COMPLEXOMETRIC TITRATION

What is complexation?

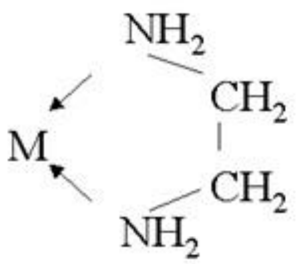
It is a process of formation of complex chemical species by coordination of group of atoms which are called as ligands to a central ion, which is a metal ion.

Chelate : it is a molecular structure where a heterocyclic ring is formed by the unshared electrons of neighbouring atoms.

Chelating agent : it is an organic compound where the atoms form more than one coordinate bond with metals in solution.

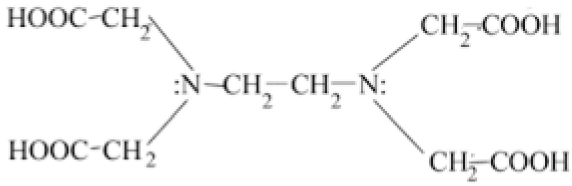
Classification of ligands (based on the number of points of attachment to the metal ion)

1. Monodentate ligand
   The NH_3 is monodentate, i.e the ligand is bound to the metal ion at only one point by the donation of a lone pair of electrons to the metal. It forms the complex with the cupric ion according to the equation,
   $$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+}$$
2. Bidentate ligand
   When the ligand has two atoms having the lone pair of electrons, then the ligand is bound to the metal ion at two points to form two coordinate bonds with the metal ion.



ethylenediamine

3. Multidentate ligand
   These ligands contain more than two coordinating atoms per molecule. The ethylenediamine tetra acetic acid (EDTA) has two donor nitrogen atoms, and four donor oxygen atoms in the molecule, can be hexadentate.



structure of EDTA

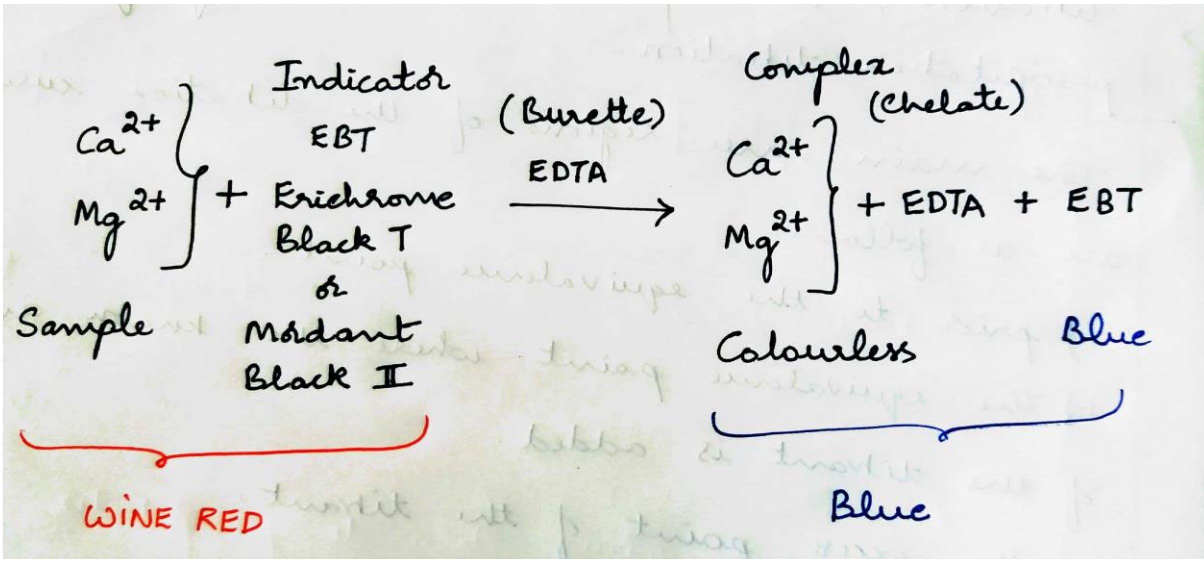
Principle and theory of the complexometric titration

The main principle is the reaction between the ligand and the metal ion to form a complex. The metal ion acts as Lewis acid and the ligand acts as Lewis base which is the complexing agent. Initially the metal ions are solvated that is, they are dissolved in the appropriate solvent and then these solvent ions are replaced by the ions or other solvent molecules to form the complex. The replacing solvent or ions are known as ligands. The ligands are defined as the charged or neutral species with lone pair of electrons forms the coordinate bond with the metal ions to form complexes.

Example for ligands: NH_3, EDTA etc.

Consider titration of a sample containing Ca^{2+} or Mg^{2+}, this is taken in a conical flask, to the same conical flask an indicator is added like eriochrome black T (EBT), also called as mordant black II or solochrome black T. This mixture of sample and indicator in the conical flask reacts to from a wine red colour. This mixture is then titrated with EDTA taken in the burette.

When the titration continues, the EDTA will react with mixture in the conical flask to form a complex with the Ca^{2+} or Mg^{2+} and the indicator i.e EBT will be in the free form while the titration continues. The complex formed between the sample and EDTA is also called a chelate, the complex colour will be colourless and the colour of free indicator will be blue. Hence at the end point of the titration, the colour of the final complex will be blue.

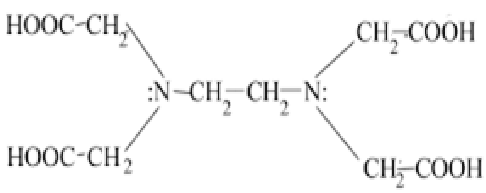


Complexometric titration is a type of polymetric analysis, in which a fixed volume of sample or analyte is titrated with a complexing agent like EDTA whose concentration will be known. Hence by using complexing agent we can calculate the amount of the metal ions present in the sample.

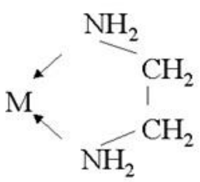
Complexing agents/chelating agents/sequestering agents

They are flexible organic molecules that can incorporate the metal ions into their molecular structure by means of chemical group called ligands.

Eg: EDTA , Ethylene diamine etc.



structure of EDTA



ethylenediamine

Metal ion indicators (Complexometric titration Indicators)

Indicators are the auxiliary substance added from the outside to the analyte solution, upon using which the end point can be detected. The end point is indicated by the change in the colour of the analyte solution. The colour change takes place after the indicator binds to the metal ion.

The most common technique to identify the end point in EDTA titration is to use metal ion indicator.

These indicators should posses the following requirements:

1. It should be chemically stable.

2. The Dye–metal complex formed should be of equal ratio.

3. The colour of the indicator should differ from colour of the metal ion.

4. It should be selective.

5. It should not compete with the EDTA.

In complexometric titration, metal ion indicators are used.

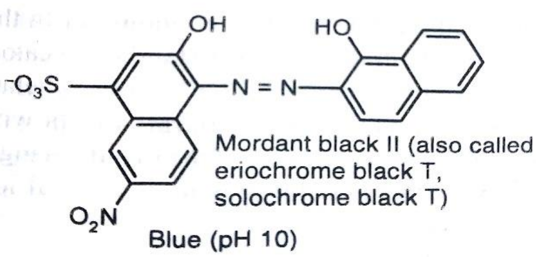
Mainly, three indicators are used in complexometric titration,

1. Eriochrome black – T
2. Xylenol orange
3. Murexide

Eriochrome black – T (EBT) is used to determine the concentration of calcium, magnesium, zinc, cadmium etc. The free indicator is blue in colour but upon the complexation with the metal ion, a pink colour is produced.

The mechanism of the colour change of the EBT can be explained as,

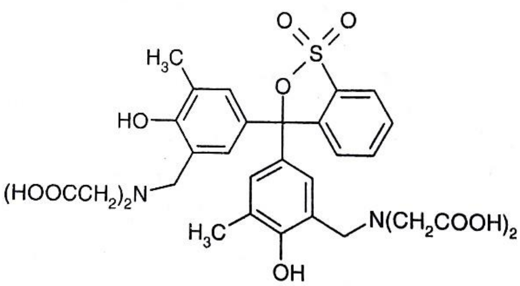
The structure of EBT is,



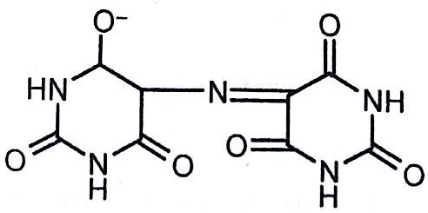
$$H_2In^{-} \rightleftharpoons HIn^{2-} \rightleftharpoons In^{3-}$$

Red	Blue	Orange
below pH 6	pH 7-11	above pH 12

The indicator will change the colour depending upon the pH of the solution. It will be wine red in acidic solution, blue in neutral solution and orange in basic solution. The structure of other indicator,



Xylenol orange



Murexide

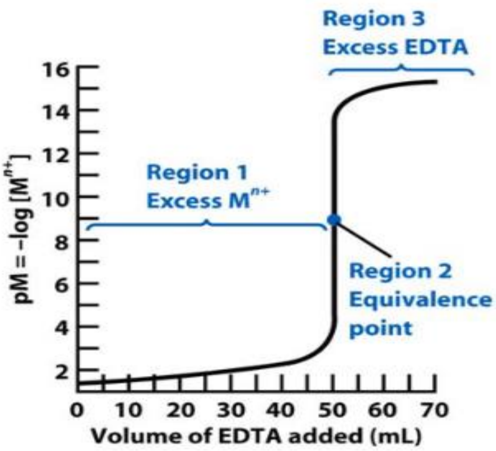
Complexometric titration curve

In the EDTA titration, the titration curve is a plot of pM versus the volume of EDTA solution.

The titration curve graph indicates the reaction of 50ml of 0.05M Metal ion solution (M) with 0.05M EDTA, where the concentration of free M decreases as the titration decreases.

There are three regions in the titration curve,

- Before the equivalence point.
- At the equivalence point.
- After the equivalence point.



In the EDTA titration, a metal ion sensitive indicator is often used to detect changes in the end point during the titration. At the beginning of the titration, the metal ion indicator (MI) is added to the metal ion solution (Analyte in the conical flask), this forms a complex.

During the titration, complexing agent like EDTA is added from the burette to the conical flask to form a complex with the metal ion solution. The EDTA has greater affinity for the metal ion and hence results in metal ion EDTA complex and liberates the free indicator.

1) Metal Ion Solution (Analyte) (colour A) + (MI) Metal Ion Indicator → MI - metal Ion complex (colour B) different colour from free indicator.

2) MI — Metal Ion Complex + EDTA (titrant) → Metal Ion - EDTA complex + MI (free form)

Depending upon the stability or formation constant of the metal ion EDTA complex, each metal ion samples end point may vary. The greater the stability constant , the sharper is the end point provided the pH is constant.

Types of complexometric titration

1. Direct titration.

   It is simplest and the most convenient method. The standard chelating agent solution is added to the metal ion solution until the end point is detected. In this method, metal ion is added to the suitable buffer solution and appropriate indicator solution and the resulting solution is titrated with the EDTA solution.

   Example: Calcium gluconate injection is assayed for determining the calcium chloride.

   The main disadvantage are the time consumption of time is more for the complex formation and also the interference of the other ions are observed. The reaction also takes place very slowly.

2. Back titration.

   This method is used in case of metals which get precipitated as hydroxides from solution at the required pH for titration. The method also finds use for insoluble substances like lead as sulphate, calcium as oxalate. This titration method is also used for substances which do not react quickly with disodium EDTA.

   Here excess of standard EDTA is treated with the metal solution. The solution is heated to have complex formation. It is then cooled. Then the disodium EDTA which is not required by the sample is then back titrated with standard solution of second metal ion. Suitable indicator is used.

   Eg : Mn determination and ZnO determination.

3. Replacement titration

   This method is used when the direct or back titration do not yield sharp end-points. By name itself it indicates the displacement of the metal ion with other metal ion takes place in this method. But it does not give the sharp end points.

   Example: $Mn^{2+} + MgEDTA^{2-} \longrightarrow Mg^{2+} + MnEDTA^{2-}$

Here, the Mn^{2+} displaces Mg^{2+} from the Mg-EDTA solution. The freed Mg metal is then directly titrated with a standard EDTA solution. This displacement takes place because the Mn^{2+} forms a more stable complex with EDTA.

This method is used for the determination of Ca, Pb and Hg using Mordant black II as an indicator.

4. Indirect titration

This method is also called alkalimetric titrations.

Here, protons from disodium edetate are displaced by a heavy metal. This is titrated with standard alkali.

This is alkalimetric titration is carried out in unbuffered solution. A visual pH indicator is used. But in cases when the colour of the complex would mask that of a pH indicator then potentiometric method of detection of endpoint is suitable.

Example : barbiturate will not react directly with EDTA and barbiturates forms complex with Hg^{2+} ions. The titration of Hg-barbiturate with EDTA gives the concentration of equivalent amount of barbiturate.

Barbiturate + $EDTA^{4-}$ $\longrightarrow$ No reaction

Barbiturate-Hg (complex) + $EDTA^{4-}$ $\longrightarrow$ $Hg\text{-}EDTA^{2-}$ + Barbiturate

Masking and Demasking agents

During the titration technique, a solution may contain wide range of cations, and also certain impurities. When it required to assay a particular ion in a mixture of ions, or to prevent the impurities to react during the titration process which may result in error during titration, we use masking agents.

The masking agents masks the the presence of other cations or impurities and allows the titration of the specific cation with the complexing agent.

Eg: During the assay of Cu, i.e based on the reaction between Cu^{2+} and I^-, Fe^{3+} which may be present in the same solution as Cu^{2+}, may react with I^- And show interference. Hence, there is a need to mask Fe^{3+}, this can be masked by using fluoride salt. Hence the interference is eliminated.

$Fe^{3+} + 6F^- \longrightarrow FeF_6^{3-}$

$FeF_6^{3-} + I^- \longrightarrow$ No reaction

Masking agent act either by precipitation or by formation of complex more stable than the interfering ion edetate complex.

I. **Masking by precipitation**

When interference due to the following ions are encountered, the precipitants are added. The collected precipitates are then estimated separately.

Interfering ions	**Precipitants**
Cu, Co, Pb	Sodium sulphide, thioacetamide.
Pb, Ba	Sulphate
Pb, Ca	Oxalate.
Pb, Ca, Mg	Fluoride.

II. **Addition of complexing agents**

This results in formation of complexes with the interfering ions. These complexes are more stable as compared to edetate complexs. So thus, impurities are eliminated and selective titration is done.

Interfering ions	complexing agents
Al, Fe, Ti	Ammonium fluoride
Ferric	Ascorbic acid + ferrocyanide
Hg, Cd, Zn	Dimercaprol in alkaline
Hg	KI

Demasking is a process in which the masked substance regains its ability to enter into the particular reaction. This enables to determine a series of metal ions in one solution containing many cations.

The cyanide complex of zinc may be demasked with formaldehyde or with chloral hydrate. Formaldehyde demasks the zinc according to the following reaction.

$$[Zn(CN)_4]^{2-} + 4H^+ + 4HCHO \longrightarrow Zn^{2+} + 4HOCH_2.CN$$

The use of masking and demasking agents permits the successive titration of many metals.

For example, consider a solution containing Ca, Cd and Cu to be titrated with EDTA. We have to find the concentration of each metal ion.

I. Initially, we have to **titrate the whole solution with the EDTA solution** from which we can find out the concentration of all the metal ions. It forms metal ion – EDTA complex.

II. In the second step, use a **masking agent like potassium cyanide**. This masks Cd and Cu. Ca is in the free form. Hence the solution with the free form of Ca and masked Cd and Cu is titrated with EDTA, hence we can find the concentration of Ca.

III. In the third step, we will adding the **demasking agent like chloral hydrate / formaldehyde** which will demask Cd, and mask Cu, and hence Ca and Cd will be in the free form. Hence we can find the combined concentration of Ca and Cd.

Hence now we can obtain the individual concentration of metal ions.

Instrumental methods of End point detection

a) **Spectrophotometric detection** : the absorption spectrum when a metal ion of a complexing agent is converted to the metal complex, or when one complex is converted to another can be detected accurately.
b) **Amperometric titration** : it is measurement of the change in the electrode potential when a metal ion is in free form to when it undergoes complexation. The diffusion current and residual current will become equal.
c) **Potentiometric titration** : in this method, platinum electrode is commonly used with any standard reference electrode. Platinum electrode measures the redox potential associated with the metal EDTA complex. The redox potential decreases when the EDTA reacts with the heavy metal ion.
d) **High frequency titration**: this method is suitable for dilute solutions. The ions are directly titrated in buffered solutions and the liberated protons are titrated with standard alkali.

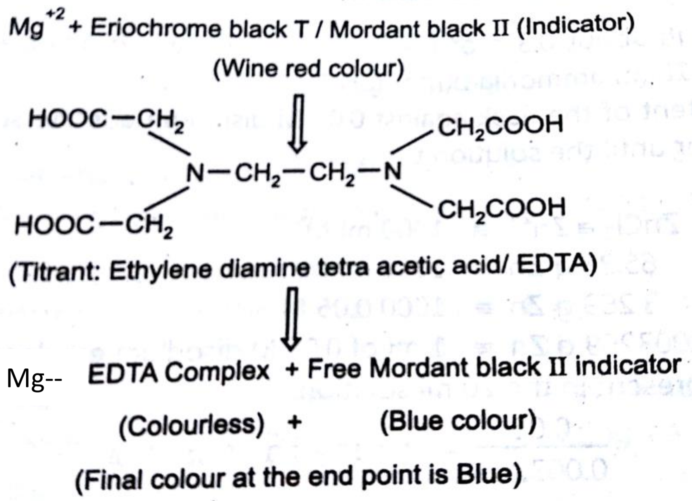
Applications of Complexometric titration

- Used to determine concentration of metal ion in solution.
- Can be used to determine how much of calcium, magnesium or other minerals is in a food product.
- Can be used to determine the concentration of certain toxic metals.
- Water hardness can be determined by titrating it with EDTA.

Estimation of Magnesium sulphate

- **Principle :** Complexometric titration is a form of volumetric analysis in which the formation of a coloured complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. Magnesium can be easily determined by EDTA titration in the pH 10 against Eriochrome Black T.

  If the solution initially contains also different metal ions, they should be removed or masked, as EDTA react easily with most cations



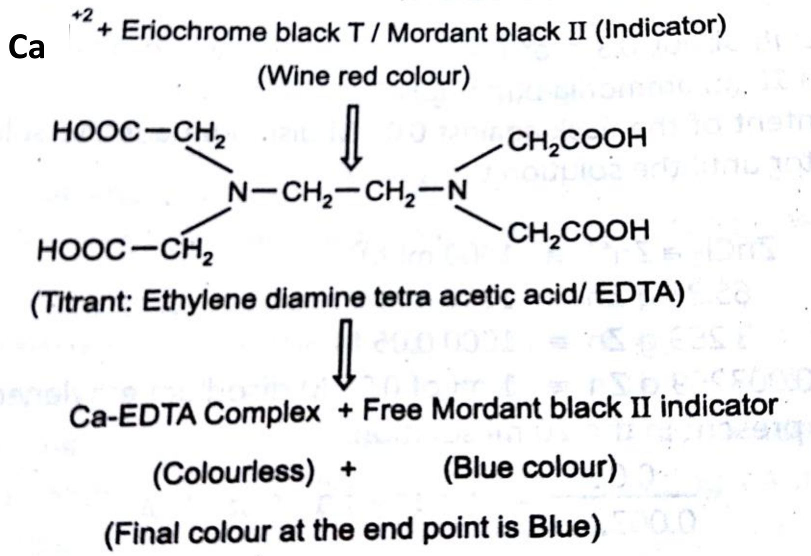
- **Procedure :**
  1) **Standardisation of EDTA:** Pipette out 20ml of calcium carbonate solution, add 10ml of ammonia, ammonium chloride solution or ammonium buffer solution. Titrate against EDTA using mordant black II mixture till the colour changes from red to blue.
  2) **Assay of Magnesium sulphate:** weigh 0.3g magnesium sulphate, add 50ml distilled water, add 10ml of ammonia, ammonium chloride solution or ammonium buffer solution. Titrate against EDTA using mordant black II mixture till the colour changes from red to blue.

- **Calculations :**
  Each ml of 0.05M EDTA = 0.01232g of Magnesium sulphate.

Estimation of Calcium Gluconate

- **Principle :** Complexometric titration is a form of volumetric analysis in which the formation of a coloured complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution.

(principle same as record)



- **Procedure :**
  3) **Standardisation of EDTA:** Pipette out 20ml of calcium gluconate solution, add 10ml of ammonia, ammonium chloride solution or ammonium buffer solution. Titrate against EDTA using mordant black II mixture till the colour changes from red to blue.
  4) **Assay of Calcium gluconate:** weigh 0.5g calcium gluconate, add 50ml distilled water, add 10ml of ammonia, ammonium chloride solution or ammonium buffer solution. Titrate against EDTA using mordant black II mixture till the colour changes from red to blue.

- **Calculations :**
  Each ml of 0.05M EDTA = 0.02242g of Calcium gluconate.