EDTA Titrations

AN INTRODUCTION TO THE THEORY AND PRACTICE

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by H. Flaschka, Ph.D.

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FOREWORD

by R. Belcher, PH.D., D.SC.

WITHIN the space of a few years, ethylene*di*amine *tetra*-*a*cetic acid (EDTA) has risen from an obscure chemical compound to the most widely used organic reagent. Elsewhere in this volume reference is made to the enormous amount of literature which has developed. The three text-books which are already available are of an advanced nature and have been written mainly for the practising analyst; from the teaching aspect a gap still remained to be filled. The few texts on the teaching of quantitative inorganic analysis which include exercises on the use of EDTA, rarely go beyond the determination of water-hardness. EDTA is worthy of more extensive treatment not only because of its importance as a titrant, but also because exercises involving its use are a valuable introduction to chelate chemistry. The need for a small teaching text was often expressed in discussions held between Professor Flaschka and the present writer, and resulted in Professor Flaschka preparing this book. It should prove indispensable to teaching institutions at all levels and a useful source of information in routine laboratories. Many of the experiments are suitable for lecture demonstrations.

Professor Flaschka is one of the outstanding analytical chemists of the post-war period and his investigations have played a great part in popularizing the use of EDTA. The value of this book must therefore be enhanced by his wide knowledge of the subject and by his great experience as a teacher.

Birmingham, 1958.

PREFACE

*E*thylene*d*amine *t*etra-*a*cetic acid is a reagent of remarkable possibilities in both theoretical and applied studies. This was recognized only a short time after the first publications of Dr. G. Schwarzenbach by many workers in many countries. More than 1,200 papers have now appeared on the application of EDTA in analytical chemistry, most of which relate to EDTA titrations. It is thus difficult even for the specialist to select the "best" procedure, indicator, buffer, etc., and the novice is overwhelmed by the flood of publications.

An introductory text such as this, must be incomplete and selective in content. The choice of experiments and the emphasis given to the various topics are a matter of personal preference, but the author will appreciate constructive criticism. A few readily available materials, reagents, and indicators have been selected for emphasis, but the omission of other procedures is *not* intended as silent disapproval. The principles and practical details given here are transferable to new procedures and indicators. An attempt has been made to cover all important types of application for EDTA titrations and full procedural details are given so that the novice can obtain correct results without additional instruction.

Neglect of certain basic facts is the most frequent cause of failure of EDTA titrations; hence, these small, but all-important facts are repeatedly emphasized. In the opening chapters, the general theoretical foundations of EDTA titrations are treated briefly. In addition, each procedure is prefaced by a summary of the relevant theory and background.

Much of the book is based on material prepared by the author for special lectures and university courses. The book should prove valuable for such advanced courses; either as a text-book in its own right or as a supplement to other monographs. The division into sections and sub-sections aids in assigning material and experiments to be covered by students. The problems at the end are of value in ensuring that the student understands the foundations of the method.

As this book is an introductory text, no extensive bibliography is provided. Some important publications are quoted and these should serve as a source of further information. The monographs and reviews cited in section I give full details of the now extensive literature.

The practising analyst has also been kept in mind in the organization of this book. The text should provide sufficient basic knowledge to permit him to adapt procedures given herein or in the journal literature to his special problems.

The author acknowledges with thanks the suggestions made by his many friends and colleagues. He is especially grateful to Drs. Ronald Belcher, Birmingham, A. J. Barnard, Jr., Phillipsburg, and C. N. Reilley, Chapel Hill. The first two have given invaluable aid in organizing the manuscript and in improving the author's imperfect English.

Atlanta, Georgia. H. FLASCHKA.
December, 1958.

CHAPTER 1

INTRODUCTION

Complex formation has been applied in chemical analysis for over a century. However, in classical titrimetric analysis only a few applications have been made, of which the titration of cyanide ion with silver according to von Liebig is probably the best known. This limited usage may appear strange, but the explanation is obvious if the essential requirements for the effective use of complex formation (i.e. complexation) in titrimetric procedures are examined. These requirements include:

(*a*) The complex reaction must be stoicheiometric so that a basis of calculation exists.

(*b*) The rate of reaction must be sufficiently fast.

(*c*) The stability of the complexes must be sufficiently high, otherwise a sharp endpoint cannot be obtained because of dissociation.

(*d*) The complex reaction should involve as few steps as possible so that a sharp endpoint is assured.

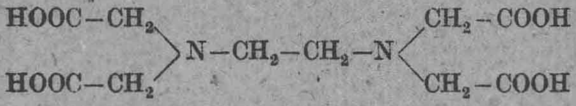
(*e*) A simple method for the location of the endpoint must be known.

(*f*) No precipitation should occur during the titration to avoid such complications as co-precipitation, adsorption and other phenomena often accompanying precipitation.

Only a few classical cases of complexation meet all of these requirements sufficiently. The greatest obstacle has always been the large number of reaction steps involved in the complexation process (see below), and the lack of suitable indicators.

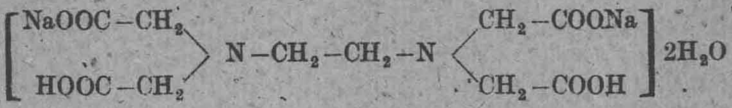
In the mid-1930s the German firm I.G. Farbenindustrie introduced under the trade name Trilon B, a polyaminocarboxylic acid possessing a remarkable ability to form very stable, water-soluble complexes with many metal ions including the alkaline earths. Among its applications were predicted its uses as a water softener (complexation of calcium and magnesium) and as a textile dyeing assistant (complexation of heavy metals). The systematic name of this substance is *e*thylene*d*iamine *t*etra-*a*cetic acid, which is now commonly abbreviated to "EDTA" in English-language publications.

The structural formulae for the acid and its disodium salt dihydrate are given in figures 1a–1b.



$$\begin{matrix} HOOC-CH_2 \\ HOOC-CH_2 \end{matrix}\!\!>N-CH_2-CH_2-N<\!\!\begin{matrix} CH_2-COOH \\ CH_2-COOH \end{matrix}$$

Figure 1a. Ethylenediamine tetra-acetic acid.



$$\left[\begin{matrix} NaOOC-CH_2 \\ HOOC-CH_2 \end{matrix}\!\!>N-CH_2-CH_2-N<\!\!\begin{matrix} CH_2-COONa \\ CH_2-COOH \end{matrix}\right]2H_2O$$

Figure 1b. Disodium ethylenediamine tetra-acetate dihydrate.

At the end of World War II, G. Schwarzenbach, professor at the University of Zürich, Switzerland, and his co-workers, initiated physicochemical studies on the metal complexes of EDTA and related compounds, including measurement of their stability constants and reaction mechanisms. In 1946, they introduced EDTA as a titrant and found some metal-sensitive indicators for detecting the endpoint. Thus, a new branch of titrimetric analysis involving chelate formation (see page 13) was originated; this is variously called complexometry, chelatometry or chelometry.

The theoretical studies of Schwarzenbach and co-workers have explained the extraordinary ability of EDTA to form metal complexes, the extreme stability of most of the complexes, and how such complexes can be used in titration processes. Some of the findings of these studies are summarized in the following paragraphs and sections.

The overall stability constant of the copper(II)-tetrammine complex can be expressed as follows and has the indicated value

$$K = \frac{[\mathrm{Cu}\,(\mathrm{NH_3})_4^{+2}]}{[\mathrm{Cu}^{+2}] \times [\mathrm{NH_3}]^4} = 4{\cdot}4 \times 10^{12} \qquad (1.1)$$

In contrast, the stability of the magnesium–EDTA complex is given as

$$K = \frac{[\mathrm{MgY}^{-2}]}{[\mathrm{Mg}^{+2}] \times [\mathrm{Y}^{-4}]} = 4{\cdot}9 \times 10^{8} \qquad (1.2)$$

Y^{-4} denotes the anion of EDTA. Magnesium can be titrated with EDTA accurately; but copper cannot be titrated with aqueous ammonia despite the higher stability of the copper-tetrammine complex. Bjerrum has demonstrated that complexes possessing more than one ligand attached to the central ion are formed stepwise. Hence, the formation of the copper-tetrammine complex may be expressed as follows:

$$\mathrm{Cu^{+2}} \underset{-\mathrm{NH_3}}{\overset{+\mathrm{NH_3}}{\rightleftarrows}} \mathrm{Cu(NH_3)^{+2}} \underset{-\mathrm{NH_3}}{\overset{+\mathrm{NH_3}}{\rightleftarrows}} \mathrm{Cu(NH_3)_2{}^{+2}} \underset{-\mathrm{NH_3}}{\overset{+\mathrm{NH_3}}{\rightleftarrows}}$$

$$\mathrm{Cu(NH_3)_3{}^{+2}} \underset{-\mathrm{NH_3}}{\overset{+\mathrm{NH_3}}{\rightleftarrows}} \mathrm{Cu(NH_3)_4{}^{+2}} \qquad (1.3)$$

For each step, the law of mass action is applicable and for each of the complexes a stability constant may be written:

$$K_1 = \frac{[Cu(NH_3)^{+2}]}{[Cu^{+2}] \times [NH_3]} = 1{\cdot}4 \times 10^4 \qquad (1.4a);$$

$$K_2 = \frac{[Cu(NH_3)_2{}^{+2}]}{[Cu(NH_3)^{+2}] \times [NH_3]} = 3{\cdot}1 \times 10^3 \qquad (1.4b);$$

$$K_3 = \frac{[Cu(NH_3)_3{}^{+2}]}{[Cu(NH_3)_2{}^{+2}] \times [NH_3]} = 7{\cdot}8 \times 10^2 \qquad (1.4c);$$

$$K_4 = \frac{[Cu(NH_3)_4{}^{+2}]}{[Cu(NH_3)_3{}^{+2}] \times [NH_3]} = 1{\cdot}3 \times 10^2 \qquad (1.4d)$$

Naturally each of these constants is smaller in value than the overall constant which is the product $K = K_1 \times K_2 \times K_3 \times K_4$. Therefore the disappearance of the "free" copper ion on addition of ammonia at the point where $Cu : NH_3 = 1 : 4$ (endpoint of a suggested titration) will be not as abrupt as in the case of magnesium. Here a 1 : 1 complex is formed in a single step. (For a more comprehensive and mathematical treatment of complexation see chapter 4, page 22.)

Schwarzenbach has demonstrated that a remarkable increase in stability is achieved if *two* monodentate ligands (these are ligands which can occupy only one co-ordinate position at the central ion) are replaced by *one* bidentate ligand (i.e. a ligand able to occupy two co-ordinate positions). If ammonia is replaced by the bidentate ligand ethylenediamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, only a two-step reaction is necessary to co-ordinate four nitrogens to the copper. The stability constants of the two complexes $Cu(en)_1^{+2}$ and $Cu(en)_2^{+2}$, where *en* denotes ethylenediamine, are 6×10^{10} and 2×10^9 respectively. A remarkable gain in stability can be noted if these figures are compared with the corresponding data on the formation of the copper-tetrammine complex.

If ammonia is replaced by the tetradentate ligand triethylenetetrammine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH \cdot NH_2$, only one single step is necessary to attach four nitrogens to the copper. The stability constant of the 1:1 complex formed is 4×10^{20}. Thus, compared with the tetrammine complex, a relative increase of about 10^8 is effected by substituting the polyamine for ammonia.

Complexes formed with polydentate ligands are called chelate complexes or simply chelates. The term is derived from the Greek "chele" for a claw such as that of the crab, and is appropriate because the ligand "grasps" the central ion from at least two sides. The gain in stability of a complex by replacing *n* monodentate ligands by a single analogous *n*-dentate ligand is called the chelate effect. This effect generally reaches its maximum if the rings formed are five or six membered. Rings with fewer members possess considerable strain; and hence are much lower in stability. A greater number of members in the ring also results in lower stability because of an entropic effect. In simple terms, if the chain between the active group in the ligand becomes too long, they behave more and more as isolated monodentate groups. Thus, through chelate formation two important requirements for titration procedures are achieved: an increase in stability of the complex and a decrease in the number of reaction steps in the complexation process.

With the above facts in mind, it is easily appreciated why only a few "classical" complexes are capable of providing the necessary basis for a titration procedure; noteworthy examples include the titration of silver, which has a co-ordination number of only two, and mercury which forms extremely stable complexes with halides.

The structure of EDTA is such that the most favourable combination of carboxylic groups (for salt formation) and amino nitrogen (for co-ordinate bonds) is achieved. All rings in the complex are five membered as shown in the figure on page 14.

Thus, EDTA forms complexes with nearly all polyvalent metal ions and also with many monovalent cations, including alkali metals (with the latter only to a slight extent). Practically all these complexes contain metal and EDTA in the ratio 1 : 1, regardless of the valency of the metal ion.

Though EDTA is frequently used as titrant, this is not its only analytical application. Growing interest exists in EDTA as a masking reagent to prevent interference and to increase the selectivity of tests. EDTA is used as a chromogenic agent in spectrophotometric procedures and plays an important rôle in polarography and ion exchange procedures. Its application in non-analytical fields is wide-spread.

The literature on the analytical applications of EDTA is extensive and has already reached about eleven hundred publications. It is impossible to cite even a selection of the more important references in a booklet such as this. Accordingly, only the minimum number of references is quoted, but there is sufficient indication of sources of further information. For more complete details the reader's attention may be called to the following standard works:

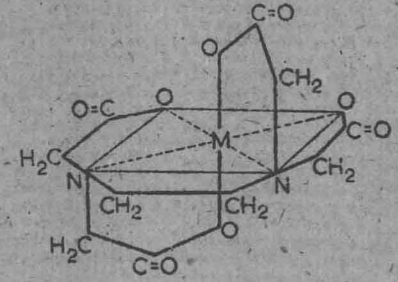


Figure 2. Steric configuration of a metal-EDTA complex. (According to A. E. Martell, *J. Chem. Education*, **29**, 270 (1952).)

G. Schwarzenbach: *Die komplexometrische Titration*. F. Encke, Stuttgart, 2nd edition (1956). English translation (H. Irving): *Complexometric Titration*. Methuen, London (1957).

F. J. Welcher: *The Analytical Use of EDTA*. Van Nostrand, Princeton (1958).

R. Pribil: *Komplexony v chemicke Analyse*. Nakladatelstvi Ceskoslov. Akad. Vad, Prague, 2nd edition (1957). An English translation is planned.

A book dealing with the analytical application of EDTA and all similar and related compounds, written by C. N. Reilley and R. W. Schmid is due to be published by John Wiley, New York.

Many reviews have been published. One of the latest, covering the literature to 1958 as completely as possible is a series of publications by the following authors:

A. J. Barnard, W. C. Broad and H. Flaschka: The EDTA Titration: Nature and Methods of Endpoint Detection. *Chemist Analyst*, **45**, 86, 111 (1956); **46**, 18, 46, 76 (1957).

H. Flaschka, A. J. Barnard and W. C. Broad: The EDTA Titration: Applications. *Chemist Analyst*, **46**, 22 (1957); **47**, 22, 52, 78, 109 (1958).

CHAPTER 2

EDTA. THE ACID, ITS SALTS AND COMPLEXES

ETHYLENEDIAMINE TETRA-ACETIC ACID, as already mentioned, is now commonly abbreviated EDTA. However, it should be noted that the abbreviation can also mean acetate and does so in most cases, because the free acid is seldom used in analytical procedures. Generally, it can easily be seen from the text whether the meaning is acid or acetate; if a special differentiation is to be made "EDTA acid" might be used.

The letter Y is used generally to denote the anion of the EDTA acid in writing formulae either with charges, e.g. Y^{-4}, or without. Charge signs in formulations are frequently omitted because they are usually unimportant.

EDTA is marketed under various trade names including: Chelaton II and III* (Czechoslovakia), Complexone II and III* (Siegfried, Switzerland), Idranal II and III* (Riedel de Haen, Germany), Sequestrene (Geigy, U.S.A.), Sequestrol (Geigy, England), Titriplex (Merck, Germany), and Versenic Acid (Dow, U.S.A.). In Russian literature the name Trilon B is frequently encountered. These are the most important ones so far as analytical grade products are concerned. Salts and complexes are also named chelonates, complexonates, versenates or trilonates.

EDTA is a white, crystalline powder, odourless and with an acid taste. It is not poisonous. It is sparingly soluble in water (0·02 g in 100 ml water at 22° C). It is insoluble in acids and common organic solvents, but is soluble in caustic and ammonia solutions. From such solutions, the acid can be precipitated by addition of mineral acids—a common and simple method of purification. It is stable at elevated

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* II refers to the free acid, III to the disodium salt dihydrate.