UNIT-3

Precipitation Titration

◪ Precipitation titration :-

Formation of precipitate with the help of precipitating agent in the titration is called as precipitation titration.

Example $AgNO_3 + NaCl \longrightarrow \underset{\text{(White ppt)}}{AgCl} + NaNO_3$

◪ Argentometric titration :-

When silver is involved in the titration, this titration is known as argentometric titration.

Four types of argentometric titration are seen. They are listed as following —

A. Mohr's method

B. Volhard's method
and
Modified Volhard's method

C. Fajan's method

D. Gay lussac method

A. Mohr's method :-

In this method identification of halide was given by scientist Mohr in 1856.

Principle :

This method involves the titration of $AgNO_3$ with a halide Solution ~~using~~ in the presence of potassium chromate indicator. End point is detected by conversion of reaction mixture into brick red colour.

$$AgNO_3 + X\ (Cl, Br, I) \xrightarrow{K_2CrO_4} AgX \text{ (White ppt)}$$

End point — brick red colour

Procedure :

Preparation of Standard Solution of Silver nitrate :

0.1 N $AgNO_3$ is prepared by dissolving 4.248 gm (AR) into distilled water and make the ~~solution~~ volume to 250 ml

↓

$AgNO_3$ dried in oven for 2 hours

↓

protect from light
Kept in amber coloured
bottle

Standardization of Silver Nitrate :

Take $AgNO_3$ in burette and in the conical flask add

Nacl (0.14 gm)
+
dried at 110°c for 2 hours
+
5ml H_2O
+
5 ml Acetic acid (CH_3COOH)
+
50 ml methanol (Ethanol)
+
0.15 ml eosin solution

then titrated it with $AgNO_3$ Solution.

Determination of Strength of Halide Solution:

Solution of $AgNO_3$ taken in burette

25 ml of unknown is taken in conical flask

+

1 ml of Potassium Chromate (Indicator)

Add $AgNO_3$ from burette to the conical flask untill brick red colour is formed. As stable colour is formed stop the titration. This is the end point of titration. Record the burette reading and calculate the quantity of halide solutions.

Theory of Mohr's method:

$$AgNO_3 + Cl^- \longrightarrow \underset{\text{(white ppt)}}{AgCl} + NO_3^-$$

$$2AgNO_3 + CrO_4^{2-} \longrightarrow \underset{\text{(Brick red ppt)}}{Ag_2CrO_4}$$

precipitate of AgCl is stable than precipitate of Ag_2CrO_4 because solubility of $AgCl < Ag_2CrO_4$.

When all Cl^- are used up then $AgNO_3$ react with

CrO_4^{2-} and form Ag_2CrO_4 (Brick red colour).

This is the end point of titration.

B. Volhard's method:

This method was given by volhard's in 1874.

This method was used both for detection of x(halide) and Ag^+ ions.

Principle:

A particular no of halide will react with $AgNO_3$ and excess of Ag^+ ions are back titrated with ammonium thiocyanate or potassium thiocyanate in the presence of nitric acid and ferric indicator. End point is detected by conversion of reaction mixture into reddish brown colour.

$$AgNO_3 + X\ (Cl, Br, I) \longrightarrow AgCl$$

$$Ag + \underset{\text{thiocyanate}}{SCN} \xrightarrow[\text{Ferric indicator}]{\text{Nitric acid}} \underset{\text{(Silver thiocyanate)}}{AgSCN}$$

End point — reddish brown colour

Procedure:

preparation of Standard Solution of Silver nitrate:

0.1 N $AgNO_3$ is prepared by dissolving 4.248 gm (AR) into distilled water and make the volume to 250 ml.

↓

$AgNO_3$ dried in oven for 2 hours

↓

protect from light
Kept in amber coloured bottle

Standardization of Silver Nitrate:

Take $AgNO_3$ in burette and in the conical flask add

NaCl (0.14 g)
+
dried at 110°c for 2 hours
+
5 ml H_2O
+
5 ml Acetic acid (CH_3COOH)

+

50ml methnol (Ethenol)

+

0.15 ml eosion solution

then titrated it with $AgNO_3$ solution.

Preparation of 0.1 M Ammonium of potassium thiocyanate solution:

→ 0.1 Molar of ammonium thiocyanate is prepared by dissolving 7.615 gm of ammonium thiocyanate in 1000 ml of distilled water

→ Similarly Potassium thiocyanate is prepared by dissolving 2.914 gm of potassium thiocyanate in 1000 ml distilled water.

Standardization of Thiocyanate Solution:

25 ml of 0.1 M $AgNO_3$ in conical flask

+

5ml of dil Nitric acid

+

1 ml of ferric alum indicator

Then titrated it with thiocyanate solution

Determination of Strength of Halide Solution :

A halide solution is added with excess of $AgNO_3$ sol. A ~~ppt~~ precipitate of silver halide is formed. Then this is back titrated with thiocyanate solution in presence of nitric acid and ferric as indicator.

When solution gives reddish brown colour this is the end point of titration. Record the burette reading and determined the concentration of Ag^+ ions.

Theory of Volhard's method :

Thiocyanate solution is added drop wise in solution of silver halide. it react with excess of Ag^+ ions and form silver thiocyanate.

$$Ag^+ + SCN^- \longrightarrow AgCNS$$

Then excess of thiocyanate is reacted with ferric indicator.

$$Fe^{+++} + 3SCN^- \longrightarrow Fe(SCN)_3$$

(reddish brow ppt)

This is the end point of titration.

Modified Volhard's method :-

Modified Volhard's method is a back titration in which excess silver nitrate is reacted with Nacl.

→ After that unreacted silver nitrate is titrated with Sodium or ammonium thiocyanate using ferric alum as indicator in acidic medium.

principal or Theory of modified Volhard's method

Excess $AgNO_3$ is react with Nacl it give

- $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$
- $AgNO_3 + NaSCN \longrightarrow AgSCN + NaNO_3$
- $\text{Ferric alum} + NaSCN \longrightarrow Fe(SCN)_3 + NO$

C. Fajan's method :-

This method was given by Scientist Fajan in 1923.

Principle :

This method involves the titration of $AgNO_3$ with a halide Solution in the presence of adsorption indicator. (like – fluorescein, Eosin).

End point is detected by conversion of reactio mixture into pink colour.

procedure:

preparation of standard solution. of silver nitrate:

0.1 N $AgNO_3$ is prepared by dissolving 4.248 gm (AR) into distilled water and make the volume to 250 ml

↓

$AgNO_3$ dried in oven for 2 hours

↓

protect from light
Kept in amber coloured
bottle.

Standardization of Silver Nitrate

Take $AgNO_3$ in burette and in the conical flask

add

NaCl (0.14 gm)

+

dried at 110°c for 2 hours.

+

5 ml H_2O

+

5ml Acetic acid (CH_3COOH)

+

50 ml methanol (Ethanol)

+

0.15 ml eosin Solution

Then titrated it with $AgNO_3$ solution.

preparation of Indicator Solution :

→ 0.2% of Fluorescein Solⁿ is prepared by dissolving 0.2 gm of fluorescein in 1000 ml of distilled water.

→ 0.1% of Eosin Solⁿ is prepared by dissolving 0.1gm of Sodium Salt of Eosin in 100 ml of distilled water.

Determination of Strength of Halide Solution:

Solution of $AgNO_3$ taken in burette

25 ml of halide solution (Cl, Br, I) is taken in conical flask

+

8-10 drops of adsorption Indicator

[illegible]

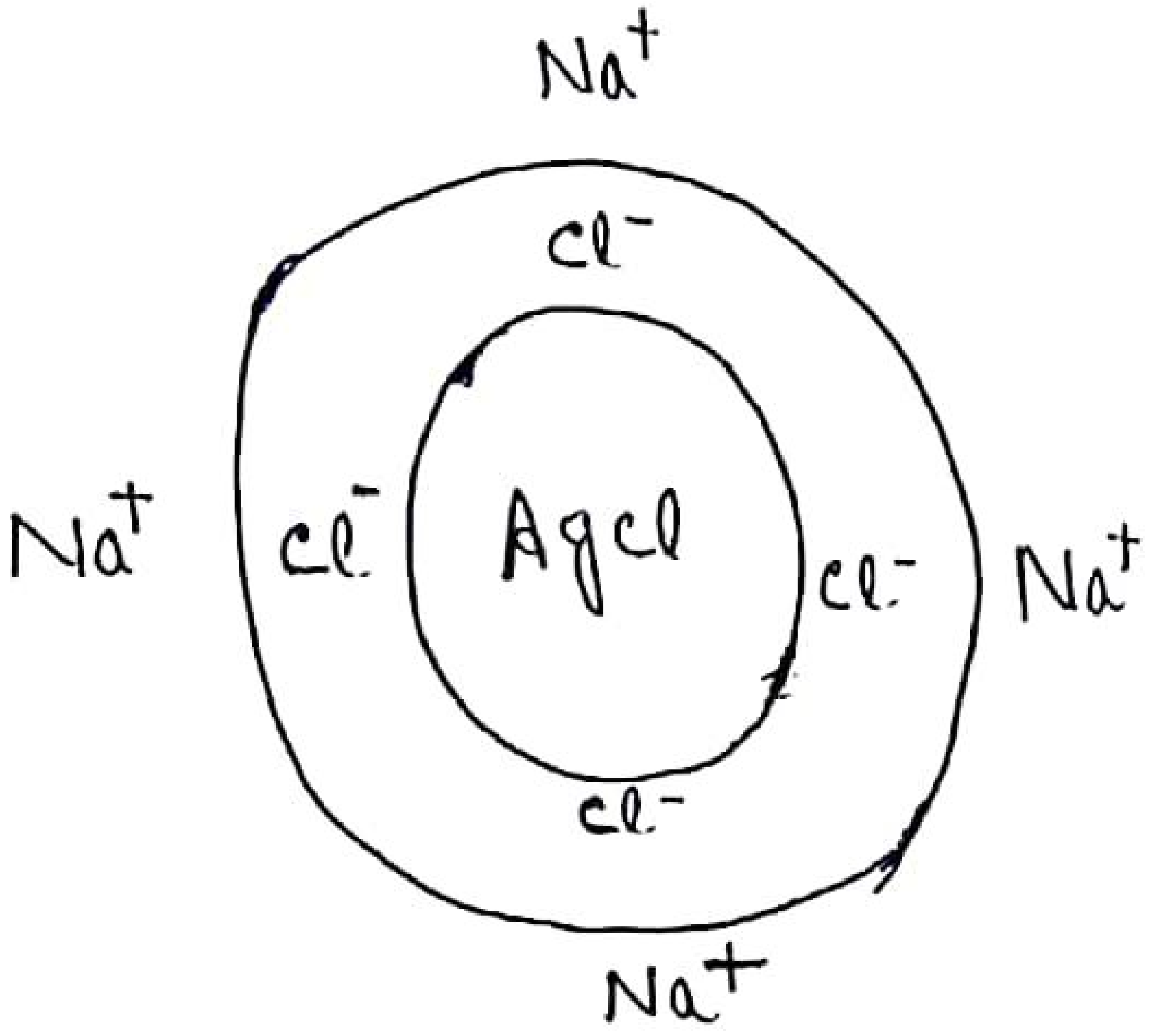
Add $AgNO_3$ from burette to the conical flask until pink colour is formed. As stable colour is formed stop the titration. This is the end point of titration. Record the burette reading and calculate the quantity of halide solutions.

<u>Theory of Fajan's method</u>:

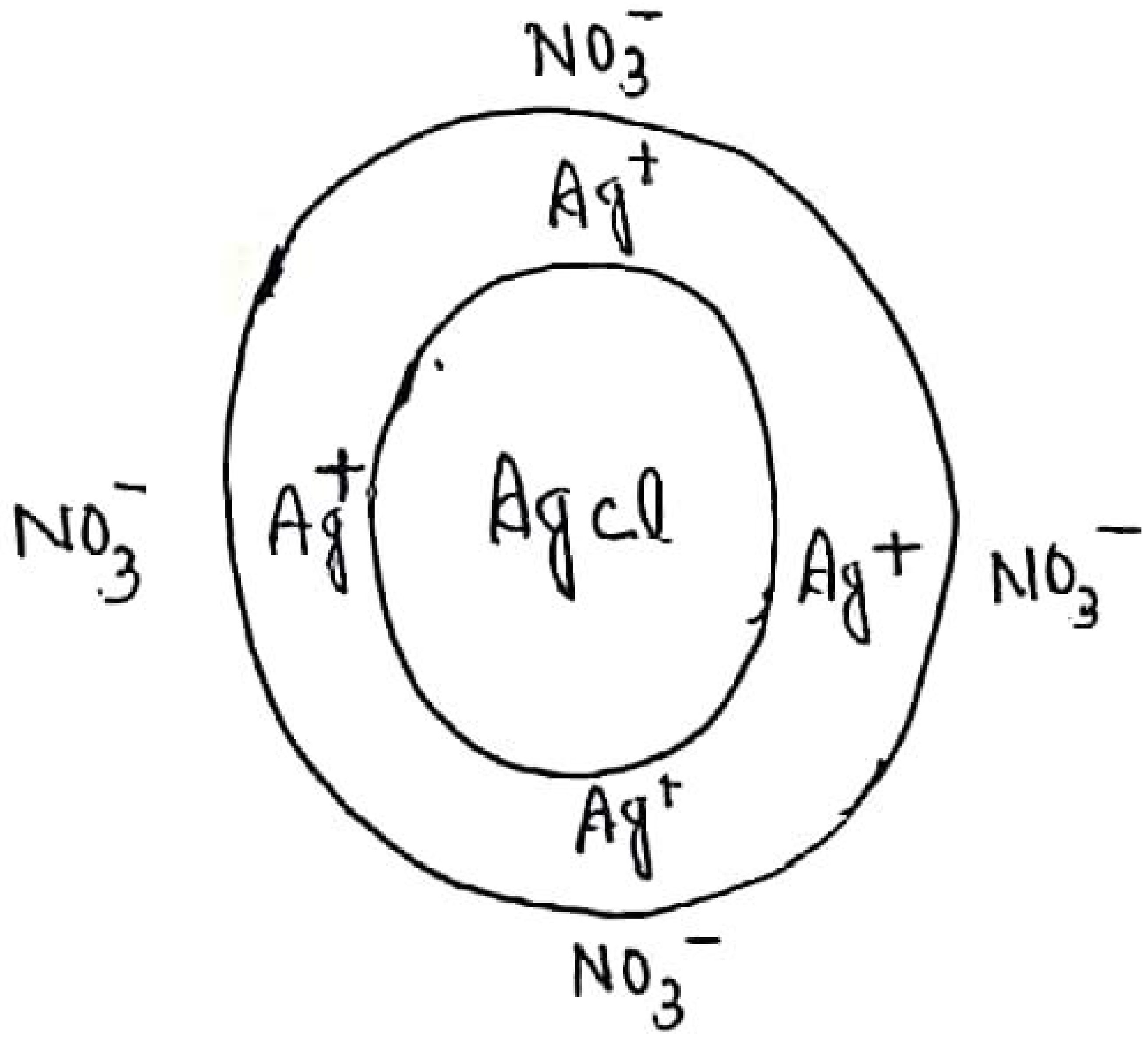
$$AgNO_3 + NaCl \longrightarrow \underset{\text{white ppt}}{AgCl} + NaNO_3$$

At I stage Cl^- will make primary adsorption layer and Na^+ will make secondary adsorption layer. This because Cl^- and Na^+ ions are in free form. Addition of $AgNO_3$ increase in Ag^+ and NO_3^- ions. Ag^+ make primary layer and NO_3^- make secondary layer. At the same time fluorescein will replace NO_3^- ions over $AgCl$ precipitate.

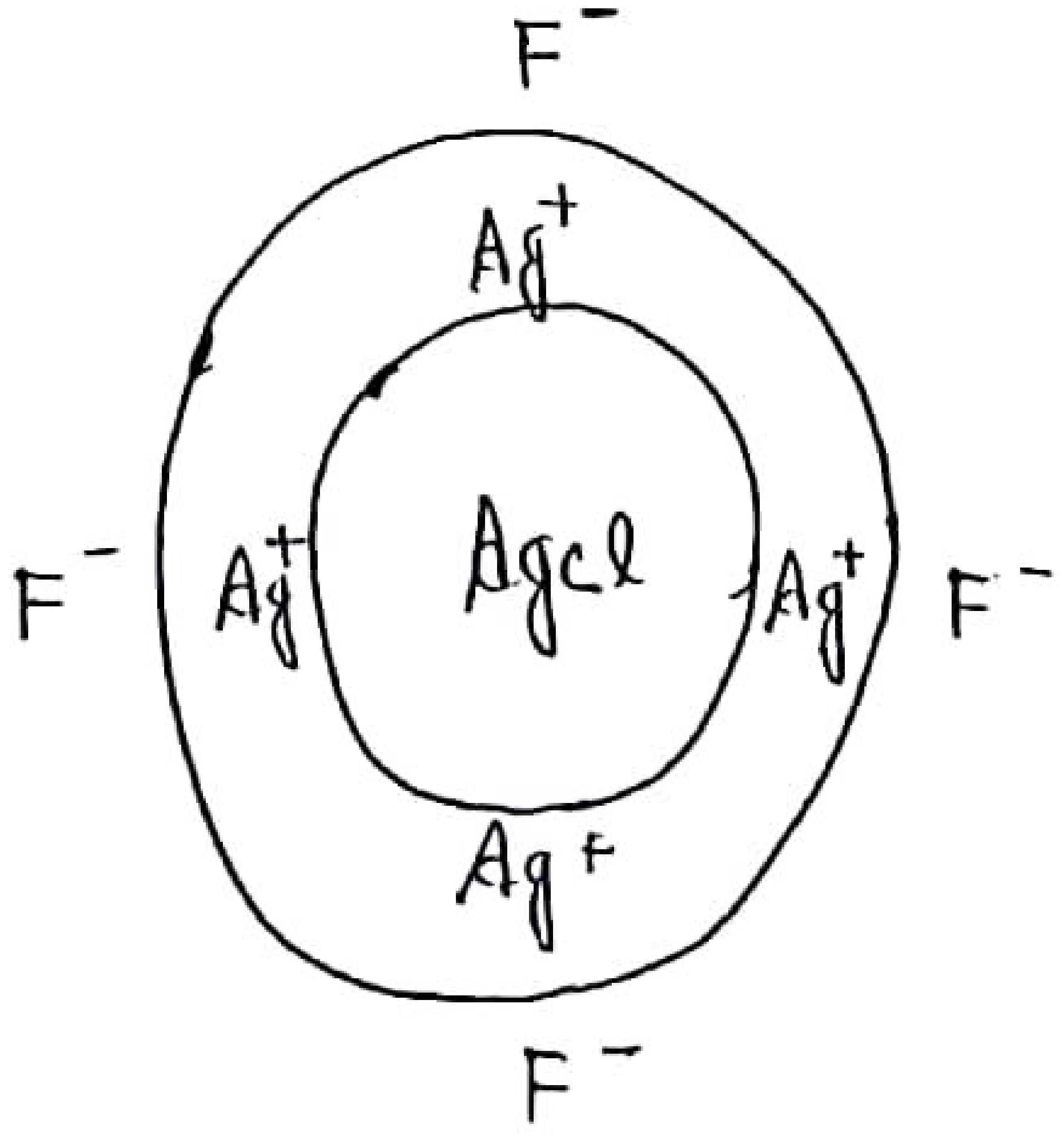
Replacement of NO_3^- ion by F^- changes the colour [illegible] to pink. This is the end point of titration.



I stage



II Stage



III Stage

Complexometric TITRATION

- Complexometric titration are those titration in which a Complexing agent is used to estimate polyvalent ions (divalent, trivalent, etc)

∝ (

- Complexing Agent : It is an electron donating ion or molecule capable of forming one or more covalent or co-ordinate bond (dative bond) with metal ion

- The group that can attach to central Cation or a metal by single bond is called Ligand.

- They are electron donating compound or ion which can form more than one covalent or co-ordinate bond with metal ion is known as Chelate

- According to IUPAC (International Union of Pure and Applied Chemistry) Chelation involves the formation or presence of two or more seperate co-ordinate bonds between a polydented ligand and a single central atom.

- If complex form between a complexing agent and metal is soluble in water it is called sequestering agent.) ∝∝

Classification

- The complexometric titration are classified into four types namely:

- Direct titration
- Back titration
- Replacement titration
- Alkalimetric titration.

Direct Titration.

In this method of titration the sample Sol^n of metal ion in the presence of Suitable buffer is titrated against standard disodium EDTA Sol^n by using metal indicator (Modent red 7) which show change in colour at the end point.

Example:- ▸ Titration of Magnesium salt like Magnesium Carbonate
- Titration of Calcium salt like Calcium
- Titration of Zinc Salt like Zinc oxide.

Back Titration.

Back titration is used in the following cases:

- Insolubility of substance like:- Lead Sulphate, Calcium oxalate
- Stability of Complex.
- Precipitate of metal hydroxide in alkaline Sol^n of buffer.
- Due to low reactivity with sodium.

$$\underset{\text{(canical)}}{\text{Analyte}(x)} + \underset{\text{(excess)}}{\text{EDTA}} \longrightarrow x\text{-EDTA} + \text{EDTA}$$

- Concⁿ of Analyte (x) can be determined by the calculation of EDTA remaing as free.

Example :- ▸ Aluminium hydroxide gel
▸ Alum.
▸ Calcium phosphate

Replacement Titration

In this titration metal ion is determined by displace of the Magnesium or Zinc ion from EDTA complex.

$$Ca^{+} + MgEDTA \longrightarrow Mg^{+} + CaEDTA$$

Concⁿ of Ca^+ can be determined by the Calculation of Mg^+ ion librated after reaction

Example :- ▹ Cadmium
▹ Lead
▹ Mercury

Alkalimetric Titration

Metal edetate complex formation reaction explain that proton are librated from disodium edetate leading to formation of acid. The acid that is formed can be titrated against standard alkali but in an unbuffered Sol^n and the end point can be detected by visual method or potentiometric method.

Metal ion Indicator.

Metal ion indicator itself act as a chelating agent but their metal complex have different Color from the reagent themself. They are called metallochromic Indicator.

After the complex formation excess amout of My^+ (metal ions) react with indicator and show change in colour.

Based on the Conc.^{n} of metal ion this indicator change the colour which indicate the end point of titration this is also pM indicator.

$$pM = -\log [M]$$

The value of pM can be derived from the equation for stability constant.

$$\cancel{K} \neq \cancel{\frac{[M][X]}{[}} \quad , \quad K = \frac{[Mx]}{[M]\,[X]}$$

$$[M] = \frac{[Mx]}{[x]\,K}$$

$$\log [M] = \log \frac{[Mx]}{[X]} - \log [K]$$

or $pM = \log \frac{[X]}{[MX]} - pk$

So, When $X = [MX]$ then,

$$\boxed{pM = pK}$$

So, the choice of indicator depends upon its stability. the indicator should be half complex and half free at pM Value.

So, pM value can also defined as value when 50% of the metallochromic indicator is complexed and 50% is in free form.

Masking

Masking may be defined as the process in which a substance is seperated or prevented to take part in the reaction, the masking agent binds with the substance and Transform it such that it can not enter into the reaction

Masking by precipitation

Many Heavy metals can be seperated either in the form of insoluble Sulphite using sodium Sulphite or as insoluble complex using thioacetamide, these are filtered decomposed and titrate with disodium edetate

Ca + EDTA ---- Ca-EDTA
Zn + EDTA ---- No Rxn
Ni + EDTA ---- No Rxn.

In this above reaction Zn and Ni is masked by masking agent which show no reaction.

Masking by Complex formation-

Masking agent form more stable complex with the interfering metal ion, the most important aspect in that masking agent must not form complex with metal ions under analysis

Example:- Ammonium floride mask aluminium
iron & titanium.
Ascorbic Acid.

Demasking

It is the process in which the masked substance regains it's ability to enter into a particular reaction.

Ca + EDTA ----- Ca-EDTA
Zn + EDTA ---- Zn-EDTA.
Ni + EDTA ----- No Rxn

Masking and demasking of Zn to get both complex Ca-EDTA and Zn EDTA

Estimation of magnesium sulphate

Synonyms = Epsom salts
chemical formula = $MgSO_4 \cdot 7H_2O$
molecular weight = 246.5

Description:- Colourless crystals or a white, crystalline powder.

∝(Preparation and standardization of 0.05M Disodium EDTA.

- 0.05M Disodium EDTA:- weight accurately about 18.6 gm of Disodium EDTA. dissolve it in sufficient quantity of distilled water in 1000 ml volumetric flask and make the volume upto the mark with the help of distilled water

- Standardization of 0.05 M Disodium EDTA:.

pipette out 25 ml of 0.05 M calcium chloride solⁿ in conical flask. Add 5 ml of ammonium chloride solⁿ to it. Add pinch of Modern black indicator and titrate it against prepared disodium EDTA solⁿ till color changes from wine red to pale blue.)∝

Assay Procedure: weight accurately about 0.3 g sample

↓

dissolve in 50 ml of water

↓

add 10 ml of strong ammonium chloride sol

↓

Titrated with 0.05 M disodium EDTA

↓

Using 0.1 g of modern black indicator

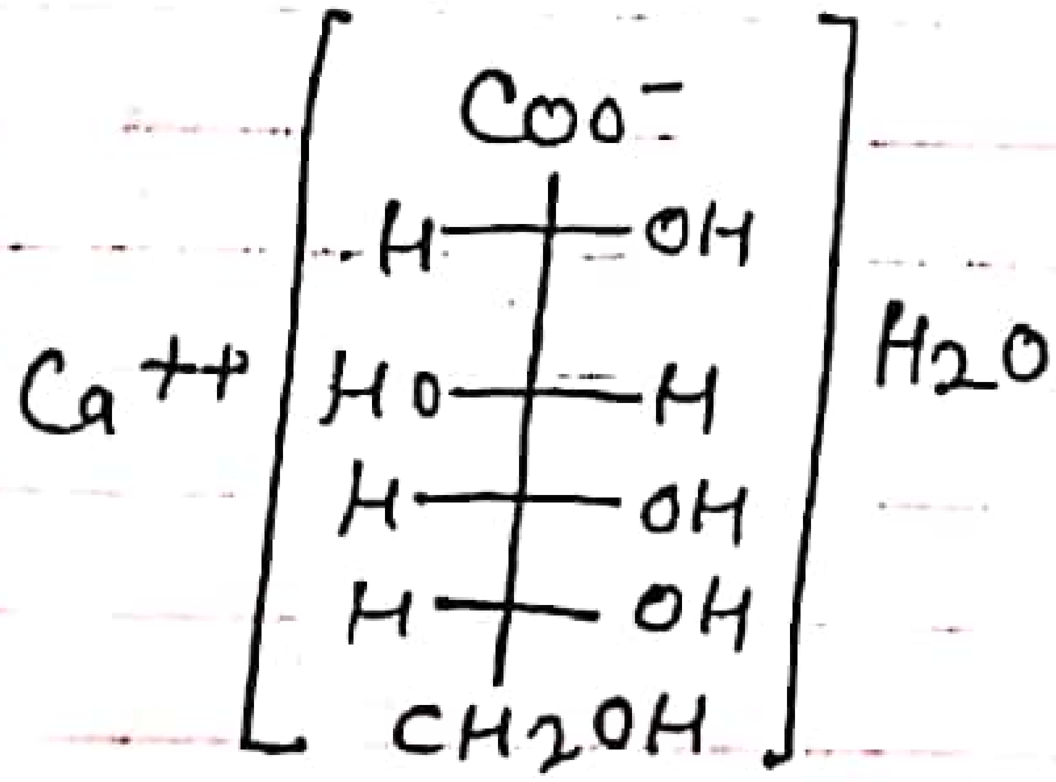
↓

Until blue colour is obtained,

I.P. Factor ⇒ 1 ml of 0.05 M disodium edetate is equivalent to 0.00602 g of $MgSO_4$.

$$MgSO_4 \rightleftharpoons Mg^{++} + SO_4^{-}$$

Estimation of Calcium gluconate



Chemical f ⇒ $C_{12}H_{22}CaO_{14} \cdot 2H_2O$

molecular weight = 448.4

∝ (Calcium gluconate is calcium D-gluconate monohydrate. Calcium gluconate contains not less than 98.5 percent and more than 102.0 percent of $C_{12}H_{22}CaO_{14}, H_2O$

(Description:- A white crystalline powder or granules.)

- 0.05 M Calcium chloride:- Weight accurately about ~~10.6 gm of Diso~~ 3.675 gm of calcium chloride, disalve it in sufficient quantity of distilled water in 500 ml volumetric flask and volume make up to help the distilled water.

- Ammonium Chloride:- weight accurately about 1.60 gm of ammonium chloride. add 14 ml of strong ammonium in 250 ml volumetric flask, shake it properly and volume make up to help of distilled water.)∝

Assay Procedure:- weight accurately about 0.5 gm ~~of~~

↓

disalve in 50 ml of warm water, cool

↓

add 5.0 ml of 0.05 M $MgSO_4$

↓

Add 10 ml strong ammonia sol^n

↓

Titrate with 0.05 M disodium EDTA.

↓

Using mordant black as indicator

↓

The volume of 0.05 M disodium EDTA.

↓

It required subtract the volume of the magnesium sulphate solution added,

I.P. Factor:- 1 ml of 0.05 M disodium EDTA is equivalent to 0.02242 gm of $C_2H_{22}CaO_{14}\cdot H_2O$.

$$C_{12}H_{22}CaO_{14}\cdot H_2O \rightleftharpoons Ca^{++} + (C_{12}H_{22}O_{14})^{-2}$$

◪ PM Indicator used in Complexometric titration

The most commonly used indicators are

① Mordant black II

② Xylenol orange

③ Murexide

④ Calcon mixture

◪ EDTA – Ethylenediamine tetra acetic acid

GRAVIMETRY

It is the estimation of substance into its measurable components as precipitate & makouss.

$Nacl + AgNo_3 \rightarrow Agcl + NaNo_3$

In this method soluble chloride (cl^-) ions are converted into insoluble white precipitate of silver chloride by treating it with silver nitrate

After precipitation precipitate of silver * chloride is filtered, washed, dried & weighed accurately.

Steps involved in Gravimetric Analysis.

1. Precipitation
2. Digestion of Precipitate
3. Filteration of Precipitate
4. Washing of Precipitate
5. Drying of Precipitate
6. Ignition
7. Weighing of Precipitate

1) Precipitation -

This involves addition of suitable precipitating agent in excess which help in the formation of precipitate.

Based on particle size two types of precipitate are formed

ⓐ colloidal precipitate - Particles having range from 10-2000 Å

ⓑ crystalline precipitate - Particle size greater then 2000 Å

Mechanism of Precipitate

① Nucleation
② crystal Growth

* Nucleation - It involves spontaneous and Induced nucleation

In spontaneous, ions join together to form a nucleus.
while in induced, a small crystal of the solute is added which acts as nucleus for crystal growth.

* Crystal Growth - On the nucleus the formation of crystal growth takes place.

(i) Diffusion - of ions on the surface of growing crystal

(ii) Deposition - these ions on crystal surface.

Contamination of Precipitates –

① Co-Precipitation
② Post-Precipitation

→ * **Co-Precipitation** – contamination of the precipitate by the substance which are soluble in mother liquor.
It is of two types

ⓐ adsorption co-precipitation
ⓑ Occulusion co-precipitation

* **Adsorption co-precipitation** – The ions impurity is adsorbed on the surface of primary precipitates during its formation.

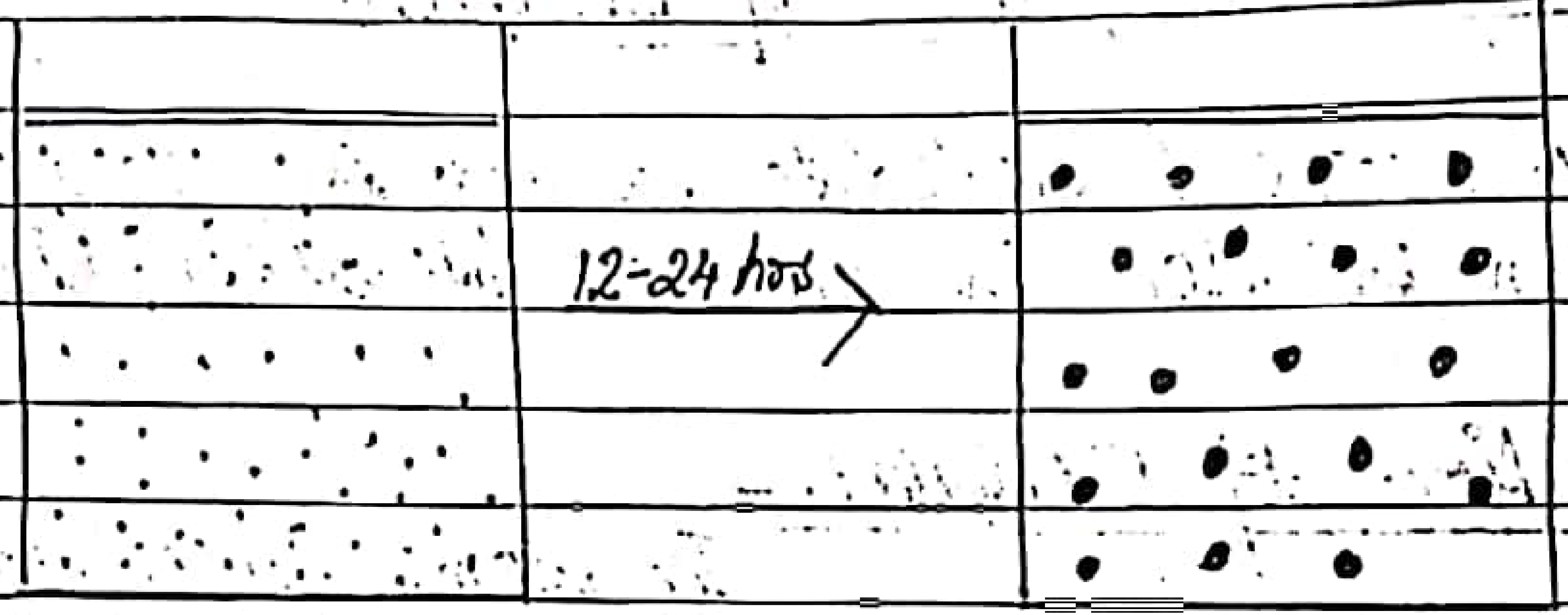
* **Occulusion co-precipitation** – It is the entrapment of ionic impurity into the crystal.

→ * **Post-Precipitation** – The precipitation of impurity on the surface of already formed primary precipitate is called Post-Precipitation.
eg- calcium is ppt as calcium oxalate in the presence of Magnesium, Magnesium oxalate deposited over ppt of calcium oxalate.

② Digestion of Precipitate -

It's purpose is to keep the precipitate and the solution from which it was precipitated in contact for about 12-24 hrs.

It help in the formation of bigger precipitate and also to avoid co-precipitation.



③ Filteration of Precipitate -

After digestion, which leads to formation of bigger particles which is filtered with the help of filter paper and sintered crucible.

Filteration Process -

The best way of filteration of precipitate is decantation Process. In this mother liquid is poured into filteration assembly using a glass rod.

④ Washing of Precipitate -

Washing of Precipitate is done to remove ions adsorbed on it.

Pure water is not used because of repeated washing some of the ppt can go into the solution.

⑤ Drying and Ignition of Precipitate -

To remove extra water & electrolyte drying is required. It can be done in an oven at about 110°-120°C.

⑥ Ignition of Precipitate -

In some precipitation ignition is required so they are kept in the pre-weighed crucible.

crucible are designed for ignition of precipitate

Two types of crucible are there -

① Silica crucible

② Sentered Glass Crucible

Silica crucible - It is bowl type apparatus consist of silica.

Sintered Glass crucible -

This allow the filteration of precipitate and then ignition. It is made up of pyrex glass. It stands for upto temperature of 1500°C.

⑦ Weighing of Precipitate - Weighing of ppt can be done by the following steps.

ⓘ wt of empty crucible = a gm.

ⓘⓘ wt of crucible + Precipitate = b gm

(iv) wt of Precipitate = (b - a) gm

Estimation of Barium Sulphate

Principle -

$BaSO_4$ may be precipitated either by the use of sulphuric acid which produces sulphate ion on boiling.

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$

(this ppt is filtered, washed, dried ignited and weighed as $BaSO_4$.)

Procedure

Take 25 ml of $BaCl_2$ in 500 ml beaker

↓

Add 0.5 ml conc. HCl + 100 ml distilled water

↓

solution is heated to boil

↓

hot distilled H_2SO_4 is added dropwise

↓

for degestion kept on water bath for 1/2 hrs.

↓

filter the precipitel + wash it

↓

Dry & weigh the precipitate