SHREE H. N. SHUKLA INSTITUTE OF PHARMACEUTICAL EDUCATION AND RESEARCH

B.PHRAM

(SEMESTER –I)

SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I

SUBJECT CODE: BP102TP

CHAPTER 3(b): COMPLEXOMETRIC TITRATION

Content

Complexometric titration: Classification, metal ion indicators, masking and demasking reagents, estimation of Magnesium sulphate, and calcium gluconate.

INTRODUCTION

Complexometric titration is important for metals and their salts, certain anions and indirectly some drugs.

Though many substances are used as titrant in complexation phenomenon, ethylene diamine tetra acetic acid disodium disodium salt, commonly known as EDTA, is most widely used.

Complexometric titrations are those reactions in which, simple metal ion is transformed into complex ion by addition of reagent which is known as ligand.

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.

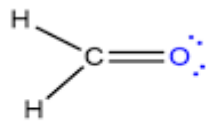
The complex formed is stable and water soluble.

THEORY OF COMPLEXOMETRIC TITRATION

Complex ion formation:

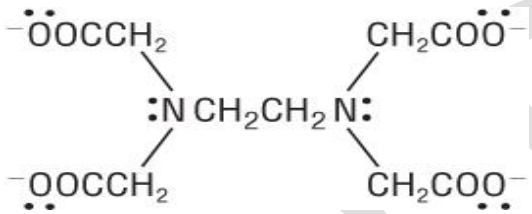
- A complexation reaction with a metal ion involves the replacement of the one or more of the coordinated solvent molecules by other nucleophilic groups. These groups are generally known as a ligand. Number of ligand that can attach to a central ion is known as coordination number (n).
- Ligands are those compounds which have some one or more lone pair of electron in outer shall of the any one atom of that compound.
- Replacement of water molecules by other ligand groups can occur until the complex is formed.
- Lone pair of electrons are useful to form a coordinated bond with the metal ion and thus formation of complex ion occurs. Thus, these types of legands having lone pair of electrons are also known as complexing agent.

Lone pair of electrons are referred to as a valence electrons that are not shared with another atom in a covalent bond and is sometimes called as unshared pair. Lone pairs are found in the outermost electron shell of atoms. e.g. HCHO Electrons in outermost shell



Formaldehyde
2 lone pairs on Oxygen

- Most widely used ligand: EDTA – multidentate
- Ethylene diamine tetra acetic acid- Disodium salt.



- EDTA is a Hexadentate. It have 6 pairs of electron which can form coordinated bond with metal ion.
- The ligand molecule usually possess oxygen, nitrogen or sulphur ion one or more number in their structure.
- Ligands may be classified on the bases of the number of point of attachment to the metal ion.

1. **Monodentate Ligannd**
2. **Bidentate Ligand**
3. **Multidentate Ligand**

Monodentate ligand: (Unidentate)

- The ligand is bound to the metal ion at only one point by the donation of a lone pair of electrons to the metal.
- Thus, we can say that only one atom of that ligand having a lone pair of electron. These types of ligands are known as monodentate ligand. For e.g. NH_3, Halide ions or the molecules H_2O.
- NH_3 is a unidentate ligand. It is capable of complexing with cupric ions (Cu^{+2}). The 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: $Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{+2}$

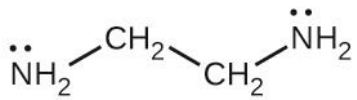
Step 4: $Cu(NH_3)_3^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_4^{+2}$

Considering the overall reaction:

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

Bidentate Ligand:

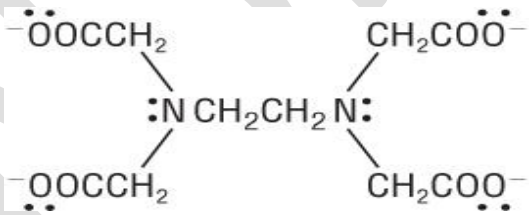
- When ligand molecules or ion has two atoms, each of which has a lone pair of electrons, then the molecule has two donor atoms, each of which has a lone pair of electrons, then the molecule has two donor atoms and it may be possible to form two coordinate bonds with the same metal ion, this is called a bidentate ligand.
- e.g. Ethylene diamine [Tris (ethylene diamine) cobalt (III) complex] – $[Co(en)_3]^{3+}$



- Here, two lone pair of electrons by two atom in one molecule

Multidentate ligand:

- Multidentate ligand contains more than two coordinating atoms per molecules.
- For e.g. 1,2- diaminoethane tetra acetic acid (EDTA). It has two donor hydrogen atoms and four donor oxygen atoms in the molecule, so it can be hexadentate.



It has been assumed that the complex species does not contain more than one metal ion, but under appropriate conditions it is possible to form a binuclear complex, i.e. one containing two metal ions, or even a polynuclear complex containing more than two metal ions.

Thus interaction between Zn^{+2} and Cl^- ions may result in the formation of binuclear complexes e.g. $[ZnCl_6]^{2-}$, in addition to simple species such as $ZnCl_3^-$ and $ZnCl_4^{2-}$.

Ethylene diamine tetra acetic acid (EDTA) disodium salt is very versatile complexing agent. The disodum salt is used in preparation of solution because of its greater water solubility. The important features of EDTA are:

1) Complexes formed are stable.
2) Complex formation is quantitative and instantaneous.
3) Complexes formed are water soluble.
4) Complexes formation occurs with most metals of periodic table in 1:1 ratio.

QUESTION - ANSWER

Sr. No.	Questions	Answer
1	Which titration method is used to analyse metals and their salts, certain anions?	**Complexometric**
2	Which type of samples are analysed by complexometric titration?	**Metal**
3	What is mostly used as titrant in complexometric titration?	**EDTA**
4	Full form of EDTA is	**Ethylene Diamine Tetra Acetic Acid**
5	Reagent which transform simple metal ion into complex ion in complexometric titration is known as	**Ligand**
6	In complexometric titration end point is indicated by formation of	**Coloured complex**
7	In which titration simple metal ion is transformed into complex ion?	**Complexometric**
8	In which titration ligand is used?	**Complexometric**
9	Nucleophilic group which replaces the one or more of the coordinated solvent molecules by the reaction with metal ion in the solution is known as	**Ligand**
10	Number of ligand that can attach to a central ion is known as	**Coordination number**
12	Coordination number is denoted by symbol	**n**
13	Compounds which have some one or more lone pair of electron in outer shall of the any one atom of that compound are known as	**Ligand**
14	Which type of bond are formed by lone pair of electrons of ligand with the metal ions?	**Coordinated bond**
15	Ligand form coordinated bond with metal ions by _____.	**Lone pair of elecctrons**
16	Ligands having lone pair of electrons which are responsible for complex formation with metal ion. Therefore ligands are known as	**Complexing agent**
17	A valence electrons that are not shared with another atom in a covalent bond is known as	**Lone pair of electrons**
18	The ligand is bound to the metal ion at only one point by the donation of a lone pair of electrons to the metal is known as	**Monodentate ligand**
19	If only one atom of ligand having a lone pair of electron is known as	**Monodentate ligand**
20	Give the example of monodentate (Unidentate) ligand	**NH_3**
21	When ligand molecules or ion has two atoms, each of which has a lone pair of electrons, this ligand is called	**Bidentate ligand**
22	When ligand molecules or ion having two lone pair of electrons which form two coordinate bonds with the same metal ion is known as	**Bidentate Ligand**

23	Give one example of bidentate ligand	**Ethylene diamine**
24	Ligand containing more than two coordinating atoms per molecules is known as	**Multidentate ligand**
25	Which ligand has two donor hydrogen atoms and four donor oxygen atoms in the molecule?	**EDTA**
26	Give the example of hexadentate or multidentate ligand?	**EDTA**
27	How many lone pair of electrons are there in EDTA?	**Six**
28	Ligand molecule having six lone pair of electron in outer most shell of their atoms is known as _____ ligand.	**Hexadentate**
29	The disodum salt of EDTA is used in preparation of solution in complexometric titration because of its	**Greater water solubility**
30	Complexes formed in complexometric titration should be stable. True or False?	**True**

- **Stability of Complexes:**

Symbolic representation of EDTA disodium salt. $Na_2H_2Y.\ H_2O$.
By ionization in water, it gives reactive species H_2Y^{2-}.
With metal ion, it gives following reaction:

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$

$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^{1-} + 2H^+$$

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

In this reaction acid is liberated. Hence, buffers are added to maintain pH of solution. pH has marked effect on stability of complex. Since reaction of M^{n+} (metal ion) with EDTA involves formation of acid. This reaction is reversible.

Due to liberation of acid alkaline range buffers are employed. If acid is not neutralized or removed, complex will break. Thus, complexes are stable in alkaline media and decompose in neutral or acidic media.

There is some exceptions are there.

- Some metals like aluminium, lead and mercury form complex under mild acidic condtition, while other like bismuth, iron and chromium are stable under distinct acidic condition.
- Monovalent ions like sodium, potassium and Silver form weak complexes. These metals have no stability in acidic media.

Stability of complex is governed by law of mass action. Complex formation is equilibrium process. Metal ion react with Ligand (L). Then,

$$M + nL = mLn$$

n= number of ligand molecule

Thus, stability constant K_s –

$$K_s = \frac{[ML_n]}{[M][L]^n}$$

As K_s increases, stability of complex is more. Concentration of unbound metal ion [M] and ligand [L] is less.

Formation of complex may be stepwise reaction. e.g. Cu^{+2} and ligand NH_3.

$$Cu^{+2} + NH_3 \rightleftharpoons Cu(NH_3)^{+2} \qquad K_1 = 2 \times 10^4$$

$$Cu(NH_3)^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{+2} \qquad K_2 = 4.7 \times 10^4$$

$$Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{+2} \qquad K_3 = 1.1 \times 10^4$$

$$Cu(NH_3)_3^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_4^{+2} \qquad K_4 = 2.0 \times 10^2$$

Overall stability constant $K_f = K_s = K_1 + K_2 + K_3 + K_4 = 2.1 \times 10^{13}$

QUESTION - ANSWER

Sr. No.	Questions	Answer
1	When EDTA disodium salt is reacted with metal ion, liberated compound is	**Acid**
2	What should be added to maintain pH in the solution of metal ion in complexometric titration?	**Buffer**
3	Why buffer is added in solution of metal ion during compexometric titration?	**To maintain pH**
4	Why pH should be maintained by adding buffer in metal ion solution during complexometric titration?	**Due to liberated acid**
5	Which type of buffer is added in metal ion solution to maintain pH?	**Alkaline buffer**
6	If solution remain acidic in the complexometric titration, what will the effect of it on complex formed?	**Complex will break**
7	Which media will be preferred mostly for stable complex in complexometric titration?	**Alkaline media**
8	In which medium complex will be decomposed?	**Neutral or Acidic media**
9	Which are the exceptions for metals which form complex under mild acidic condition?	**Aluminium, Lead and Mercury**
10	Which metal's complex are stable in acidic condition?	**Bismuth, Iron and Chromium**
11	Stability of complex is governed by law of	**Mass action**

DETECTION OF END POINT

In complexomteric titration, end point detection is done by following methods:

I. By using visual indicator (pM indicator)

II. Instrumental method detecting end point

I. VISUAL INDICATOR METHOD:

(a) Metallochromic /pM indicator

- These are dyes which show one colour in presence of metal ion. They do not show any colour or show different colour in absence of metal ion.
- Initially, indicator makes complex with metal ion and gives their unique colour. As the titration proceed further and metal ion titrated with EDTA, metal-indicator complex will break and metal-EDTA complex will form.
- Indicator will become free. Free indicator will give its original colour. Change in colour due to free indicator will help to detect end point.

$$M + In \longrightarrow MIn$$

$$M + EDTA \longrightarrow M\text{-}EDTA \text{ (More stable)}$$

Properties of metal ion indicator:

1) Metal ion indicator should be sufficient stable. It should not dissociate otherwise colour change will not be observed.
2) Metal indicator (MIn) complex should be less stable than metal-EDTA complex so that EDTA will take metal ion from MIn complex which will give sharp colour change by liberation of lidicator at the end point.
3) The colour reaction should be such that before end point the solution is strongly coloured.
4) The colour contrast between the free indicator and metal indicator complex is sufficient so that it can be readily observed.
5) The indicator must be sensitive to metal ion concentration.
6) The colour reaction is either specific or selective.
7) All the above requirements must be fulfilled with in the pH range at which the titration is performed.

The indicator act by following mechanism.

- When metal ion M reacts with indicator ion In. Complex MIn is formed. Stability constant of which is given by:

$$KIn = \frac{[MIn]}{[M][In]}$$

- During titration of metal ion M by titrant EDTA, metal-EDTA complex formation occurs. Stability of this complex is given by:

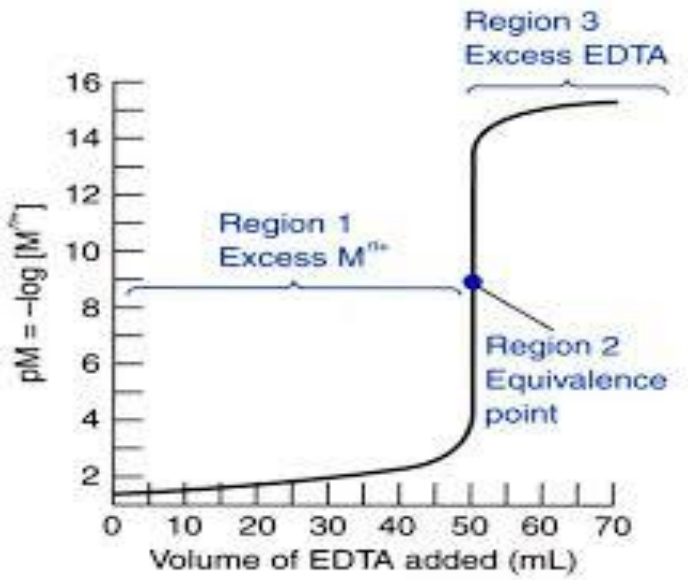
$$K_s = \frac{[M-EDTA]}{[M][EDTA]}$$

- Here, K_s is greater than KIn (K_s > KIn).

- Thus, before addition of EDTA in to metal ion solution, metal forms complex with indicator and after addition of EDTA, metal-indicator complex starts to dissociate and metal-EDTA complex starts to form due to more stability of that complex.

Graphical Representation:

- Graph of **Concentration of metal ion [M]** Vs **Concentration of sodium edetate** in appropriate buffered solution. It shows sharp break near equivalent point. The rate of change of metal ion concentration is initially slow and it becomes rapid at equivalence point.



- The colour of indicator and those of complexes vary with pH. This fact and the stability of metal indicator complex should be taken into consideration while deciding selection of indicators. e.g. Calcon, Catechol violet, Eriochrome Black T, Mordant Blue 3, Mordant Red 7, Murexide, Pyridylazonaphthol (PAN), Xylenol orange.

(b) pH indicator:

- Metal indicator complex formation results in liberation of acid, if formed.
- Complex is stable in acidic media. Completion reaction goes even in presence of acid then the quantitatively produced acid can be titrated with standard alkali. This reaction then can become acid-base titration and therefore pH indicators like methyl red and methyl orange can be used to detect end point.

II. INSRUMENTAL METHOD:

- **Potentiometric Titration:** In this method potassium electrode is commonly employed along with standard reference electrode.

  Platinum electrode measures redox potential associated with metal-EDTA complex. Potential of electrode is a function of ratio of two oxidation states of metal.

$$E = E_o \log e \frac{[Oxi]}{[Red]}$$

E = The potential of the electrode

E_o = The standard electrode potential (Reference)

[Oxi] = Concentration of ions in oxidation state

[Red] = Concentration of ions in reduced state

Another electrode used is a mercury electrode which measures the potential changes with replacement reaction.

QUESTION - ANSWER

Sr. No.	Questions	Answer
1	How many methods are there for end pint detection?	**Two**
2	Which methods are used to detect end point in complexometric titration?	**1. pM indicator** **2. Insttrumental**
3	The dyes which shows one colour in presence of metal ion or show different colour in absence of metal ion. These dyes are known as	**Metallochromic or pM indicator**
4	pM indicator shows colour in presence of	**Metal ion**
5	In complexometric titration, which complex form initially?	**Metal-indicator**
6	As the titration proceed, which complex will form when metal-indicator complex will break?	**Metal-EDTA**
7	As the titration proceed in complexometric titration, colour change is observed due to	**Free indicator**

8	Whose changed colour will help to detect end point in complexometric titration?	**Free indicator**
9	Metal ion indicator should dissociate to give colour change. It is true or false?	**False**
10	Which complex is more stable? Metal indicator (MIn) complex or metal-EDTA complex?	**Metal-EDTA complex**
11	Why EDTA will take metal ion from MIn complex?	**Metal-EDTA complex is more stable**
12	Give the formula for stability constant for metal indicator complex.	**KIn =** $\frac{[MIn]}{[M][In]}$
13	Give the formula for stability constant for metal-EDTA complex.	$K_s = \frac{[M-EDTA]}{[M][EDTA]}$
14	Which factor mainly affect complex formation in complexometric titration?	**Stability of complex**
15	Which factors should be taken into consideration while deciding selection of indicators?	**pH and stability**
16	Give two examples of pM indicator?	**Eriochrome Black T, Mordant Blue 3**
17	pH indictors are also used in detection of end point in complexometric titration. It is true or fslde?	**True**
18	Which electrodes are used in potentiometric titration for complexometric titration?	**Platinum electrode**
20	What is measured about metal-EDTA complex by platinum electrode for complexometric titration?	**Redoxpotential**
21	The redox potential of the complex is measured by the equaion	$E = E_o \log e \frac{[Oxi]}{[Red]}$

TYPES OF COMPLEXOMETRIC TITRATION

1) Direct Titration:

- In this method metal ion solution in a suitable buffer is titrated with EDTA using pM indicator. At the equivalent point colour change is observed.
- Important elements which could be detected by direct titration are: Cu, Mn, Ca, Ba, Al, Fe, Co etc.

Principle & Procedure: Example: Determination of Mg

Dissolve accurately weighed sample (75 mg) in 100 ml water

↓

Pipette out 50 ml of this solution

↓

Add 50 ml of water

↓

Add 5 ml of NH_3 Buffer solution

↓

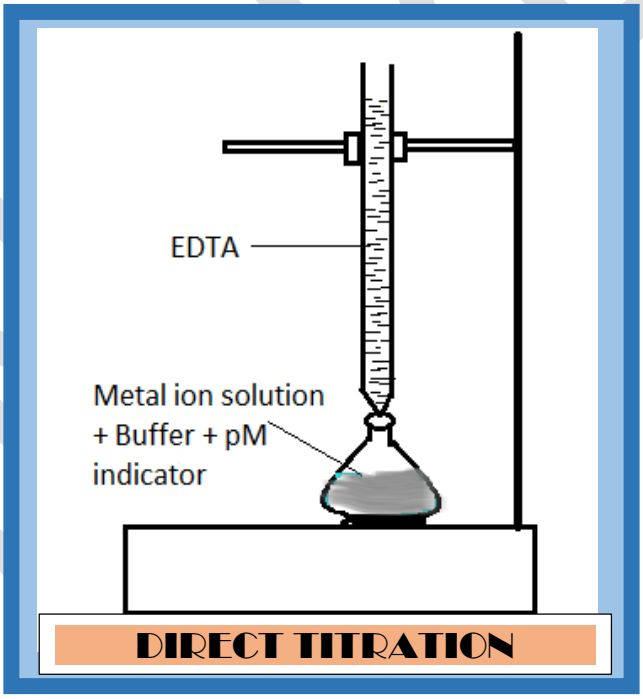
Add Eriochrome Black T (EBT) indicator.

↓

Titrate with EDTA

Colour change: Deep Blue in colour

1 ml of 0.5 M disodium EDTA $\cong$ 0.02432 gm of Mg



2) Back Titration:

- When direct titration is not possible because of-
  - Insolubility of substance
  - Instability of complex
  - Precipitation of metal hydroxide
- In above situation, Back titration method is adopted.

Procedure:

General Procedure:

To metal ion solution

↓

Excess EDTA solution

↓

Add suitable buffer solution (Heated for complete complex formation)

↓

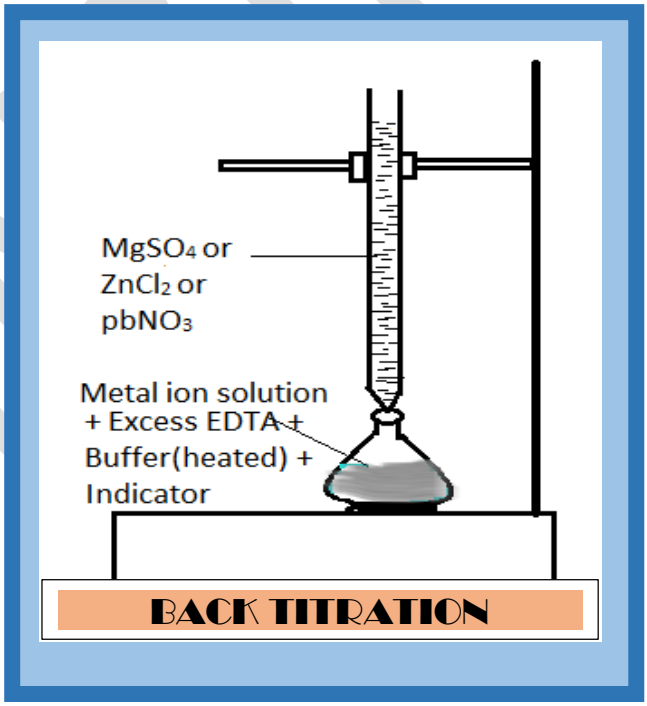
Titrate against $MgSO_4$ or $ZnCl_2$

Colour change: Deep Blue in colour

1 ml of 0.5 M disodium EDTA $\cong$ 0.02432 gm of Mg

Example: Manganese (Mn) or Aluminium (Al) Salt is back titrated.

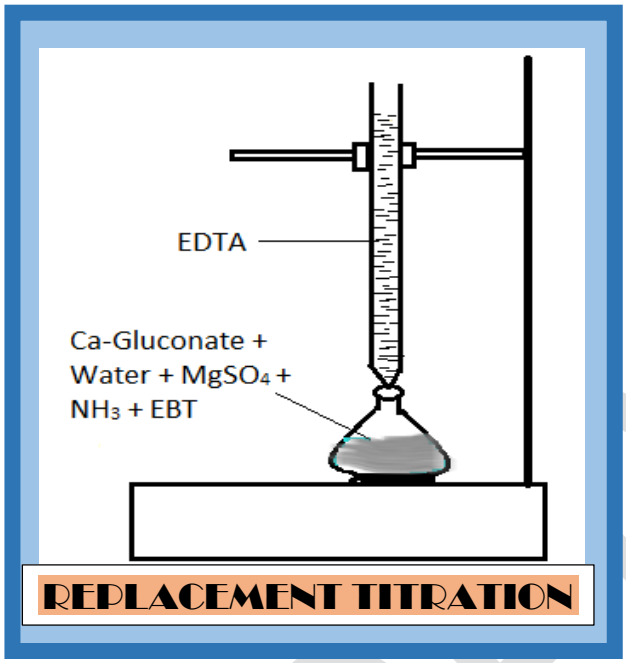
- To aluminium salt, 6 pH buffer is added followed by excess of EDTA solution. Excess of EDTA is back titrated with $pbNO_3$.



3) Replacement Titration:

- When direct or back titration is not possible, metal ions estimated by replacement technique.

- **Example:** Analysis of calcium salt (Ca^{+2}) is carried out by replacement method.



- In this method additional metal ion is added with analyte. This additional metal ion initially forms complex with indicator which will later break by analyte. Thus analyte replaces the metal ion from initially formed complex.
- Displaced metal ion is titrated with EDTA.
- In estimation of calcium gluconate, $MgSO_4$ is added with analyte solution. Initially Mg-In and Ca-In complex are formed. Here, Stability of Ca-In complex is more than Mg-In complex. Therefore, Mg-In complex more easily break by EDTA and form Mg-EDTA complex.
- But, Mg-EDTA complex is less stable than Ca-EDTA complex. Thus, calcium ion replaces the Mg^{+2} from the Mg-EDTA complex. Free Mg is then titrated with EDTA.

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

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

QUESTION - ANSWER

Sr. No.	Questions	Answer
1	If metal ion solution in a suitable buffer is directly titrated with EDTA using pM indicator. Which method is this?	**Direct titration**
2	Which elements could be detected by direct titration?	**Cu, Mn, Ca, Ba, Al, Fe, Co etc**
3	Determination of Magnesium can be done by _____ method of complexometric titration.	**Direct Titration**

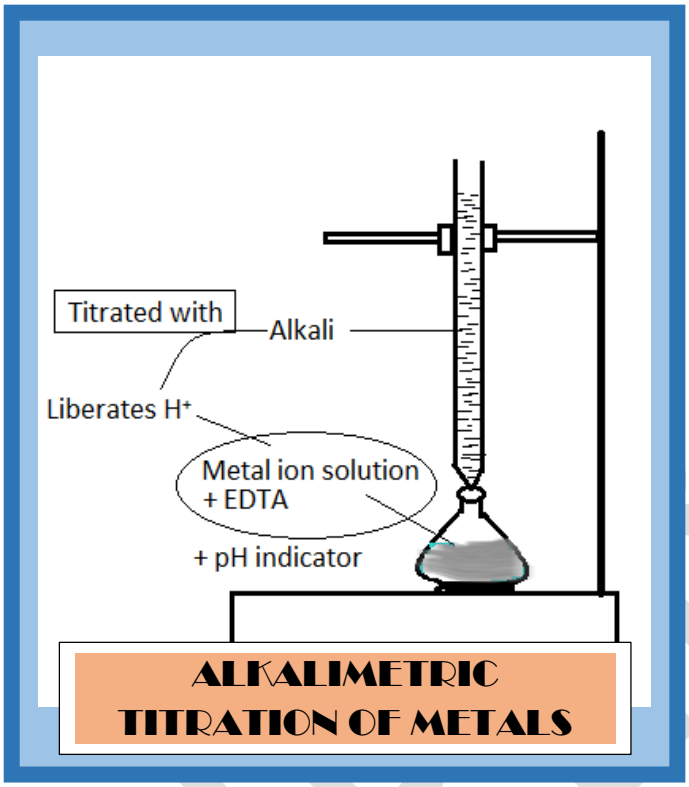
4	Which indicator is used in direct titration of complexometric titration?	**Eriochrome Black T**
5	Which colour change is observed at the end point of direct complexometric titration?	**Colorless to deep blue**
6	Sometimes, direct titration is not possible of metal ions. Why?	Insolubility of substance Instability of complex Precipitation of metal hydroxide
7	If complex is not sufficient stable in titration mixture, which type of titration method is carried out in case of metal ion?	**Back titration**
8	If substance is insoluble in titration mixture, which type of titration method is carried out in case of metal ion?	**Back titration**
9	If precipitation of metal hydroxide occurs in titration mixture, which type of titration method is carried out in case of metal ion?	**Back titration**
10	In back complexometric titration, reaction mixture is titrated against	**$MgSO_4$ or $ZnCl_2$**
11	Which sample is analysed by back method of complexometric titration?	**Manganese or Aluminium**
12	In back titration which solvent is added in excess in complexometric titration?	**EDTA**
13	In case of estimation of aluminum, excess EDTA is back titrated with	**$pbNO_3$**
14	Which method of complexometric titration is used for estimation of aluminium & magnesium?	**Back titration method**
15	When direct or back titration is not possible, metal ions estimated by	**Replacement Titration**
16	Which method is used for analysis of calcium ion?	**Replacement method**
17	Which ion is estimated by replacement method? Give one example.	**Calcium ion**
18	In which method of complexoetric titration, additional metal is added with analyte metal?	**Replacement method**
19	Which metal ion form complex with indicator from both additional and analyte metal ion?	**Additional metal ion**
20	Who will replace the metal ion from initially formed additional metal ion-indicator complex?	**Analyte metal ion**
21	Which metal ion is used with calcium as additional metal ion?	**Magnesium**

4) Alkalimetric titration of metals:

- Metal-EDTA complex formation undergoes ionization and liberates proton (H^+). Proton from disodium EDTA are displaced by heavy metal. Liberated acid is titrated with disodium alkali.

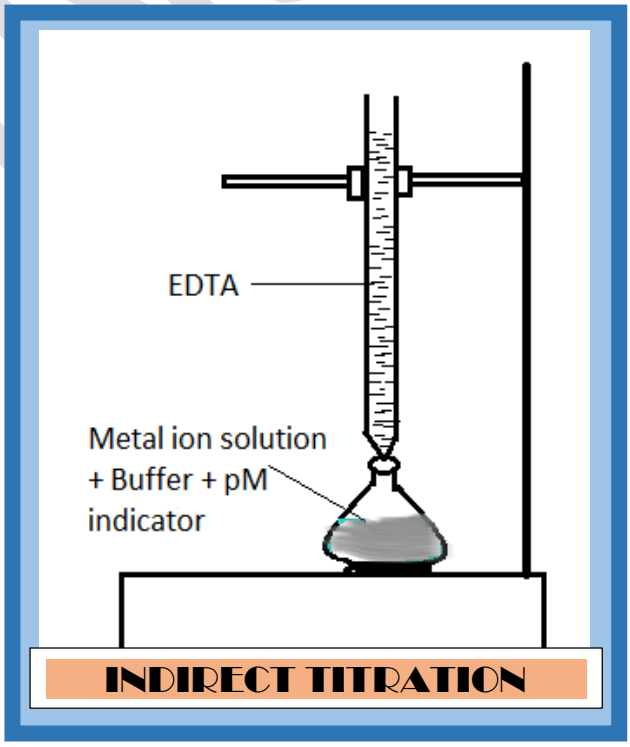
- Here, end point can be detected by visual pH indicator or potentiometric method.

- If metal ion + Iodide – Iodate mixture is added to the solution and EDTA is also added, it will liberate iodine (I_2). This liberated I_2 is then titrated with thiosulphate using starch indicator.



5) Indirect method of titration

- This method is not used for metal ion.
- Organic substances can be analysed by indirect method. For e.g. Codeine, Chlorpromazine.
- In this method, organic substance is precipitated by addition of excess metal ion solution. Excess of metal ion solution is back titrated with EDTA.



6) Complexometric titration by masking and demasking agent

- This method is used when two or more metals are present in the same solution.
- There are two ways for detection of single metal ion from mixture
  1. This can be done either by selection of suitable pH at which one metal forms complex without involvement of other metal ion.
  2. Another way is by using suitable masking agent.
- EDTA is a very unselective reagent because it complexes with numerous cations so, it is not selective for solution containing mixture of metals. The following procedure will help to increase the selectivity.
  1. Use of masking and demasking agent
  2. pH control
  3. Use of selective metal indicator.

Masking Agent:

- It is auxiliary chelating agent or complexing agent that will form complex more strongly with the metal than the titrant under the condition of titration.

e.g. Triethanolamine is a masking agent for aluminium and iron.
Triglycerol for copper
Potassium cyanide for heavy metals
Ammonium fluoride for iron and aluminium.

- Masking agent act by masking one of the metal ion from the mixture, thus estimation of another metal become easy because masked metal cannot interfere in estimation of another metal present in mixture.
- Masking is done by one of the following two mechanisms.
  1. Masked by precipitation
  2. Masked by complexation
- Masked metal by precipitation are filtered, decomposed and then titrated with disodium EDTA.

Masking Agent act by Precipitation

Sr. No.	Masking agent	Metal masked
1	Sodium sulphide	Co, Cu, Pb
2	Sulphate	Pb, Ba
3	Oxalate	Ca, Pb
4	Fluoride	Ca, Mg, Pb
5	Ferrocyanide	Zn, Cu

6	Thioglycerol	Cu
7	Dimercaprol	Hg, Cd, Zn, Ar, Pb, Bi

Masking Agent act by Complex formation

Sr. No.	Masking agent	Metal masked
1	Ammonium Fluoride	Al, Fe, Ti
2	Ascorbic acid	Fe (III)
3	Dimercaprol	Ni
4	Potassium cyanide	Ag, Co, Hg, Fe, Zn, Cd, Co, Ni
5	Potassium iodide	Hg(II)
6	Tiron	Al, Ti
7	Triethanolamine	Al, Fe(III), Mn

Demasking Agent:

- They are defined as the agents which reverse the process of masking.
- It is the substance which release the masked metal ion. Example: The cyanide complex of Zinc and Cadmium can be demasked by formaldehyde (HCHO).
- Demasked agent now able to enter in particular reaction.

$$[Zn(CN)_4]^{2-} + 4H^+ + 4\,HCHO \longrightarrow Zn^{2+} + 4\,HO.CH_2 + CN$$

(Masked complex) (Demasked)

- Thus masking and then selective demasking permits successive titration of many metals.

E.g. Cu, Cd, and Ca from solution containing can be determined selectively by use of masking and demasking agent. Cu and Cd masked by cyanide ion, not Ca, determine separated Ca with disodium EDTA. Cd demasked from cyanide by formaldehyde, free Cd determine separated Ca with disodium EDTA.

QUESTION - ANSWER

Sr. No.	Questions	Answer
1	Which type of indicator is used to detect end point in alkalimetric type of complexometric titration?	**pH indicator**
2	When Metal-EDTA complex formation undergoes ionization and liberates proton, titration of that liberated acid is done with	**Alkali**
3	Dissociation of which complex is responsible for acid liberation in alkalimetric type of comlexometric titration?	**Metal-EDTA**

4	Which titrant is used when mixture of metal ion and Iodide-Iodate is added to the solution in complexometric titration?	**Sodium thiosulphate**
5	Which indicator is used when mixture of metal ion and Iodide-Iodate is added to the solution in complexometric titration?	**Starch**
6	Which substances can be analysed by indirect method of complexometric titration?	**Organic substances**
7	Organic substances can be analysed by _____ method of complexometric titration.	**Indirect**
8	Give the example of substance which can be analysed by indirect method.	**Codeine, Chlorpromazine**
9	In indirect method of complexometric titration, _____ is precipitated by addition of excess metal ion solution.	**Organic substance**
10	When complexometric titration by masking and demasking agent is used?	**When 2 or more metals are present**
11	Which method of detection is used when two or more metals are present?	**Titration by Masking/Demasking agent**
12	How many ways are there for detection of single metal ion from mixture?	**2**
13	If suitable masking agent is not available for detection of single metal ion from mixture, what will be another option?	**Selection of suitable pH**
14	Auxiliary chelating agent or complexing agent that will form complex more strongly with the metal than the titrant under the condition of titration is known as	**Masking agent**
15	Masking agent is _____or_____ agent that will form complex more strongly with the metal than the titrant under the condition of titration.	**Auxiliary chelating agent or Complexing agent**
16	Which compound is used as a masking agent for aluminium and iron?	**Triethanolamine**
17	Which compound is used as a masking agent for copper?	**Triglycerol**
18	Which compound is used as a masking agent for heavy metals?	**Potassium cyanide**
19	Which metal is masked by Triglycerol?	**Copper**
20	Which metal is masked by Triethanolamine?	**Aluminium & Iron**
21	Which metals are masked by Potassium cyanide?	**Heavy metals**
22	How many mechanisms are involved in masking of any metal ion?	**2**
23	Which mechanisms are involved in masking of any metal ion by masking agent?	**Precipitation or Complexation**

24	The agents which reverse the process of masking are known as	**Damasking agent**
25	Which demasking agent is used to damask cyanide complex of Zinc and Cadmium?	Formaldehyde (HCHO)
26	Formaldehyde is used for damasking of	**Cyanide complex of Zinc and Cadmium**

ESTIMATION OF MAGNESIUM SULPHATE

Dissolve accurately weighed sample (75 mg) of Mg in water 100 ml.

↓

Pipette out 50 ml of this solution in titration flask, add 50 ml of water.

↓

5 ml of NH buffer solution and a few drops of Eriochrome black T as indicator.

↓

Titrate it with EDTA until the solution is deep blue in colour.

Factor: 1 ml of M/20 Disodium EDTA = 0.02432 g of Mg

ESTIMATION OF CALCIUM GLUCONATE

Principle:

- It is complexometric titration which involves replacement of Mg^{2+} ions from its [Mg-In] complex. Indicator do not give distinct colour change at the end point with ca-gluconate. Therefore a known volume of 0.05 M $MgSO_4$ solution is added.
- Initially when calcium on and magnesium ions are present in solution and when indicator is added. It forms complex with Mg as [Mg-IN] is stronger than [Ca-In] complex and impact pink colour to solution.
- When titration commences added EDTA forms complex with calcium ions as [Ca-EDTA] is stronger than [Mg-EDTA] complex, when all the Ca^{+2} ions are complexes then free Mg^{+2} forms complex with EDTA and end point reached then [Mg-In] complex breaks liberating free Mg^{+2} and In^{-} which forms complex with EDTA.

Procedure:

Weight accurately about 0.5 gm calcium gluconate

↓

Dissolve it in 50 ml warm water and cool it.

↓

Add 5 ml 0.05 M $MgSO_4$ (x M) and 10 ml ammonia solution.

↓

Titrate it against 0.05 M EDTA solution using EBT as an indicator.

QUESTION - ANSWER

Sr. No.	Questions	Answer
1	Which indicator is used in estimation of magnesium sulphate?	**Eriochrome black T**
2	What is added as a buffer in estimation of magnesium sulphate?	**NH_3**
3	Which colour will be observed at the end point in estimation of magnesium sulphate?	**Deep blue**
4	Which complex is formed first in estimation of calcium gluconate from the following? 1. Mg-In 2. Ca-In	**Mg-In**
5	Why Mg-In complex is formed first instead of Ca-In complex?	**Mg-In is More stronger**
6	As titration of calcium gluconate proceed, which complex will form from?	**Ca-EDTA**
7	Which ion will be replaced by Ca^{+2} in estimation of calcium gluconate?	**Mg^{+2}**
8	Which complex will break to give Mg^{+2} ion in estimation of calcium gluconate?	**Mg-In**