

Lecture No. 6

**COMPLEXOMETRIC TITRATIONS - ITS APPLICATION
TO SILICATE ANALYSIS**

by

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COMPLEXOMETRIC TITRATION AND ITS APPLICATION TO SILICATE ANALYSIS

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Chemical analysis for knowing the quantitative composition of a substance is considered important and essential for evaluation and characterization of silicate raw materials and finished products. However, the classical 'wet' chemical methods involving lengthy and time consuming steps of successive separations of groups by precipitation and reprecipitation can not serve the purpose of quality control since the effectiveness of quality control is largely determined by the speed with which the determination of critical parameters, compositions and properties involving evaluation of raw materials and finished products are made. Attempts have therefore, been constantly made for development of rapid and accurate methods of chemical analysis. The literature on silicate analysis reveals spectacular advancement both in wet chemical and instrumental methods of analysis after the last World War II. In wet chemical analysis complexometric titration with EDTA (Ethylene Diamine Tetra Acetic Acid), a versatile complexing agent first introduced by Schwarzewbach is probably the best contribution till now in 20th century.

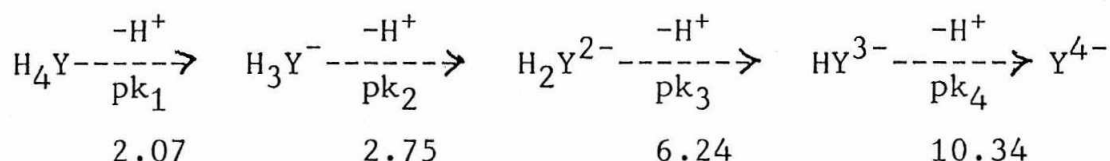
This article deals with some basic concepts of EDTA, preparation of solution of silicates and the application of EDTA for the rapid determination of some important constituents.

PROPERTIES OF EDTA

With almost all metals, EDTA practically instantaneously forms slightly dissociated water soluble complexes which are usually colourless. All the complexes have 1:1 composition. Because of these exceptional properties, EDTA was predestined to be a most important analytical reagent. It still keeps its dominant position in complexometry, although in some cases other compounds have proved to be either a little more suitable or to differ in complex formation. These include:

EGTA: ethylene glycol-bis (2-aminoethyl ether) tetra acetic acid
 DCTA: 1,2-diaminocyclohexane tetra acetic acid
 DTPA: Diethylene triamine penta acetic acid
 TTHA: Triethylene tetramine hexa acetic acid

- (a) **Acid base properties of EDTA:** EDTA is tetrabasic acid. Stepwise dissociation of EDTA can be written schematically as



At pH >10, EDTA is completely dissociated.

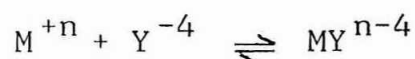
- (b) **Complex forming properties of EDTA:** The EDTA molecule is sufficiently flexible to bond through the two nitrogen atoms and four oxygen atoms. The bonds of a EDTA molecule hook the metal ion like Crab's claws and the complex is known as chelate. This is the basis of the high stability of EDTA complexes.

STABILITY OF EDTA COMPLEXES

Although complexometric titrations are very simple, they cannot be developed properly without basic theoretical knowledge. Analytical chemists are mainly interested in how stable these complexes are under various analytical conditions and which factors influence their stability. All these theoretical problems were solved by Schwarzenbach. We will try to describe as simply as possible the background theory and explain some basic terms.

Stability Constants of EDTA Complexes

If only the fully ionized anion of EDTA is taken into consideration the complex formation between a metal M^{+n} of the oxidation state n , and Y^{-4} takes place according to the equilibrium:



and the stability constant of MY is identical with the equilibrium constant for the reaction:

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

Thus the absolute stability constant is defined in terms of only the EDTA that is present in the completely dissociated form Y^{-4} . The metal ion concentration refers to the 'free' metal, that is, not complexed with EDTA, and present solely as the aquo complex. The EDTA, however, will be present totally as Y^{-4} only in strongly alkaline solution at a pH higher than 10. At lower pH values the uncombined EDTA will be present also in its protonated forms HY^{-3} , H_2Y^{-2} , H_3Y^{-1} and H_4Y . These forms will vary in their amounts

according to the pH of the solution. To account for this fact, the stability constant under the actual solution conditions must be calculated and the resulting constant is called the apparent, conditional or effective stability constant. A factor $\alpha_{Y(H)}$ (the subscript denotes the H^+ dependence) can be used to calculate the apparent from the absolute stability constant. Thus

$$\log K'_{MY} = \log K_{MY} - \log \alpha_{Y(H)}$$

apparent
stability
constant

In solutions another complex forming substance may be present in addition to EDTA. Then according to the stability constants of the complexes formed with the metals and this substance, more or less of the metal is transferred to those complexes. $[M^{+n}]$ can no longer be considered to be the total amount of 'free' metal ion though it is the total amount of metal not complexed with EDTA. To account for that effect a factor α_M may be introduced.

In order to evaluate the titration conditions and to understand what is going on in the course of a titration, it is important to become, completely familiar with these two factors. Considering these coefficients (α_M and α_Y) have been introduced for measuring the extent of side reactions of the metal ion (M) and of the ligand (Y) which compete with the main reaction. These coefficients for the metal ion and the ligand may be expressed as

$$\alpha_M = \frac{M'}{M} ; \quad \alpha_Y = \frac{Y'}{Y}$$

where M' denotes the total concentration of the free metal ion plus the metal ion in solution that has not reacted with

the complexing agent but has participated in a side reaction. Similarly, Y' represents not only the concentration of the free ligand but also those of all the species or the complexing agent which have reacted with other metal ions present. Under such conditions the conditional stability constants of complexes obtained with pure systems need correction according to the following equations

$$K'_{MY} = \frac{K_{MY}}{\alpha_M \alpha_Y} \quad \dots (5)$$

K'_{MY} : conditional stability constant,
 K_{MY} : stability constant in pure system, and
 α_M & α_Y : are side reaction coefficients

$$\begin{aligned} \log K'_{MY} &= \log K_{MY} - \log \alpha_M - \log \alpha_Y \\ \text{or } \log K_{MY} - \log K'_{MY} &= \log \alpha_M + \log \alpha_Y \end{aligned}$$

The left hand side, thus gives a measure of the extent of side reactions. It has been observed that a visual titration of the metal (M) with a ligand Y(EDTA) can be performed only when $\log K' \geq 7$.

Detection of the Titration End Point

The course of the titration and the change in free metal ion concentration in the neighbourhood of the equivalent point can be calculated from the equation for the complexation equilibrium, and the end point can be detected very simply from the colour change of the so called complexometric indicators.

Metallochromic indicators: The term metallochromic indicators was chosen for organic dyes capable of forming with metal cations distinctly coloured chelates, with colours as different as possible from the original colour of the dye.

Usually the indicators contain at least two oxygen atoms as well as two nitrogen atoms which can co-ordinate with the metal cation, forming five or six membered rings. Suitably disposed oxygen or nitrogen ligand atoms are possessed by the -OH and -COOH radicals, -N=N- azo group, -NH₂ group etc.

The properties of metallochromic indicators

1. The colour reaction must be sensitive so that near the end-point when nearly all the metal is bound to the EDTA complex, a sufficiently strong colour persists in the solution.
2. The colour reaction should be specific or selective, and subject to as few interferences as possible.
3. The colour difference between the metal indicator complex and the free indicator must be sufficiently large to be observed by the human eye.
4. The metal indicator complex must be sufficiently stable. The desired value of log K is between 4 and 5. Otherwise owing to marked dissociation, a sharp colour change at the end-point is not obtained.
5. The metal indicator complex must be less stable than the corresponding metal-EDTA complex. The difference between the values of log K for M-EDTA complex and M-indicator complex should be at least 4 to 5. Otherwise the EDTA is unable to remove the metal from the indicator complex at the end-point.
6. The reaction between metal indicator complex and EDTA must be sufficiently rapid to permit exact location of the end-point. Slow substitution reactions cause over titration of the solution. Very slow reaction leads to blocking of the indicator.
7. The metal indicator complex should be formed at the titrating pH.
8. The reaction between the indicator and the metal ion should be rapidly reversible.
9. The indicator should be stable enough in aqueous or alcohol solution to be stored for reasonable periods.
10. It should be pure.

Blocking of indicators: In many titrations some cations block the indicator. This blocking is due to the formation of indicator complexes that are stable towards ligand exchange with EDTA. That makes the direct titrations impossible. This type of reaction occurs with xylenol orange, methyl thymol blue, EBT etc. It has been found in the determination of Cu with EDTA and xylenol orange that the blocking is eliminated in the presence of minute traces of 1,10-phenanthroline, 2,2'-bipyridyl has similar deblocking action.

Selectivity of EDTA Titrations

Masking reagents - EDTA is very unselective as a titrimetric reagent, forming more or less stable chelates with almost all metal cations. It becomes very valuable if we can increase its selectivity in such a way that we make only one cation determinable, even in the presence of others. A very ingenious and quick method for the elimination of interference is to bind the interfering elements in undissociated water soluble complexes directly in the solution. Such an operation is called masking and the compound used is called a masking reagent. In the narrow sense of the term we understand masking to mean binding of metals in the form of chelates that are more stable than the corresponding EDTA chelates, and that these complexes should be as colourless as possible and soluble in water.

Masking may be effected by one or more of the following means:

1. pH adjustment

Lowering the pH may cause the EDTA complex of a very weakly combined metal to dissociate completely. Then another metal which has a highly stable EDTA complex can be titrated.

2. Complex formation

If a solution of two metals is treated with a reagent which forms a stable complex with one and a very weak or no complex with the other metals, it is possible to increase sufficiently the difference of the two apparent stability constants of the metal-EDTA complexes to effect a selective titration.

Zn, Cu, Ni, Co and some other metals form very stable cyano complexes. In contrast the corresponding complex of Pb or Mn is very weak, whereas Ca and Mg do not form cyano-complexes at all. Accordingly the latter metals can be titrated when the formers are masked by addition of KCN. The cyano complexes are so stable that Zn, Cu etc are virtually removed completely from their EDTA complexes.

Zn can be demasked selectively from its cyano complex by addition of formaldehyde.

Triethanolamine forms a stable complex with Al, Fe and Ti. Al in strong alkaline medium is also masked by hydroxyl ions, in as much as it is transformed into the aluminate ion, a process which can also be considered as complex formation.

The complex HgI_4^{2-} is very stable; hence potassium iodide can be used for a highly selective masking of mercuric ion.

3. Precipitation

Mg can be titrated in presence of Ca if the latter has been precipitated with oxalate. Calcium can be titrated in presence of Mg if the latter is precipitated as hydroxide.

Al, Ca and Mg can be precipitated with fluoride. Bi can be masked by hydrolysing with a chloride containing solution so that the sparingly soluble bismuth oxychloride is formed.

It may be seen that many precipitating reactions could be used for masking purposes, but this approach is relatively limited. Precipitation reactions are in most cases affected by occlusion, Co- and post precipitation, adsorption and other phenomena which cause serious trouble. Further more, the colour change of an indicator can be obscured by the presence of a precipitate.

4. Oxidation and reduction

Oxidation or reduction may convert a metal ion to a state where a weaker EDTA complex or no complex at all is formed. Fe(III) can be reduced to Fe(II) by addition of ascorbic acid in slightly acid medium. The stability constant of the EDTA complex of iron(II) is about eleven log K units lower than that of Fe(III), thus the interference due to iron can be eliminated when titration is done in acid medium. Ascorbic acid reduces Hg(II) to metal which does not interfere, Cr(III) can be oxidised to chromate with H_2O_2 in alkaline solution. Chromate as an anion does not form an EDTA complex and the interference is eliminated.

5. Kinetic masking

Al forms complex with DCTA in cold whereas Cr does not form complex in cold condition. This is an example of kinetic masking.

Decomposition of Samples:

One of the most important steps in silicate analysis is the proper decomposition of the sample for bringing the sample into solution. Two general methods are usually used for decomposition of silicates. The first is the fusion with fluxes followed by dissolution in acid and the other is treatment with HF in conjugation with H_2SO_4 or $HClO_4$.

Fusion with Fluxes:

There are two types of fluxes, acid and alkali. Among acid fluxes, potassium bisulphate or potassium pyrosulphate is important and used for decomposition of metallic oxide - like iron ore, insoluble metal oxide. Potassium bisulphate or pyrosulphate is sometimes used for fusion of undecomposed silicate sample after treatment with $\text{HF} + \text{H}_2\text{SO}_4$ and is usually carried out at low temperature in platinum or silica crucible. Acid fluxes fail to decompose samples containing significant amount of silica.

Alkali Fluxes:

Sodium carbonate, an equimolar mixture of sodium and potassium carbonates (fusion mixture) and alkali hydroxides and peroxides are the important alkaline fluxes. Usually sodium carbonate or fusion mixture is used for decomposition of aluminosilicates and high silica bearing materials like clay, feldspar, fire bricks etc with moderate amounts of alumina. While sodium carbonate-boric acid fusion for high alumina refractories, chrome and zirconia bearing materials, kyanite, sillimanite etc. Sodium hydroxide is a good flux for rapid decomposition of aluminosilicate and high silica bearing materials. Sodium peroxide is used in classical analysis for decomposition of chrome ores and chrome refractories in iron or nickel crucible. The modern trend of fusion is to carry out with flux only 2-3 times of the sample.

In recent advances of decomposition, lithium metaborate LiBO_2 or $\text{Li}_2\text{CO}_3 + \text{H}_3\text{BO}_3$ and acid decomposition at high temperature and pressure are found to be very effective and important. Lithium metaborate fusion of silicate samples has certain advantages over the alkali fluxes. The decomposition

can be carried out in platinum crucible at a much lower temperature than with alkali carbonates. Lithium metaborate is effective for decomposition of complicated refractories which do not usually contain Li and B therefore, the solution obtained after the dissolution of lithium metaborate melt in acid permits the complete analysis of silicate samples.

Acid Decomposition:

The use of HF as a decomposing agent for silicate materials avoids the introduction of large quantities of foreign ions as flux. Generally HF in conjugation with H_2SO_4 or $HClO_4$ is used for decomposition. Acid decomposition by high temperature - pressure technique in HF in Teflon lined bomb received probably the highest attention for effective decomposition without any loss of silica due to volatilization. This method of decomposition is advantageously used in complete analysis of samples by atomic absorption spectrophotometer. The method is however, not very effective for decomposition of samples like zircon, sillimanite, kyanite, high alumina refractories and chrome ores which can better be done with lithium metaborate fusion.

Application of Complexometric Titration to Silicate Analysis

The introduction of complexometric titration for successful and rapid determinations of Ca, Mg, Al, Zr, Ba and Pb is probably the most valuable contribution in schemes of rapid silicate analysis. Below are cited a few interesting determinations advantageously utilised in rapid analysis of silicates.

Aluminium:

It can be determined by back titration method based on

addition of EDTA solution, titration of excess EDTA and then selective release of EDTA from Al by boiling with ammonium fluoride and titration with standard Zn solution at pH 5.2 using xylenol orange as indicator, Ti interferes. However, Ti is usually present in small amounts and can be corrected by accurate determination by spectrophotometric method.

Calcium and Magnesium:

Rapid determination of Ca and Mg together is possible by direct titration with EDTA at pH 10 using indicator like EBT, methyl thymol blue or screened indicator comprising of EBT, orthocresolphthalexone and naphthol green B indicator. Screened indicator has been found to give sharp end-point. Ca is titrated with EDTA at pH 12 when Mg precipitates out as hydroxide using calcon, calcein or P&R indicator. Polyvinyl alcohol is added to prevent coprecipitation.

Lead and Barium:

The method is based on precipitation of lead and barium sulphate followed by selective dissolution of lead sulphate in excess of EDTA at pH 4.3. The excess EDTA is then titrated with ferric sulphate using sulfosalicylic acid as indicator. Lead is calculated from the equivalent EDTA consumed. Ba is determined by dissolving BaSO_4 in ammonical excess EDTA and then titrating the excess with MgCl_2 at pH at 10°C .

Zirconium:

Complexometric titration of zirconyl ion in 1N HNO_3 (HCl or HClO_4) in hot $>80^\circ\text{C}$ using xylenol orange as indicator is very selective. The colour change is from pink to yellow. The titration can be done in the presence of Al, Ti, Fe, Cr,

Pb, Zn, Ni, Co, Ca, Mg and Ba. Only phosphate interferes and required to be leached out in water after sodium carbonate and boric acid fusion. The determination is very rapid and accurate.

In conclusion it may be well said that adoption of improved methods in wet analysis is a necessity to accelerate the speed of chemical analysis and to achieve good accuracy, and in this direction complexometric titration has many potential applications.

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