Complexometric Titration with EDTA

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Paper VI
Inorganic Chemistry
Department of Chemistry

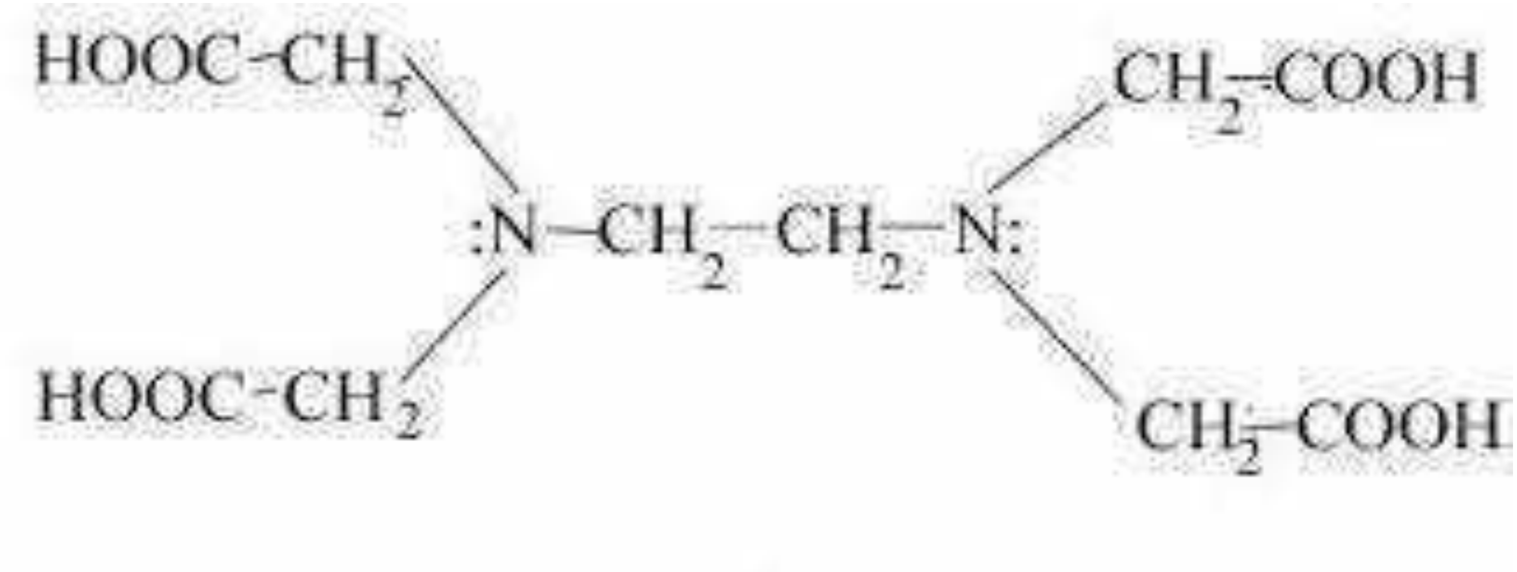
L.S COLLEGE MUZAFFARPUR
B. R. A. BIHAR UNIVERSITY
Dr. Priyanka

EDTA Titrations:

What is EDTA???

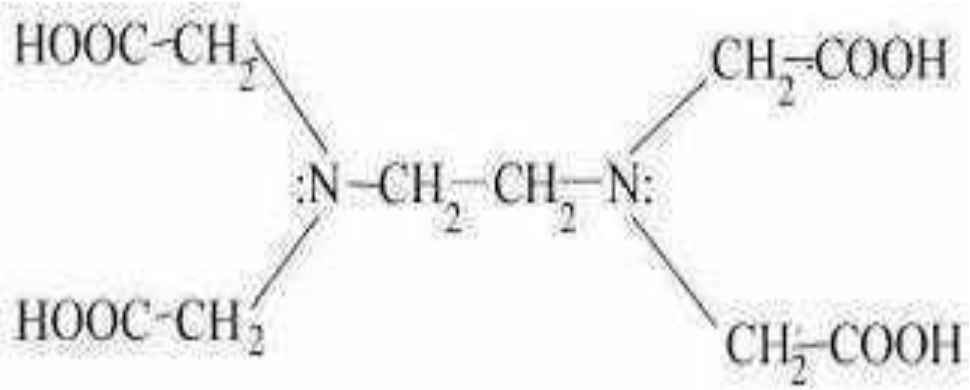
✓ EDTA is Ethylene Diamine Tetra Acetic acid.

✓It has four carboxyl groups and two amine groups.



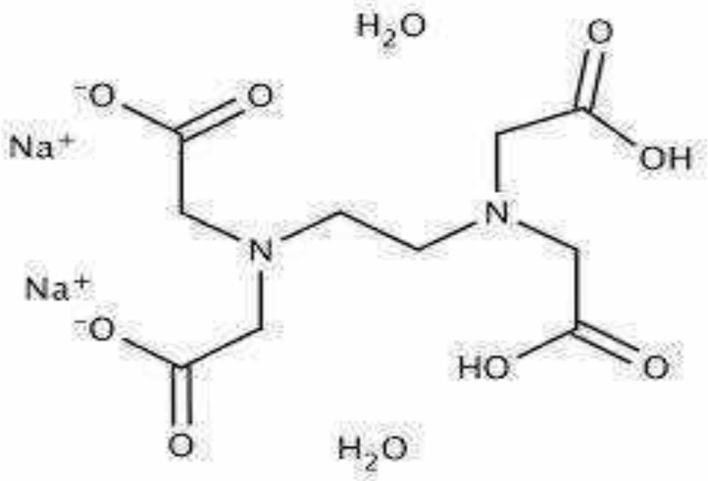
structure of EDTA

Commonly EDTA is represented in the acid form as H_4Y.



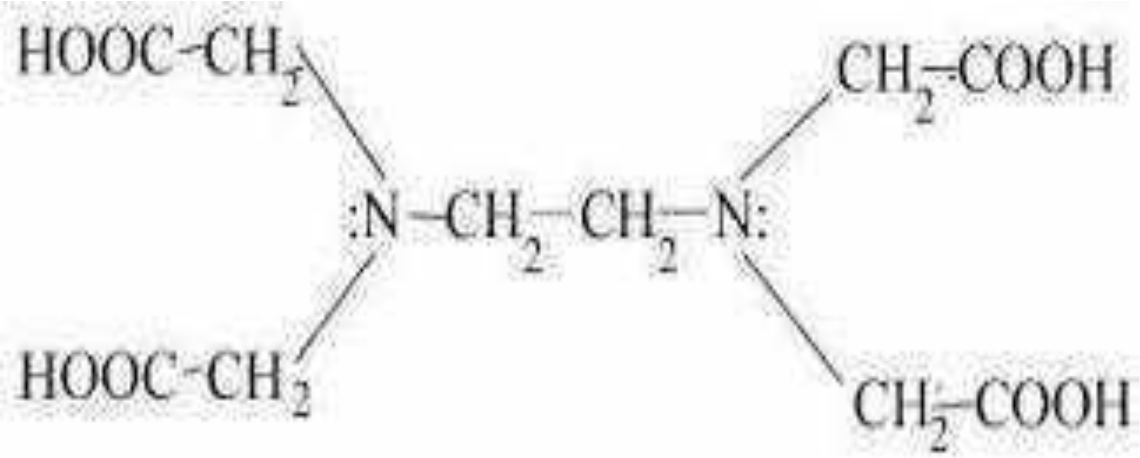
EDTA = H_4Y

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



disodium dihydrate EDTA = $Na_2H_2Y.2H_2O$

Different Forms of EDTA



$EDTA = H_4Y$

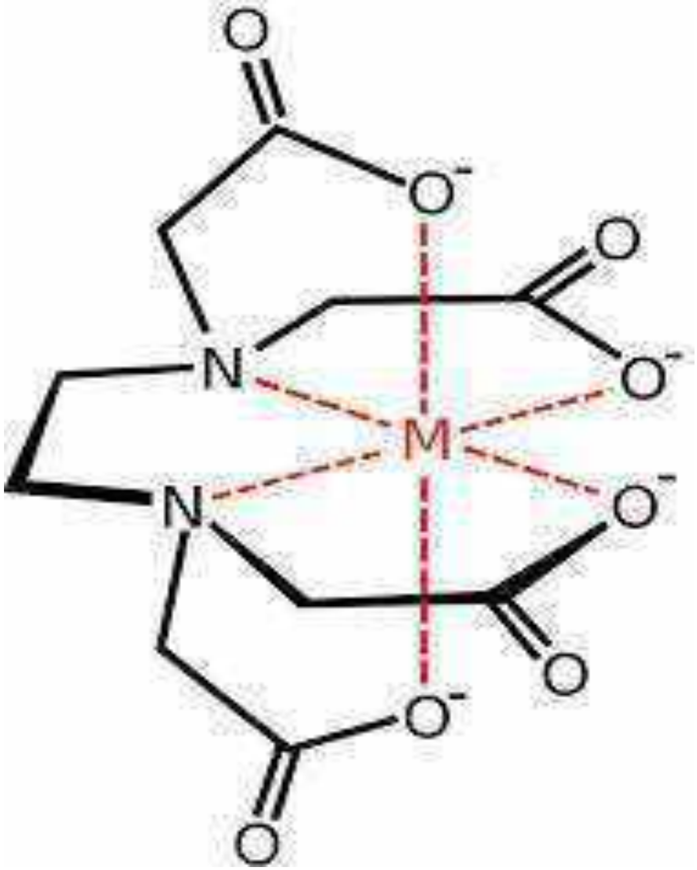
The fully protonated form H_4Y is only a major component in very acidic solutions (pH<3).

Throughout the pH range of 3 to 10 the species H_2Y^{2-} and H_3Y^{-} are predominant.

The fully unprotonated form Y^{4-} is dominant only in very basic solutions (pH>10).

EDTA has four carboxyl groups and two amine groups.

EDTA is polydenated ligand as it donate its six lone pairs of electrons for the formation of coordinate covalent bonds with metal cations to form Metal-EDTA complex.



Metal-EDTA complex

Stability of Metal-Ligand Complexes

The stability of complexes is influenced by a number of factors related to the ligand and metal ions.

1. Nature of the metal ion: Small ions with high charges lead to stronger complexes.

2. Nature of the ligand: The ligands forming chelates impart extra stability (chelon effect). For example the complex of nickel with a multidentate ligand is more stable than the one formed with ammonia.

3. Basicity of the ligand: Greater basicity of the ligand results in greater stability of the complex.

4. Size of chelate ring: The formation of five- or six - membered rings provides the maximum stability.

5. Number of metal chelate rings: The stability of the complex is directly related to the number of chelate rings formed between the ligand and metal ion. Greater the number of such rings, greater is the stability.

7. Steric effects: These also play an important role in the stability of the complexes.

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. ETDA **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:

$$M^{n+} + H_2Y^{-2} + H_2O \longrightarrow MY^{(n-4)} + 2H^3O^+$$

Limitations of EDTA as titrant:

1. Formation of insoluble hydroxides:

   Many ETDA titrations are carried out under alkaline pH which may lead to formation of insoluble hydroxides or basic salts that may compete with the complexation process .

2. Lack of selectivity:

   Since EDTA forms stable complexes with most of the metal ions, it lacks selectivity if it is used to estimate a single metal cations from a solution of mixture of metal ions.

Absolute formation constant

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. If fully unprotonated form of EDTA (Y^{-4}) is react with metal ion as follows:

$$\mathbf{M^{+n} + Y^{-4} \rightleftharpoons MY^{(n-4)+}}$$

Then absolute formation constant K_{MY} is given as,

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

K_{MY} is also referred as absolute stability constant. Higher the value of K_{MY}, higher is the stability of complex formed.

Metal Cation	K_{MY}	Log K_{MY}	
Mg^{2+}	4.9×10^{8}	8.69	**Group I Titrated in pH 8-11**
Ca^{2+}	5.0×10^{10}	10.70	
Sr^{2+}	4.3×10^{8}	8.63	
Ba^{2+}	5.8×10^{7}	7.76	
Mn^{2+}	6.2×10^{13}	13.79	**Group II Titrated in pH 4-8**
Fe^{2+}	2.1×10^{14}	14.33	
Co^{2+}	2.0×10^{16}	16.31	
Ni^{2+}	4.2×10^{18}	18.62	
Cu^{2+}	6.3×10^{18}	18.80	
Zn^{2+}	3.2×10^{16}	16.50	
Cd^{2+}	2.9×10^{16}	16.46	
Al^{3+}	1.3×10^{16}	16.13	
Pb^{2+}	1.1×10^{18}	18.04	
Hg^{3+}	6.3×10^{21}	21.80	**Group III Titrated in pH 1-4**
Fe^{3+}	1.3×10^{25}	25.1	
V^{3+}	7.9×10^{25}	25.9	
Th^{4+}	1.6×10^{23}	23.2	

Conditional formation constant

In absolute formation constant only fully unprotonated form of EDTA (Y^{-4}) is taken consideration. EDTA is tetra protonic acid. It is represented as H_4Y. The four different stages of dissociation of this tetra protonic acid can be represented as follows:

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad K_{a1} = \frac{[H^+][H_3Y^-]}{[H_4Y]}$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{-2} \qquad K_{a2} = \frac{[H^+][H_2Y^{-2}]}{[H_3Y^-]}$$

$$H_2Y^{-2} \rightleftharpoons H^+ + HY^{-3} \qquad K_{a3} = \frac{[H^+][HY^{-3}]}{[H_2Y^{-2}]}$$

$$HY^{-3} \rightleftharpoons H^+ + Y^{-4} \qquad K_{a4} = \frac{[H^+][Y^{-4}]}{[HY^{-3}]}$$

✓Due to such important role of pH in complex formation with EDTA , normally the solution of metal ions are buffered so that the pH will remain constant.

✓In this way the Conditional formation constant (K'_{MY}) can be estimated and it is possible to calculate and construct the titration curve from which it is possible to judge the feasibility of the Complexometric titration.

✓Instrumental methods used for end point detection in Complexometric titrations are : Spectrometric analysis, Ampheromtric analysis, Potentiometric analysis

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.
2. The colour contrast between the indicator and Metal-indicator complex should be readily observable.
3. The Metal-indicator complex should possess sufficient stability to ensure a sharp colour change, however it should be less stable than Metal-EDTA complex.
4. The change in equilibrium from metal-indicator complex to the Metal-EDTA complex should be sharp and rapid.

5. The colour reaction of the indicator should be selective.
6. The indicator must be very sensitive to metal ions so that the colour change occurs at near the equivalence point.
7. The indicator must be stable in the titration medium.
8. The indicator must be stable on storage also.
9. All the above requirements must be fulfilled in the pH range in which the proposed titration is to carried out.
10. It should be commercially available in adequate purity.

Theory of metal ion indicators

The reaction corresponding to use of a metal ion indicator in an EDTA titration can be represented as

$$\text{M-In} + \text{EDTA} \longrightarrow \text{M-EDTA} + \text{In}$$

This reaction will take place only if the M-EDTA complex is more stable than the M-In complex.

$$\text{M} + \text{In} \longrightarrow \text{M-In}$$

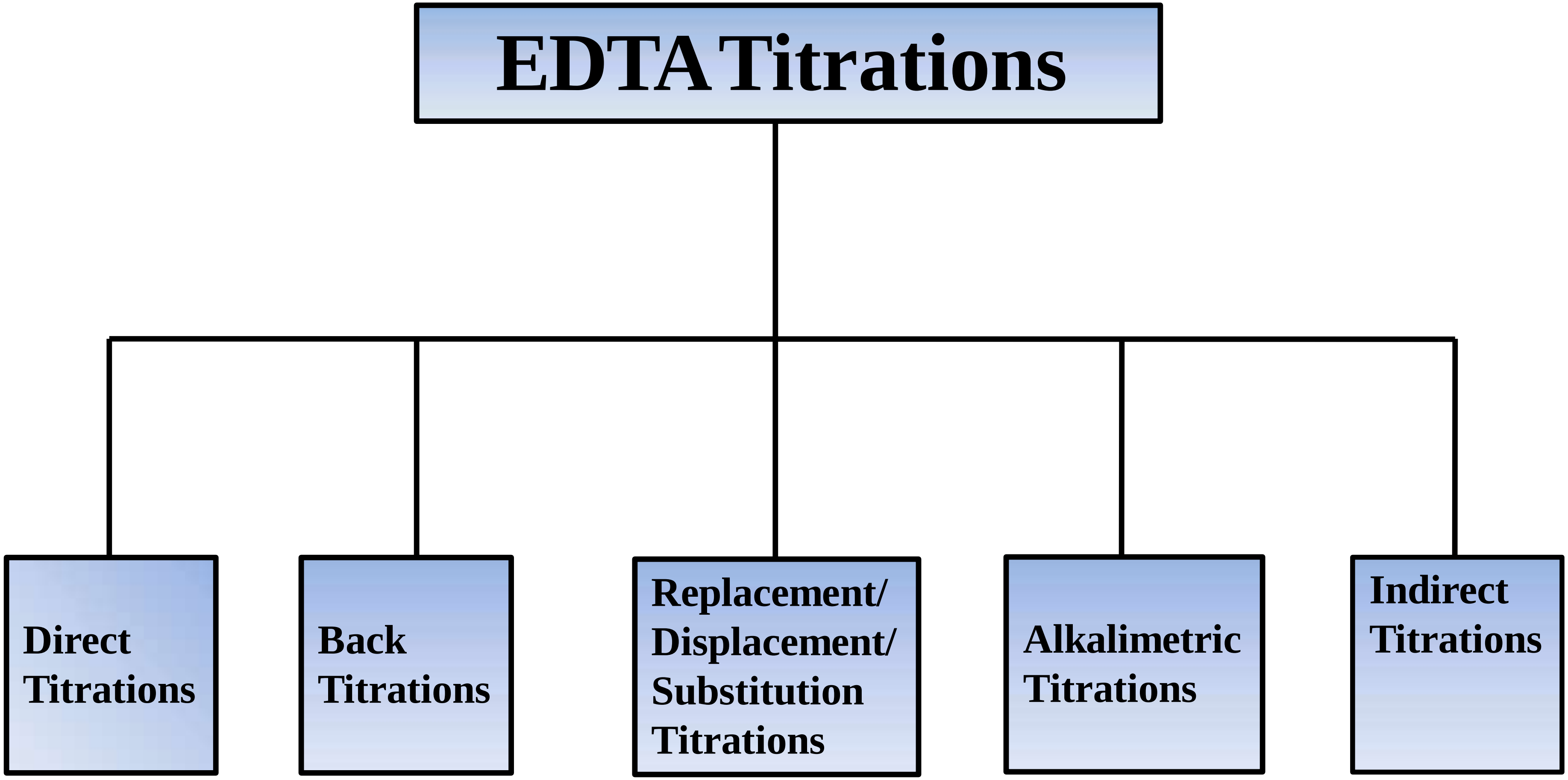
Stability of the Metal-Indicator complex K_{In}, is given by the equation

$$K_{In} = \frac{[\text{M-In}]}{[\text{M}]\ [\text{In}]}$$

Since, the indicator colour change also affected by the hydrogen ion concentration, so it is convenient to define the conditional indicator constant K’In which varies with pH.

For small the error, $K'_{In} > 10^4$ and the ratio of conditional formation constant of the metal-EDTA complex K'_{MY} to K'_{In} should be of the order 10^4 to provide a good end point.

Types of EDTA Titrations:



EDTA Titrations

- Direct Titrations
- Back Titrations
- Replacement/ Displacement/ Substitution Titrations
- Alkalimetric Titrations
- Indirect Titrations

Direct Titrations:

- ✓ This is a direct determination of a metal ion by adding standard EDTA titrant to the sample solution.

Metal ion + EDTA → [Metal-EDTA] complex

- ✓ The solution containing the metal ion is buffered to the desired pH and titrated directly with standard EDTA solution.
- ✓ Some auxiliary complexing agent such as tartarate can be added to prevent the prevent the precipitation of the hydroxide of metal ion.
- ✓ Cu^{+2}, Zn^{+2}, and Ni^{+2} can be determine by using direct titration method.

Back Titrations:

- ✓ This is method, an excess of standard EDTA is added to the sample solution of metal ion.
- ✓ The resulting solution will contain unreacted EDTA which is then back titrated with standard metal ion solution in the presence of indicator.

$ZnCl_2$, $ZnSO_4$, $MgCl_2$, $MgSO_4$ is used as standard metal ion solution.

- ✓ Al^{+3}, Co^{+2}, Pb^{+2}, Mn^{+2}, Hg^{+2}, and Ni^{+2} can be determine by using Back titration method

Replacement, Displacement or Substitutions Titrations:

- ✓ This is method, weak EDTA complex of another metal ion (M2) is added to the solution of metal ion (M1) to be determined.
- ✓ Mg-EDTA & Zn-EDTA are frequently used weak EDTA complex
- ✓ The weaker metal EDTA complex is replaced with strong metal EDTA complex.
- ✓ The equivalent amount of metal M2 freed from the weaker complex can be titrated with standard EDTA solution.
- ✓ This method is useful for the determination of Ca^{+2} ion.

Alkalimetric Titrations:

- ✓ This method, use the principle of liberation of free H^+ ions during the complexation.
- ✓ The reaction between metal ion and EDTA H_2Y^{-2} produce H^+.

$$\mathbf{M^{+n} + H_2Y^{-2} \longrightarrow MY^{(n-4)+} + 2H^+}$$

- ✓ The free H^+ ions is titrated with standard solution of alkali like NaOH by using suitable acid-base indicator.
- ✓ The H^+ ions can also be determined by instrumental method.

Indirect Titration:

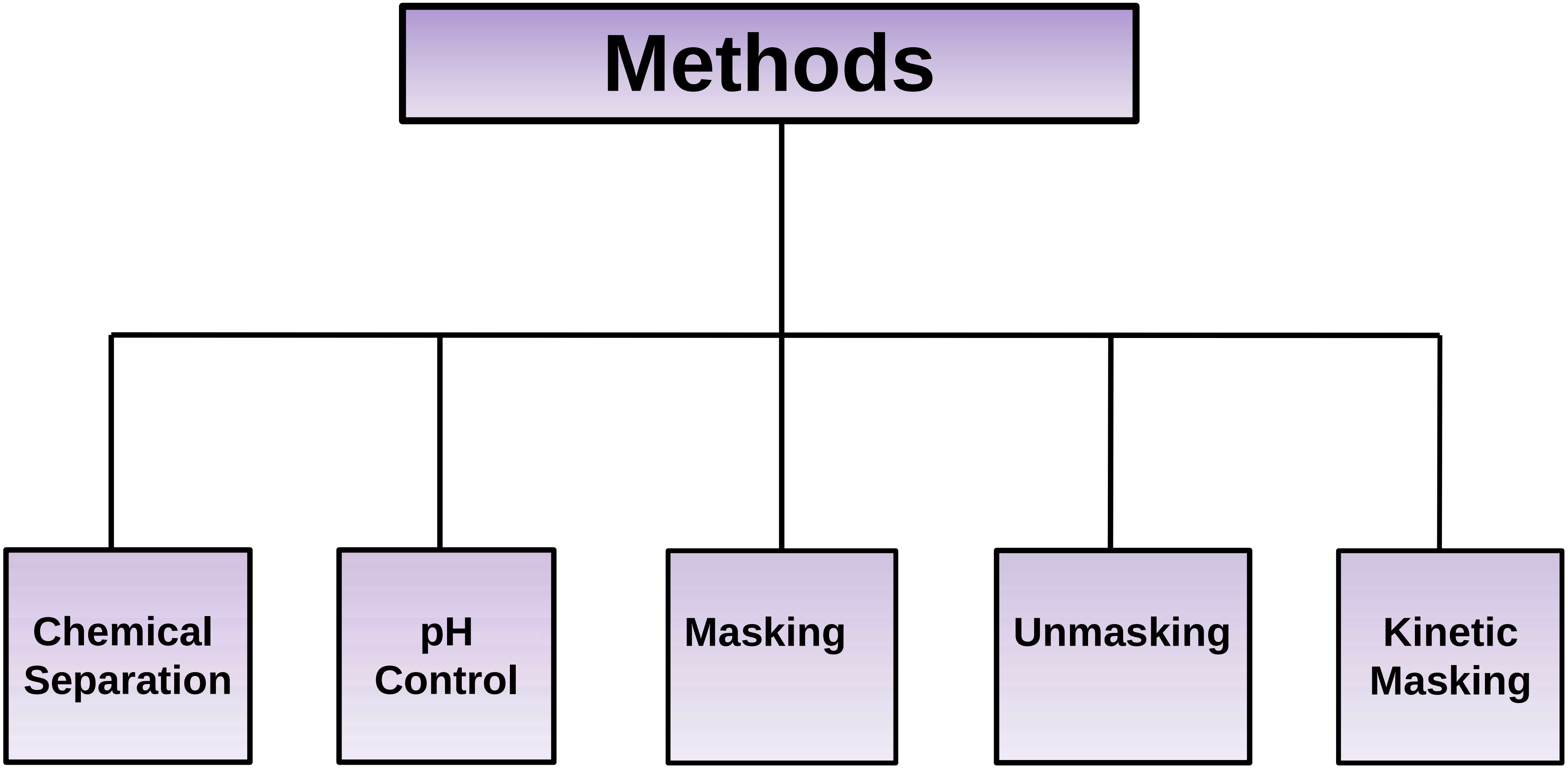
✓This method is used to determine the ions such as Halides, phospates, and sulphates that do not form complex with EDTA.

✓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.

Methods of increasing the selectivity of EDTA as Titrations



Methods

Chemical Separation

pH Control

Masking

Unmasking

Kinetic Masking

Chemical Separation

- In this technique, the selectivity is increases by separating the species from other components from the sample solution.

- The separated species is then dissolved in suitable solvents and then titrated against EDTA using indicator.

- Eg: Ca^{+2}, Mg^{+2}, Ni^{+2} and Cu^{+2} ions can be first separated as Ca-oxalate, Ni-DMG (Nickel bis(dimethylglyoximate)), Mg-ammonium phosphate and Cu-thiocyanide.

- These precipitate are then dissolved in separate suitable solvents and then titrate against EDTA using indicator.

Control of acidity of pH of the solution

- In this technique, the selectivity is increases by controlling the pH of the solution. That is depend on the hydrogen ion concentration.

- So by adjusting the pH of the sample solution containing several metal ions, it is possible to allow only a single species to react with EDTA.

- E.g.: Ca^{+2} can be determined in the presence of Mg^{+2} in strongly alkaline solution (pH < 10).

- Trivalent ions like Bi+3, Fe+3 can be selectively determined from the solution of bivalent metal ions in strongly acidic solution (pH ~ 2).

Use of masking and demasking agents:

Masking agents act either by precipitation or by formation of complexes more stable than the interfering ion-EDTA complex. Masking is a process in which substance is prevented to take part in the reaction without physical separation of it. he reagent used in masking is known as masking agent

a) Masking by Precipitation

b) Masking by Complex formation

a) Masking by Precipitation: Many heavy metals e.g.- Co, Cu and Pb, can be separated either in the form of insoluble sulphides using Sodium sulphide, or as insoluble complexes using thioacetamide.

These are filtered, decomposed and titrated with disodium EDTA.

Other common precipitating agents are :

-sulphate for Pb and Ba,

-oxalate for Ca and Pb,

- fluoride for Ca, Mg and Pb,

- ferrocyanide for Zn and Cu,

- 8-hydroxy quinoline for many heavy metals.

Eg. Thioglycerol ($CH^2SH.CHOH.CH^2OH$) is used to mask Cu by precipitation in the assay of lotions containing Cu and Zn.

4.Potassium cyanide reacts with silver, copper, mercury, iron, zinc, cadmium, cobalt and nickel ions to form complexes in alkaline solution

5.Potassium iodide is used to mask the mercury(II) ion as $(HgI^{4})^{2-}$ and is specific for mercury. It can be used in the assay of mercury(II) chloride.

6.Tiron (disodium catechol-3,5-disulphonate) will mask aluminium and titanium as colourless complexes. Iron forms highly coloured complex

7.Triethanolamine [N(CH2.CH2.OH)3] 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

Use of Demasking

In this technique, the one of the cation is first masked and remaining free cation is titrated with standard EDTA.

Then previously masked cation is damasked by using suitable reagent to get free cation. This free cation is then titrated by using standard EDTA.

Formaldehyde , chloral hydrate and methanol acetic acid mixture (3:1): use to demask cyanide complexes of cadmium and zinc

- eg. Formaldehyde is used to damasked Zn-CN complex

$$[Zn(CN)_4] + 4HCHO + 4H \longrightarrow Zn^{+2} + 4HOCH_2CN$$

(Hydroxy ACN)

- This free Zn+2 ion is then titrated by using standard EDTA.
- Thus it is possible to determine Zn in the presence of Ca.

Kinetic masking

- Some of the metal undergoes fast complexation some of undergoes slow complexation with EDTA .

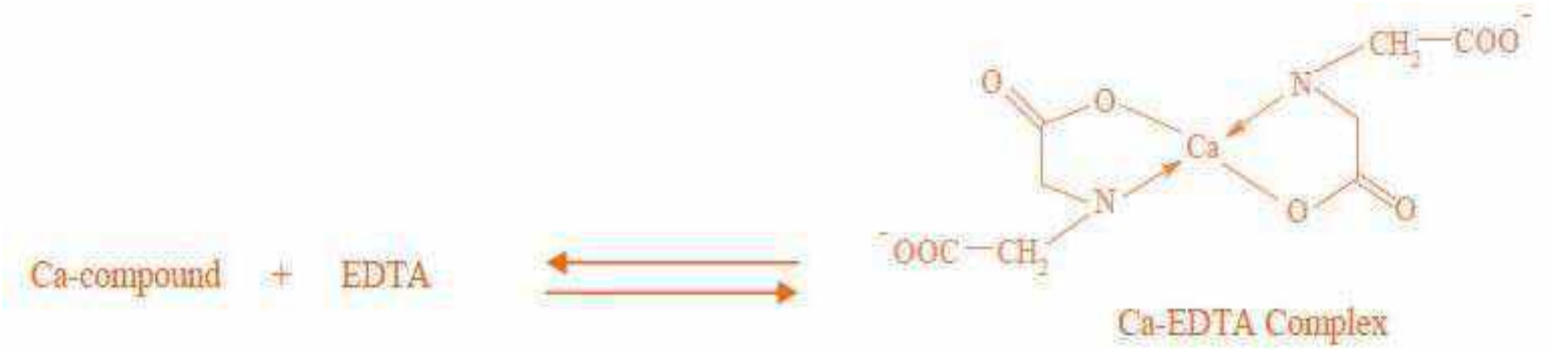
- Hence it is possible to titrate the metal ions which undergoes fast complexation with EDTA in the presence of those metal ions which undergoes slow complexation with EDTA .

- eg. Fe^{+3} can be easily estimated in the presence of Cr^{+3}, because Cr^{+3} reacts slowly with EDTA to form complex as compared to Fe^{+3}.

- Applications of Complexometric Titrations

Complexometric titrations have been employed with success for determination of various metals like Ca, Mg, Pb, Zn, Al, Fe, Mn, Cr etc. in different formulations that are official in I.P., and also for the determination of Hardness of water.

-Determination of Calcium in different formulations: Calcium can be determined in almost every formulation by EDTA-titrations. e.g.- Five membered heterocyclic rings are formed with EDTA, which are stain-free, and thus highly stable.



Assay of $CaCO^3$
Calcium Lactate tablets
Calcium Lactate injection
Calcium Gluconate
Calcium Gluconate injection
Calcium Gluconate tablet

-Determination of Magnesium: for the assay of Mg stearate and Mg sulphate

-Determination of Hardness of Water: Water hardness due to Ca and Mg is expressed as the amount of Ca and Mg ions in ppm. Actually, the hardness is due to both Ca and Mg salts but he two are determined together in the titration.

Titration curve for metal-EDTA titrations

In the Case of metal-EDTA titration, the EDTA is added to the buffered solution of metal and pM is calculated by using

$pM = -\log_{10} [M^{n+}]$ during the titration. The obtained pM values is plotted on Y-axis against the volume of EDTA solution added on x axis. This curve give the point of inflexion at the equivalence point. The curve of pM agaist volume of EDTA added is known as Titration curve of metal-EDTA titrations.

Example: Titration curve of Ca^{+2} with EDTA

Example: Titration curve of Ca^{+2} with EDTA

Absolute formation constant (K_{MY}) for CaY^{-2} is 5.0×10^{10} and α_4 at pH 10 is 0.35.

$\therefore$ $K'_{MY} = K_{MY} . \alpha_4 = 5.0 \times 10^{10} \times 0.35 = 1.8 \times 10^{10}$

Solution:

❖ Take 10 cm^3 of 0.01 M ca^{+2} solution buffered at pH 10 and titrate with 0.01 M EDTA solution.

❖ Calculate the pCa at different stages of titration such as,

1. At the start of the titration
2. After addition of 1.0 cm^3 of titrant EDTA
3. At the equivalence point
4. After addition of 11.0 cm^3 of titrant.

1. At start of Titration:

At start of Titration when no titrant EDTA is added to the solution, only Ca^{+2}, will be present in the solution.

The concentration of Ca^{+2} can be given as,

$$\therefore \quad [Ca^{+2}] = 0.01$$

$$pCa = -\log_{10}[Ca^{+2}] = -\log_{10}[0.01] = 2.0$$

$$\mathbf{pCa = 2.0}$$

2. At the addition of 1.0 cm^3 of titrant:

When 1.0 cm^3 of titrant EDTA is added to the solution, 1.0 cm^3 Ca^{+2} will react with EDTA and it will form complex. The 9.0 cm^3 of Ca^{+2} will remained unreacted in the solution and total volume of solution will become 11 cm^3.

The concentration of Ca^{+2} present in the solution can be given as,

$$[Ca^{+2}] = \frac{0.01 \times 9}{11} = 0.0082\ M$$

$$pCa = -\log_{10}[Ca^{+2}] = -\log_{10}[0.0082] = 2.09$$

$$\mathbf{pCa = 2.09}$$

3. At the equivalence point: (when 10 Cm^3 of EDTA is added)

When 10.0 cm^3 of titrant EDTA is added to the solution, 10.0 cm^3 Ca^{+2} will react with EDTA and it will form complex and total volume of solution will become 20 cm^3.

The concentration of Complex [CaY^{-2}] present in the solution can be given as,

$$[CaY^{-2}] = \frac{0.01 \times 10}{20} = 0.005\ M$$

At equivalence point, concentration of Ca^{+2} will be equal to the concentration of EDTA . As EDTA is present in its all form.

So the concentration of EDTA is given by C_Y

$$[Ca^{+2}] = C_Y$$

Conditional formation constant (K'_{MY}) for CaY^{-2} is $108 \times 10^{10,}$
Now Conditional formation constant (K'_{MY}) is

$$K'_{MY} = \frac{[CaY^{-2}]}{[Ca^{2+}].\ C_Y} = 1.8 \times 10^{10}$$

Since $[Ca^{+2}] = C_Y$

$$K'_{MY} = \frac{[CaY^{-2}]}{[Ca^{2+}].\ [Ca^{+2}]} = 1.8 \times 10^{10}$$

By substituting,

$$K'_{MY} = 1.8 \times 10^{10}$$

$$[CaY^{-2}] = 0.005$$

In the above equation and we can calculate the concentration of $[Ca^{2+}]$

$$\therefore \quad 1.8 \times 10^{10} = \frac{0.005}{[Ca^{2+}]^{2}}$$

$$\therefore \quad [Ca^{2+}] = \sqrt{\frac{0.005}{1.8 \times 10^{10}}}$$

$$[Ca^{2+}] = 5.2 \times 10^{-7}$$

$$pCa = -\log_{10}[Ca^{+2}] = -\log_{10}[5.2 \times 10^{-7}] = 6.28$$

$$\therefore \quad pCa = 6.28$$

4. After the addition of 11 Cm^3 of EDTA:

When 11.0 cm^3 of titrant EDTA is added to the solution, 10.0 cm^3 Ca^{+2} will react with EDTA and it will form complex and 1.0 cm^3 of EDTA will remain excess in the solution. Total volume of solution will become 21 cm^3.

The concentration of Complex $[CaY^{-2}]$ present in the solution can be given as,

$$[CaY^{-2}] = \frac{0.01 \text{ X } 10}{21} = 4.76 \text{ X } 10^{-3} \text{ M}$$

The 1.0 cm3 of EDTA is excess,

concentration of excess of EDTA present in the solution can be given as,

$$[\text{Excess of EDTA}] = \frac{0.01 \times 1}{21} = 4.76 \times 10^{-4}\ \text{M}$$

The concentration of EDTA in the solution given by C_Y

$$\therefore \quad C_Y = 4.76 \times 10^{-4}\ \text{M}$$

Conditional formation constant (K'_{MY}) for CaY^{-2} is $1.8 \times 10^{10,}$ Now Conditional formation constant (K'_{MY}) is

$$K'_{MY} = \frac{[CaY^{-2}]}{[Ca^{2+}].\ C_Y} = 1.8 \times 10^{10}$$

By substituting,

$$K'_{MY} = 1.8 \times 10^{10}$$

$$[CaY^{-2}] = 4.76 \times 10^{-3}$$

$$[C_Y] = 4.76 \times 10^{-4}\ M$$

In the above equation and we can calculate the concentration of $[Ca^{2+}]$

$$\therefore \quad 1.8 \text{ X } 10^{10} = \frac{4.76 \text{ X } 10^{-3}}{[Ca^{2+}] \text{ X } 4.76 \text{ X} 10^{-4}}$$

$$\therefore \quad [Ca^{2+}] = \frac{4.76 \text{ X } 10^{-3}}{1.8 \text{ X } 10^{10} \text{ X } 4.76 \text{ X} 10^{-4}}$$

$$[Ca^{2+}] = 5.55 \text{ X } 10^{-10}$$

$$pCa = -\log_{10} [Ca^{+2}] = -\log_{10} [5.55 \text{ X } 10^{-10}] = 9.26$$

$$\therefore \quad pCa = 9.26$$

Table of pCa Value

Volume in Cm^3 of 0.01 M EDTA added	pCa
0.0	2.0
1.0	2.09
5.0	2.48
10.0	6.28
11.0	9.26
12.0	9.56

When the pCa is plotted against volume of titrant added, it gives the Familiar S shaped titration curve with sharp increse in the curve in the value of pCa in the vicinity of the equivalence point.

Titration curve for Ca^{+2} - EDTA titrations