

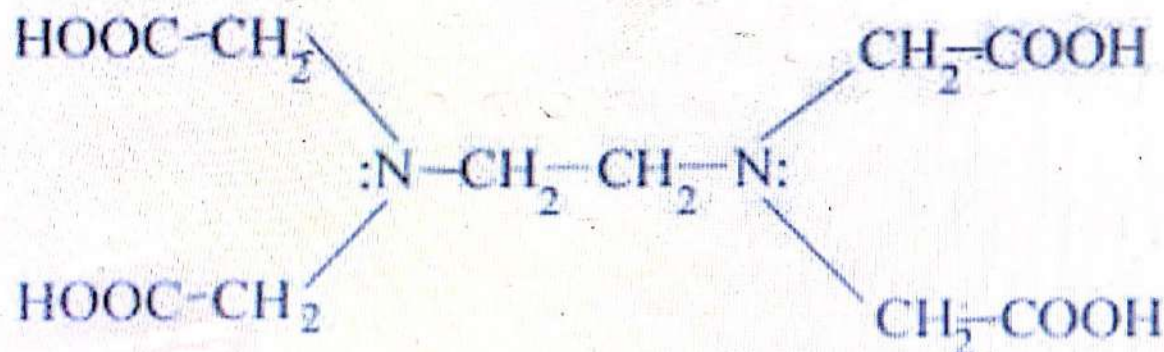
Complexometric Titrations:

- ❖ A complexometric titration is technique of volumetric analysis in which a **soluble, undissociated, stiochimetric complex is formed during the addition of titrant** to the sample solution.
- ❖ Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution.
- ❖ An indicator capable of producing an definite color change is usually used to detect the end-point of the titration.

EDTA Titrations:

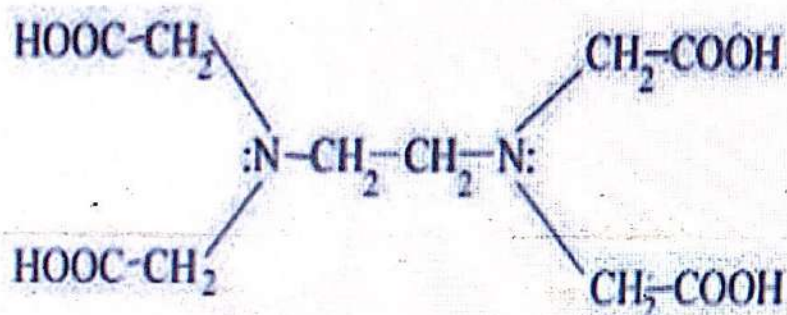
What is EDTA???

- ✓ **EDTA** is **E**thylene **D**iamine **T**etra **A**cetic acid.
- ✓ It has four carboxyl groups and two amine groups.



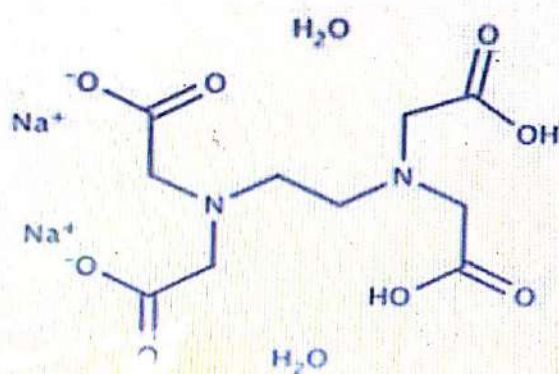
structure of EDTA

Commonly EDTA is represented in the acid form as H_4Y .

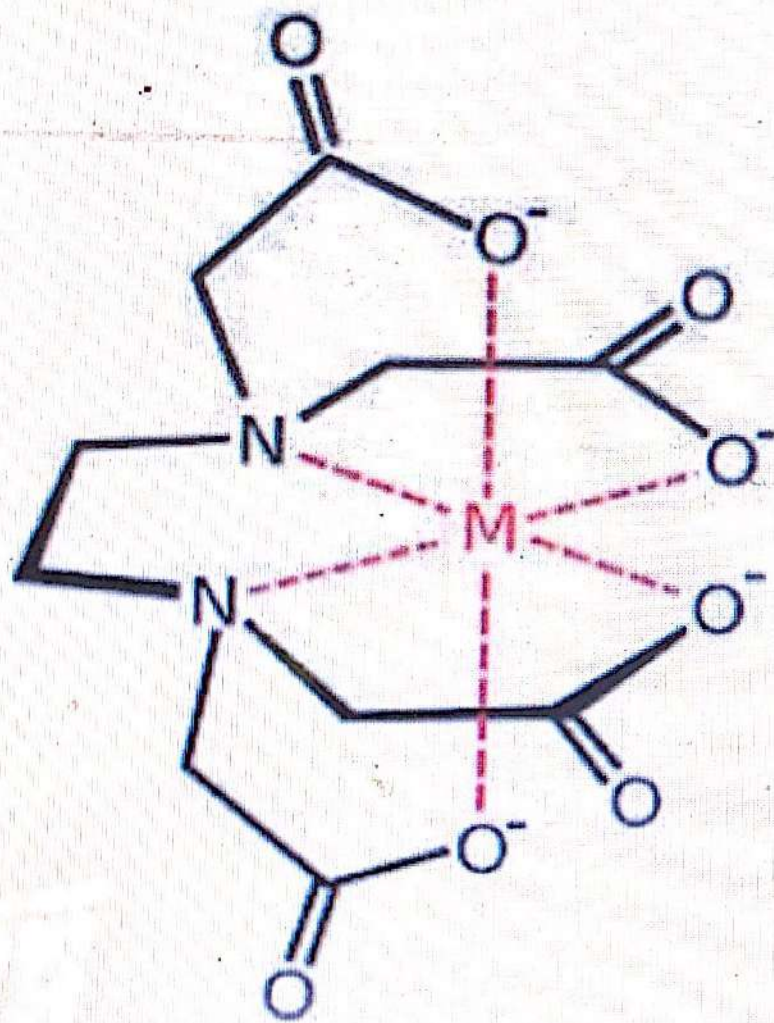


EDTA = H_4Y

Due to low solubility of acid form of EDTA in water, its disodium dihydrate EDTA salt i.e. $Na_2H_2Y \cdot 2H_2O$ is used



**disodium dihydrate EDTA
= $Na_2H_2Y \cdot 2H_2O$**



Metal-EDTA complex

Role of pH in EDTA titrations

- EDTA titrations are carried out in buffered solution of the metal ions to be estimated.
- The use of proper pH is important and is related to the stability constant of a metal-EDTA complex.
- E.g. Alkaline pH is required for the metals having low stability constant.
- Low Alkaline to mild acidic pH is required for the metals having high stability constant.
- The dissociation reactions of acid form EDTA, H_4Y are also pH dependant. pH is also an important criteria for the proper functioning of the indicator substance.

Thus it is very important to maintain the pH during the EDTA titrations

Advantages of EDTA as titrant:

1. EDTA **form stable complex** with various metal ions.
2. The complexation occurs in a **single step** and hence the titration of the metal **produce a sharp change** in the metal ion concentration at the equivalence point.
3. The **Metal-EDTA complexes are all water soluble** and hence all studies can be performed in aqueous media.
4. EDTA **forms 1:1 complex with all metal ions** irrespective of all charge on the metal ions. The stoichiometry is hence same for all metal ions. The reaction can be represented as:



Metallochromic indicator

- ✓ The metallochromic indicators are organic compounds which are capable of forming intensely coloured complex with EDTA.
- ✓ This metal –indicator complex is weaker than the Metal-EDTA complex and it has different colour than uncomplexed indicator.
- ✓ During the course of titration, the metal ion from metal –indicator complex is replaced to form Metal-EDTA complex.

Requirement for Metal ion indicator

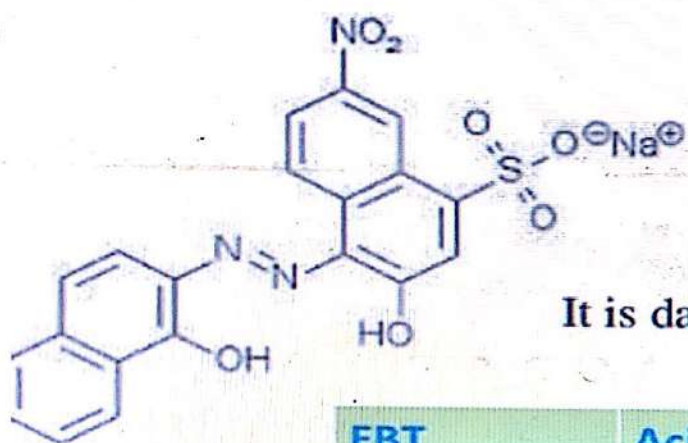
1. The **colour** must be sufficiently **intense**, so that a minimum amount of indicator can be used.

The **Metal-indicator complex** should possess **sufficient stability** to ensure a sharp colour change, however it **should be less stable than Metal-EDTA complex**.

The **change in equilibrium** from metal-indicator complex to the Metal-EDTA complex should be **sharp and rapid**.

Eriochrome Black T Mordant black II EDT

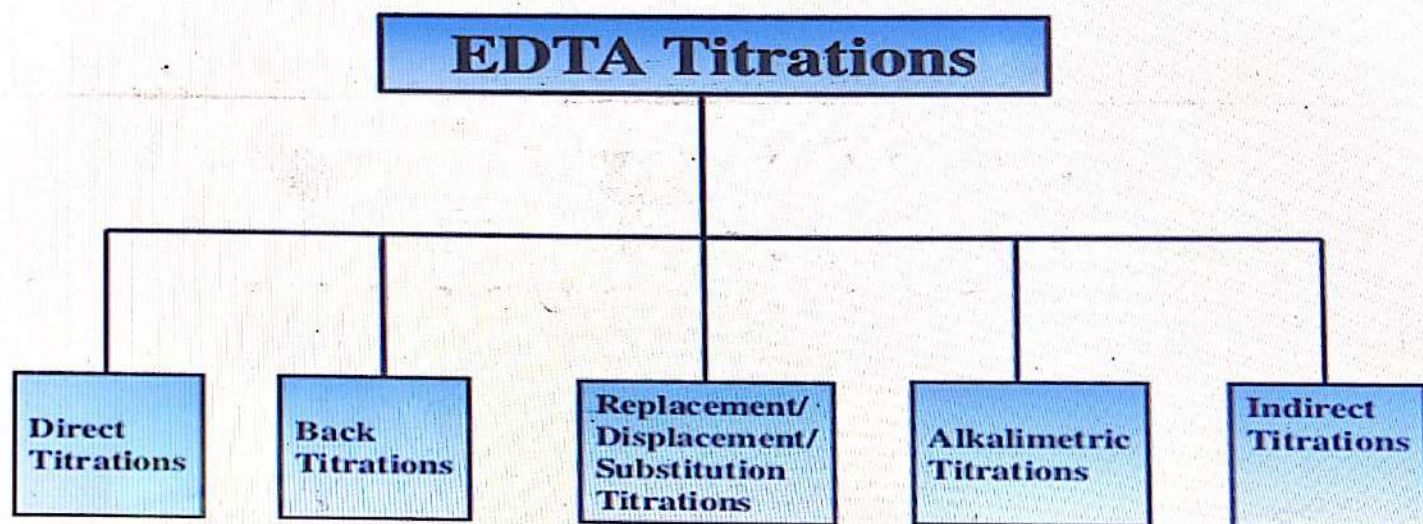
Chemically it is sodium salt of 1-(1-hydroxy-2 naphthylazo)-6 nitro-2-naphthol-4-sulphonic acid.



It is dark powder with a slight metallic luster

EBT	Acidic pH	H ₃ D	Black
EBT	pH- 6	H ₂ D ⁻	Red
EBT	pH- 7-11	HD ⁻²	Blue
EBT	pH > 12	D ⁻³	Orange

Types of EDTA Titrations:



DIRECT TITRATION:

In this type of titrations, the sample solution of metal ion, in the presence of a suitable buffer, is titrated against standard disodium EDTA solution.

M-EDTA complex must be more stable than M- Ind. complex in buffered medium.

The compound to be determined is water soluble.

The reaction between EDTA and metal must be rapid. If the reaction is slow it must be catalyzed.

M^{n+} should not be ppt. at the pH of titration. If M^{n+} is ppt. as MOH, auxiliary reagent must be added to prevent pptn. of M^{n+} .

Metal ion + Buffer + indicator Titrate with EDTA solution.

It is a simplest and most convenient method in which the standard solution of EDTA is slowly added to the metal ion solution till the end point is achieved.

The solution containing the metal ion is buffered to the desired pH and titrated directly with the standard EDTA solution.

A blank titration may be performed by omitting the sample to check the presence of impurities in reagents. Eg: Ca^{2+} , Mg^{2+} & Zn^{2+} ion are determined by direct titration with EDTA.

BACK TITRATION:

In a back titration an excess of EDTA is added to the metal ion solution

Excess EDTA is titrated with a known concentration of a second metal ion.

The second metal ion must form a weaker complex with EDTA than the analyte ion so the second metal does not displace the analyte ion from its complex with EDTA

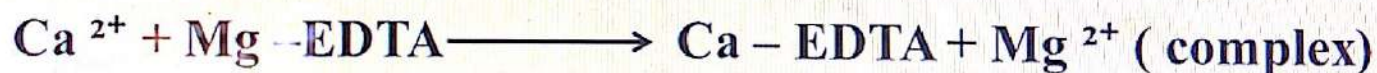
when the metal-EDTA complex forms too slowly, or when the metal precipitates in the absence of EDTA.

SUBSTITUTION & DISPLACEMENT TITRATION

This type of titration is used for metal ions which form EDTA complexes which are more stable than other metals such as Mg^{2+} and Ca^{2+} .

Eg: To the calcium salt solution, ammonia-ammonium buffer is added. To this, a standard known volume of Mg-EDTA solution is added.

In the reaction, stable Ca-EDTA complex is formed and Mg ions are liberated which may be titrated with a standard EDTA solution.



ALKALIMETRIC TITRATION

The solution of disodium EDTA is added to a solution containing metallic ions ,complexes are formed with liberation of hydrogen ions.

The Hydrogen ions are titrated against alkali solution (standard) using an acid indicator.

Indirect Titration

This method is used to determine the ions such as Halides, phosphates and sulphates that do not form complex with EDTA .

In the determination of sulphate ion, SO_4^{-2} ion solution is treated with excess of standard solution of Barium ion.

The formed precipitate of BaSO_4 is filtered off and unreacted Barium ions present in filtrate is titrated with EDTA.

In this way, we are able to indirectly determine the amount of sulphate ion present in the sample solution.

Aim 1 To determine the ^(strength) amount of $Mg(II)$ in
from the ~~the~~ given $MgSO_4$ solution using ~~an~~ EDTA ($\frac{M}{40}$)
as an intermediate & Erichrome black-T
as an indicator.

② Standardization of EDTA with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solⁿ
(Titratⁿ of std $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solⁿ with EDTA solⁿ)

EDTA

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ + 10 ml + buffer + EBT
Water (2 ml) (1-Pinch)

↓ Δ 30-35°C
Red to blue

③ Titratⁿ of given $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solⁿ with EDTA solⁿ.

Above procedure is repeated with unknown solⁿ.

Procedure:

- Firstly, the standard Magnesium sulphate soln. was prepared by weighing 0.246 g in the weighing bottle.
- Then 10 ml. from the standard soln. was pipetted out in a conical flask which had 10 ml. of distilled water, 2-3 ml. buffer (10% CH₃COOH) and a pinch of Eriochrome Black T.
- The pink soln. was then titrated with EDTA till the colour changed to blue.
- The whole process was repeated to obtain 3 concordant readings.
- Now the same titration was performed using the given sample of MgSO₄ · 7H₂O.
- And again the 3 concordant readings were obtained.