viscous solvent must be used, warming is often employed to decrease the viscosity.

5) Solvents which form stable emulsions with water cause difficulties in phase separation. Surfactants are often helpful in "breaking" the emulsion.

6) Although solvents with a low vapor pressure are preferred, many solvents with a high vapor pressure such as diethyl ether and hexane are in common use. Frequent venting of the separatory funnel is necessary when using these solvents.

7) and 8) These two requirements are self explanatory.

#### Distribution Equilibria

Equilibrium is eventually established when a solute is distributed between two immiscible solvents in contact with each other. This

equilibrium is governed by the distribution law: At a given temperature, the ratio of the equilibrium concentrations of a species distributed between two immiscible solvents is constant (6). In this discussion it is assumed that one of the solvents is water and the other is an immiscible organic solvent.

The distribution equilibrium for a species A is written as



where the subscripts a and o refer to the aqueous and organic phases, respectively. In (I-1) it is assumed that the molecular weights of  $A_a$  and  $A_o$  are identical. The distribution law is expressed as:

$$P = \frac{[A]_o}{[A]_a} \quad (I-2)$$

where  $[A]$  denotes the molar concentration of the species A. P is commonly called the partition coefficient or the distribution constant. The numerical value of P depends upon the temperature and the solvents employed.

In the case where the two phases are equilibrated in the presence of an excess of a sparingly soluble solute, the partition coefficient can be expressed as the ratio of the solubilities of the compound in the two phases:

$$P = \frac{S_o}{S_a} \quad (I-3)$$

where S refers to the formal solubility of the solute in each phase.

In analytical chemistry, the distribution ratio is usually preferred over the partition coefficient. The distribution ratio is defined by

$$D = \frac{C_{A,o}}{C_{A,a}} \quad (I-4)$$

where  $C_{A,o}$  and  $C_{A,a}$  are the formal concentrations of the species A in each phase. The distribution ratio has the advantage over the partition coefficient in that the concentration terms refer to the total formal concentration of the solute in a phase rather than to the molarity of a particular form of the solute.

The percentage of species A extracted, % E, is of interest in determining the number of repetitions of the extraction, using fresh portions of organic solvent, necessary to remove the species A from water. The % E is written as

$$\% E = \frac{C_{A,o} \times V_o}{C_{A,o} \times V_o + C_{A,a} \times V_a} \times 100 \quad (I-5)$$

where  $V_o$  and  $V_a$  refer to the volume of organic and aqueous phases, respectively. Equation (I-5) is also written in terms of D by:

$$\% E = \frac{V_o \times D}{V_o \times D + V_a} \times 100 \quad (I-6)$$

In the special case where the volumes of the two phases are equal, (I-6) simplifies to

$$\% E = \frac{D}{D + 1} \times 100 \quad (I-7)$$

### Classification of Extraction Systems

Most solutes are strongly solvated in aqueous solution and the hydration energy is quite high. In order for the solute to be extracted from the aqueous phase into the organic phase, this hydration energy must be overcome, which is possible by chemical bond formation, ion pair formation, organic phase solvation, or by combinations of these. In all extractions, the species which crosses the boundary between the two immiscible liquid phases is electrically neutral: charged species cannot be extracted; only atoms, molecules or ion pairs can be extracted. Thus the mechanism by which the hydration energy is overcome and the neutral species is formed from ions in aqueous solution enables the classification of extraction systems (5). The classification system for the extraction of inorganic solutes as proposed by Kolthoff (7) is summarized below.

#### Class I

In Class I the solute is a simple molecule (or atom) in both the aqueous and organic phases. In the aqueous phase there is little

solvation and sufficient energy is released by solvation in the organic phase to permit extraction (5). Examples of Class I extractions are iodine, ( $I_2$ ), and other halogens,  $OsO_4$ ,  $RuO_4$ , and covalent halides such as  $AlCl_3$ ,  $GeCl_4$ , and  $SnI_4$ . These compounds are all nonpolar as is evidenced by their high volatility (7).

In Class I systems, the organic solvent is inert in that it dissolves the solute but does not react with it chemically. A covalent molecule is more easily accommodated in the disordered organic solvent than within the ordered structure of water, and the solute distributes preferentially into the organic solvent. Nonpolar solvents such as carbon tetrachloride or chloroform are used as organic solvents for Class I extractions.

#### Class II

In Class II, the solute is an uncharged chelate complex of a metal ion. Many neutral complexes of metal ions such as 8-hydroxyquinolates, dithiozonates, and diethyldithiocarbamates are extracted into a variety of organic solvents. In most of these types of complexes, the cation is completely surrounded by the anionic hydrophobic complexing agent. In general, these complexes are slightly soluble in water and much more soluble in organic solvents.

In some complexes of Class II, however, not all of the coordination sites of the metal cation are occupied by the complexing agent. For example, a divalent metal cation  $M$  with a coordination number of six, which forms a 1:2 complex with a monoprotic bidentate ligand  $HL$ , has two coordination sites not occupied by the anionic ligand. These sites are

occupied by water molecules, uncharged ligand, or organic solvent molecules. If water molecules occupy both coordination sites, then the neutral complex is only slightly soluble in organic solvents and essentially nonextractable. In general, replacement of the water molecules of the complex by organic solvent molecules or neutral chelate molecule HL increases the solubility of the complex in organic solvents and consequently its extractability. Nonpolar solvents are preferred for Class II extractions (7).

### Class III

In Class III, the solute is an unsolvated ion-association compound. Large anions and cations are usually not solvated in aqueous media. The compounds formed from large ions are sparingly soluble in water but are quite soluble in some organic solvents. Examples of compounds of Class III extractions are: tetraphenylarsonium perrhenate  $(\text{Ph}_4\text{As})^+(\text{ReO}_4)^-$ ; cuprous biquinoline-halide salt  $(\text{CuBq}_2)^+(\text{X})^-$ ; cesium tetraphenylborate  $(\text{Cs})^+(\text{BPh}_4)^-$ .

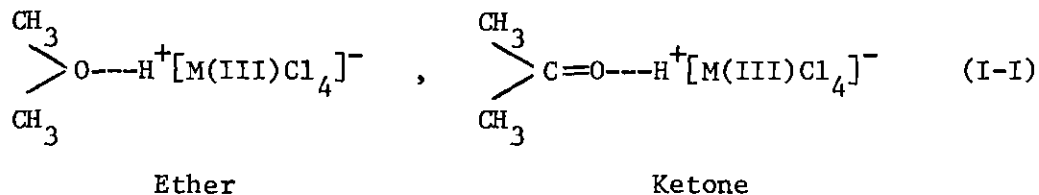
Ion-association compounds formed from singly charged ions are more extractable than those formed from nonsymmetrically charged ones. For example,  $(\text{Ph}_4\text{As})^+$  forms a chloroform-extractable compound with  $(\text{ReO}_4)^-$  but not with molybdate  $(\text{MoO}_4)^{2-}$ . Nonpolar organic solvents are used for Class III extractions (7).

### Class IV

In Class IV the solute is a neutral inorganic species which is coordinated by the solvent. In highly concentrated hydrochloric acid, metal ions such as iron(III) and other trivalent cations,  $\text{M(III)}$ , form



metallo-acids of the general form  $(H)^+(M(III)Cl_4)^-$ . These metallo-acids are extracted from hydrochloric acid solutions into oxygenated organic solvents such as ethers and ketones. The hydrogen of the metallo-acid bonds to the basic oxygen of the organic solvent as illustrated by (I-I).



An ion-pair is formed from the large cation of the solvent molecules and the proton, and the anion of the metallo-acids. The water-immiscible organic solvent serves as both the coordinating agent and the solvent. Non-oxygenated solvents such as chloroform and benzene do not extract metallo-acids (7).

### Extraction of Iron

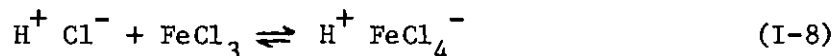
#### Diethyl Ether

One of the oldest known examples of Class IV extractions is that of iron from aqueous hydrogen chloride into diethyl ether. Rothe (8,9) demonstrated in 1892 that large amounts of iron can be separated from many other elements from 6 F hydrochloric acid into diethyl ether. With modifications (10-13), this method has been used for the isolation of iron from a large variety of sample components. This extraction has also been used extensively for removing large quantities of iron that would otherwise interfere in the determination of other elements. The elements that are extracted from 6 F hydrochloric acid into diethyl ether are shown in Table 1.

Table 1. Extraction of Various Ions from 6 F  
Hydrochloric Acid Into Diethyl Ether (12)

Element	% Extracted	Element	% Extracted
Fe(III)	99	Cu	Trace
Ga	97	V(V)	Trace
Au	95	Zn	Trace
Tl(III)	90-95	Al	0
Mo(VI)	80-90	Bi	0
Sb(V)	81	Cd	0
As(III)	68	Cr	0
Ge	40-60	Cu	0
Sn(IV)	17	Fe(II)	0
Sn(II)	15-30	Pb	0
Sb(III)	6	Mn	0
As(V)	2-4	Ni	0
Ir	5	U	0

Although several oxygenated solvents extract iron from chloride media, diethyl ether is by far the most studied and merits discussion because its behavior serves as a model for other solvents employed. In hydrochloric acid, the following equilibrium exists:



Because  $\text{HFeCl}_4$  is a stronger acid than  $\text{HCl}$ , it is completely dissociated at low concentrations of hydrogen chloride. At higher concentrations (greater than 4  $\text{F}$ ), the formation of the molecular species  $\text{HFeCl}_4$  is favored. In diethyl ether the metallo-acid is present as the ion pair  $(\text{H})^+ (\text{FeCl}_4)^- \cdot \text{Et}_2\text{O}$  which does not dissociate.

The effect of the formality of the hydrochloric acid upon the extraction of iron(III) is shown in Figure 1. The value of the distribution ratio rises to a maximum at around 6  $\text{F}$  and then decreases with increasing acid concentration. Figure 2 shows the equilibrium volumes of diethyl ether and hydrochloric acid as a function of initial acidity after 20 ml of each are shaken together. With an initial hydrochloric acid concentration of 8  $\text{F}$ , the equilibrium volumes of the organic and hydrochloric acid phases are 5 ml and 35 ml, respectively.

Figure 3 shows the equilibrium concentration of the acid in the aqueous phase after shaking various hydrochloric acid solutions with equal volumes of diethyl ether. At equilibrium, the acid concentration in the aqueous phase is always less than the initial one. The acidity of the aqueous phase increases linearly with respect to initial aqueous

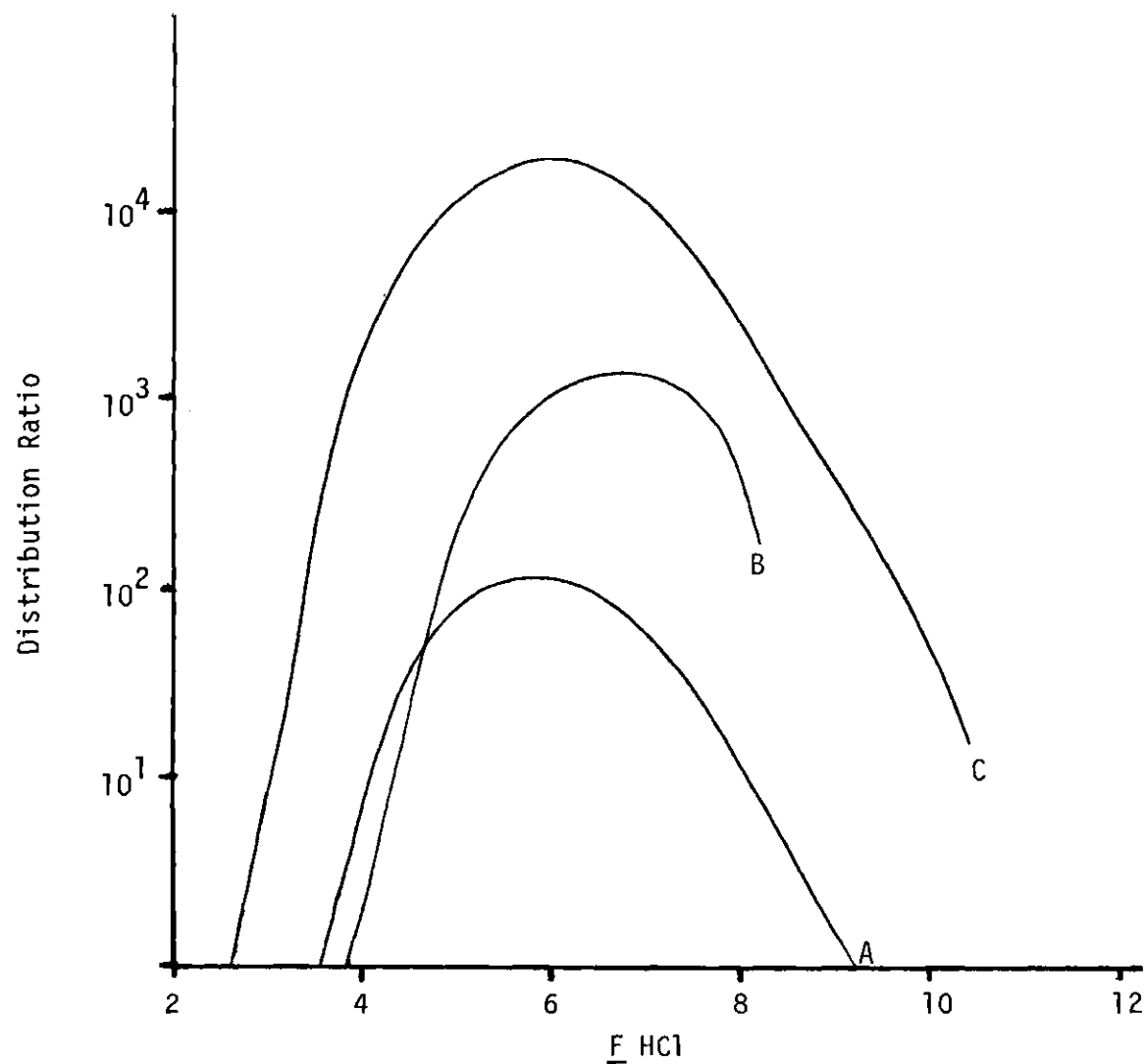


Figure 1. Extraction of Iron(III) from Hydrochloric Acid Solutions Into Various Solvents (14).

- A. Diethyl Ether
- B. Diisopropyl Ether
- C. Methyl Isobutyl Ketone

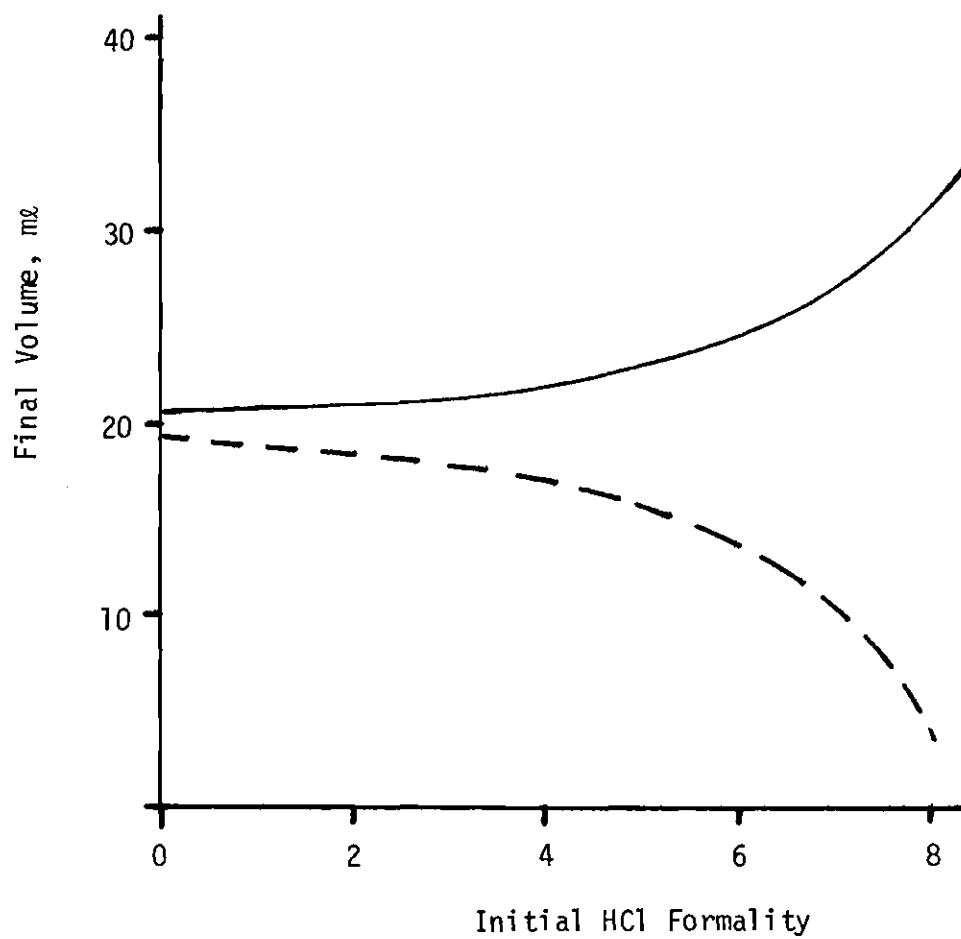


Figure 2. Volume Changes on Equilibrating Equal Volumes of Ether and HCl (5).

— Aqueous Phase      - - - Ethereal Phase

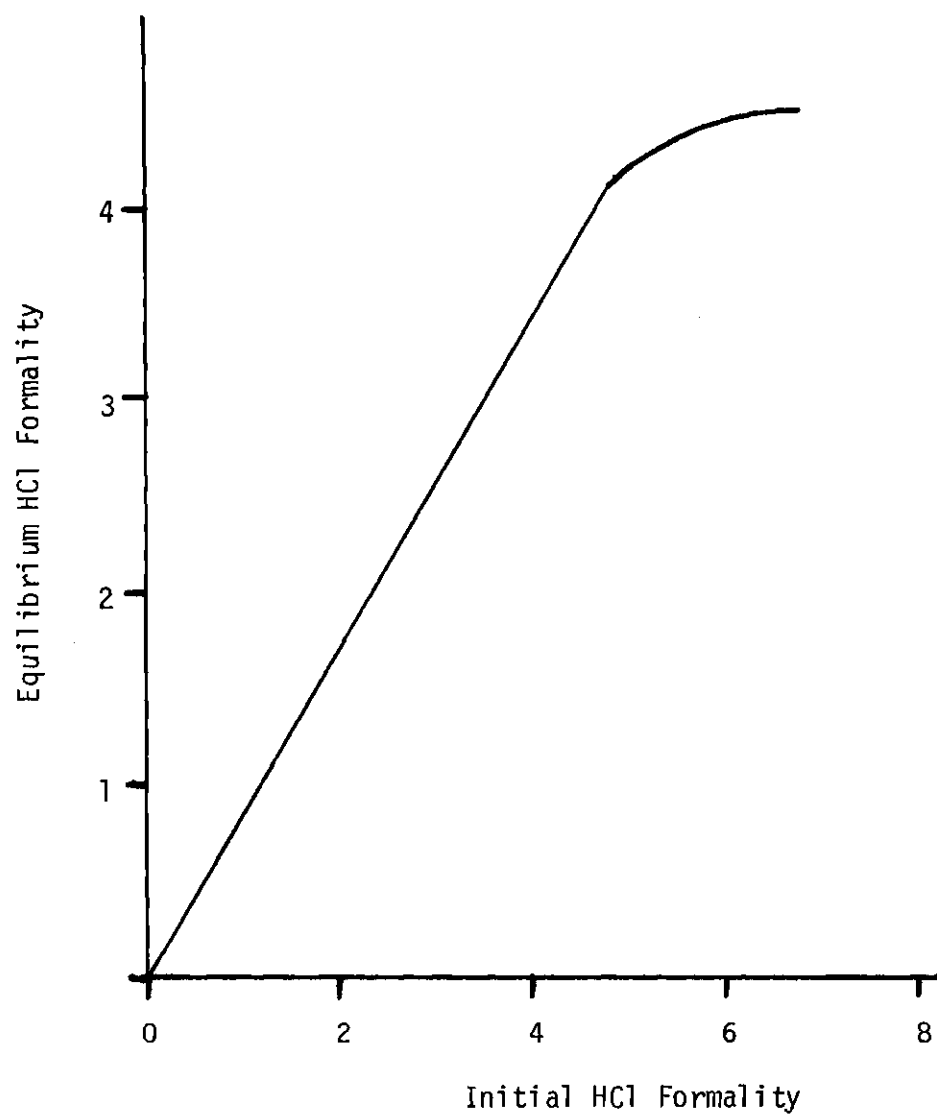


Figure 3. Final Formality at Equilibrium as a Function of Initial Formality (5).

phase acidity up to about 6 F. Above 6 F hydrochloric acid, the equilibrium acidity decreases rapidly with increasing initial acidity. This is due to the fact that the solubility of diethyl ether in hydrochloric acid increases greatly above 6 F. Consequently, the volume increase of the aqueous phase due to the incorporation of diethyl ether is greater than the corresponding increase in the initial aqueous acidity. Concentrated hydrochloric acid and diethyl ether are miscible in all proportions.

Diethyl ether is by no means the best solvent for the extraction of iron from chloride media. The disadvantages of diethyl ether are well known: extraction is only possible from a very limited range of acidity; the distribution ratio is small ( $\sim 100$ ); complete extraction of iron(III) is difficult because diethyl ether usually contains a small amount of peroxide which reduces some of the iron(III); and the vapor pressure of the solvent is quite high. Other oxygen-containing solvents allow better extraction of iron as is shown in Figure 1. Diisopropyl ether is somewhat less sensitive than diethyl ether with regard to acidity and has a lower vapor pressure. Diisopropyl ether as a solvent for the extraction of iron has been studied by several authors (15-21).

#### Methyl Isobutyl Ketone

Methyl isobutyl ketone (MIBK) or "hexone" is one of the best solvents for the extraction of iron from aqueous chloride solutions. The solvent has a low vapor pressure (B.P. = 117°C), low flammability and does not easily form peroxide compounds, even upon prolonged contact

with air. In addition, a high distribution ratio ( $\sim 10,000$ ) is realized. The elements that are extracted from 5-7 F HCl and 6-7 F LiCl into MIBK are shown in Table 2.

Several researchers have studied the extraction of iron into MIBK (22-26); the most extensive work seems to be that of Wickbold (27). Some of the details of his method are as follows. To the iron solution contained in a separatory funnel is added a few drops of nitric acid to ensure that all of the iron is in the trivalent form. Concentrated hydrochloric acid is added to make the solution 6 F in hydrogen chloride. A portion of MIBK is added, the system is shaken, and the aqueous phase is withdrawn and discarded. Ammonium thiocyanate, acetate buffer, and distilled water are added to the separatory funnel containing the MIBK. Upon shaking, the iron is reextracted into the aqueous phase, the red thiocyanato complex of iron is formed immediately, and the complex is extracted into the MIBK. An extractive titration is performed by adding increments of EDTA solution with shaking after each addition. As the titration proceeds, the ketone phase becomes less colored (destruction of the iron-thiocyanato complex) and the aqueous phase becomes progressively yellow (formation of iron - EDTA complex). The point where the MIBK becomes completely colorless is taken as the endpoint (28).

While Wickbold's method gives good results for higher concentrations of iron, problems arise in its use at the lower levels. This can be seen from Table 3, which represents a portion of Wickbold's results. As the method is applied to solutions of decreasing iron content, increasingly high results are obtained. The fact that high results are



Table 2. Extraction of Metal Ions Into Methyl Isobutyl Ketone (27)

Metal	% Extracted from 5-7 <u>F</u> HCl	% Extracted from 6-7 <u>F</u> LiCl
Fe(III)	100	100
Ga	100	100
Cr(VI)	98	0
Mo	96	0
IN	94	60
Sn(IV)	93	91
As(III)	88	33
V(V)	81	0
Sb(III)	69	47
U(VI)	22	5
Cd	13	0
Zn	6	1
Cu	4	1
As(V)	4	0
Co	3	0
Ni	1	0
Th	1	0
Mn(II)	0.7	0
Bi	0.3	0

Table 3. Results of Wickbold in the Form Shown by Tinsley (28)

Concentration of titrant, <u>F</u>	0.1	0.01	0.0001	0.00001
Number of titrations	20	10	10	10
Arithmetic mean, ml	24.95	25.00	25.09	25.86
Relative standard deviation %	$\pm 0.09$	$\pm 0.08$	$\pm 0.08$	$\pm 1.5$

obtained is rather surprising; one would actually expect the opposite. Since the disappearance of the last trace of pink is taken as the end-point, one would expect that, with the inadequacy of the human eye, a colorless solution is seen when in fact there is still some color left. Thus the titration would be stopped too early. High results could be explained by iron impurities in the reagents but this is unlikely, considering the reliability of Wickbold who, incidentally, did not suggest a reason for the high values. The problem is most likely due (28) to an unfortunate situation in which the equilibria involved cause slightly more than the equivalent amount of EDTA to be required in removing all of the iron from the organic phase.

As indicated, considerable improvement is needed in Wickbold's method for use at the trace level. One of the possibilities is to switch from an extractive titration to a single phase titration. The titration of the iron in the MIBK, namely a non-aqueous titration, was investigated in this study.

The visual titration should be abandoned and replaced by a photometric titration which is inherently more reliable. Thus the accuracy should be increased and a considerable improvement in the precision realized.

A redox titration should be employed rather than the complexometric titration proposed by Wickbold. Although EDTA is an important titrant in analytical chemistry, it is non-selective. A redox titration should be more selective for iron than the EDTA titration when considering the elements that are coextracted with iron using MIBK (see Table 2).

These proposed improvements in Wickbold's method comprise the basis for the research conducted in order to develop an improved method for iron using the MIBK extraction.

## CHAPTER II

### COMPLEXING AGENTS FOR IRON(II)

#### Introduction

The complexation behavior of iron is very important in analytical chemistry. One need only make a superficial survey of the literature to note the many methods of detection, separation, masking, indication, and determination that are based on this behavior.

Literally hundreds of iron complexes are known. Most complexing agents form more stable complexes with ferric than with ferrous ion. Notable exceptions are certain aromatic amines and imines (e.g. pyridine, quinoline, and 1,10-phenanthroline). For reasons which will be discussed in some detail in the next chapter, only those compounds which preferentially complex iron(II) are of interest here. The remainder of this chapter is devoted to a discussion of 1,10-phenanthroline and related compounds.

The importance of 1,10-phenanthroline is convincingly demonstrated by the fact that some mention of it is included in nearly all quantitative analytical chemistry textbooks. Most practicing analytical chemists have, at some time in their career, employed the reagent for the determination of iron, or used its iron complex as a redox indicator. The history of the discovery of and the early work with 1,10-phenanthroline is both interesting and informative; a brief discussion of this subject follows (3).

### 1,10-Phenanthroline

#### Historical Remarks

In 1888 Fritz Balu (29) synthesized 2,2'-bipyridine, and demonstrated its remarkable ability to form an intensely red-colored compound with iron(II) in aqueous media. These discoveries prompted him to investigate the synthesis and possible application of other compounds similar to 2,2'-bipyridine. His paper, published in 1898 (30), reported the following findings: synthesis of 1,10-phenanthroline and demonstration of its similarity to 2,2'-bipyridine; preparation and elucidation of the iron(II) and iron(III) complexes; discovery of the reversible oxidation of the iron(II) complex; and recognition of the complexes as Werner type coordination compounds (3).

It is of historical interest to note that Gerdeissen (31) in 1889, reported the synthesis of 2-methyl-1,10-phenanthroline without any mention of its reaction with ferrous ion. This compound does not form a colored complex with iron, otherwise Gerdeissen might have shared with Blau the credit of discovering a new class of chromogenic compounds.

A number of years passed before further investigations were reported. This is rather surprising when considering that the possible analytical applications of these compounds as chromogenic reagents for iron as well as redox indicators was clearly evidenced in Blau's publications. Bode (32) was the first to employ 2,2-bipyridine for quantitative purposes. He determined iron in beer after digestion with sulfuric acid and hydrogen peroxide.

Blau's compounds received widespread interest after publication of a paper by Hammett, Walden and Chapman (33) in 1931, who described the use of iron(II) complexes as high potential redox indicators. Since then, many have contributed to the development of the use of 1,10-phenanthroline and related compounds for numerous applications in analytical chemistry. Particularly significant in this regard is the investigation into the substituent effects by G.F. Smith in conjunction with the outstanding synthetic work by F.H. Case. These cooperative efforts have led to the production of a number of important chromogenic reagents as well as a host of redox indicators covering a range of 0.87 to 1.33 volts. Notable in this respect is that the systematic approach taken led to tailor-made reagents for specific purposes (3).

Interest in the practical applications and the theoretical aspects of Blau's compounds continues to grow. The literature is replete with diverse studies of and uses for these compounds. 1,10-Phenanthroline also has applications other than as an analytical reagent. Examples include use in bacteriocides and fungicides, as virus inactivators, paint and oil dryers, enzyme activators and inhibitors, polymerization agents and catalysts, and electroplating agents (3).

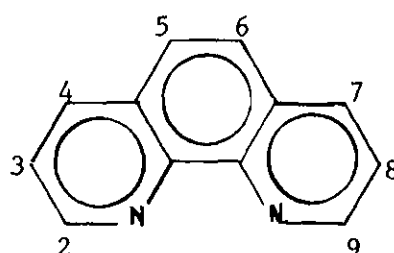
#### Nomenclature

The terms 1,10-phenanthroline and 2,2'-bipyridine are names recommended by Chemical Abstracts and the International Union of Pure and Applied Chemistry. To simplify the use of these terms the abbreviations "phen" and "bipy" are commonly used. A few trivial names are popular, e.g. ferroin and ferriin for the tris-1,10-phenanthroline

complex of iron(II) and iron(III), respectively; bathophenanthroline for 4,7-diphenyl-1,10-phenanthroline; and nitroferrion for the tris-5-nitro-1,10-phenanthroline ferrous complex.

### Properties

1,10-Phenanthroline is a planar molecule. The structure is depicted in (II-I) with the numbering of the carbon atoms as shown.



(II-I)

The compound readily acts as a bidentate ligand to form a five-membered chelate ring with either a metal or the hydrogen ion. No monodentate behavior is known; the close proximity of the nitrogen atoms in the molecule precludes such action.

The relative inertness of 1,10-phenanthroline toward chemical reaction other than salt-formation and complexation is an asset for analytical applications. The mono-hydrate of 1,10-phenanthroline melts at 98-100°C. 1,10-Phenanthroline is soluble to the extent of 0.38 g/100 ml in water. It is much more soluble in organic solvents such as alcohols, benzene, and diethyl ether.

### Applications to Iron

1,10-Phenanthroline has several features that make it ideally suited for trace iron determinations. The stability constant of the



iron complex is high enough to ensure its quantitative formation, even in dilute solutions. Another desirable feature is that some of the salts of the complex can be extracted into organic solvents, thus affording the possibility for enrichment.

When extreme sensitivity is not required, the reagent usually selected for iron determinations is 1,10-phenanthroline. The molar absorptivity of the orange-red complex is 11,100 at 510 nm; the complex forms quantitatively over the pH range 2.0-9.0. The absorption spectrum of the complex is shown in Figure 4. A pH range of 3.0-6.0, maintained by acetate buffer, is often employed. In the case where the analytical solution contains heavy metals in large amounts, a citrate buffer is used to prevent their precipitation.

In most cases, the iron is present in the analytical solution as iron(III) or as a mixture of iron(III) and iron(II), and a reducing agent must be employed. Numerous reducing agents have been evaluated. These include hydroxylamine hydrochloride, hydrazine, sodium sulfite, ascorbic acid, hydroquinone, stannous chloride, sodium formate, and sodium hypophosphite. The one most often used is hydroxylamine hydrochloride.

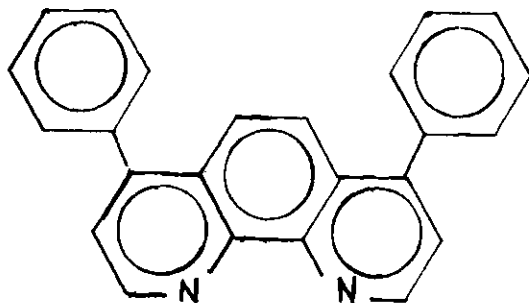
The rate of color development is very high, except when the iron(II) must be displaced from relatively non-labile complexes such as those with pyrophosphate or EDTA. The color is stable for long periods of time (at least 6 months) and is unaffected by exposure to ultraviolet light provided the pH is maintained between 3.0 and 6.0.

Beer's law is followed over the concentration range of 0-8 ppm. Few metals interfere in the determination. Mercury, copper, cobalt, and nickel are the worst offenders when present in high concentrations. Masking can be employed to minimize these interferences.

#### 1,10-Phenanthroline Derivatives

Several other phenanthroline compounds are used for iron determinations.

Bathophenanthroline (II-II) is particularly useful when high sensitivity is required. The trivial name derives from the fact that the absorption maximum of the complex is at a higher wavelength (bathochromic shift) than is that of 1,10-phenanthroline. The reagent is quite expensive, but iron determinations can be made in the concentration range of 0.001 to 0.1 ppm. The iron(II) chelate forms over the pH range 2-9, has good color stability, and a high molar absorptivity (22,400). Because of the low solubility of the complex in water, the complex is extracted into solvents such as n-hexyl alcohol, chloroform, nitrobenzene, or isoamyl acetate prior to the measurement of the color. Few metals interfere; nickel, cobalt, and copper interfere by consuming the reagent.

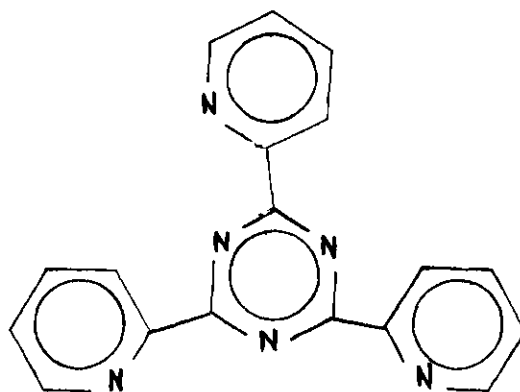


(II-II)

4,7-Dihydroxy-1,10-phenanthroline is used for the determination of iron in strongly alkaline solution. The compound is insoluble in most solvents, but is highly soluble in sodium hydroxide solution. Above pH 8, the red iron(II) chelate forms; it has a molar absorptivity of 14,800 at 520 nm. The color fades because of atmospheric oxidation of the iron(II) chelate, unless a suitable reductant is present in large excess.

#### Triazine Derivatives

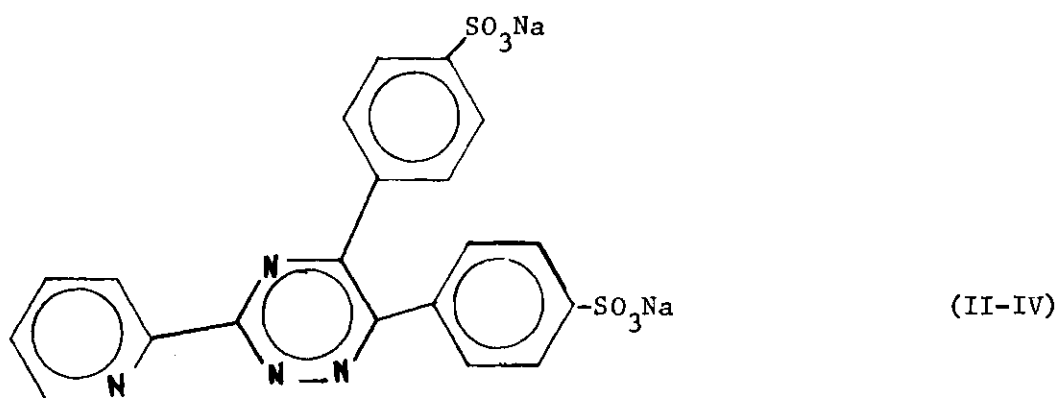
Tris(2'-pyridyl)-1,3,5-triazine, TPTZ (II-III), forms an intensely violet bis-chelate with ferrous ion over the pH range 3.4-5.8. The complex has a molar absorptivity of 22,600 at 595 nm. The reagent is comparable to bathophenanthroline in sensitivity toward iron but the method is subject to more interferences. The chief advantage of TPTZ over bathophenanthroline is its much lower cost.



(II-III)

Since its introduction by Stookey (34) in 1970, 3-(2-pyridyl)-5,6-bis-(4-phenylsulfonic acid)-1,2,4-triazine (II-IV) has been applied to

the determination of iron in a variety of samples. This compound is commonly called FerroZine and is abbreviated Fz. Its advantages include reasonable water solubility, low cost, and high sensitivity. A number of procedures (35-37) have been developed using FerroZine.



The iron(II) FerroZine complex forms over the pH range 2.0-8.5. The absorption spectrum of the complex is shown in Figure 4. The tris-complex formed with iron(II) has a molar absorptivity of 28,600 at 562 nm. Few interferences are encountered in its use for the determination of iron; only cobalt and copper form colored complexes with FerroZine. The same reducing agents that are applicable to the 1,10-phenanthroline methods can be used with FerroZine.

The rate of color development is quite high (5-10 minutes). The iron(II) FerroZine complex is stable in acid solution ( $1 \text{ F HClO}_4$ ) where the iron(II)-1,10-phenanthroline complex slowly dissociates (Figure 5).

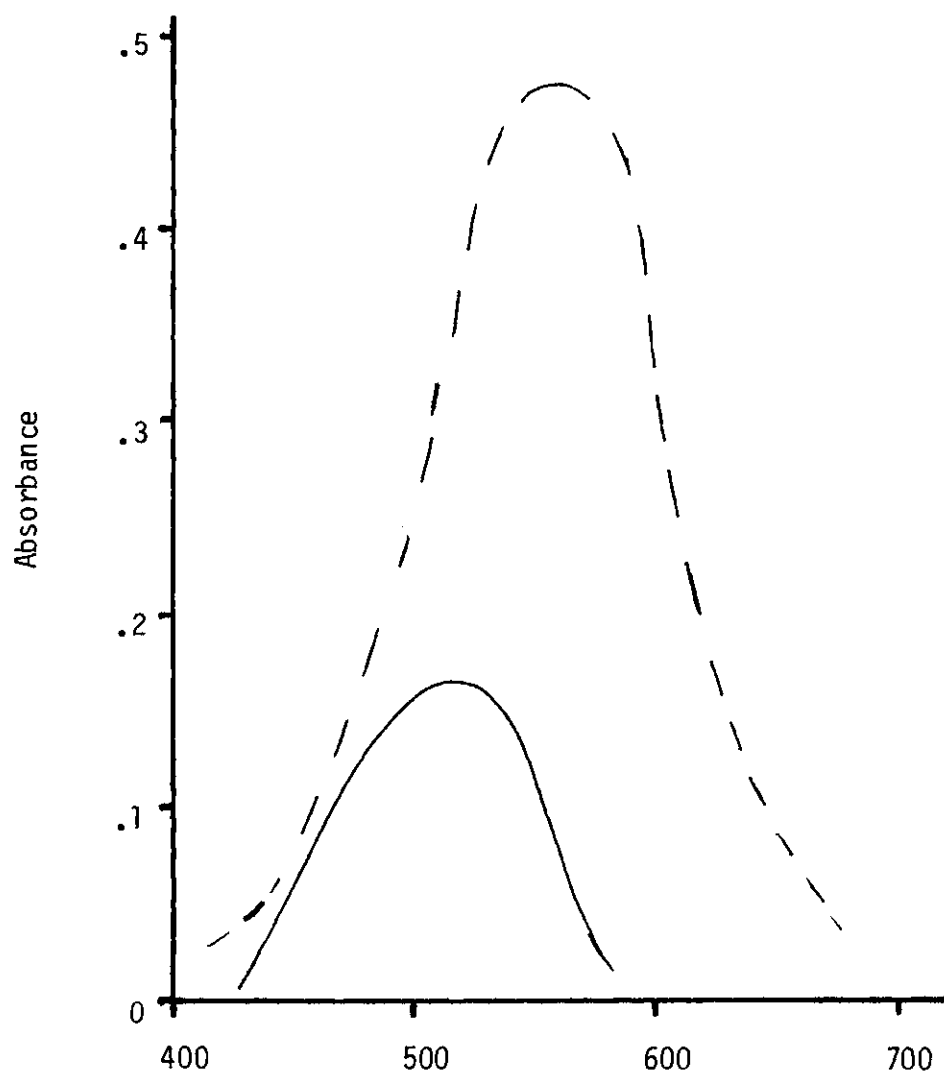


Figure 4. Absorbance Curves of Iron(II) Complexes (Same Iron Concentrations).

-- -- Ferrozine      ——— 1,10-Phenanthroline

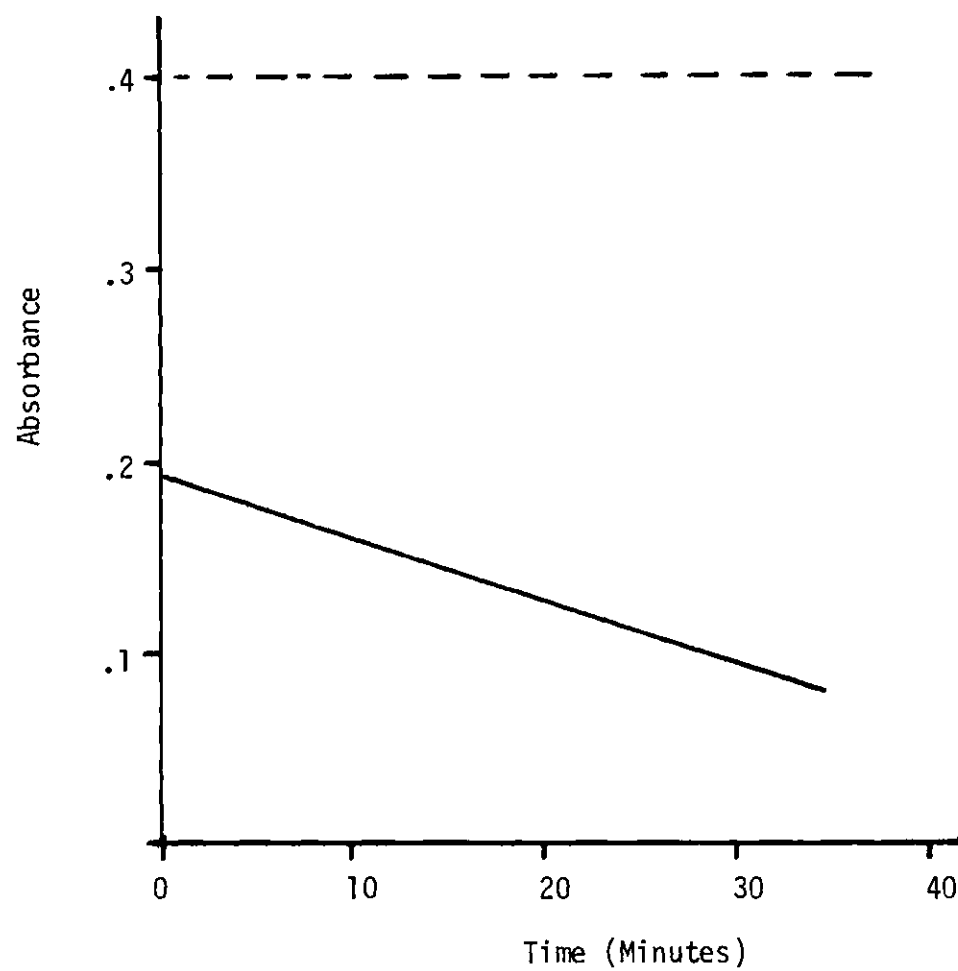


Figure 5. Dissociation of Iron(II) Complexes in 1 F  $\text{HClO}_4$ .

---- FerroZine      ——— 1,10-Phenanthroline

### CHAPTER III

#### BACKGROUND TO THE EXPERIMENTS

The stated goal of this investigation is the development of a photometric titration of iron at the trace level in sequence to the extractive separation into MIBK. Much data was already available on this subject and they provide a base from which can be selected the more prospective approaches. For redox titrations of iron, the number of procedures is legion. When considering a photometric indication, however, many approaches can immediately be excluded, and when scaling down to the trace level, the field of choices narrows considerably more. From what is then left, a number of approaches can be selected that seem to offer the best possibilities for further experimental testing. Some of the reasoning applied in the selection processes will be discussed in the following sections and should provide a background for the appreciation of the actual tests described in later chapters.

Off hand the simplest way to titrate the iron without further processing seemed to be in the MIBK extract. A titration such as this can be classified as a non-aqueous redox titration. Unfortunately very little is known on this subject. Of the few papers at hand, the majority deal with "water-like" organic solvents and scant mention is made of "non-water-like" media such as MIBK. Therefore the considerations in developing a redox method for iron on the trace level in aqueous media

will be discussed as background before relating the possibilities in MIBK.

Iron can be titrated equally easily in the divalent or the trivalent state. In general practice the choice of which state is titrated depends more on considerations of convenience. When the titrimetric determination is not performed routinely, the titration of iron(II) is usually preferred, even though the sample solution will normally contain iron(III). It is simpler to reduce iron(III) to iron(II) and titrate the latter with an oxidant that is stable in storage, than to titrate iron(III) with a reductant that requires special storage. However, when the titration is performed routinely and frequently, the titration of iron(III) becomes more appealing. When processing a large number of samples, the time saved by eliminating the preliminary reduction step more than offsets the time spent initially in setting up the apparatus for the storage of the oxygen-sensitive reducing titrant.

Such latitude in possibilities is due to the fact that, while iron(II) is subject to oxidation by dissolved oxygen, the reaction is so slow that, for practical purposes, no interference in the titration results. This statement, however, holds only for macro samples and macro amounts of iron. When operating on the micro scale, and even more so on the trace level, the situation is entirely different. In a macro titration the amount of iron oxidized by dissolved oxygen during the titration may be a negligible fraction of the total amount present, but this same minute amount may be a multiple of the total amount of iron present in a trace titration. Thus the problem of oxygen becomes a very



important factor in the present work, especially since a photometric titration is intended, which requires a longer time for the titration because of the necessity for repeated absorbance measurements.

The titration of iron(III) with a reductant may seem to be the better approach in the present study because of the problems concerning the effect of dissolved oxygen when titrating small amounts of iron(II). In addition, after the Wickbold extraction, the iron is present in the trivalent state.

However, the case for the titration of iron(III) is not as strong as it appears. Although the reducing titrant is protected from oxygen, dissolved oxygen in the sample solution still may cause problems. It may react with the titrant before the iron is titrated. Whether this causes an interference depends on what substance is used to indicate the titration, namely, the titrant, the iron, or another entity. Even under the best circumstances, the oxygen would show as a "pretitration" portion of the curve. In the case where oxygen does not rapidly react with the titrant, it may cause incorrect results because the iron(II) formed during the titration may be reoxidized. If the oxygen is titrated after the iron, and the endpoint is already established, no interference results unless the titrant itself or its oxidized form is used for indication. Thus, while under favorable conditions oxygen may be tolerated in the reductometric approach, the general situation is such as to warrant its exclusion.

Although the iron is present in the trivalent state after the Wickbold titration, many factors point toward an oxidimetric titration

as being more advantageous. Reduction of the iron(III) can be made by a variety of means which have to be screened for suitability on the trace level. At this point of discussion, however, the obvious problem with oxygen, once the reduction has been performed, is of prime interest.

The most common method of removing dissolved oxygen is bubbling an inert, oxygen-free gas through the solution. However, there are problems with this approach. When performing a photometric titration, time must be allowed for gas bubbles floating in the solution to clear, thus prolonging the titration. Bubbles may cling to the wall of the titration vessel and prevent light from passing through in the correct path.

Another problem may arise with the use of cylinder gases which sometimes contain traces of oxygen. Although the minute amount of oxygen frequently present in the gas may be tolerable in a macro titration, the amount may be prohibitive in trace level titrations. To achieve complete freedom from oxygen may require the use of copper turnings in a heated tube or an equivalent arrangement.

Because of the problems associated with the removal of oxygen, another approach should be investigated, namely, creating a situation where the oxygen is allowed to stay but is prevented from doing harm. Such would be the case when the iron(II) is transferred into a complex that is unaffected by oxygen, but can still be titrated with an appropriate oxidant. The iron(II) complexes of 1,10-phenanthroline and related compounds (see Chapter II) satisfy these conditions and in addition are intensely colored. This latter feature is of particular moment

here because it affords the opportunity for self-indication in the photometric titration.

When it is desired that the iron(II) be titrated, a prereduction becomes necessary. Many ways to achieve this are known, but again the restriction when applied to the trace level narrows the choices. The prime difficulties are not connected with the reductant as such, but rather with the removal or destruction of its excess.

At first glance, substances like sulfurous acid, hydrazine or hydrogen sulfide that have been employed on the macro level seem to offer advantages. They are readily available in highly pure state, i.e. iron-free, and their excess is removed by boiling. However, boiling is not a preferred operation in work on the trace level and in some cases may even not be adequate to reach the completeness of removal required.

Thus some of the solid reductants seem to offer better choices. As such, powdered zinc has been in use for a long time. The main disadvantage in its use is the time necessary for complete dissolution of the metal. The same holds for powdered aluminum which can also be used for the same purpose. These metals, and nickel, are often employed as spirals or shot. In either form, the removal of the excess metal is simple but the spiral or shot must be rinsed to recover all of the sample solution. This may lead to an undesirable dilution of the sample solution and also offers ready means for oxygen to reenter. Thus the best possibility seems to be application of the metal in the form of a reductor column, which can be designed and constructed to suit any level.

The most common reductor in use is the Jones reductor, which is constructed from zinc. With very small Jones reductors, the formation of hydrogen gas bubbles (occurring even when amalgamation is applied) poses a great problem. The silver reductor, also called the Walden reductor, seems to be a much better choice because with it no hydrogen bubbles are formed, hydrogen peroxide formation is not a problem, and the silver is more readily available in high purity, i.e. iron-free, than zinc.

Silver is a much milder reductor ( $E^{\circ} = +0.22V$ ) than the other metals discussed and is much more selective. A few reductions of analytical importance are (6): Fe(III) to Fe(II), Cr(VI) to Cr(III), Ce(IV) to Ce(III), V(V) to V(IV), Mo(VI) to Mo(V), Mo(III), and Cu(II) to Cu(I). The oxidation of silver proceeds according to



The formal potential depends upon the chloride concentration. This fact is of advantage because the reductor can be made even more selective in its reducing properties by appropriate adjustment of the chloride concentration.

In connection with the reduction of iron(III) to iron(II) using the Walden reductor, two interesting possibilities for the stabilization of the iron(II) present themselves. Should the solution containing the iron(II) exiting the column flow into the complexing solution, or should the complex former be added to the solution that is poured into the

reductor? The latter choice seems the better one because then the existing solution contains the iron in a protected form. However, whether the approach is feasible cannot be judged in advance because too many parameters are involved. Here the experiment has to decide.

Whatever the outcome of these experiments, the point now is that the iron as iron(II) is present and ready for titration with a strong oxidant.

Although a host of compounds oxidize iron(II) in aqueous media, the important ones are permanganate, dichromate and cerium(IV). Permanganate suffers from stability problems and was not considered further. Dichromate was also eliminated as a possibility because it is subject to problems due to side reactions and it was felt that these difficulties would be even more pronounced in titrating on the trace level. Cerium(IV) was thought to have great promise. Solutions of it are very stable. Because only a one electron change is involved in its use as an oxidizing titrant, no side reaction should result. The formal potential of the Ce(IV)/Ce(III) couple is high, amounting in 1 F perchloric, nitric, sulfuric, and hydrochloric acids to +1.70 V, +1.61 V, +1.44 V, and +1.28 V respectively (6).

The preceding considerations were based on aqueous solutions for which the relevant facts are at hand. When investigating the possibility of operating in non-aqueous medium, the following considerations come into play.

For direct titration of the iron(III) in the MIBK extract, the problems mentioned for the aqueous solution are compounded. The bubbling

of an inert gas here will have the additional effect of greater temperature changes and, as a consequence, cause formation of Schlieren that hamper the photometric measurement. Furthermore, with the more volatile organic solvent, a decrease in volume may result which is quite undesirable in a photometric titration.

Thus, in non-aqueous media, the titration of iron(II) with an oxidant seems to be preferable. Selection of the mode of the then required prereduction is based on considerations analogous to those for aqueous media. When employing the Walden reductor, or for that matter any type of reductor, additional questions must be pondered. Will the electron transfer at the metal surface be as fast and complete with the solvated ion as with the hydrated ion? What will be the possibility of interaction between the reductor and the solvent? Answers to these questions all need actual experimental treatment.

The choice of oxidizing titrant must be reviewed in the same manner as for aqueous media, with the added difficulties of possible insolubility in and interaction with the solvent. Further, since a photometric titration is intended, the solubility of the reduced form of the titrant is also of importance.

Should the MIBK itself cause problems, then these problems may be alleviated by, for example, adding a solvent of more water-like nature, or by adding water plus a mediator to ensure a homogeneous solution.

Finally, the case has to be considered in which operation in non-aqueous or even partially aqueous media is impossible. In this case a reextraction into a water phase has to be applied and then all of the considerations for the aqueous media apply.

Still the situation is not as simple as it appears. The development of a redox titration involves much more than merely scaling down a macro-titration, as discussed previously. One point that could be a source of trouble is that MIBK is soluble in water to the extent of 1.9 g/100 ml. While this amount of MIBK is probably tolerable in a macro-titration, its effect on a trace titration is unknown. MIBK is a methyl ketone, and these types of compounds react with strong oxidants.

## CHAPTER IV

## TITRATIONS IN MEDIATED MIBK

Titration of Iron(II)Prereduction of Iron(III)

The Walden Reductor was investigated for the prereduction of iron(III) in MIBK. This reductor was first tested as follows: a portion of the MIBK extract containing the chlorocomplexes of iron(III) was passed through the reductor and collected in a small volume of ethanolic FerroZine. The residual solution was removed from the column by washing with several bed volumes of MIBK. The reduction of the iron(III) should be indicated by the formation of the purple iron(II)-FerroZine complex. Repeated attempts with this procedure failed to indicate any reduction of the iron(III). It was suspected that the bulky MIBK molecules present in the solvation sphere of the iron(III) inhibit the electron transfer between the metallic silver and the iron(III). For this reason, the addition of a polar organic solvent whose size is much smaller than that of MIBK was investigated. The thought here was that the replacement of the bulky MIBK molecules in the solvation sphere of the iron(III) by smaller molecules would permit the electron transfer. The solvents investigated for this purpose were glacial acetic acid, methanol, and ethanol.

The solvents were added in various amounts to the MIBK containing the iron(III) prior to passing through the reductor. The addition of



glacial acetic acid to the MIBK did not help; still no reduction of the iron(III) was observed. However, with methanol or ethanol, the situation was entirely different. In a 50% V/V solution of MIBK and the respective alcohol, some of the iron(III) was reduced to iron(II) in the Walden Reductor, but in an irreproducible manner. The inconsistency was felt to be due to the fact that most of the iron(II) is rapidly oxidized by atmospheric oxygen as the MIBK solution exits the column. This supposition was supported by the fact that when atmospheric oxygen was excluded (by bubbling oxygen-free nitrogen through the ethanolic FerroZine solution) from both the ethanolic FerroZine solution and the solution exiting the column, the reduction of iron(III) was quantitative. This requirement of the exclusion of oxygen, however, poses the disadvantages mentioned in the preceding chapter.

Next, the addition of both the FerroZine and the alcohol to the MIBK extract prior to passing it through the reductor was investigated. The expectation here was that the iron(II) formed by the reduction of the iron(III) with silver would be complexed by the reagent within the column. This in situ reduction and complexation would protect the iron(II) from oxidation by atmospheric oxygen. This expectation was fully realized experimentally as follows. To the MIBK extract containing the chlorocomplexes of iron(III) was added an equal volume of alcohol (methanol or ethanol) and 1 ml of ethanolic FerroZine. This iron solution was passed through the reductor. The reduction of the iron(III) using this procedure was quantitative and the color of a solution containing 5 PPM of iron(II) is stable for several hours; then the color

begins to fade. This procedure is also applicable when using other iron(II) complexing agents such as 1,10-phenanthroline and bathophenanthroline.

#### Oxidizing Titrants

Because iron(II) in MIBK is rapidly oxidized by atmospheric oxygen, either oxygen must be excluded or the iron(II) must be protected (by complexation) when the iron(II) in MIBK is titrated with an oxidizing titrant. The advantages and disadvantages of each of these two approaches were discussed in the last chapter. Only the second approach, namely titration of the protected iron(II), was investigated.

Since ethanol is required when the Walden Reductor is used for the prereduction of iron(III) in MIBK, this method was not used in the preliminary investigations of the various oxidizing compounds tested as possible oxidizing titrants for iron(II). Ethanol reacts with strong oxidants in aqueous media and although it could not be predicted that this reaction will take place in MIBK, it was thought best to consider another way of preparing MIBK solutions of the iron(II) complex. The following way was chosen. A very small amount of the aqueous iron(II)-FerroZine complex was added to glacial acetic acid (used as a mediator) and the solution diluted with a large volume of MIBK. Such a solution is stable for several days. This solution was used in the evaluation of the oxidizing compounds tested.

The oxidizing compounds studied are shown in Table 4. None of these compounds are appreciably soluble in MIBK and a solvent mediator is necessary. Each of these compounds was tested as follows. The

Table 4. Compounds Investigated as Oxidizing Titrants

Compound	Formula	MIBK Mediator
Antimony pentachloride	$\text{SbCl}_5$	Chloroform
N-bromosuccinimide	$\text{C}_4\text{H}_4\text{O}_2\text{NBr}$	Acetone
N-chlorosuccinimide	$\text{C}_4\text{H}_4\text{O}_2\text{NCl}$	Glacial HAc
Chloramine-T	$\text{CH}_3\text{C}_6\text{H}_4\text{O}_2\text{NCl} \cdot \text{Na}$	Glacial HAc
Ammonium hexanitratocerate	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Glacial HAc

appropriate mediator was added to the MIBK containing the iron(II)-FerroZine complex and increments of the titrant solution were added. The titration was followed photometrically (oxidation of the purple iron(II) complex to the corresponding colorless iron(III) complex).

Antimony pentachloride, N-bromosuccinimide, N-chlorosuccinimide, and chloramine-T did not oxidize the iron(II)-FerroZine complex in the mediated MIBK. Cerium(IV) slowly oxidized the iron(II) complex when glacial acetic acid was present. This oxidation was quite rapid, however, in 10% perchloric acid. Several titrations of the iron(II)-FerroZine complex in a solution containing 10% perchloric acid, 70% glacial acetic acid and 20% MIBK were performed but the results were disappointing in that considerably more titrant than expected was required to reach the endpoint. In addition, after the endpoint was reached (colorless), the purple color reappeared within about thirty seconds.

It was thought that these problems were caused by some side-reaction of cerium(IV) with MIBK. This was tested as follows. To a 10% perchloric acid solution in glacial acetic acid were added a few drops of aqueous iron(II)-FerroZine complex and sufficient cerium(IV) solution so that the color was just discharged. The solution was split into two portions and after about one hour, one drop of MIBK was added to one of the solutions.

The results of this test are quite interesting. Both solutions remained colorless for the one hour observed. However, color reappeared within about 30 seconds in the solution to which the MIBK had been added. Ethanol showed the same effect as does MIBK. Because MIBK reacts

with cerium(IV) and most likely also reacts with any oxidizing compound which oxidizes the iron(II)-FerroZine complex, this approach was abandoned and instead the titration of iron(III) in MIBK with a reducing compound was investigated.

#### Titration of Iron(III)

The reducing compound investigated for the titration of iron(III) in MIBK was ferrocene (see Chapter VI). As was the case in the previous section, the exclusion of oxygen from the solution to be titrated was not considered; rather the investigation here was restricted to titrations of iron(III) in the presence of iron(II) complexing agents, so as to prevent reoxidation.

Several iron(II) complexing agents were investigated and a study of the time necessary for the complete reduction of iron(III) in MIBK by ferrocene (added as ethanolic solution) and complete formation of the respective iron(II) complex is shown in Figure 6.

Because the reduction and complexation occurs fastest in the presence of 1,10-phenanthroline, this complexing agent was investigated further. Photometric titrations of the chlorocomplexes of iron(III) in the MIBK extract with ferrocene was conducted as follows. To the MIBK extract was added an equal volume of ethanol and one milliliter of ethanolic 1,10-phenanthroline. An increment of ethanolic ferrocene was added every three minutes until several points beyond the endpoint were established. A typical titration curve is shown in Figure 7. The titration curves are reasonably well defined, but the endpoints are not

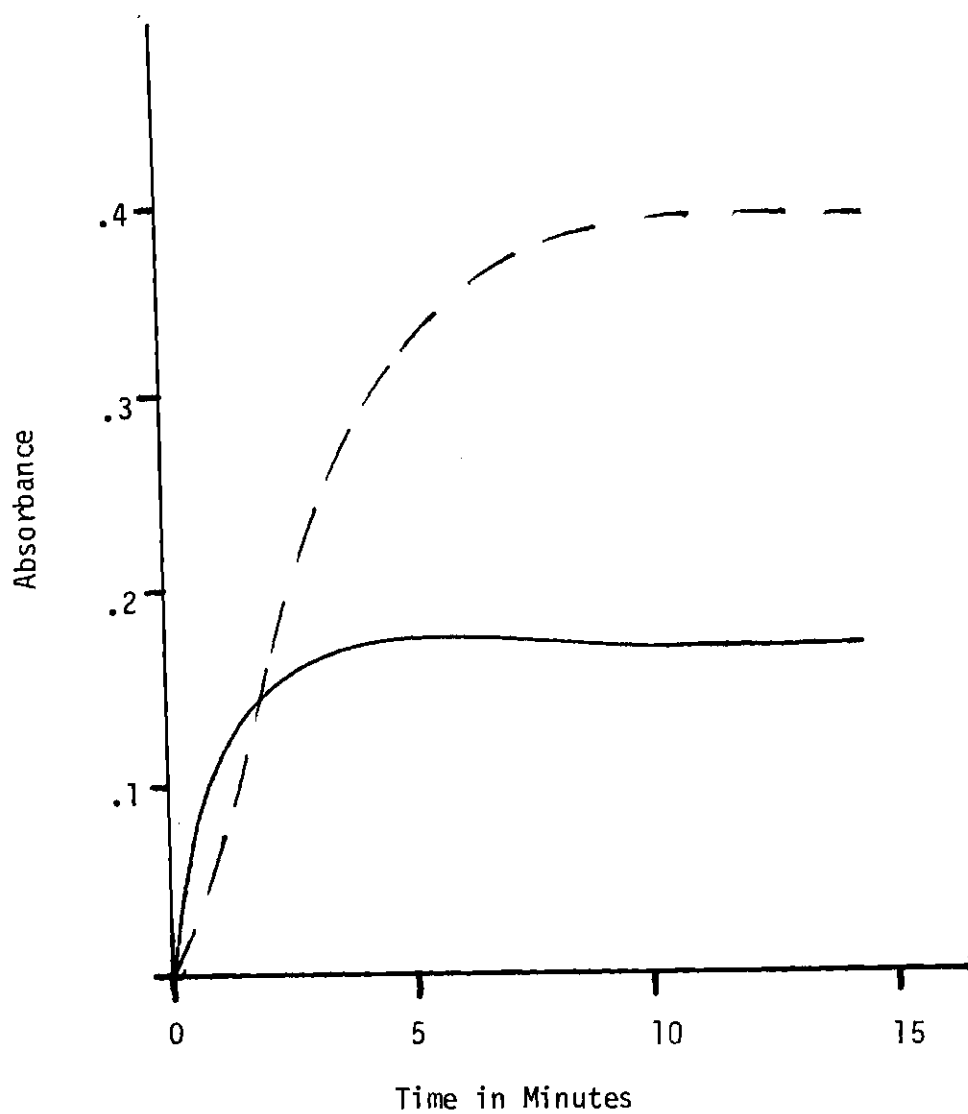


Figure 6. Time Necessary for the Complete Reduction of Iron(III) by Ferrocene.

In the Presence of

— 1,10-Phenanthroline      - - - FerroZine

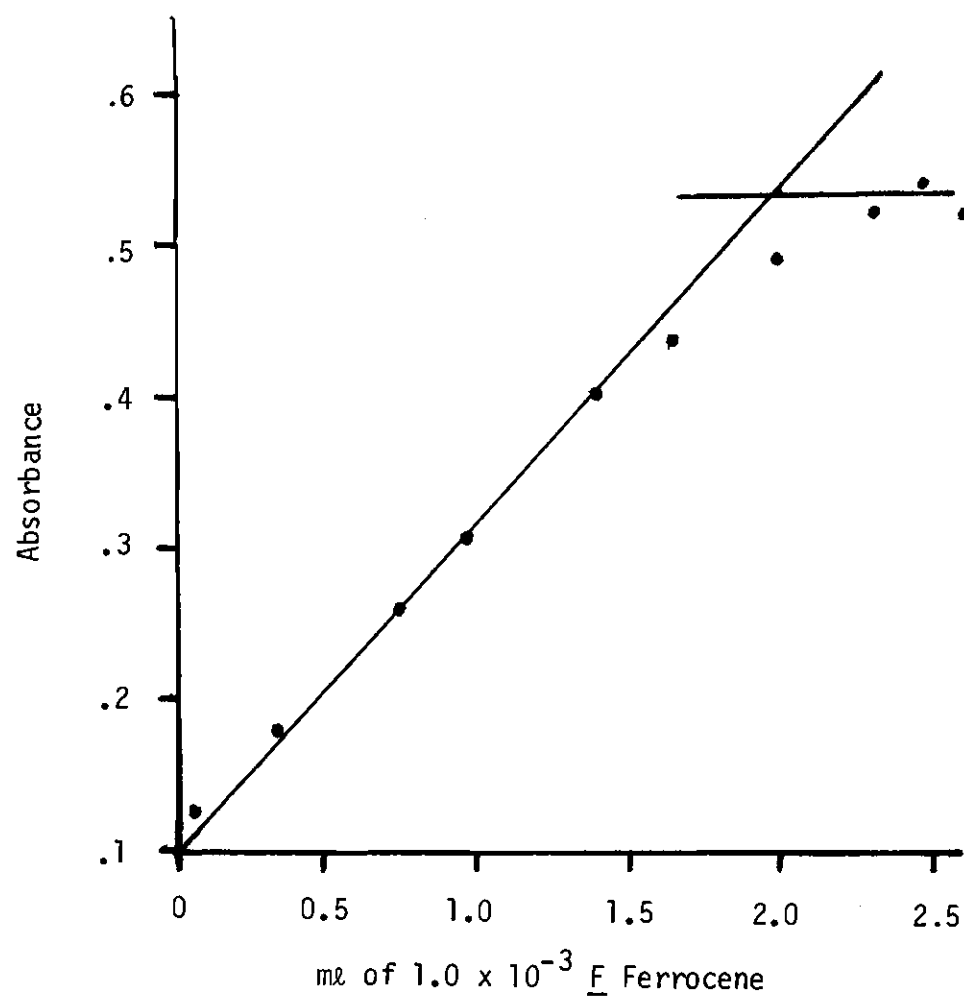


Figure 7. Curve for the Photometric Titration of Iron(III) with Ferrocene.

reproducible. In addition, about 50% more ferrocene than expected is required to reach the endpoint.

The conclusion was drawn that since several minutes are required for all of the iron(II) to be complexed by 1,10-phenanthroline (and thus protected from oxygen), that some of the iron(II) formed by the reduction of the iron(III) in MIBK with ferrocene was reoxidized by dissolved oxygen. This explained the high results and the non-reproducible endpoints.

Because of the problems encountered in developing a method for the photometric redox titration of iron in MIBK, it was decided next to operate with a reextraction into an aqueous medium. By doing so, the advantages mentioned in the last chapter would be realized. However, the possible problems anticipated, particularly the effect of the small amount of MIBK dissolved in the aqueous phase, had to be kept in mind.



## CHAPTER V

### THE DETERMINATION OF IRON AFTER REEXTRACTION

#### Introduction

As discussed in detail in Chapter III, the preferred method for the determination of iron after its reextraction from MIBK into water is to prereduce the iron(III), protect the iron(II) formed by complexation, and titrate the iron(II) complex with an oxidizing titrant. The four major areas that had to be investigated in developing such a method were: 1) the extraction of iron(III) into MIBK; 2) the reextraction of the iron(III) from MIBK into water; 3) the reduction of the iron(III) to iron(II); and 4) the titration of the iron(II) with an oxidizing titrant. The extraction of iron(III) into MIBK had been worked out (see Chapter I) and no further work in this area was necessary. The other three areas, however, required a great deal of investigation in developing the method. The details of this work are as follows.

#### The Reextraction

For the reextraction, water alone is employed. The reasoning here was that since there is no excess chloride present in the aqueous phase, the iron(III) chlorocomplexes in the organic phase would break up readily and the iron, no longer complexed, should move easily into the aqueous phase.

This was tested as follows. To 10 ml of the MIBK extract containing the chlorocomplexes of iron(III) in a separatory funnel was added 0.5 ml of water and the system shaken for about 30 seconds. The aqueous layer was withdrawn and the amount of iron in this phase determined via the FerroZine Method (see Part II, Chapter II). The reextraction with fresh portions of water was repeated until no more iron could be detected in the aqueous phase.

It was found that in order to completely recover the iron from 10 ml of MIBK, two reextractions with 0.5 ml portions of water are sufficient. This reextraction is applicable to a wide range of iron concentrations ( $1 \times 10^{-2} \text{ M}$  to  $1 \times 10^{-5} \text{ M}$ ).

#### The Prereduction of Iron(III)

The reductor selected for the reduction of the iron(III) in the aqueous phase obtained by the reextraction was again the Walden Reductor. As mentioned earlier, it was deemed necessary that the iron(II) produced by the prereduction be protected from dissolved oxygen by complexation. The complexing agent investigated for this purpose was FerroZine. Two possibilities exist with respect to its use: adding the FerroZine to the iron(III) solution prior to passing through the reductor and collecting the solution exiting the reductor in the FerroZine solution. The first approach offers the advantage over the second approach in that the in situ reduction and complexation ensures that the iron(II) exiting the reductor is protected against oxygen.

### pH Dependence

Because the iron(II)-FerroZine complex forms over the pH range 2.0-8.5, it was felt that the in situ reduction and complexation in the Walden Reductor would also be pH dependent. Consequently a pH study was undertaken using the following approach. To a series of aqueous solutions containing very small amounts of iron(III) and 0.1M in chloride ion, were added FerroZine solution and different amounts of hydrochloric acid, acetate buffer, or sodium hydroxide so that the series represented a wide pH range. Each solution was passed through the reductor, and the absorbance of the solution exiting the column measured at 562 nm ( $\lambda_{\text{max}}$  of the iron(II)-FerroZine complex).

The results of this study are shown in Figure 8. The in situ reduction and complexation is quantitative over the pH range 1.7 to 3.2.

### Procedural Details

Several important points were discovered during the course of these investigations. Prior to adding the iron(III)-FerroZine solution, the reductor should be conditioned with several bed volumes of "wash solution". The purpose of this is twofold: 1) to ensure that any iron (or other impurities) left on the column is removed; 2) to ensure that the solution on the column is within the pH range 1.7 to 3.2. The "wash solution" can be prepared from a variety of materials as long as the chloride concentration is at least  $1 \times 10^{-2}$  and the pH of the solution is between 1.7 and 3.2. For example, this solution can be prepared from any of the following: 1)  $10^{-2}$  F hydrochloric acid; 2) acetate buffer to which sufficient hydrochloric acid is added to bring the pH within the

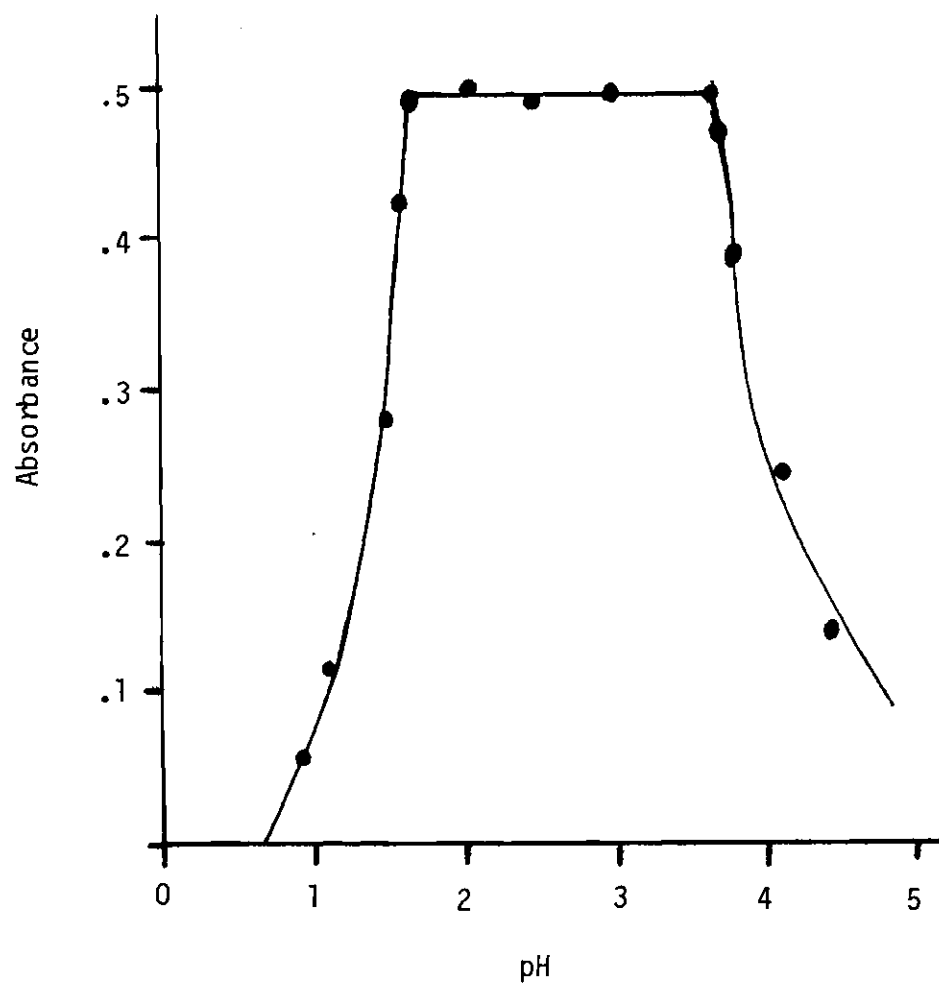


Figure 8. pH Dependence of In Situ Reduction and Complexation.

range prescribed; 3) dilute monochloroacetic acid/monochloroacetate buffer.

After eluting the sample solution, at least  $1\frac{1}{2}$  bed volumes of "wash solution" are used to ensure that all sample solution is removed from the column. With a typical reductor (constructed from the lower part of a 50 ml buret and containing about 4 grams of "Walden" silver) the flow rate should be maintained at 1 ml/minute or less.

#### Procedure

The procedure highlighted in this section can be used for the prereduction of iron(III) to iron(II) followed by the titration of the iron(II) with an oxidizing titrant, or for the photometric determination of iron at trace levels. This procedure was found in many tests to give the reliable results reported in Table 5.

- 1) To the sample solution containing up to 150  $\mu\text{g}$  or iron, add sufficient sodium chloride to ensure that the final chloride concentration is  $10^{-2}$  F.
- 2) Add 1 ml  $10^{-2}$  F FerroZine solution.
- 3) Add strong acid or base as needed to bring the pH to within the range 1.7 to 3.2.
- 4) Pass the solution through the reductor and wash as described in the Procedural Details section.
- 5a) Titrate the solution as outlined in Procedure I, or
- 5b) Bring to defined volume and measure the absorbance at 562 nm.
- 6) Obtain the results in the usual manner: a) from the titration curve, or b) from a calibration curve established under identical conditions.

Table 5. Typical Results Using the Prereduction Method

Fe TAKEN $\mu\text{g}$	Fe FOUND $\mu\text{g}$
90.0	90.0
	90.1
	90.3
	89.8
	90.4
	90.0
	89.6
	90.3
	89.9
	90.2
$\bar{x} = 90.1 \quad s = \pm 0.2$	



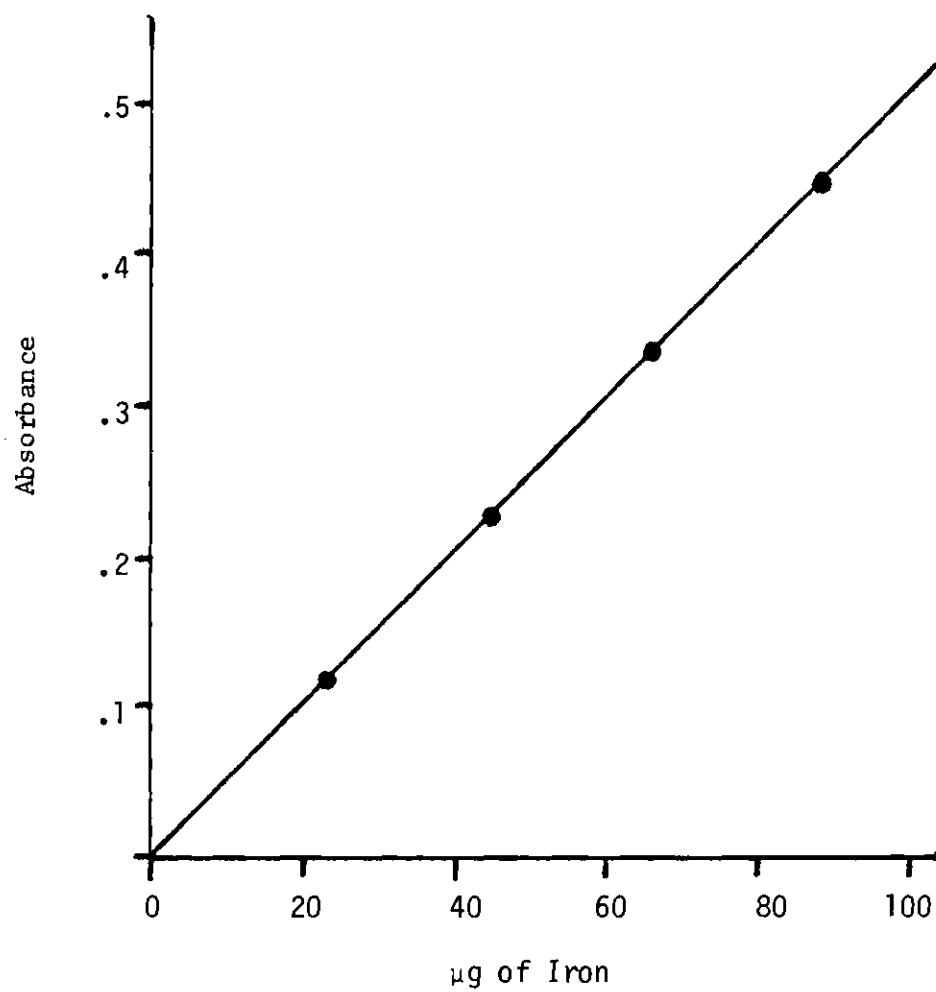


Figure 9. Calibration Curve Using the Prereduction Method.



the colorless iron(III)-FerroZine proceeds very slowly. However, in 1 F perchloric acid the reaction is very rapid and analytically useful.

A large number of titrations were performed of the iron(II)-FerroZine in 1 F perchloric acid with cerium(IV); a typical titration curve is shown in Figure 10.

#### Stability of Cerium(IV)

At first, titrant solutions ( $10^{-3}$  F or lower) of cerium(IV), 1 F in perchloric acid, were prepared by diluting the stock solution ( $10^{-2}$  F cerium(IV), 2.5 F perchloric acid) and adding enough perchloric acid to give a final concentration of 1 F in the acid. However, it was noticed that the titer of the cerium(IV) stock solution decreases by as much as 0.05% per day. This decrease was thought to be due to contamination by dust, etc., when the flask was opened, but even when care was taken to exclude such events, the same decrease in the titer was still observed. When the cerium(IV) stock solution was kept in the dark, however, the titer remained fairly constant.

This decrease in the titer of cerium(IV) in perchloric acid has been observed by others. Weiss (38) found that cerium(IV) solutions in perchloric acid are sensitive to photochemical reduction by water. Furman (39), however, stated that  $10^{-2}$  F solutions of cerium(IV) in sulfuric acid are stable for at least 6 years.

Furman's observation was very helpful in work in this laboratory: solutions  $10^{-2}$  F in cerium(IV) and 2.5 F in sulfuric acid were found to be stable for at least three months as long as normal precautions are followed to exclude dust. It was also found that as long as the solution

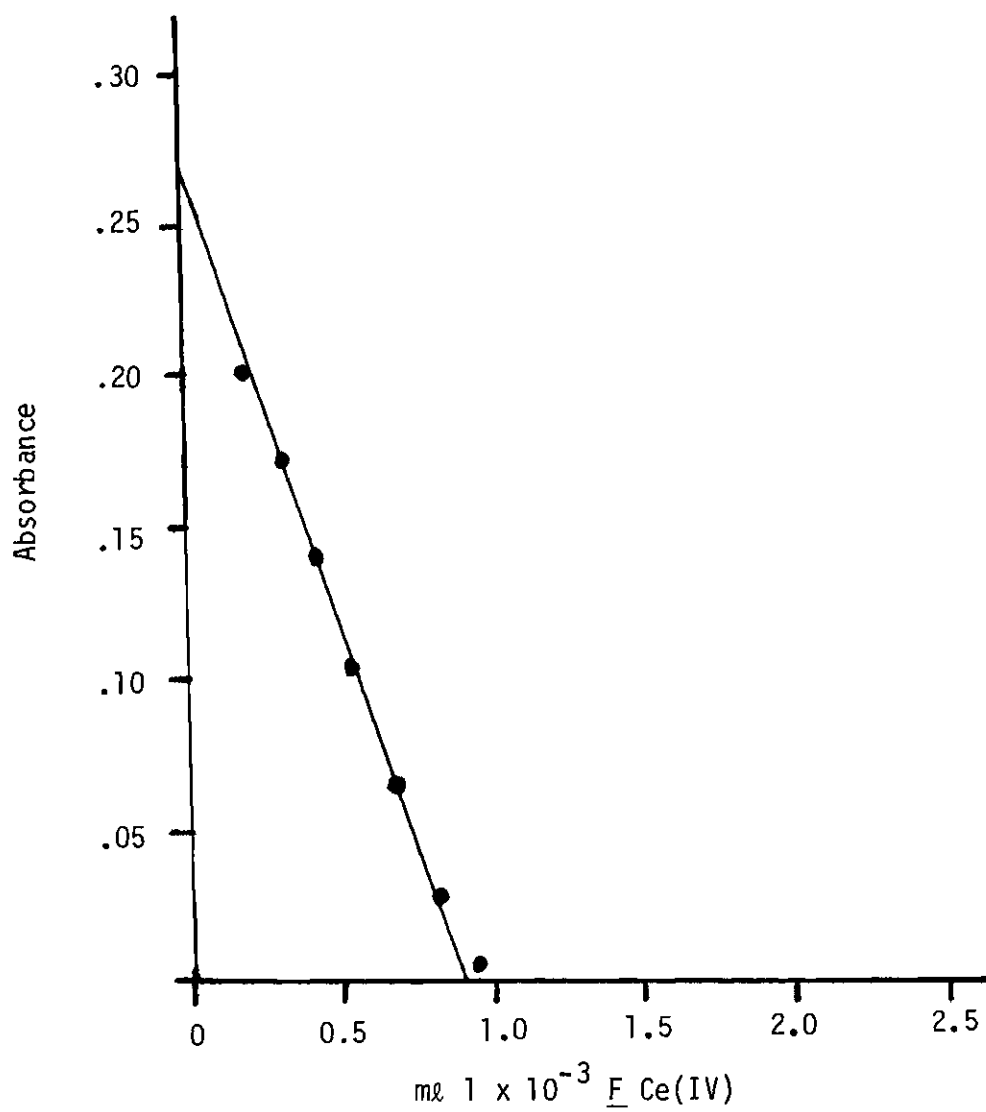


Figure 10. Typical Curve for the Titration of Iron(II)-Fz with Cerium(IV).

containing the iron(II)-FerroZine is about 1  $\underline{\text{F}}$  in perchloric acid, the titrant solution need not contain perchloric acid. The titrant solutions used in the present work were  $2.5 \times 10^{-1}$   $\underline{\text{F}}$  sulfuric acid, with no perchloric acid present.

#### The Effect of Dissolved MIBK

When the titration described was employed for the determination of the iron in the aqueous phase, obtained from the reextraction, problems similar to those mentioned in Chapter IV were encountered. Much more cerium(IV) than expected was necessary to reach the endpoint, and again the purple color returned within about thirty seconds. Both these problems were found to be due to the MIBK, which is soluble in the aqueous phase to the extent of about 1.9 g/100 ml.

Thus, the removal of the MIBK from the aqueous solution was deemed necessary. The term "removal" does not imply complete removal; rather, it suffices to reduce the amount of MIBK such that what is left after the separation step does not exert any influence upon the titration of the iron(II)-FerroZine with cerium(IV). The two approaches for MIBK removal investigated were volatilization and extraction.

Dissolved MIBK is eliminated by boiling the aqueous solution for at least thirty minutes. However, this approach opens the way for contamination from the atmosphere and the walls of the vessel.

The better approach is extraction of the MIBK into a water immiscible organic solvent such as benzene. It was found that shaking the aqueous phase, obtained from the reextraction, with an equal volume of benzene for about thirty seconds eliminates the effect of the

dissolved MIBK upon the titration. The small amount of benzene present in the aqueous phase after such an extraction has no effect upon the titration of the iron(II)-FerroZine with cerium(IV).

### Interferences

The elements which are coextracted with iron(III) from 6 F hydrochloric acid into MIBK are shown in Table 2 (see Chapter I). Several of the more common elements coextracted were tested for interference as follows. To 1  $\mu$ mole of iron(III) was added 1  $\mu$ mole of the metal ion. The solution was passed through the reductor, and titrated with cerium(IV). The metals tested in this manner were Cr(VI), Mo(VI), Sn(IV), As(III), V(V), Sb(III), Cd, Zn, and Cu.

Of these, cadmium, zinc and tin do not interfere at all. With molybdenum, arsenic, and antimony, a small "pretitration" portion of the titration curve was evident. However, these elements do not interfere because when the amount of cerium consumed in the "pretitration" is subtracted from the total amount of cerium(IV) required to reach the endpoint, the difference corresponds to the amount of iron present. Copper shows a very large "pretitration" curve (see Figure 11). Again, this represents no problem with the iron determination provided the amount of cerium(IV) consumed in the "pretitration" portion is taken into account.

Both chromium and vanadium interfere in the method. In the presence of Cr(VI), the in situ reduction and complexation of iron(III) is incomplete (about 50% of expected). It is suspected that in solutions low in chloride the reduction of Cr(VI) by silver is slow, and the Cr(VI)

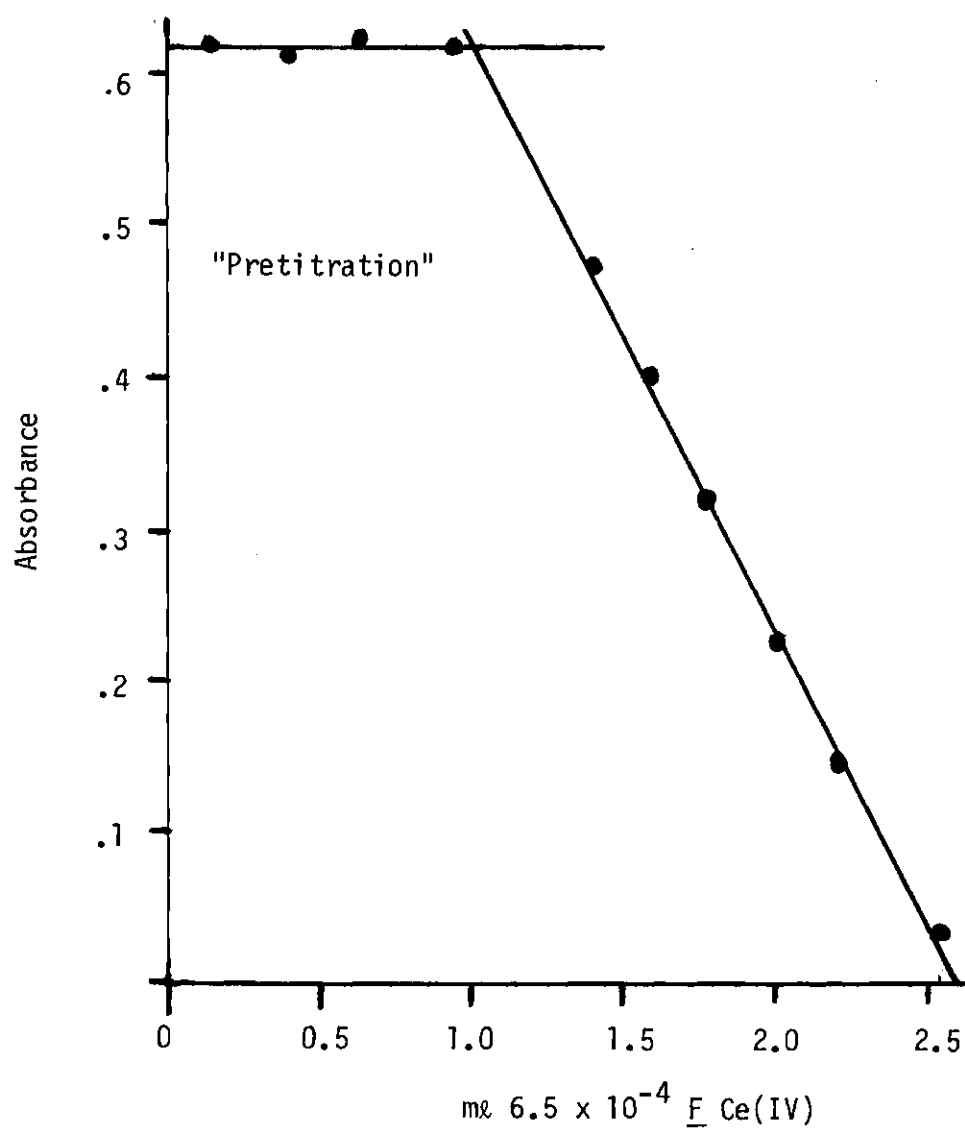


Figure 11. Effect of Copper Upon the Titration.

reoxidizes the iron(II). Vanadium interferes in that some of it is titrated with the iron(II)-FerroZine. However, the interference by chromium and vanadium are easily taken care of. For those sample solutions which contain either one or both of the elements, the extraction into MIBK is performed from 6 F lithium chloride rather than from 6 F hydrochloric acid. Neither chromium nor vanadium are then extracted.

#### The Determination of Large Amounts of Iron

The procedure presented in this section is the product of the four areas investigated: the extraction, the reextraction, the prereduction, and the titration.

#### Procedural Details

If it is suspected that the sample solution is more than  $10^{-4}$  F in either Cr(VI) or V(V), then step 2 should be modified by substituting 12 F lithium chloride for the concentrated hydrochloric acid.

The blank is established as follows. Three different amounts of standardized iron(III) solution are carried through the procedure. A graph of iron concentration versus volume of cerium(IV) required is constructed. The Y-intercept (0 iron concentration), represents the amount of cerium(IV) required to titrate the blank, and this amount is subtracted from all titration results. Figure 12 illustrates such a graph.

#### Procedure I: More Than 10 $\mu$ g of Iron

1. Deliver 10 ml of the aqueous iron solution into a separatory funnel, add 5 drops of concentrated nitric acid, and mix well.

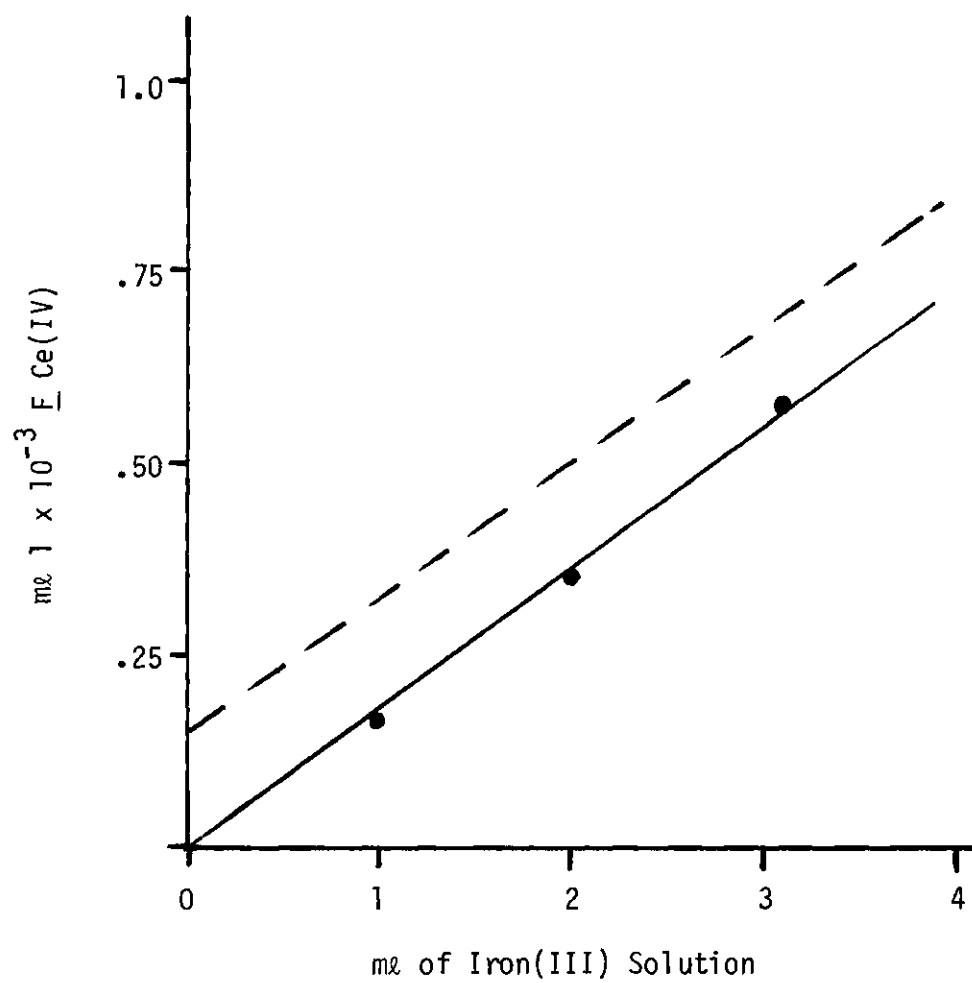


Figure 12. Calibration Curve Using Procedure I.

— Blank Subtracted    - - - Blank Not Subtracted

2. Add 10 ml of concentrated hydrochloric acid, 5 ml MIBK, and shake for about 1 minute.
3. Allow phase separation and discard the lower, aqueous layer.
4. Add a 2-ml portion of water to the separatory funnel containing the MIBK and shake for about 1 minute.
5. Allow phase separation (about 1 minute) and drain the lower aqueous layer into a second separatory funnel containing 10 ml of benzene. Rinse the funnel tip with a couple of drops of water.
6. Repeat steps 4 and 5 with a fresh 2-ml portion of water.
7. Shake the funnel containing the benzene and the aqueous phase for about 2 minutes.
8. Allow about 5 minutes for phase separation, and drain the lower, aqueous layer into a small beaker. Rinse the funnel tip with a couple of drops of water.
9. Repeat steps 4, 5, 7, and 8 with a 1-ml portion of water.
10. Add 0.5 ml of  $10^{-2}$  F FerroZine solution, adjust the pH of the solution to 1.7-3.2, and mix well.
11. Pass through the Walden Reductor (see Prereduction Section), and collect in a small beaker containing a magnetic stirring bar.
12. Wash the column with two 3-ml portions of "wash solution".
13. Add sufficient 2.5 F  $\text{HClO}_4$  so that the solution is approximately 1.0 F in  $\text{HClO}_4$ .



14. Add increments of standard cerium(IV) solution, stir after each addition and read the absorbance of the solution at 562 nm until several points beyond the endpoint are reached.
15. Correct for dilution and plot absorbance versus volume of cerium(IV) in the usual manner.

### Results

The results presented in Table 6 are representative of determinations using this method. Although the method works well, fairly large amounts of iron (10 to 60  $\mu\text{g}$ ) were determined. Such amounts were used in order to have comfortable working conditions.

As the next step, a scaling down was performed by appropriately diluting both the iron(III) and cerium(IV) solutions by a factor of 10. Immediately, several problems arose. The relative blank value increased. This was attributed to iron impurities in the reagents. For example, reagent grade hydrochloric acid contains about 0.1  $\mu\text{g}$  per ml of iron. It was found that if the amount of reagents used in the procedure were kept to a minimum, the relative blank value was not prohibitively high.

Even with the blank problem solved, the results were still very disappointing. A small increase in the standard deviation was anticipated when scaling down the amount of iron to be determined, but the results were sporadic and irreproducible beyond expectation. The problem was traced to the introduction of impurities from the laboratory environment.

Table 6. Determination of Large Amounts of Iron

TAKEN $\mu\text{g}$	FOUND $\mu\text{g}$	$\Delta$ $\mu\text{g}$
11.2	11.2	0.0
17.2	17.6	+0.4
22.3	22.8	+0.5
24.8	25.0	+0.2
33.5	33.5	0.0
38.5	38.2	-0.3
44.7	45.1	-0.4
49.7	49.4	-0.3
49.9	49.4	-0.5
55.8	55.9	+0.1
$s = \pm 0.3$		

### The Dust Problem

Iron is an omnipresent element, and dust usually contains at least traces of iron in various forms.

Although ambient dust is the scourge of any trace determination, the problem was particularly aggravating to the present work. Despite the fact that the Bogg's Chemistry Building is a fairly new facility with a "modern" ventilation system, iron-containing dust abounds in the Analytical Laboratory. While no experiments were performed to quantify the amount of dust, it is interesting to note that a sheet of white paper left in the working area for only one hour was covered with dust and "black specks".

It is important to point out that the results in Table 6 were obtained using Procedure I in which all operations were carried out in the open, i.e. no precautions out of the ordinary were taken to exclude dust. Because of the problems in scaling down the amount of iron to be determined via Procedure I, it was decided to perform the extraction and all operations in one of the laboratory exhaust hoods. Some relief was provided, that is the precision improved, but dust was still a problem because the exhaust hood was of the negative pressure type which draws air in.

A positive pressure or laminar flow hood was then tried (see Chapter VII). With such a hood, filtered air is blown through the hood and out of the front, keeping contamination minimal. By carrying out the operations of Procedure I in such a hood, application of Procedure II was possible and very small amounts of iron could then be determined.

All solutions for operations such as the extraction, the reextraction, the prereduction and the titration were kept in the hood.

### The Determination of Small Amounts of Iron

#### Procedural Details

The problems caused by Cr(VI) and V(V) are handled and the blank is determined in the same manner as discussed for Procedure I.

All operations are performed under the laminar flow hood. To minimize the amounts of solutions required in the procedure the small Walden Reductor (see Chapter VII) is used.

#### Procedure II: Less Than 10 $\mu$ g of Iron

With the exception of the changes discussed in the Procedural Details, and the fact that the volumes employed are smaller, Procedure II is very similar to Procedure I. Consequently only the changes need be listed.

1. Deliver 2 ml of aqueous iron solution.
2. Add 2 ml concentrated hydrochloric acid, and 2 ml of MIBK.
4. Add a 1-ml portion of water.
6. Repeat with a 1-ml portion of water.
9. Omit this step.
12. Wash with one 3-ml portion of "wash solution".

#### Results

The results of a series of determinations of small amount of iron using Procedure II are given in Table 7. The standard deviation compares very favorably with other trace methods for iron.

Table 7. Determination of Small Amounts of Iron

TAKEN $\mu\text{g}$	FOUND $\mu\text{g}$	$\Delta$ $\mu\text{g}$
1.65	1.32	-0.33
2.62	2.43	-0.19
4.46	4.46	0.00
4.82	4.68	-0.14
6.42	6.56	0.14
6.79	6.56	-0.23
8.03	7.96	-0.07
8.90	8.78	-0.12
9.60	9.90	0.30
9.97	9.68	-0.29
$s = \pm 0.22$		

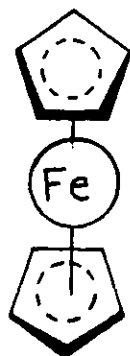
A practical lower limit using Procedure II is about 1  $\mu\text{g}$  iron. With less than 1  $\mu\text{g}$  of iron, the reaction of the iron(II)-FerroZine with cerium(IV) is very slow and the results are not reproducible.

## CHAPTER VI

## A NOVEL APPLICATION OF FERROCENE

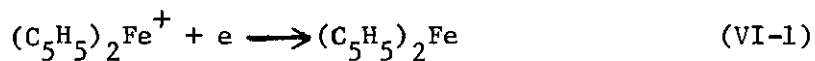
Introduction

Bis-(pentahaptocyclopentadienyl) iron, commonly called ferrocene, is a remarkable compound first synthesized by Kealy and Pauson (40) in 1951. Ferrocene has the "sandwich" structure depicted in VI-I.



(VI-I)

The formal potential of the system



in 75% acetic acid (0.034  $\text{F}$   $\text{HClO}_4$ ) is +0.466V (41). Solutions of ferrocene in solvents such as MIBK or benzene are yellow. Ferrocenium ion, the oxidized form of ferrocene, is pale blue in these solvents.

Ferrocene is very soluble (>0.1  $\text{M}$ ) in organic solvents such as ethanol, benzene, or MIBK, and the solutions are quite stable with regard to

oxidation by air. The "sandwich" compound is, however, only slightly soluble (42) in water ( $2 \times 10^{-5}$  M) and at acid conditions oxidized by air.

As mentioned in Chapter IV, ferrocene was thought to be very promising as a possible non-aqueous redox titrant for iron(III) in MIBK. However, because of the problems mentioned, ferrocene was abandoned for this application.

Due to its low solubility in water, ferrocene was investigated for the preliminary reduction of iron(III) in the aqueous solution obtained from the reextraction from MIBK. It was felt that the reduction of the iron(III) could be accomplished by shaking the aqueous solution with a benzene or MIBK solution of ferrocene. The details of this work follow.

### The Reduction

#### Introduction

Because of problems associated with the dissolved MIBK after the reextraction (see Chapter V), it was decided to try shaking the aqueous iron(III) solution with a benzene solution, 0.01 F, in ferrocene. The purpose of this was twofold: removal of the MIBK from the water and reduction of the iron(III) to iron(II). Both of these goals were realized but only the second is of relevance to the present discussion.

#### Shaking-Time

The reduction of iron(III) by ferrocene was tested as follows. A series of solutions containing various amounts of iron(III), 0.1 F in



hydrochloric acid, were shaken with 0.01  $\underline{\text{F}}$  ferrocene (in benzene) for about 1 minute. Each solution was then transferred to a volumetric flask containing  $1 \times 10^{-2} \underline{\text{F}}$  FerroZine and acetate buffer, diluted to mark, and after a few minutes the absorbance measured. The results of such tests were erratic.

After considering a number of factors, it was decided that the irreproducibility was due to shaking-time dependence and a study in this direction was conducted as follows. To a series of iron solutions was added ferrocene in benzene and the solutions shaken for different periods of time. The aqueous phases were withdrawn and handled as before. The results of this study are shown in Figure 13. For 20  $\mu$ grams of iron(III), shaking with  $1 \times 10^{-2} \underline{\text{F}}$  ferrocene for 100 seconds is sufficient for complete reduction of the iron(III).

#### Addition of Buffer and FerroZine

Because the possibility existed that some of the iron(II) formed during the reduction would be reoxidized by air during the withdrawal of the aqueous phase, the addition of both the agent for complexing the iron(II) and the buffer to the iron(III) solution, prior to shaking with the ferrocene solution, was investigated. The reasoning here was similar to that applied in the use of the Walden Reductor (see Chapter V).

At first only FerroZine was added and the experiment carried out as discussed earlier. In the presence of FerroZine the reduction of iron(III) by ferrocene was quantitative. However, when an iron(III) solution containing both the buffer and the FerroZine was shaken with the ferrocene solution, turbidity developed in the lower (aqueous)

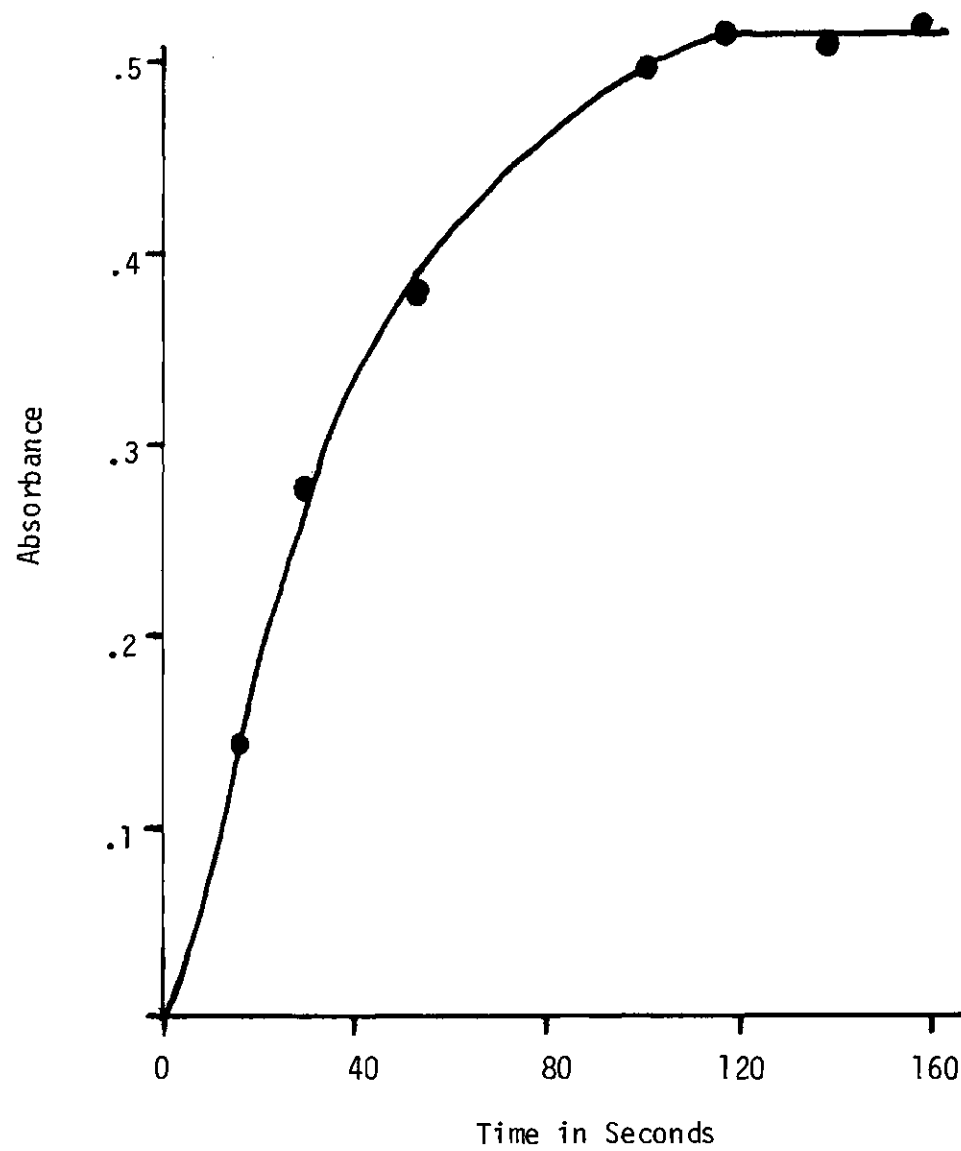


Figure 13. Influence of Shaking Time on Complete Reduction.

phase. By visual inspection the reduction appeared to be quantitative, but the haze made an absorbance measurement impossible. The turbidity was most likely caused by the formation of a water-benzene emulsion in the presence of the acetate buffer. Because of this problem, the approach of adding the buffer prior to reduction was abandoned, and a photometric method for the determination of iron using FerroZine with ferrocene as the reducing agent was developed.

### Ferrocene Method for the Photometric Determination of Iron

#### Procedural Details

The pH of the iron(III) solution should be less than about 3. The reduction is quantitative in strongly acidic solutions (approximately 1 F) but a large amount of buffer or strong base must be added to the solution after shaking with ferrocene to ensure complete formation of the iron(II)-FerroZine complex.

The ferrocene is purified and its solution in benzene is prepared as detailed in Chapter VII. When stored in a plastic bottle, this solution is stable for at least 3 months.

#### Procedure

1. To 10 ml of sample solution containing up to 30.0  $\mu\text{g}$  of iron add strong acid or base as needed to bring the pH within the range 1-2.5.
2. Transfer the solution to a separatory funnel, add 10 ml of  $10^{-2}$  F ferrocene in benzene, and shake for at least 2 minutes.
3. Allow phase separation (about 5 minutes) and drain the lower,

aqueous layer into a 25 ml volumetric flask containing 1 ml of  $10^{-2}$  F FerroZine solution. Rinse the funnel tip with a couple of drops of water.

4. Dilute to mark with acetate buffer and measure the absorbance at 562 nm after 5 minutes.
5. Obtain the results in the usual manner from a calibration curve established under identical conditions.

### Results

A calibration is shown in Figure 14. The method works well. The critical step of the procedure is the shaking. When determining 25-30  $\mu$ g of iron, the solution must be shaken for at least 2 minutes in order for the reduction to be quantitative.

Next, this method was investigated for the prereduction of iron(III) prior to the titration with cerium(IV).

### Ferrocene as a Prereductor

The ultimate purpose of these investigations with ferrocene was the development of a simple method for the prereduction of the iron(III) obtained from the reextraction from MIBK. The use of a benzene solution of the ferrocene had the two advantages mentioned earlier.

Ferrocene as a prereductant for iron(III) was first tested using aqueous iron solutions. The reduction was carried out as described in the last section and titration with cerium(IV) was carried out as described in Chapter V. However, the results were very disappointing. While the reduction proceeded as expected, the titration with Ce(IV)

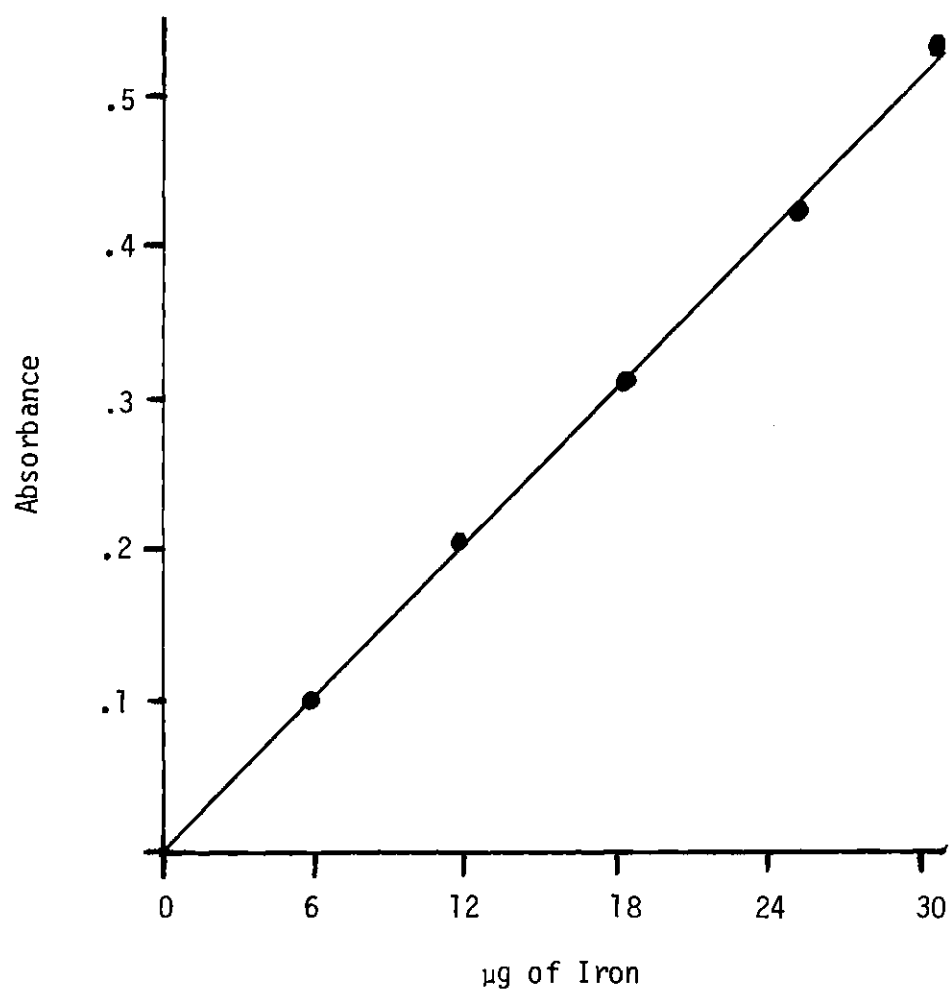


Figure 14. Calibration Curve for the Ferrocene Method.

failed. In the titration, the same problems were encountered as those described in Chapter V with the dissolved MIBK, and it was suspected that the problem was caused by dissolved ferrocene. However, this assumption was based upon the level of solubility of ferrocene in water while the pH of the iron(III) solutions in these tests was less than 2. Evidently ferrocene is much more soluble in solutions of pH less than 2 than in pure water. This was tested as follows. A 0.1 F HCl solution was shaken with  $10^{-2}$  F ferrocene in benzene for several minutes. The aqueous phase was withdrawn and added to an iron(II)-FerroZine solution obtained from the prereduction method discussed in Chapter V. The titration with cerium(IV) was carried out as previously described, and the problems described earlier were encountered again.

Several approaches were investigated with the hope of eliminating the effect of the dissolved ferrocene but none was successful. Consequently the prereduction of iron(III) with ferrocene was abandoned.

## CHAPTER VII

### EQUIPMENT AND CHEMICALS

#### Laboratory Equipment

##### Spectrophotometers

All spectral curves were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer. All quantitative measurements (including the photometric titrations) were made with a Bausch and Lomb Spectronic 20 spectrophotometer.

##### pH Meter

All pH measurements were made with a Fisher Accumet Model 230 pH Meter. This device was calibrated with Fisher buffer of pH 7.00.

##### Glassware

The usual glassware such as beakers, flasks, separatory funnels, etc., were used as needed. For volumetric measurements, class A volumetric glassware was used exclusively and without additional calibration.

##### Small Walden Reductor

A small Walden reductor was constructed to minimize the volumes required. The reductor was constructed according to Figure 15 (drawn to actual size) using about 1.5 grams of silver. The diameter and length of the outlet are chosen so that the liquid level in the reductor does not fall below the top of the silver.

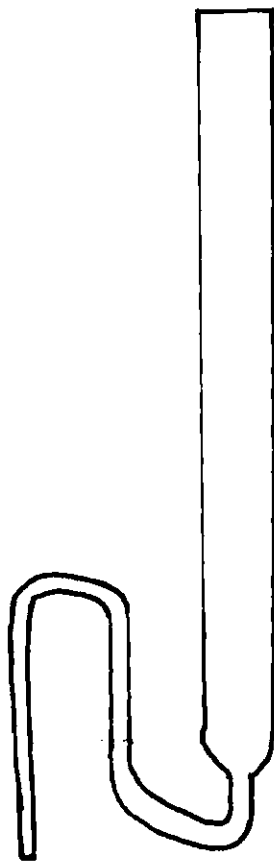


Figure 15. The Small Walden Reductor (Drawn to Size).



Hood

An Environmental Air Control Incorporated Portable-Positive-Pressure Hood was used in the determinations of small amount of iron. This type of hood is very effective in excluding ambient dust.

ChemicalsWater

Distilled - deionized water was used exclusively.

Perchloric Acid

Fisher reagent grade perchloric acid was used.

Sodium Acetate Buffer

Sodium hydroxide pellets (40 g) and concentrated acetic acid (92 ml) were dissolved and diluted to one liter.

FerroZine Solution

Hach Chemical Company FerroZine was used. A  $10^{-2}$  F solution was prepared by adding 0.6 g of FerroZine to a 100-ml volumetric flask. A couple of drops of concentrated hydrochloric acid were added and the solution diluted to mark with water.

Cerium(IV) Solution

Fisher ceric ammonium nitrate was used. A  $1.00 \times 10^{-2}$  F solution, 2.5 F  $\text{H}_2\text{SO}_4$ , was prepared by adding 5.4825 g of ceric ammonium nitrate to a one liter flask. Water was added, followed by 139 ml of concentrated sulfuric acid. This solution was diluted to one liter with water. This concentration was accepted at face value without further standardization.

### Iron Solution

About 5.5 g of high purity iron wire was dissolved in the minimum amount of hydrochloric acid with warming. After complete dissolution the solution was diluted to one liter with water.

### Hydrochloric Acid

Fisher hydrochloric and sulfuric acids were used.

### Ferrocene Solution

Eastman practical grade ferrocene was used. This compound was purified by sublimation. A  $1.00 \times 10^{-2}$  F solution was prepared by dissolving 0.4651 g ferrocene to one liter with benzene.

## BIBLIOGRAPHY

1. G.E.F. Lundell, H.A. Bright, and J.I. Hoffman, Applied Inorganic Analysis, 2nd Ed., John Wiley and Sons, Inc., New York, 1953.
2. I.M. Kolthoff and P.J. Elving, Ed., Treatise on Analytical Chemistry, Volume 2 (Part II), Interscience Publishers, New York, 1962.
3. A.A. Schilt, Analytical Applications of 1,10-Phenanthroline and Related Compounds, Pergamon Press, New York, 1969.
4. R.B. Fischer and D.G. Peters, Quantitative Chemical Analysis, Third Ed., W.B. Saunders Company, 1968.
5. R.V. Dilts, Analytical Chemistry, Methods of Separation, D. Van Nostrand Company, New York, 1974.
6. H.A. Flaschka, A.J. Barnard, Jr., and P.E. Sturrock, Quantitative Analytical Chemistry: Vol. I, Barnes and Noble, Inc., New York, 1969.
7. I.M. Kolthoff, E.B. Sandell, E.J. Meehan, and S. Bruckenstein, Quantitative Chemical Analysis, 4th Ed., The MacMillan Company, New York, 1969.
8. J.W. Rothe and U. Stahl, Eisen, 12, 1052 (1892).
9. J.W. Rothe and U. Stahl, Eisen, 13, 333 (1893).
10. A.C. Langmuir, J. Am. Chem. Soc., 22, 102 (1900).
11. E.F. Keen, J. Am. Chem. Soc., 23, 689 (1901).
12. F.N. Speller, Chem. News, 83, 124 (1901).
13. I. Wada and S. Atsu, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1, 70 (1922).
14. H.F. Walton, Principles and Methods of Chemical Analysis, Second Ed., Prentice Hall, Inc., Englewood Cliffs, 1964.
15. R.W. Dodson, G.J. Forney, and E.H. Swift, J. Am. Chem. Soc., 58, 2573 (1936).
16. N.H. Nachtrieb and J.G. Conway, J. Am. Chem. Soc., 70, 3547 (1948).

17. N.H. Nachtrieb and R.E. Fryell, J. Am. Chem. Soc., 70, 3552 (1948).
18. R.J. Myers, D.E. Metzler, and E.H. Swift, J. Am. Chem. Soc., 72, 3767 (1950).
19. R.J. Myers and D.E. Metzler, J. Am. Chem. Soc., 72, 3772 (1950).
20. M. Barrachina and M.A. Villar, J. Inorg. Nucl. Chem., 28, 2407 (1966).
21. R. Karlsson and L. Gorton, Talanta, 23, 672 (1976).
22. A. Claassen and L. Bastings, Z. Anal. Chem., 160, 403 (1958).
23. E. Gagliardi and H.P. Woss, Z. Anal. Chem., 248, 302 (1969).
24. H.M. Widmer, J. Phy. Chem., 74, 3251 (1970).
25. H.M. Widmer, Proceedings of the International Solvent Extraction Conference, The Hague, paper no. 129 (1971).
26. H.M. Widmer, Chimia, 26, 229 (1972).
27. R. Wickbold, Z. Anal. Chem., 244, 372 (1969).
28. R.W. Tinsley, M.S. Thesis, Georgia Institute of Technology (1971).
29. F. Blau, Ber., 21, 1077 (1888).
30. F. Blau, Monatsh., 19, 647 (1898).
31. Gerdeissen, Ber., 22, 245 (1889).
32. B. Bode, Wochschr. Brau., 50, 321 (1933).
33. G.H. Walden, Jr., L.P. Hammett, and R.P. Chapman, J. Am. Chem. Soc., 53, 3908 (1931).
34. L.L. Stookey, Anal. Chem., 42, 779 (1970).
35. S.K. Kundra, M. Katyal, and R.P. Singh, Anal. Chem., 46, 1605 (1974).
36. P. Carter, Anal. Biochem., 40, 450 (1971).
37. J.P. Persijn, W. Van Der Slik, and A. Riethorst, Clin. Chim. Acta, 35, 91 (1971).
38. J. Weiss and D. Porret, Nature, 139, 1019 (1937).

39. N.H. Furman, in Forward to G.F. Smith "Cerate Oxidimetry", G.F. Smith Chemical, Columbus, Ohio, 1942.
40. Kealy and Pauson, Nature, 168, 1039 (1951).
41. J.G. Mason and M. Rosenblum, J. Am. Chem. Soc., 82, 4206 (1960).
42. J.F. Coetzee and J.J. Campion, J. Am. Chem. Soc., 89, 2513 (1967).

PART II

A FIELD METHOD FOR THE DETERMINATION  
OF EDTA IN NATURAL WATER

## CHAPTER I

### A SURVEY OF EDTA METHODS

#### Introduction

Ethylenediamine tetra-acetic acid (EDTA) is a widely employed reagent in analytical chemistry. In recent years EDTA and analogous complexing agents, such as nitrilotriacetic acid (NTA), have been used as detergent builders, for water treatment, metal cleaning, in food processing, and in many other applications. With an annual production of both EDTA and NTA numbering millions of pounds, it is reasonable to assume that substantial quantities of the compounds will ultimately be discarded into waste water, and end up in various bodies of water (1). Consequently, interest in determining complexing agents such as EDTA on the trace level has grown immensely in recent year, despite the fact that their impact upon the environment is not clearly understood.

The current interest in complexing agents in the environment prompted the development of a reliable, rapid and simple method for determining EDTA on the trace level. The first step in this investigation was an extensive survey of the literature.

#### Existing Methods

The literature is replete with reports of methods for the determination of EDTA and other complexing agents. A compilation of such

methods for the determination of EDTA and related compounds is presented in table form (see Table 8).

The methods for such determinations are diverse, but can be placed in the following general categories (2):

1. Titration of the complexing agent with a metal.
2. Addition of excess metal and determination of the metal in excess of the complexing capacity.
3. Spectrophotometric measurement of the complexing agent or one of its metal complexes.
4. Solubilization of a metal ion from an insoluble material, or cation exchange followed by determination of the amount of solubilized metal.
5. Decolorizing of a relatively weak complex by the reaction with the sought-for complexing agent.
6. Derivatization to a volatile form followed by gas chromatographic analysis.
7. Electrochemical measurement of the complexing agent as a metal complex.
8. Determination by kinetic methods of analysis.
9. Separation of complexing agent or metal complex by chromatography and determination of complexing agent.

The methods surveyed in Table 8 are grouped according to these eight categories.



Table 8. Survey of Methods for EDTA and Related Compounds

Category	Reference	Species Determined			Remarks		Lowest Concentration Determined (if shown)
		EDTA	NTA	Other	Titrant	Indication	
1	4	X			Cu(II)	Diff. Pulse. Pol.	--
	5	X			Pb(II)	Const. Cur. Pot.	30 PPM
	6	X		DCYTA	Hg(II)	Amperometric	$1 \times 10^{-4} \underline{M}$
	7	X			Cu(II)	Visual	--
	8	X	X		Cu(II)	Visual	--
	9		X	MIDA, EIDA	Ce(IV)	Pot.	--
	10	X			Cu(II)	Visual	$1 \times 10^{-2} \underline{M}$
	11		X		Cu(II)	Pot.	$5 \times 10^{-5} \underline{M}$
	12	X	X		Cu(II), Fe(III) Zn(II), Pb(II)	Visual	--
	13	X			Cu(II)	Photometric	--
	14	X	X	Several	Ca(II)	Visual	--
	15		X		Cu(II)	Photometric	$1 \times 10^{-5} \underline{M}$
	16	X			Cd(II)	Stripping Analysis	--

Table 8 (continued)

Category	Reference	Species Determined			Remarks		Lowest Concentration Determined (if shown)
		EDTA	NTA	Other	Excess Metal	Method	
2	17	X			Bi(II)	Tit.-Photometric	4 PPM
	18	X		X	Cd(II)	Tit.-pH	0.1 PPM
	19			Complexing Capacity	Cu(II)	Diff. Pulse Pol.	Approx. $1 \times 10^{-7}$ <u>M</u>
	20	X	X	Several	Ca(II)	Ca Selective Electrode	1 PPM
					Metal Complex		
3	21	X	X		Co(III)		10 PPB (with preconcentration)
	22	X			Fe(III)		0.3 PPM
					Metal Solubilized	Method of Determination	
4	23	X	X		Cu	A.A.	$1 \times 10^{-6}$ <u>M</u>
	24	X	X		Cu	A.A.	$1 \times 10^{-6}$ <u>M</u>
					Complex Decolorized		
5	25		X		Zn - Zincon		
	26	X			Zn - Zincon		0.70 PPM
					Bi - XO		0.70 PPM
					Zr - XO		0.74 PPM
					Bi - PCV		0.70 PPM
					Th - XO		0.74 PPM
					Cu - PCV		0.70 PPM

Table 8 (continued)

Table 6 (continued)

Category	Reference	Species Determined			Remarks		Lowest Concentration Determined (if shown)
		EDTA	NTA	Other	Complex Decolorized		
5 (cont.)	27	X			Fe - TPTZ		$1 \times 10^{-4}$ <u>M</u>
	28	X		others	Zn - dithiozonate		3 PPM (visual)
	29	X			Fe - thiocyanate		$2 \times 10^{-2}$ <u>M</u>
	30	X			Zr - XO		--
	31		X		Ga - Oxine (Fluor)		$1 \times 10^{-7}$ <u>M</u>
	32	X	X	DCTA, others			Identification Test
					Derivative	Detector	
6	33	X	X	DTPA	methyl ester	FID	EDTA - $1 \times 10^{-2}$ PPM DTPA - $1 \times 10^{-2}$ PPM NTA - $2 \times 10^{-2}$ PPM
	34		X		trimethylsilyl	FID	1 PPM
	35		X		propyl ester	FID	20 PPB
	36		X	others	butyl ester	FID	25 PPB
	37		X	others	butyl ester	FID	1 PPB
	38		X		trimethylsilyl	FID	0.1 PPM
					Metal	Technique	
7	39	X	X	others	Cu(II)	Polar.	--
	40		X	EDDA	Cd(II)	Polar.	$5 \times 10^{-5}$ <u>M</u>
	41		X		Bi(III)	a.c. Polar.	0.50 PPM

Table 8 (continued)

Category	Reference	Species Determined			Remarks		Lowest Concentration Determined (if shown)
		EDTA	NTA	Other	Metal	Technique	
7 (cont.)	42		X		Cd(II)	Polar.	1 PPM
	43	X	X		Cd(II)	Differential Pulse Polar.	$5 \times 10^{-6}$ <u>M</u>
	44		X		Pb(II)	Differential Pulse Polar.	10 PPM
	45		X		Bi(III)	Oscillographic Polar.	10 PPM
	46		X		In(III)	Polar.	25.7 PPB
					Reaction System	Technique	
8	47	X			$\text{IO}_4^-$ -malachite green	Photometric	$2 \times 10^{-6}$ <u>M</u>
	48	X		others	$\text{IO}_4^-$ -malachite green	Photometric	$1 \times 10^{-5}$ <u>M</u> (EDTA)
	49	X		others	Cu(II)-ascorbic acid	Photometric	$2 \times 10^{-6}$ <u>M</u> (EDTA)
	50	X			periodate-diethylaniline	Pot.	$7.5 \times 10^{-5}$ <u>M</u>
	51		X	EDDA, EGTA	Ni-cyanide	Photometric	10 PPB
	52		X		$\text{IO}_4^-$ -malachite green	Photometric	10 PPB
	53	X			$\text{Cu-H}_2\text{O}_2$	Pot.	--

Table 8 (continued)

Category	Reference	Species Determined			Remarks		Lowest Concentration Determined (if shown)
		EDTA	NTA	Other	Chromatographic Method	Detection	
9	3	X		HEDTA,DTPA	Ion-exchange	Photometric	--
	54	X			TLC	Visual	--
	55	X			TLC	Visual	--
	56	X	X		TLC	Visual	--
	57	X			TLC	Visual	--
	58	X		CYDTA,EDDA	TLC	Visual	--
	59	X	X	others	TLC	Visual	--
	60	X	X	many	Paper	Visual	--
	61	X	X	EGTA,EDTA		A.A.	0.1 - 0.2 PPM

Abbreviations Used in Table 8

DCYTA - 1,2-cyclohexanediamine - N,N,N',N'-tetraacetic acid

MIDA - methyliminodiacetic acid

EIDA - ethyliminodiacetic acid

PCV - pyrocatechol violet

XO - xlenol orange

TPTZ - bis-(2,4,6-tripyridyl-s-Triazine)

DTPA - diethylenetriaminepenta-acetic acid

EDDA - N,N'-ethylene diglycine

Despite the large number of existing methods for the determination of EDTA, research is continually being conducted in this area. While many of the methods are well-working and highly sensitive, they suffer from such drawbacks as lack of selectivity and simplicity.

In reviewing the various methods, one approach which seems to show promise for further development is reported in the work of Wallace (3). This researcher determined EDTA in the presence of lanthanum(III) and samarium(III) by the following method. An excess of iron(III) is added to the solution containing the EDTA. The solution is then passed through a cation-exchange column containing resin in the sodium form. This resin retains the lanthanum, samarium, and uncomplexed iron, but not the iron(III)-EDTA complex. The amount of complexing agent is determined by determining the amount of iron present in the eluate.

Although many of the details were not included in the paper, it was felt that the possibility for extending this approach to the determination of EDTA in the presence of many other metals warranted further investigation. The work by Wallace formed the basis of the methods developed in the present work.

## CHAPTER II

### THE DETERMINATION OF EDTA

#### Introduction

In developing the method for the determination of trace amounts of EDTA by the approach introduced in Chapter I, four major areas had to be investigated: 1) the formation of the iron(III)-EDTA complex; 2) the separation of the iron(III)-EDTA complex; 3) the determination of the iron in the iron(III)-EDTA complex; and 4) the indirect determination of EDTA in the presence of other metal ions. The first two areas had been worked out (3) and no further work was necessary. The third and particularly the fourth area required a great deal of investigation. The details of this work follow.

#### The Formation and Separation of Iron(III)-EDTA

The separation of the iron(III)-EDTA complex from other ions by ion-exchange chromatography was reported by Wallace (3). His work was repeated in this laboratory to gain familiarity with the situation; a summary of the results is as follows. It was found that in the absence of cations, which form stable complexes with EDTA, the reaction of iron(III) with EDTA is fairly rapid at pH = 2.00 and goes to completion within a few minutes provided the initial iron(III) concentration is about five times that of the EDTA. The iron(III)-EDTA complex is separated from the excess iron(III) by passing the solution through a



strong cation exchange resin in the sodium form; here the uncomplexed iron is retained and the complexed iron is passed. The sodium form of the resin must be used because it was found that when the separation is attempted with the resin in the hydrogen form, the results are erratic. Since iron forms only a 1:1 complex with EDTA, the amount of EDTA in the eluate can correctly be found by determining the amount of iron(III) present. The determination of the iron in the eluate, in the presence of the EDTA, was the next area which had to be investigated.

#### The Iron Determination

Both FerroZine and 1,10-phenanthroline were investigated for the determination of the iron present in the iron(III)-EDTA complex. With both complexing agents, 10% hydroxylamine hydrochloride solution was used to reduce the iron(III) to iron(II).

The two complexing agents were tested as follows in evaluating whether either could be used in the determination of iron(III) in the presence of EDTA. To a small amount of iron was added an equivalent amount of EDTA and the solution allowed to stand for about thirty minutes to ensure complete formation of the complex. Hydroxylamine hydrochloride, the complexing agent and buffer were added to each of the two solutions, and the absorbance of the solution (after dilution to a known volume) was measured at the wavelength maximum of the respective iron(II) complex.

The results of this study were quite interesting. It was found that even after about one day with FerroZine the color of the iron(II)

complex was not completely developed when EDTA was present. However, with 1,10-phenanthroline (see Figure 16) the color development was complete in less than one hour. Because of the slow reaction of the FerroZine, 1,10-phenanthroline was chosen for the determination of the iron.

#### Interference Study

A few metals representative of a wide range in stability of their respective EDTA complexes were tested for interference as follows. To solutions containing 0.4  $\mu$ moles of EDTA were added various amounts of the metal ion. After about two hours, 2  $\mu$ moles of iron(III) were added. After about thirty minutes, each solution was passed through the cation exchange resin and the iron determined by the 1,10-phenanthroline method. The results of this study are shown in Table 9.

The only metals which interfere to any extent in the determination are lead and copper, but it was found that these interferences can easily be taken care of. For the procedure described in the last section, the lead interference is removed by passing the lead-containing solution through the ion-exchange resin prior to adding the iron(III).

The copper is handled in a similar way except that, in addition to the preelution step, more iron must be present. If about 50  $\mu$ moles of iron(III) are added to the copper solution obtained from the preelution, the copper does not interfere in the indirect determination of the EDTA.

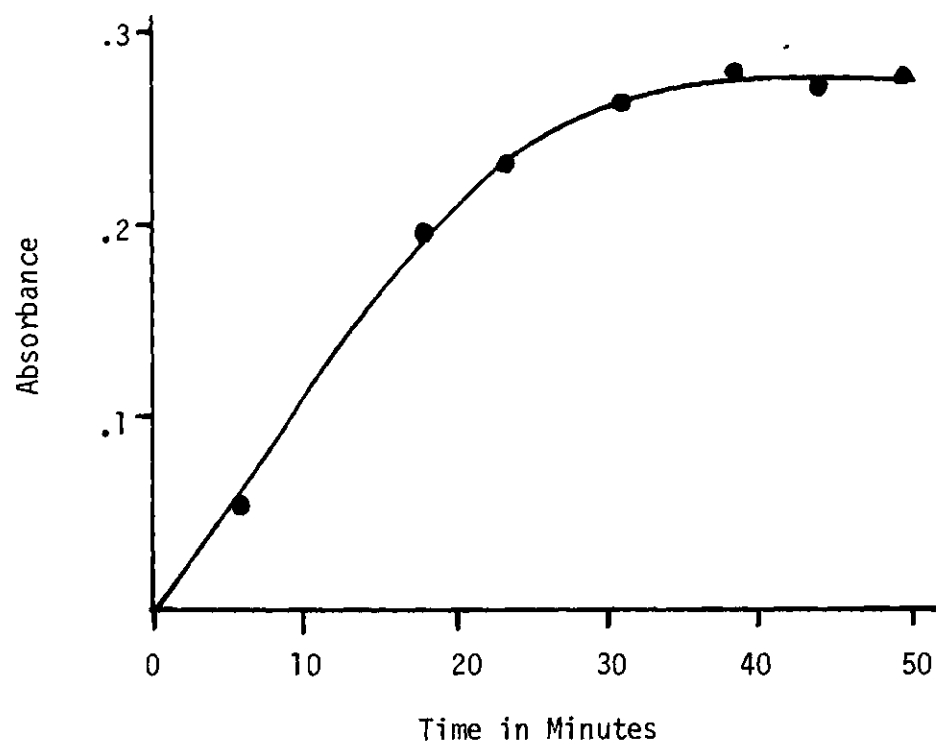


Figure 16. Time Required for Complete Color Development with 1,10-Phenanthroline.

Table 9. Recovery of 0.4  $\mu$ moles of EDTA in  
the Presence of Certain Metals

Metal	Log $K_{st}$	Recovery of EDTA at a Metal to EDTA Ratio of:		
		25:1	2.5:1	1:1
Mg(II)	8.69	0.397	0.400	0.398
Ca(II)	10.70	0.393	0.398	0.396
Mn(II)	13.79	0.400	0.396	0.400
Co(II)	16.31	0.380	0.393	0.402
Cd(II)	16.46	0.400	0.403	0.400
Zn(II)	16.50	0.402	0.400	0.400
Pb(II)	18.04	0.330	0.393	0.400
Cu(II)	18.80	0.286	0.344	0.369

It is important to note that chromium and nickel were also tested, and each found to interfere severely. A somewhat different approach was necessary to deal with the problems caused by chromium and nickel. Therefore, the interferences due to these elements will be discussed later in the chapter.

#### The Determination of EDTA in the Absence of Cr and Ni

The procedure in this section is the product of the four areas of investigation.

##### Procedural Details

If the sample solution is more than  $1 \times 10^{-2} \text{ F}$  in total metal concentration or contains copper or lead, the sample solution must be passed through the cation-exchange resin prior to following the procedure.

The resin is prepared in the sodium form by washing with several bed volumes of each of the following: 1) 4.0 F hydrochloric acid; 2) distilled water; 3) 1.0 F sodium chloride; 4) distilled water. As long as solutions low in metal ion concentration are handled, the resin need be regenerated every 20-40 times.

##### Procedure I: Chromium and Nickel Absent

1. Add sufficient strong acid (nitric acid) or base to 5 ml of the sample solution to bring the pH within the range 2.0-3.0.
2. Add 1 ml (5 ml if the presence of copper is suspected) of  $10^{-2} \text{ F}$  iron(III) to the sample solution, mix well, and let stand for about 30 minutes.

3. Pass the solution through 3 ml of strong cation exchange resin (see Procedural Details) and collect in a 25-ml volumetric flask containing 1 ml each of  $10^{-2}$  F 1,10-phenanthroline and 10% hydroxylamine hydrochloride.
4. Wash the column with two 4-ml portions of distilled water.
5. Add 5 ml of acetic acid, sodium acetate buffer and dilute to mark with distilled water.
6. Measure the absorbance of the solution at 510 nm after about one hour.
7. Obtain the results in the usual manner from a calibration curve established under identical conditions.

### Results

The results presented in Table 10 are representative of determinations using Procedure I. The test solutions were prepared by mixing equal amounts of solutions of the metals shown in Table 10 with standard EDTA so that the total metal concentration was  $1 \times 10^{-2}$  F. Because both copper and lead were present in the test solution, the preelution step described in the Procedural Details was necessary. Procedure I is applicable to solutions which contain EDTA in the concentration range of about 3.0 to 60 ppm.

A typical calibration curve for Procedure I is shown in Figure 17.

### The Chromium and Nickel Interference

When conducting the interference study with chromium(III) and nickel(II), the recovery of the EDTA by the indirect determination was

Table 10. Representative Results Obtained from Procedure I

EDTA TAKEN $\mu\text{mole}$	EDTA FOUND $\mu\text{mole}$
0.400	0.396
	0.396
	0.399
	0.394
	0.391
	0.400
	0.401
	0.397
	0.401
	0.400
$\bar{x} = 0.398 \quad s = \pm 0.003$	

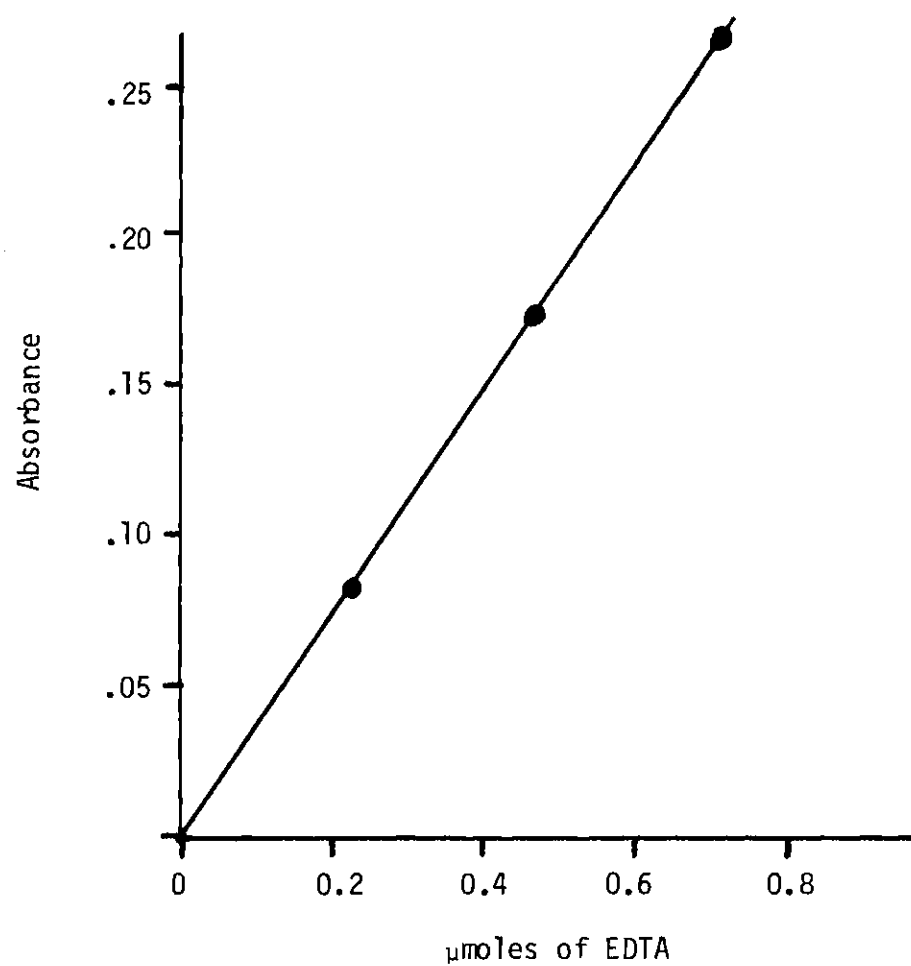


Figure 17. Calibration Curve for Procedure I.



erratic and low results were obtained. This problem was traced to the fact that the complexation reaction of either metal with EDTA is very slow. In addition, once formed, both the Cr(III)-EDTA and Ni(II)-EDTA are relatively inert and neither metal is displaced from the EDTA by iron(III). This was a rather perplexing situation because, with the exception of chromium and nickel, the method was found to work quite well in the presence of the other metals tested. However, the following observation provided relief to the problem at hand: the iron(III) will preferentially react with the EDTA as long as the solution is not boiled. This is due to the very low reaction rate of chromium or nickel with EDTA.

An idea was hit upon to circumvent these interference problems. If the solution containing chromium and/or nickel and EDTA is made strongly acidic, the respective EDTA complexes are completely dissociated. When iron(III) is then added and the pH raised to about 2.0, the iron(III) preferentially reacts with the EDTA.

This hypothesis was tested experimentally as follows. To two series of solutions containing small amounts of chromium(III)-EDTA complex was added iron(III) and various amounts of concentrated hydrochloric acid. In one series the solutions were heated on a boiling water bath, and in the other series no heating was involved. The absorbance of each solution was measured at 540 nm (the wavelength maximum of the Cr(III)-EDTA complex). The results of this study are shown in Figure 18.

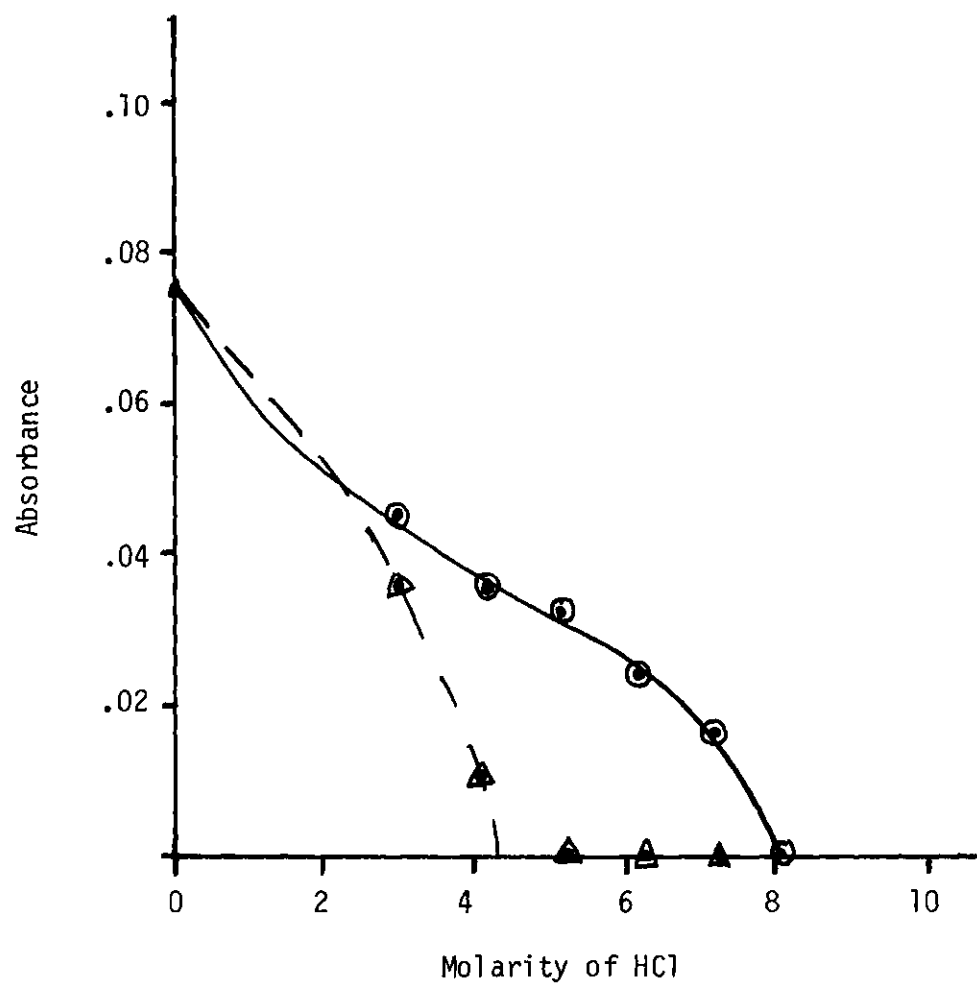


Figure 18. Dissociation of Cr(III)-EDTA as a Function of Acidity.

----- Heated      ——— Not Heated

From Figure 14, it is obvious that the Cr(III)-EDTA complex is completely dissociated in 4.5 F hydrochloric acid after the solution is boiled for about thirty minutes. The next step was to take the solution containing the dissociated chromium-EDTA and also an excess of iron(III) and then sodium hydroxide until the pH is about 2.0. When 2.0 F sodium hydroxide is used, the temperature of the solution, due to the heat of neutralization, increases by only about 8°C. After the addition of the sodium hydroxide, the EDTA can be determined as mentioned previously.

#### The Determination of EDTA in the Presence of Chromium and/or Nickel

##### Procedural Details

As in Procedure I, if the sample is more than  $10^{-2}$  F in total metal concentration or contains copper or lead, the sample solution must be passed through the cation-exchange resin prior to following the procedure.

At least 10 ml resin should be used and regenerated after each analysis. Otherwise some residual iron comes off the column and interferes with the determination.

##### Procedure II: Chromium and/or Nickel Present

1. Add 2 ml of sample solution to a small test tube or flask.
2. Add 2 ml of concentrated hydrochloric acid, and 1 ml (5 ml if the presence of copper is suspected)  $10^{-2}$  F iron(III) to the sample solution and mix well.
3. Place the sample tube into a boiling water bath for 30 minutes.
4. Remove the sample tube from the water bath, allow to cool to room temperature, and transfer the solution to a small beaker.

5. Deliver 2 F sodium hydroxide from a buret (about 12 ml) to the sample solution to bring the pH within the range 2.0 to 3.0.
6. Pass through at least 10 ml of strong cation resin (see Procedural Details) and collect in a 50-ml volumetric flask containing 1 ml each of  $10^{-2}$  F 1,10-phenanthroline and 10% hydroxylamine hydrochloride.
7. Wash the column with one 10-ml portion and one 5-ml portion of water.
8. Add 5 ml of acetic acid/sodium acetate buffer and dilute to mark with water.
9. Measure the absorbance of the solution at 510 nm after about 1 hour.
10. Obtain the results in the usual manner from a calibration curve established under identical conditions.

### Results

The results presented in Tables 11 and 12 are representative of determinations of EDTA using Procedure II in the presence of nickel and chromium, respectively. Each metal was present in the sample solution in an amount equivalent to that of the EDTA. Procedure II is applicable to solutions containing EDTA in the concentration range of about 15.0 to 300 ppm.

Table 11. Determination of EDTA in the Presence of Nickel

TAKEN $\mu\text{mole}$	FOUND $\mu\text{mole}$
0.400	0.390
	0.394
	0.398
	0.402
	0.397
	0.400
	0.391
	0.398
	0.397
$\bar{x} = 0.396 \quad s = \pm 0.004$	

Table 12. Determination of EDTA in the Presence of Chromium

TAKEN $\mu\text{mole}$	FOUND $\mu\text{mole}$
0.400	0.408
	0.391
	0.387
	0.401
	0.396
	0.400
	0.403
	0.393
	0.392
$\bar{x} = 0.397 \quad s = \pm 0.007$	

## CHAPTER III

### EQUIPMENT AND CHEMICALS

#### Laboratory Equipment

##### Spectrophotometers

All spectral curves were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer. All quantitative measurements were made with a Bausch and Lomb Spectronic 20 spectrophotometer.

##### pH Meter

All pH measurements were made with a Fisher Accumet Model 230 pH Meter. This device was calibrated with Fisher buffer of pH 7.00.

##### Glassware

The usual glassware such as beakers, flasks, etc., were used as needed. For volumetric measurements, class A volumetric glassware was used exclusively and without additional calibration.

#### Chemicals

##### EDTA Solution

Baker "Analysed" disodium ethylene dinitrilotetraacetate dihydrate was used. A  $1.00 \times 10^{-2}$  F solution was prepared by dissolving 0.9306 g to 250 ml in water. The concentration of this solution was taken at face value without further standardization.

Cation-Exchange Resin

Rexyn 101(H) beads-strong cation exchange resin, 40-100 mesh, was used. This reagent was "swelled" overnight prior to its use.

1,10-Phenanthroline

Fisher Scientific 1,10-phenanthroline was used. To 0.2 g of the reagent contained in a 100-ml volumetric flask was added a couple of drops of concentrated hydrochloric acid and the solution was brought to mark with water.

Metal Salts

All metal salt solutions for the interference study were prepared from the highest grade reagent available in the laboratory.

Hydroxylamine Hydrochloride

Fisher practical grade was used.



## BIBLIOGRAPHY

1. S.E. Manahan and M.J. Smith, Water and Sewage Works, Sept., 102 (1973).
2. S.E. Manahan, "Complexation and Chelation in Natural Waters: Results of a Computerized WRSIC Bibliographic Literature Search", Fifth Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Jekyll Island, Georgia, May 19-21, 1975.
3. R.M. Wallace and J.F. Hinton, Anal. Chim. Acta, 51, 536 (1970).
4. K.W. Hanck and J.W. Dillard, Anal. Chim. Acta, 89, 329 (1977).
5. C.O. Huber and D.R. Tallant, J. Electroanal. Chem., 18, 421 (1968).
6. D. Roubalova and J. Dolezal, Chemist-Analyst, 49, 76 (1960).
7. W.W. White and P.J. Murphy, Anal. Chem., 47, 2054 (1975).
8. G.G. Clinckemaille, Anal. Chim. Acta, 43, 520 (1968).
9. H. Holzapfel and K. Dittrich, Talanta, 13, 136 (1966).
10. A.K. Rishi, B.S. Garg, and R.P. Singh, Curr. Sci., 41, 117 (1972).
11. G.A. Rechnitz and N.C. Kenny, Anal. Lett., 3, 509 (1970).
12. D.L. Fuhrman, G.W. Latimer, and J. Bishop, Talanta, 13, 103 (1966).
13. H.V. Malmstadt and T.P. Hadjiivanou, Anal. Chim. Acta, 23, 288 (1960).
14. H.W. Furssell, Galvanotechnik, 66, 803 (1975).
15. L. Harju and R. Sara, Anal. Chim. Acta, 73, 129 (1974).
16. M.S. Shuman and G.P. Woodward, Anal. Chem., 45, 2032 (1973).
17. J. Vanderdeelen and A. Van Den Hende, Chim. Anal., 50, 237 (1968).
18. B. Van't Riet and James E. Wynn, Anal. Chem., 41, 159 (1969).
19. Y.K. Chan, J. Chromatogr. Sci., 11, 579 (1973).

20. J.A. Blay and J.H. Ryland, Anal. Lett., 4, 653 (1971).
21. K.L. Kaiser, Water Research, 1, 1465 (1973).
22. S.N. Bhattacharyya and K.P. Kundu, Talanta, 18, 446 (1971).
23. R. Kunkel and S.E. Manahan, Anal. Chem., 45, 1465 (1973).
24. S.E. Manahan and D.R. Jones IV, Anal. Lett., 6, 745 (1973).
25. G.F. Longman, J.J. Stiff, and K.K. Gardiner, Water Res., 5, 1171 (1971).
26. A. Šťáhlavská and M. Malát, Scientiae Pharmaceuticae, II, 193 (1965).
27. B. Kratochvíl and M.C. White, Anal. Chem., 37, 111 (1965).
28. I. Stone, J. Ass. Off. Agr. Chem., 47, 714 (1964).
29. C.J. Parker, Jr., Anal. Chem., 36, 236 (1964).
30. C.A., 69, 73781 q (1968).
31. J.L. Robinson and D.F. Lott, Microchem. J., 18, 128 (1973).
32. R. Příbil and V. Veselý, Chemist-Analyst, 56, 51 (1967).
33. L. Rudling, Water Res., 6, 871 (1972).
34. R.J. Stolzberg and D.N. Hume, Anal. Chem., 49, 374 (1977).
35. Y.K. Chau and M.E. Fox, J. Chromatogr. Sci., 9, 271 (1971).
36. C.B. Warren and E.J. Malec, J. Chromatogr., 64, 219 (1972).
37. W. Ave, et al., J. Chromatogr., 72, 259 (1972).
38. R.J. Stolzberg and D.N. Hume, Anal. Lett., 6, 829 (1973).
39. W. Hoyle, I.P. Sanderson, and T.S. West, J. Electroanal. Chem., 2, 166 (1961).
40. R.B. LeBlanc, Anal. Chem., 11, 1841 (1959).
41. G. den Boef, R. Oostervink, and F. Freese, Fresenius' Z. Anal. Chem., 264, 147 (1973).
42. J. Asplund and E. Wanninen, Anal. Lett., 4, 267 (1971).

43. R.J. Stolzberg, Anal. Chim. Acta, 92, 139 (1977).
44. B.K. Afghan and P.D. Goulden, Environ. Sci. Tech., 5, 601 (1971).
45. B.K. Afghan, P.D. Goulden, and J.F. Ryan, Anal. Chem., 44, 354 (1972).
46. J.P. Haberman, Anal. Chem., 43, 63 (1971).
47. H.A. Mottola and H.A. Freiser, Anal. Chem., 39, 1294 (1967).
48. H.A. Mottola, Anal. Chem., 42, 630 (1970).
49. H.A. Mottola, M.S. Haro, and H. Freiser, Anal. Chem., 40, 1263 (1968).
50. T.P. Hadjiioannuu, M.A. Koupparis, and C.E. Erstathiuu, Anal. Chim. Acta, 88, 281 (1977).
51. L.C. Coombs, J. Vasiliades, and D.W. Margerum, Anal. Chem., 44, 2325 (1972).
52. H.A. Mottola and G.L. Heath, Anal. Chem., 44, 2322 (1972).
53. F.F. Gaal, et al., Fresenius' Z. Anal. Chem., 286, 222 (1977).
54. M. Qureshi and J.P. Rawat, Sep. Sci., 6, 451 (1971).
55. Z. Masoomi and D.T. Haworth, J. Chromatogr., 48, 581 (1970).
56. F.J.M. Rajabalee, M. Potvin, and S. Laham, J. Chromatogr., 79, 375 (1973).
57. J. Vanderdeelen, J. Chromotogr., 39, 521 (1969).
58. J.L. Swain and J.L. Sudmeier, Anal. Chem., 40, 418 (1968).
59. E.A. Fitzgerald, Anal. Chem., 47, 356 (1975).
60. D.G. Hill-Cottingham, J. Chromatogr., 8, 261 (1962).
61. D.R. Jones IV and S.E. Manahan, Anal. Chem., 48, 502 (1976).

## VITA

John Joseph Tice IV, known as Jay to his friends, was born July 4, 1948, in Corpus Christi, Texas, to Capt. John Joseph Tice III and Mary JoAnne Davenport Tice. His pre-college years were spent in many locations, typical of any "Navy Junior". In September, 1966, he entered the Virginia Military Institute and received a B.S. degree in chemistry as a Distinguished Military Graduate in May, 1970.

In September, 1970, he was appointed Graduate Teaching Assistant at the Georgia Institute of Technology, and in August, 1972, he received the degree Master of Science in Chemistry.

In December, 1971, he was married to Elizabeth Lyle Stansell of Richmond, Virginia. He accepted the position of Analytical Chemist at the Monsanto Textiles Company, Pensacola, Florida, in October 1972. In March, 1975, he returned to the Georgia Institute of Technology on an academic leave of absence.

In December, 1977, he accepted a position as Senior Process Chemist with the Monsanto Company in Pensacola, Florida.