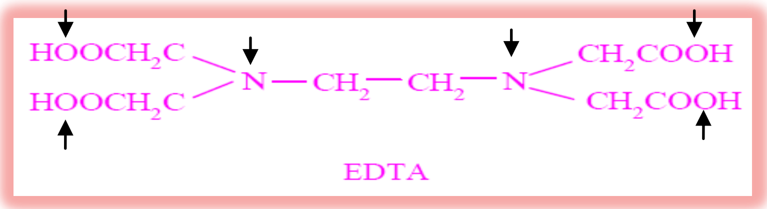
COMPLEXOMETRIC TITRATIONS

- Complexometric Titration is a type of 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.
- The technique involves titrating metal ions with a complexing agent or chelating agent (Ligand) and is commonly referred to as complexometric titration.

Chelate Compound or Chelate

- Complexes involving simple ligands, i.e., those forming only one bond are described as **simple complexes**.
- A complex of a metal ion with 2 or more groups on a multidentate ligand (e.g. EDTA) is called a **chelate**.
- The stability of a chelate 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**. EDTA has six binding sites and therefore it is also called as multidentate (hexadentate) ligand.



- EDTA forms chelates with nearly all metal ions and this reaction is the basis for general analytical method for these ions by titration with a standard EDTA solution. Such titrations are called complexometric or chilometric or EDTA titrations.

Types of EDTA Titrations

1. **Direct Titration**

- In direct titration, a suitable indicator is added to the metal-ion complex solution and titrated with disodium- EDTA until the indicator just changes colour.
- In the initial stages of the titration, magnesium ions are displaced from the EDTA complex by calcium ions and are free to combine with the Eriochrome Black T, therefore imparting a red color to the solution. When all of the calcium ions have been complexed, however, the free magnesium ions again combine with the EDTA until the end point is observed.

2. **Back titration**

- In actual practice, an excess of the standard solution of disodium edetate is added to the sample, pH is adequately adjusted for the back titration with a metal-ion solution e.g., $ZnSO_4$ and employing an appropriate indicator which is sensitive enough to the respective titrant. However, the metal ion under estimation remains complexed with the EDTA and offers little interference with the Zn-EDTA complex formed.

- Back-titrations are useful for the determination of cations that form stable EDTA complexes and for which a satisfactory indicator is not available. The method is also useful for cations such as Cr(III) and Co(III) that react slowly with EDTA.
- Extra amount of standard EDTA solution is added to the solution containing metal ions. After the reaction is judged complete, the excess EDTA is back-titrated with a standard magnesium or zinc ion solution to an Eriochrome Black T or Calmagite.
- For this procedure to be successful, it is necessary that the magnesium or zinc ions form an EDTA complex that is less stable than the corresponding analyte complex.
- Back-titration is also useful for analyzing samples that contain anions that could form precipitates with the analyte under the analytical conditions. The excess EDTA complexes the analyte and prevents precipitate formation.

3. **Replacement Titration**

- In this method the metal, which is to be analyzed, displaces the other 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 MnEDTA solution. The free 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, Hg may be determined using Eriochrome blackT indicator.

Masking and Demasking Agents

- The disodium EDTA usually complexes with a wide variety of cations, which may give false results of the titration procedure. There are chances that metal impurities can be titrated along with the ion it is aimed at for actual estimation.
- Therefore, in a situation where one or two ions present in a mixture of cations is specifically required to be determined with a view to eliminate completely the possible effects of unwanted impurities that may enhance the titre value, a third substance is added, which is known as the **Masking Agent**. **This agent forms the complex with the metal ions that are not required in the estimation.**
- Cyanide ion is used as a masking agent to permit the titration of magnesium and calcium ions in the presence of ions such as cadmium, cobalt, copper, nickel, zinc,

and palladium. All of these ions form sufficiently stable cyanide complexes to prevent reaction with EDTA.

Masking Agent	Interferences
Cyanide	Zn, Cd, Cu, Ni, Co
Fluoride	Fe, Al, Ca, Mg
Phosphate	Ti
Iodide	Hg(II)
Citrate	U, Al
Diethyldithiocarbamate	Pb, Cd, Cu
Sulfide	Heavy metals
Thiosulfate	Ag

Table. List of masking agents and metal ions with which they react

- After completion of titration, if needed, a demasking agent can be added to set free the previously masked metal ions so that they can be determined.
- **Demasking agents are the compounds which are use to bring those metal ions which are masked by masking agent.**
- For example, Cd and Zn ions can be demasked by addition of chloral hydrate or formaldehyde: acetic acid solution.

Indicators

- The endpoint for an EDTA titration is usually found by using a metallochromic indicator – this is a dye that can act as a complexing agent to the metal being titrated.
- The colour of the indicator depends on whether it is attached to the metal ion or free.

$$\underbrace{\text{MI}}_{\text{(Colour of metal-indicator complex)}} + \text{M} + \text{EDTA} \longrightarrow \text{M-EDTA} + \underbrace{\text{I}}_{\text{(original color of indicator)}}$$

- At the beginning of a titration, some of the analyte metal ion is complexed by the indicator.

S.No.	Name of the Indicator	Colour change	pH range	Metals detected
1.	Mordant black II Eriochrome blackT Solochrome blackT	Red to Blue	6-7	Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg
2.	Murexide or Ammonium purpurate	Violet to Blue	12	Ca, Cu, Co
3.	Catechol-violet	Violet to Red	8-10	Mn, Mg, Fe, Co, Pb
4.	Methyl Blue	Blue to Yellow	4-5	Pb, Zn, Cd, Hg
	Thymol Blue	Blue to Grey	10-12	
5.	Alizarin	Red to Yellow	4.3	Pb, Zn, Co, Mg, Cu
6.	Sodium Alizarin sulphonate	Blue to Red	4	Al, Thorium
7.	Xylenol range	Lemon to Yellow	1-3	Bi, Thorium
			4-5	Pb, Zn
			5-6	Cd, Hg

Table. Metallochromic/ Complexometric indicators