2.5. COMPLEXOMETRIC TITRATION

Complexometric titration (**chelatometry**) 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. An indicator capable of producing an unambiguous colour change is usually used to detect the end point of the titration. The formation of a complex during a chemical reaction may serve as the basis of assay of complexometric titration.

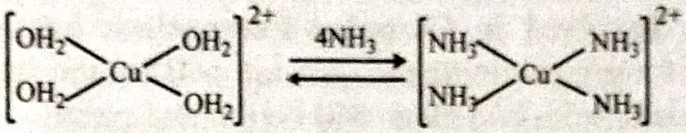
2.5.1. Principle

In complexometric titrations, the metal ions are titrated with a complexing or a chelating agent (ligand). This method is an analytical application of a complexation reaction. This method involves transforming a simple ion into a complex ion and determining the equivalence point using metal indicators or electrometrically. This method is also termed as **chilometric titrations**, **chilometry**, **chilatometric titrations**, and **EDTA titrations**. These terms have resulted from the use of EDTA (Ethylene Diamine Tetra Acetic Acid) and other chilons which react with metal ions forming a chelate complex:

		Chilon		**Chelate**
Metal ion (Analyte; Cation)	+	Complexing agent	Metal-ion indicators	Complex ion
		Chelating agent Ligand Sequestering agent	pM indicators →	Metal coordination compound Metal complex Chelate compound

Solvated metal ions are present in solution, i.e., a definite number of solvent molecules (usually 2, 4, or 6) and the metal ion are bound together. However, some other solvent molecules or ions replace these bound solvent molecules during the formation of a metal complex or metal coordination compound.

Ligands or complexing or chelating agents are the molecules or ions displacing the solvent molecules. They can be electron donating entity with the ability to bind to the metal ion and produce a complex ion. An **example** of a complexation reaction between Cu (II) ion and four ammonium molecules in an aqueous solution may be expressed by the following equation:



The **ligands are classified** as follows:

1) **Unidentate Ligands:** These ligands are bound to metal ions only at one place (one toothed). **For example,** NH_3 is a unidentate ligand capable of complexing with cupric ions. Halide ions, cyanide ions, and NH_3 are common **examples** of unidentate ligands. The formation of complex $Cu(NH_3)_4^{2+}$ proceeds in the following steps:

Step 1: $Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+}$

Step 2: $Cu(NH_3)^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+}$

Step 3: $Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{2+}$

Step 4: $Cu(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$

Considering the overall reaction:

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

2) **Bidentate and Multidentate Ligands:** These ligands are known to contain more than one group, and are capable of binding with metal ions. They include bidentate ligands (2 donor atoms), tridentate ligands (3 donor atoms), quadridentate ligands, etc.

Example:

i) Bidentate Ligand – Ethylene Diamine,

ii) Multi-Dentate Ligand – Ethylene Diamine Tetra Acetic Acid.

2.5.2. Theory

Complexometric titrations involve the disappearance of the free metal ions as they are changed into complex ions. As in acid-base titrations, the pH changes suddenly at the end point; in complexometric titrations, in the plot pM (negative log of metal ion concentration) *versus* volume of titrant, the pM rapidly increases at the end point (**figure 2.6**).

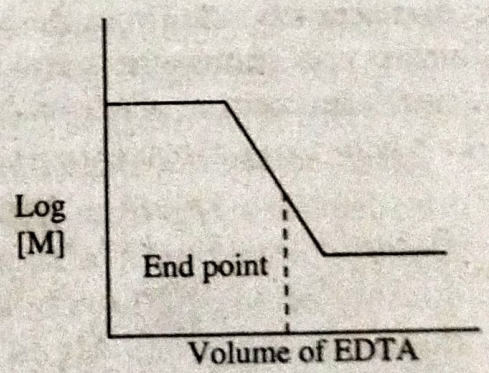


Figure 2.6: Titration Curve

This sudden rise in pM is the result of removal of traces of metal ions from the solution by EDTA. A method which can determine this sudden disappearance of free metal ions can detect the end point in complexometric titrations. Detection of end point can be brought about using an indicator or instrumentally by potentiometric or conductometric (electrometric) method.

The **factors** which need consideration while determining the magnitude of break in titration curve at the end point are:

1) **Complex Stability:** Greater is the stability constant for complex formed, larger will be the charge in free metal concentration (pM) at the equivalent point and more clear will be the end point.

2) **Number of Steps Involved in Complex Formation:** Less the number of steps required for forming complexes, greater will be the break in titration curve at the equivalent point and clear will be the end point.

3) **Effect of pH:** A constant pH should be maintained during a complexometric titration with the aid of a buffer solution. The pH should be controlled as the H^+ ion has a significant role to play in chelation. The ligands mostly are basic, thus, bind to H^+ ions throughout a wide range of pH. During the formation of chelate some of these H^+ ions are frequently displaced from the ligands (chelating agents) by the metal. Complexation between metal ion and H^+ ion for ligand is shown below:

$$M^{2+} + H_2\text{-}EDTA^{2-} \rightleftharpoons M\text{-}EDTA^{2-} + 2H^+$$

Thus, pH significantly influences the stability of metal complex. **Lower the solution pH, less stable will be the complex** (because more H^+ ions are available to compete with the metal ions for ligand). Metals forming very stable complexes can be titrated in acidic solution, and metals forming weak complexes can be titrated in alkaline solution.

2.5.3. Classification

Complexometric titrations are of the following four types:

1) **Direct Titration:** This method is similar to acid-base titrations, and involves adding the standard chelon solution to the metal ion solution till the end point is attained.

2) **Back Titration:** In this method, excess of a standard EDTA solution is added to the metal solution (to be analysed), and the excess is back titrated with a standard solution of a second metal ion.

3) **Replacement Titration:** In this method, the metal to be analysed quantitatively displaces the metal from the complex. When direct or back titrations do not give sharp end points, the metal may be determined by the displacement of an equivalent amount of Mg or Zn from a less stable EDTA complex:

$$Mn^{+2} + Mg\,EDTA^{-2} \longrightarrow Mg^{+2} + Mn\,EDTA^{-2}$$

Mn displaces Mg from Mn-EDTA solution. The freed Mg metal is then directly titrated with a standard EDTA solution. In this method, excess quantity of Mg-EDTA chelate is added to Mn solution. Mn quantitatively displaces Mg from Mg-EDTA chelate. This displacement takes place because Mn forms a more stable complex with EDTA. By this method Ca, Pb, and Hg may be determined using Eriochrome black T indicator.

4) **Indirect Titration:** This is also known as **alkalimetric titration**. It is used for the determination of anions which do not react with EDTA chelate. Protons from disodium EDTA are displaced by a heavy metal and titrated with sodium alkali.

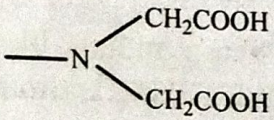
$$M^{n+} + H_2X^{-2} \longrightarrow MX^{(n-4)} + 2H^+$$

2.5.4. Chelates (Chelate Compounds)

Complexes involving simple ligands, i.e., those forming only one bond are described as **coordination compounds**. A **chelate** or a **chelate compound** is a complex of a metal ion with two or more groups on a multi-dentate ligand. The coordination and a chelate compound does not differ from each other, except that in the latter ring influences its stability. Thus, a chelate is a heterocyclic ring structure in which a metal atom is a member of ring. The chelate stability is usually much greater than that of corresponding unidentate metal complex.

Chelating Agent

Ligands having more than one electron donating groups are called **chelating agents**. The most effective complexing agent in ligands are amino and carboxylate ions. All the multi-dentate ligands important in analytical chemistry contain the structure component as follows:

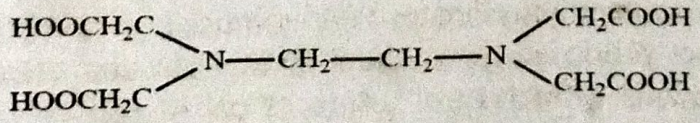


The solubility of metal chelates in water depends on the presence of hydrophilic groups such as COOH, SO_3H, NH_2, and OH.

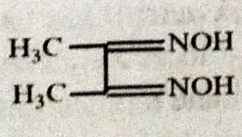
The complex containing both acidic and basic groups is soluble over a wide range of pH. The solubility of the chelating agent as well as the metal chelate is low in the absence of hydrophilic groups, but they are soluble in organic solvents.

Sequestering agents are the chelating agents forming water-soluble complexes with bi- or polyvalent metal ions. Thus, even if the metals remain in solution, they do not give normal ionic reactions. **For example,** EDTA is a sequestering agent, while dimethylglyoxime and salicylaldoxime are chelating agents forming insoluble complexes.

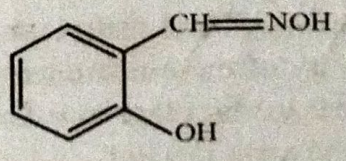
EDTA forms water-soluble complexes by reacting with the most polyvalent metal ions. The resultant complexes cannot be extracted from aqueous solutions with organic solvents. Dimethylglyoxime and salicylaldoxime form water insoluble complexes which are soluble in organic solvents, **e.g.,** nickel dimethylglyoxime with low water solubility is used in gravimetric assay. EDTA chelates with almost all the metal ions and this forms the basis for **complexometric** or **chilometric** or **EDTA titrations**.



EDTA



Dimethylglyoxime



Salicylaldoxime

In complexometric titrations, a complex ion is formed by the analyte and titrant, and the equilibrium constant is called the **formation constant** (K_f). The complexes formed by chelating (multi-dentate) ligands are more stable than those formed by monodentate ligands. This is because the entropy of complex formation favours the binding of a large ligand rather than small ligands. Synthetic amino carboyxlic acids (such as EDTA), widely used in analytical chemistry, have large metal-binding constants.

2.5.4.1. Masking Reagents

A masking reagent is a complexing agent which prevents a component (in a solution) to interfere in a determination by selectively reacting with it. These agents either act by precipitation or by forming complexes with stability more than that of the interfering ion-EDTA complex.

Methods of Masking

1) **Masking by Precipitation:** The heavy metals like Co, Cu, and Pb, can be separated either as insoluble sulphides using sodium sulphide, or as insoluble complexes using thioacetamide. These separated components are filtered, decomposed, and titrated using disodium EDTA.

   Using sulphate for Pb and Ba, oxalate for Ca and Pb, fluoride for Ca, Mg, and Pb, ferrocyanide for Zn and Cu, and 8-hydroxy quinoline for many heavy metals are some other precipitating agents used for separation.

2) **Masking by Complex Formation:** Masking agents using interfering metal ions result into complexes with high stability. The masking agent should not form complexes with the metal ion being analysed. Some of the masking agents used are:

   i) **Ammonium Fluoride:** It is used for masking aluminium, iron, and titanium by complex formation.

   ii) **Ascorbic Acid:** It is used for reducing iron(III) and then masking it by forming a stable hexacyanoferrate(II) complex. The stability of this complex is more and its colour intensity is less than that of the hexacyanoferrate(III) complex.

   iii) **Dimercaprol (2,3-Dimercaptopropanol) ($CH_2SH.CHSH.CH_2OH$):** It reacts with mercury, cadmium, zinc, arsenic, tin, lead, and bismuth cations in weakly acidic solution, forming precipitates or complexes soluble in alkaline solution. These colourless complexes are stronger than the corresponding edetate complexes. Cobalt, copper, and nickel form intense yellowish-green complexes with the reagent under the above conditions. Dimercaprol displaces cobalt and copper (not nickel) from their edetate complexes.

   iv) **Potassium Cyanide:** It reacts with silver, copper, mercury, iron, zinc, cadmium, cobalt, and nickel ions to form complexes in alkaline solution. The stability of these complexes is more than the corresponding edetate complexes, so that other ions (such as lead, magnesium, manganese, and the alkaline earth metals) can be determined in their presence.

v) **Potassium Iodide:** It is used for masking the mercury (II) ion (HgI_4) and is specific for mercury. It can also be used in the assay of mercury (II) chloride.

vi) **Tiron (Disodium Catechol-3,5-Disulphonate):** It masks aluminium and titanium forming colourless complexes. Iron forms highly coloured complexes and is best masked as its hexacyanoferrate (II) complex.

vii) **Triethanolamine [$N(CH_2.CH_2.OH)_3$]:** It forms a colourless complex with aluminium, a yellow complex with iron(III), the colour of which is almost discharged by adding sodium hydroxide solution, and a green manganese(III) complex which oxidises mordant black II. For these reasons, if murexide is used in the presence of iron and manganese, it is best to mask them with triethanolamine; similarly, mordant black II can be used in the presence of triethanolamine-aluminium complex.

2.5.4.2. Demasking Reagents

A demasking reagent enables the masked substance to enter into a particular reaction. This enables to determine a series of metal ions in one solution containing many cations.

Example of using masking and demasking agents in complexometry is the analysis of three metals, i.e., Cu, Cd, and Ca.

Methods of Demasking

1) **pH Control Method:** The formation of a metal chelate is dependent on the pH of the reaction medium. In weakly acidic solution, the chelates of many metals completely dissociate such as alkaline earth metals, whereas chelates of Bi, Fe^{3+}, or Cr are readily formed at this pH.

   Thus, in acidic solution, Bi can be effectively titrated with a chelating agent in the presence of alkaline earth metals. This method is based upon the differences in stability of the chelates formed between the metal ions and the chelating agent.

2) **Use of Selective Metal Indicators:** These indicators are the metal complexing agents which react with different metal ions under various conditions. Several selective metal indicators specific for a particular ion have been used.

3) **Classical Separation:** These methods may be applied if they are not tedious; thus the following precipitates may not be used for separations after being re-dissolved. Cations that can be determined complexometrically are CaC_2O_4, nickel dimethylglyoximate, $Mg(NH_4)PO_4$, $6H_2O$, and CuSCN.

4) **Solvent Extraction:** This method of demasking is used occasionally. **For example**, zinc can be separated from copper and lead by adding excess of ammonium thiocyanate solution and extracting the resulting zinc thiocyanate with 4-methyl pent-2-one (isobutyl methyl ketone); the extract is diluted with water and the zinc content is determined with EDTA solution.

5) **Removal of Anions:** Anions, such as orthophosphate, which can interfere in complexometric titrations, may be removed using ion exchange resins.

6) **Kinetic Masking:** This is a special case in which a metal ion does not effectively enter into the complexation reaction because of its kinetic inertness. Thus, the slow reaction of chromium (III) with EDTA makes it possible to titrate with other metal ions which react rapidly, without the interference from Cr (III).

2.5.4.3. Metal-EDTA Titration Curves

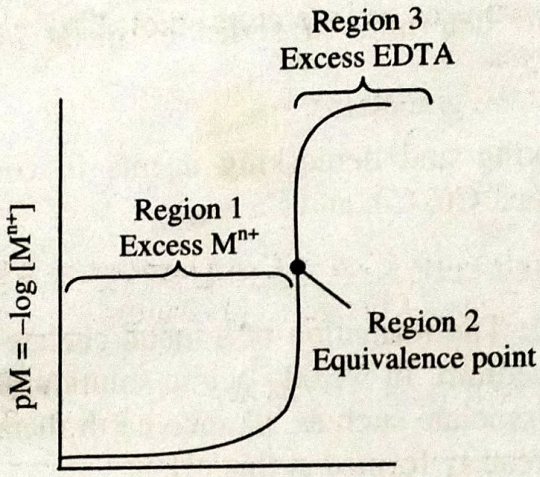
The titration of a metal ion with EDTA is similar to the titration of a strong acid (M^+) with a weak base (EDTA).

$$M^{n+} + EDTA \rightleftharpoons MY^{n-4}$$

The **titration curve** has three distinct **regions**:

1) Before the equivalence point (excess M^{n+}).
2) At the equivalence point ([EDTA] = $[M^{n+}]$).
3) After the equivalence point (excess EDTA).

$$pM = -\log[M^{n+}]$$



2.5.5. Methods of End Point Detection

End point in complexometric titrations can be detected by the following two methods:

1) Complexometric/metal ion indicators, and
2) Instrumental methods.

2.5.5.1. Complexometric/Metal Ion Indicators

Similar to acid-base indicators, metal ion indicators are metal complexing agents which may produce different colours on binding to metal ions.

These indicators have several acid base functional groups whose ionisation state affects the colour of the unbound indicator. Thus, the colour of the unbound indicator varies with the solution pH.

The metal indicators should comply with the following **requirements**:

1) The compound should be chemically stable throughout the titration.
2) It should form 1:1 complex weaker than the metal chelate complex.
3) Colour of the indicator and the metal complexed indicator should be different.
4) Colour reaction should be selective for the metal being titrated.
5) The indicator should not compete with the EDTA.

Mechanism of Action

Let the metal be denoted with M, indicator by I, and chelate with EDTA. At the onset of titration, the reaction medium contains the Metal-Indicator complex (MI) and excess of metal ion. When EDTA titrant is added to the system, a competitive reaction takes place between the free metal ions and EDTA. Since the Metal-Indicator complex (MI) is weaker than the metal-EDTA chelate, the EDTA which is being added during the course of the titration chelates the free metal ions in the solution at the expense of the MI complex.

Finally, at the end point, EDTA removes the last traces of the metal from the indicator and the indicator changes from its complexed colour to its metal free colour. The overall reaction is given by:

$$\underset{\text{(Colour of metal-indicator complex)}}{MI} + M + EDTA \longrightarrow M\text{-}EDTA + \underset{\text{(Original colour of indicator)}}{I}$$

Many compounds have been used as indicators (**table 2.4**), like:

1) Triphenyl methane dyes,
2) Phthalein and substituted phthaleins,
3) Azo dyes, and
4) Phenolic compounds.

Table 2.4: Indicators Used in Complexometric Titrations

Indicators	Colour Change	pH Range	Metals Detected
Mordant black II	Red to Blue	6-7	Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg
Eriochrome blackT			
Solochrome blackT			
Murexide or Ammonium purpurate	Violet to Blue	12	Ca, Cu, Co
Catechol-violet	Violet to Red	8-10	Mn, Mg, Fe, Co, Pb
Methyl blue	Blue to Yellow	4-5	Pb, Zn, Cd, Hg
Thymol blue	Blue to Gray	10-12	
Alizarin	Red to Yellow	4.3	Pb, Zn, Co, Mg, Cu
Xylenol range	Lemon to Yellow	1-3	Bi, Thorium
		4-5	Pb, Zn
		5-6	Cd, Hg

2.5.5.2. Instrumental Methods

Following are the instrumental methods used for complexometric end-point detection:

1) **Spectrophotometric Detection:** When a metal ion of a complexing agent converts into the metal complex, or when one complex converts into another, the absorption spectrum changes which is accurately detected by spectrophotometric methods. Thus, in disodium EDTA titrations an accurate end point can be obtained using 0.001M solutions. In practice, an indicator giving a colour change in the visible region is generally employed, but coloured ions may be titrated without an indicator using spectrophotometric methods. Also it is sometimes possible to use an end point in the UV region for ions and complexes colourless in the visible region.

2) **Amperometric Titration:** The effect of complex formation on the half-wave potential of an ion is to render it more negative. If the electrode potential is adjusted to a value between that of the half-wave potential of the free cation and that of the complex, and disodium EDTA solution is added slowly, the diffusion current will fall steadily until it equals the residual current, i.e., until the last trace of free cation has been complexed. This is the end point and the amount of standard disodium EDTA solution added is equivalent to the amount of metal present.

3) **Potentiometric Titration:** Since disodium EDTA prefers to react with the higher valency state of an ion, it will reduce the redox potential according to the equation:

$$E = E_0 + \log_e [Ox]/[Red]$$

Where, E = Potential of the electrode.
E_0 = Standard electrode potential.
[Ox] = Activity of the ions in the oxidised state.
[Red] = Activity of the ions in the reduced state.

This method is of limited application owing to the lack of suitable indicator electrodes. Iron (III) and copper (II), however can be titrated by this method. Back titration of excess disodium EDTA with ferric chloride in acid solution is possible for some ions.

4) **High Frequency Titration:** This method is particularly suitable for dilute solutions, in some cases with concentrations as low as 0.0002M. The ions may be titrated directly in buffered solution or excess reagent can be added to the un-buffered solution and the liberated protons titrated with standard alkali. Since buffer solution and other extraneous electrolytes reduce the sensitivity of the titration, their concentration must be kept to a minimum.

2.5.6. Applications of Complexometric Titrations

The pharmaceutical applications of complexometric titrations are:

1) **Determination of Permanent and Temporary Hardness of Water Separately:** If a water sample is boiled for some time, bicarbonates of Ca and Mg (which causes temporary hardness) is precipitated as white insoluble carbonates and are removed by filtration. The filtered water sample may now be titrated with EDTA salt which gives only permanent hardness. Now the temporary hardness can be manipulated by subtracting the permanent hardness from the total hardness of water sample.

Calculations for Water Hardness: The concentration of EDTA solution is found by:

$$M\ EDTA = \frac{(\text{wt. of } CaCO_3)(V_{10}/100\ ml)}{(\text{mol. wt. } CaCO_3)\ (\text{ml EDTA}/1000)}$$

Where, V_{10} = Calibrated volume of the 10ml pipette.

Water hardness, expressed in parts per million or milligrams per litre of $CaCO_3$, can be calculated by:

$$\text{Hardness in ppm} = \frac{(\text{ml EDTA}/1000)(\text{M EDTA})(\text{mol. wt. } CaCO_3)(1000 \text{ mg/g})}{(\text{vol. of sample in litres})}$$

The hardness in ppm value represents the $CaCO_3$ concentration in the solution prepared from the unknown sample. The result as ppm of $CaCO_3$ in the solid unknown sample was reported.

2) **Determination of Total Hardness of Water (Permanent and Temporary):** The hardness of water is generally due to dissolved calcium and magnesium salts and may be determined by complexometric titration.

3) **Determination of Magnesium and Silicon Dioxide in Magnesium Trisilicate:** The MgO in magnesium trisilicate is determined complexometrically with EDTA solution by first dissolving it in dilute H_2SO_4/HCl, when its magnesium contents are converted to either soluble magnesium sulphate or magnesium chloride respectively. This is filtered and collected quantitatively and assayed by complexometric titration. At the same time a waxy white precipitate of H_2SiO_3 (silicic acid) is obtained. It is filtered, dried, and ignited at 1000°C in a fused silica crucible to SiO_2 and then weighed to a constant weight.

4) **Determination of Calcium and Lead in a Mixture:** With methyl-thymol blue, lead may be titrated at a pH of 6 without interference by calcium; the calcium is subsequently titrated at pH 12.

5) **Determination of Chromium (III) and Iron (III) in a Mixture (Kinetic Masking):** Iron (and nickel, if present) can be determined by adding an excess of standard EDTA to the cold solution, and then back-titrating the solution with lead nitrate solution using **xylenol orange** as an indicator; provided the solution is kept cold, chromium does not react.

   The solution from the back titration is then acidified, excess of standard EDTA solution is added and the solution is boiled for 15 minutes when the red-violet Cr(III)-EDTA complex is produced. After cooling and buffering to pH 6, the excess EDTA is then titrated with the lead nitrate solution.

6) **Determination of Manganese in the Presence of Iron (Ferromanganese):** After dissolution of the alloy in a mixture of concentrated nitric and hydrochloric acids, the iron is masked with triethanolamine in an alkaline medium, and the manganese is titrated with standard EDTA solution using **thymolphthalexone** as an indicator. The amount of iron (III) present should not exceed 25mg per 100ml of solution, otherwise the colour of the iron (III)-triethanolamine complex is so intense that the colour change of the indicator is obscured. Consequently, the procedure can only be used for samples of ferromanganese containing more than about 40% manganese.

7) **Determination of Lead and Tin in a Mixture (Solder):** A mixture of tin (IV) and lead (II) ions may be complexed by adding an excess of standard EDTA solution, the excess EDTA being determined by titration with a standard solution of lead nitrate, the total lead-plus-tin content of the solution is thus determined. Sodium fluoride is then added which displaces the EDTA from the tin (IV)-EDTA complex; the liberated EDTA is determined by titration with a standard lead solution.