

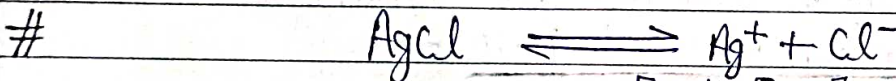
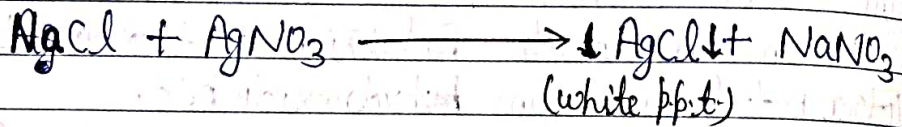
i) # Advantage of Non-aqueous Titration:-

Unit - III

# Precipitation Titration

Precipitation reaction is a reaction in which a sparingly soluble compound (precipitate) is formed as a product and precipitation titration is a method of titration which involves precipitation reaction.

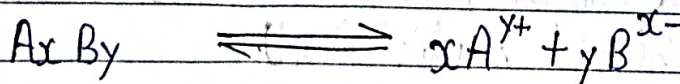
Example:-



$$K_{sp} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

\* If  $K_{sp}$  (Solubility product) is greater than the solubility product <sup>then it</sup> is soluble and if ionic product are greater than  $K_{sp}$  it form precipitation.



$$K_{sp} = \frac{[\text{A}^{y+}]^x [\text{B}^{x-}]^y}{[\text{A}_x\text{B}_y]}$$

$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

\* It means  $K_{sp}$  is the product of molar conc. of ions forms raised to the power of number of ions in molecule.

# Q: How does the precipitate form?

⇒ A precipitate is a form when the product of its ionic concentration is greater than its solubility product.

Ionic product  $\gg K_{sp}$ . (for precipitation).

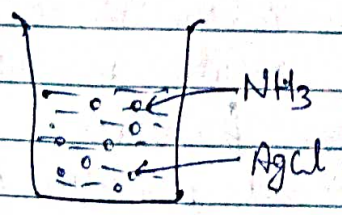
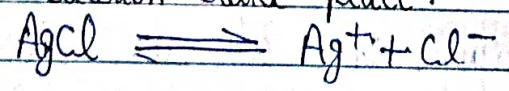
# Factors Affecting Precipitation:

(i) Common Ion Effect :- In presence of common ion solubility generally decreases and this is why precipitation increases.

(ii) Solvent Effect :- Solubility of most inorganic compound is generally decreases in organic solvent and therefore precipitation increases.

(iii) Complexation Effect :- Due to complex formation solubility increases and hence precipitation decreases.

E.g. :- By adding  $NH_3$  to  $AgCl$  precipitate following reaction take place.



## 1 # Argentometric Titration

# \* Precipitation titration is the formation of Insoluble Compound (precipitate) as a result of titration of analyte and titrant. If this titration take place using Silver nitrate ( $\text{AgNO}_3$ ) as titrant it is called as Argentometric titration.

\* This titration is used to determine the presence of halides ( $\text{Cl}^-$ ,  $\text{Br}^-$  etc.) ~~with~~ by titration with  $\text{AgNO}_3$ .

\* According to the indicator used there are 3 methods -

(i) Mohr's Method } Direct method

(ii) Fajan's Method }

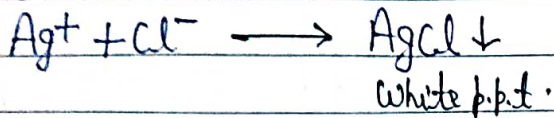
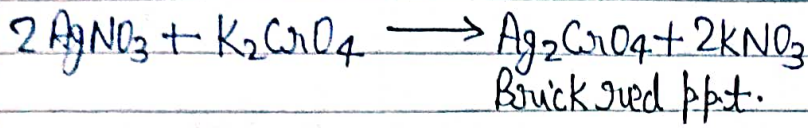
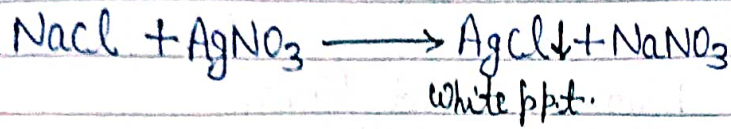
(iii) Volhard's Method } Indirect Method

# (i) Mohr's Method :-

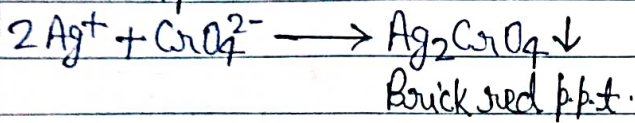
\* This method uses Potassium Chromate [ $\text{K}_2\text{Cr}_2\text{O}_7$ ] as an indicator for the titration of Chloride ( $\text{Cl}^-$ ), Bromide ( $\text{Br}^-$ ), Cyanide ( $\text{CN}^-$ ) containing compounds (analyte) with a silver nitrate solution (titrant).

\* During this titration, once all the chloride ions has been precipitated as white silver chloride, the first excess of titrant results in the formation of silver chromate precipitate.

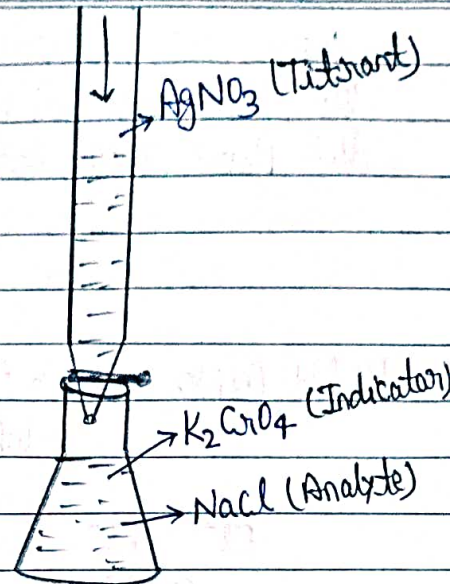
\* The end point is determined by the formation of brick red colour precipitate of silver chromate [ $\text{Ag}_2\text{Cr}_2\text{O}_7$ ].



$$K_{sp} = 1.8 \times 10^{-10}$$



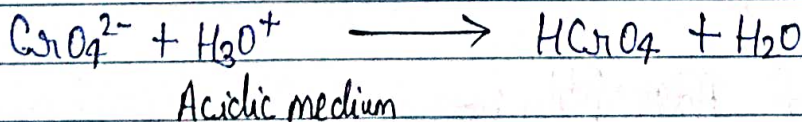
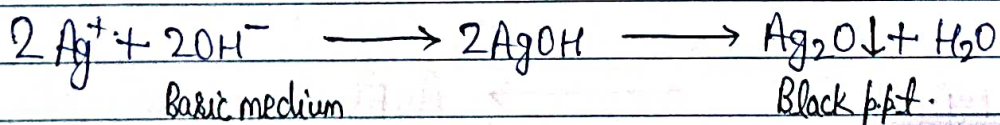
$$K_{sp} = 1.2 \times 10^{-12}$$



### \* Condition for Mohr's Method

Titration are perform only in Neutral or Slightly Basic medium and not in strong basic medium or Acidic medium.

(pH should be Between 7-10.)



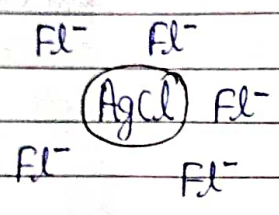
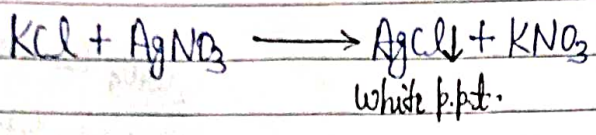
### (ii) Fazank Method :-

\* This is the direct titration method which is used for titration of Halides Ions ( $\text{Cl}^-$ ) for titration using Internal adsorption Indicators.

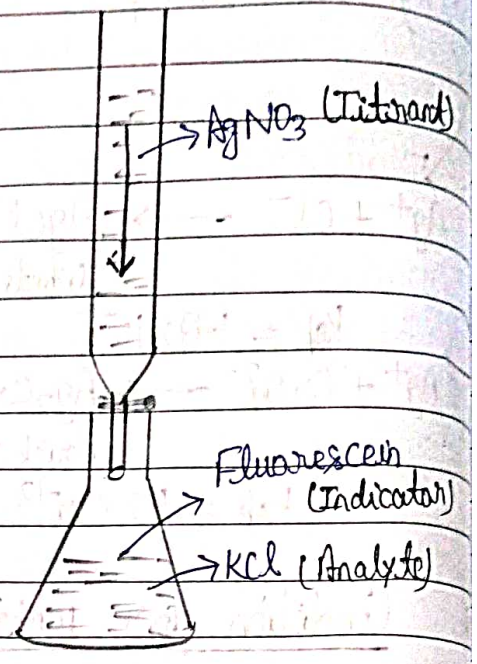
\* This indicators are adsorbed by  $\text{AgCl} \downarrow$  precipitate molecules at the end point and a colour change occurs.

- iii) There are two type of Adsorption Indicator -  
 (i) (a) Acid Dyes Such as Fluorescein and Eosin  
 (b) Basic Dyes Such as Rhodamine and Phenolphthalein

#

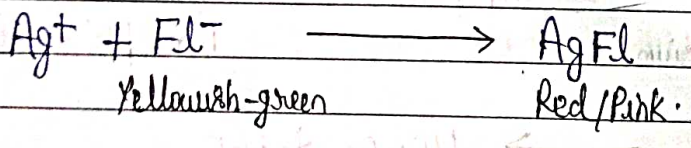


Adsorption of  $Fl^-$  on  $AgCl$  molecule & Colour Change from Yellow green to Red/Pink.



#

\* Once all chloride is used up by  $AgNO_3$  to form  $AgCl$ , the 1st drop of  $AgNO_3$  will react with fluorescein ( $Fl^-$ ) to produce red/pink colour.

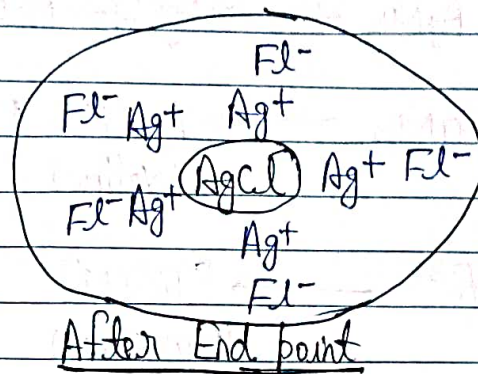
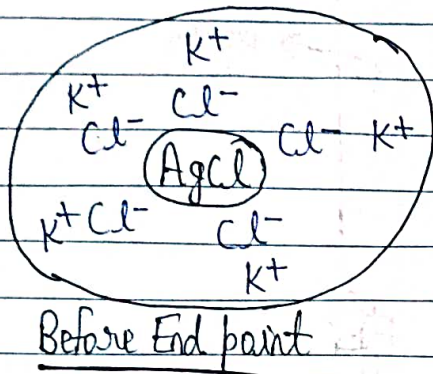


# Principle of Adsorption :-

\* In the titration of  $Cl^-$  with  $Ag^+$  :-

- (i) Before End Point :-  $Cl^-$  is in excess and ~~it~~ forms the primary layer on  $AgCl$  ppt molecule. This repulses the indicator Anion  $Fl^-$  and attract ~~the~~  $K^+$  Ion from the solution.

(ii) After End Point:-  $\text{Ag}^+$  is in excess and form a layer of positively charged  $\text{Ag}^+$  on the surface of  $\text{AgCl}$  molecule. It will now attract the Indicator Anion  $\text{Fl}^-$  and adsorb it on  $\text{AgCl}$  surface.



### # Factors Affecting Adsorption of Indicator:-

(i)  $\text{H}^+$  ion Concentration:- Fluorescein is a very weak acid and hence the colour change is sharp at pH 7 to 10. Eosin is a strong acid and hence the colour change is sharp at pH = 3.

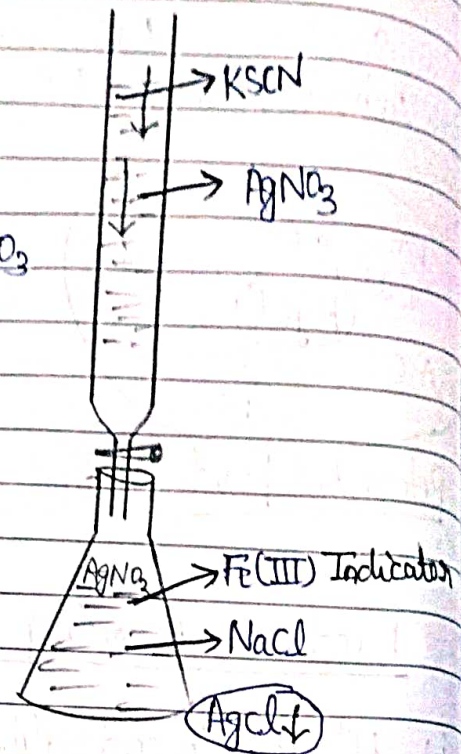
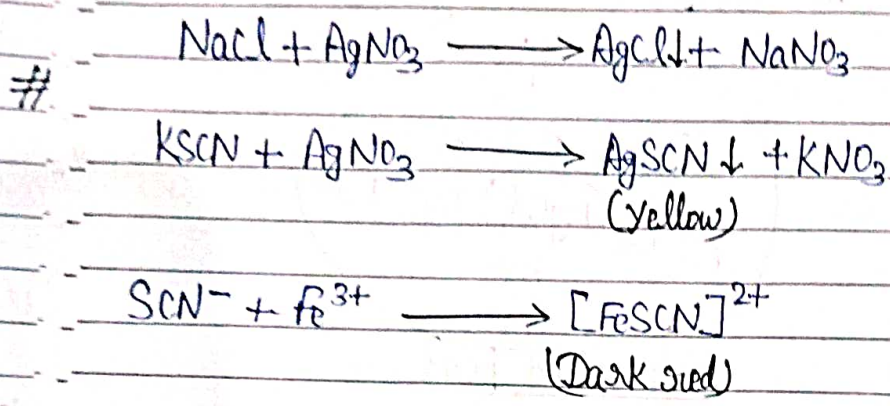
(ii) Effect of Salt:- A large quantity of salt cause coagulation of precipitate which results into poor end point.

### (iii) Volhard's Method:-

\* This method uses a back titration with potassium thiocyanate ( $\text{KSCN}$ ) to determine the concentration of chloride ions in a solution.

\* Note:- Back titration:- A back titration is a method of titration where the concentration of an analyte is determined by reacting it with a known amount of excess reagent. The remaining excess reagent is then titrated with another second reagent to

- (i) determine excess reagent.
- (ii)



# \* Before the titration an excess volume of Silver nitrate solution is added to the solution containing Chloride Ion forming a precipitate of silver chloride.

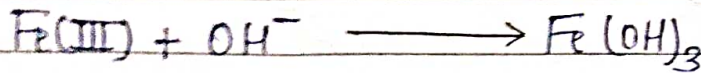
\* The Indicator  $\text{Fe}^{3+}$  is then added and the solution is titrated with the potassium thiocyanate solution (KSCN) forming silver thiocyanate ( $\text{AgSCN}$ ) which gives yellow colour to the solution.

\* Once all the silver ion have reacted the first excess of thiocyanate reacts with  $\text{Fe}^{3+}$  to form a dark red complex of  $[\text{FeSCN}]^{2+}$ .

\* Now, the concentration of chloride ion is determined by subtracting the moles of silver ions reacted with thiocyanate from the total no. of moles of silver nitrate added to the solution.

## \*\* Conditions for Volhard's method

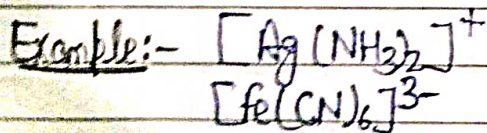
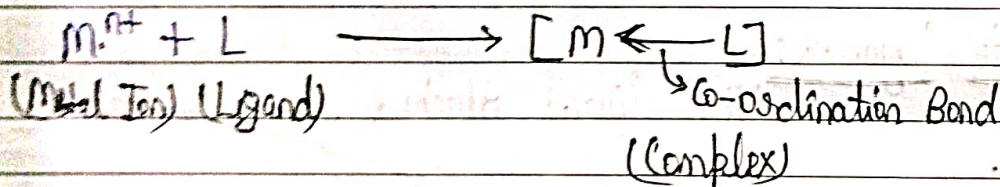
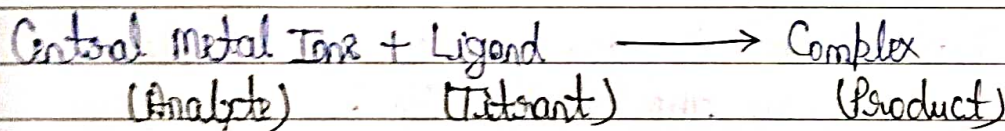
- \* The solution must be Acidic with 1 M conc. of Nitric Acid to prevent the precipitation of Iron [Fe(III)] indicator as Ferric hydroxide



## ## Complexometry Titration:-

### Complex formation: (Co-ordination Compound)

- \* Compound obtained from combination of metal ion (Analyte) Acceptor) with donor molecule (Ligand) through the formation of Co-ordination bond.



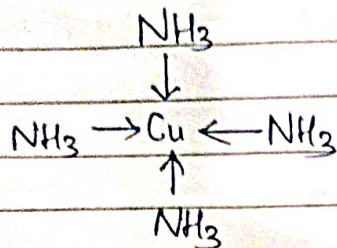
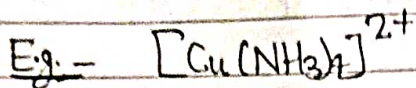
### Complexometry:-

- \* A titration that involves the formation of soluble complex between metal ion (acceptor) and Ligand (Donor) to form Co-ordination Bond.
- \* The metal ion is known as Central metal atom & Anion or neutral molecule is known as Ligand.



## Co-ordination number :-

\* The number of co-ordination bond formed to a metal ion by their ligand.



→ There is 4. co-ordination number in complex molecule.

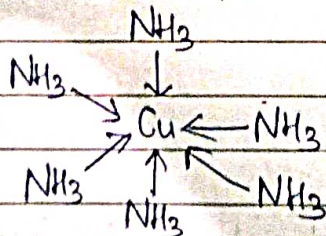
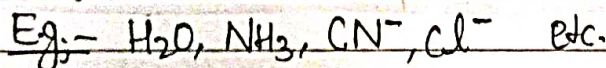
\* Co-ordination number may be defined as the number of e<sup>-</sup> pairs that a metal ion can accept from the ligand.

## Types of Complexing Agent (Ligands)

This classification is according to the number of sites attached to the metal ion.

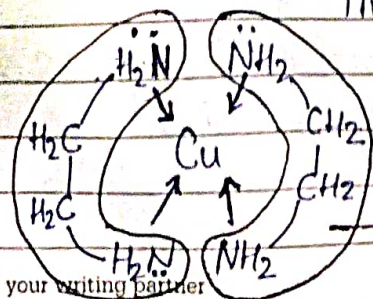
### (i) Unidentate Ligands :-

The ligand attached to the metal at one site.



### (ii) Bi-dentate Ligands :-

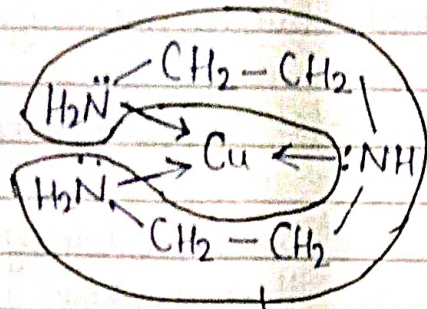
The ligand attached to metal at two sites.



Ethylene Diamine (Ligand)

(iii) Tri-dentate Ligands:-

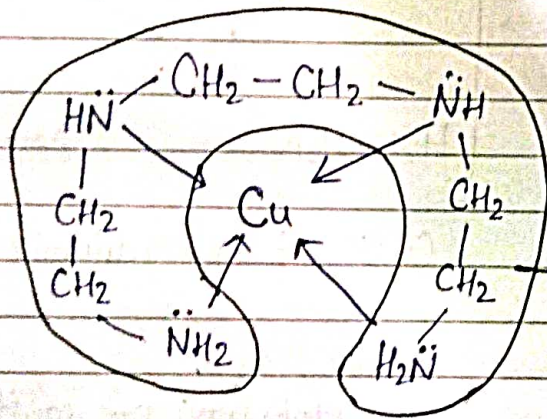
The Ligand attached to metal at three site.



↓ di-ethylene tri-amine

(iv) Tetra-dentate Ligands:-

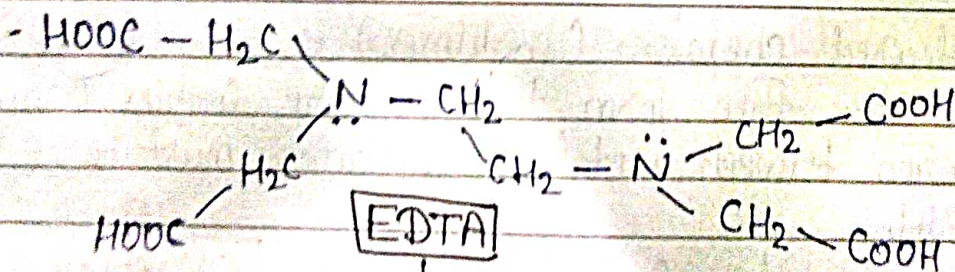
The ligand attached to the central metal at four site.



Tri-ethylene Tetra-amine

(v) Multi-dentate Ligands:-

The ligand attached to central metal at more than four site.



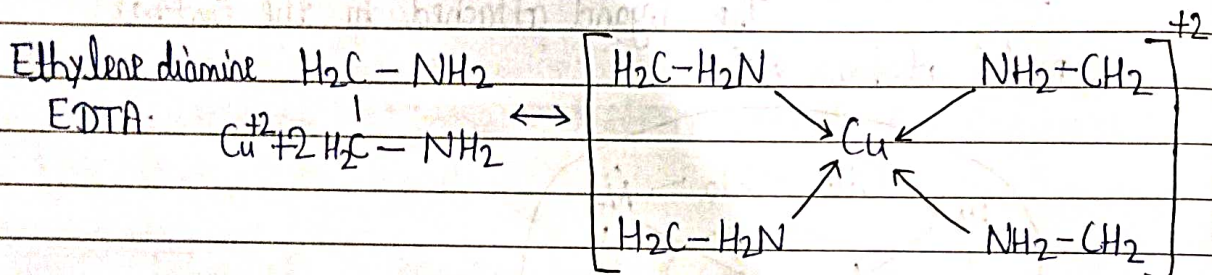
Ethylenediamine Tetra Acetic Acid

## # Chelation :-

Chelate :- A complex formed between the ligand containing two or more donor atoms & a metal, forming ring structure (heterocyclic rings or chelate rings).

Chelating agents :- Organic molecules containing two or more donor groups that combine with metal to form a complex of ring structure.

### Examples :-



$\text{Cu(II)}$  Ethylenediamine Chelate

### Chelate effect :-

Enhancing the stability of multidentate complexes than unidentate complexes.

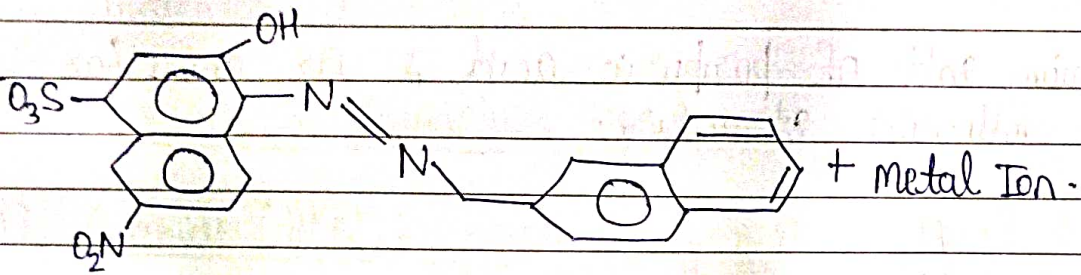
### Characteristics of Metal Ion Indicators :-

- 1). Form coloured chelates (complexes) & exhibit a different color in the free form than in the complex form.
- 2). The reaction between metal & indicator must be reversible.
- 3). The metal-indicator complex should be less stable than the metal-EDTA complex.  
Metal-indicator + EDTA  $\rightarrow$  metal-EDTA + free indicator.
- 4). The color reaction should be specific or at least selective.
- 5). Changes its color according to the pH of the medium.

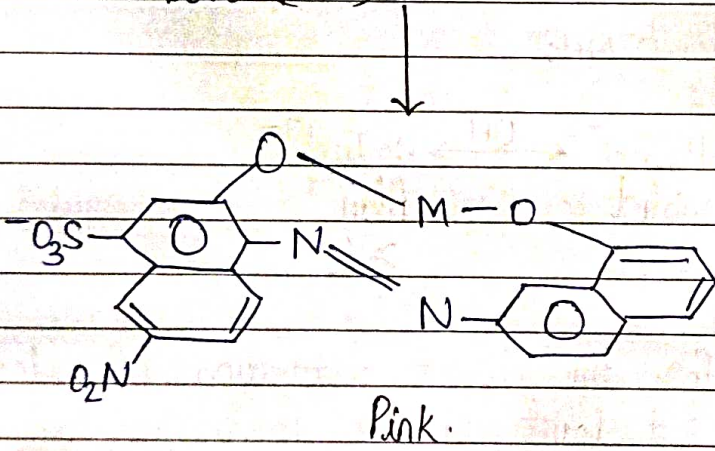
Examples of Metal Ion Indicators :-

1. Eriochrome black T (EBT) :-

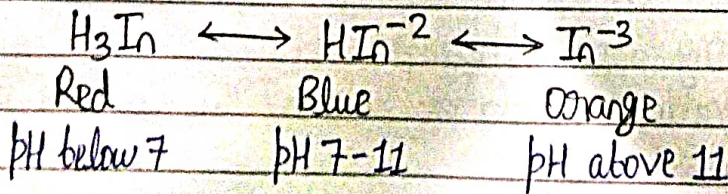
- It can be represented by  $H_2In^-$ . The colour of Indicator change with the change of pH.
- EBT contains 2 replaceable phenolic hydrogen.



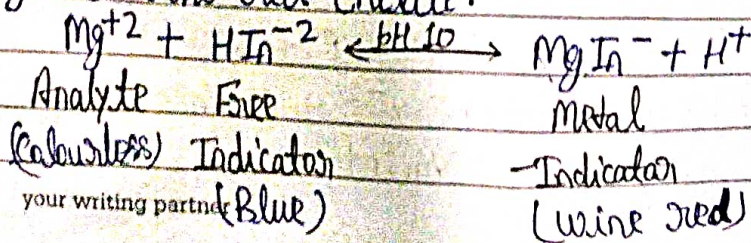
(Eriochrome black T, solochrome black T)  
Blue (pH 10)



→ EBT is a tribasic acid at pH 10, exists as blue  $HIn^{2-}$ .



→ The blue form of the indicator reacts with metal ions, to give a wine red chelate.

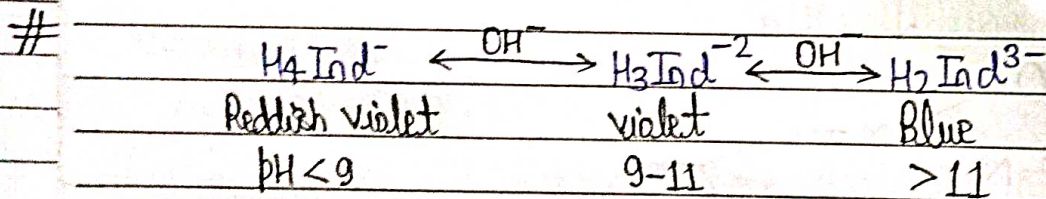
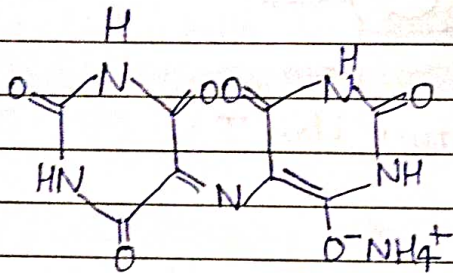


(i) → EBT is used for the determination of  $Mg^{+2}$ ,  $Zn^{+2}$ ,  $Ca^{+2}$ ,  $Pb^{+2}$ ,  $Hg^{+2}$  &  $Mn^{+2}$  salt at pH 7-11 using ammonia buffer (pH=10).

# → EBT cannot be used for the determination of  $Cu^{+2}$ ,  $Fe^{+3}$ ,  $Al^{+3}$ ,  $Co^{+2}$  &  $Ni^{+2}$ .

## 2. Murexide :-

Ammonium salt of purpuric acid & its anion has the following structure.

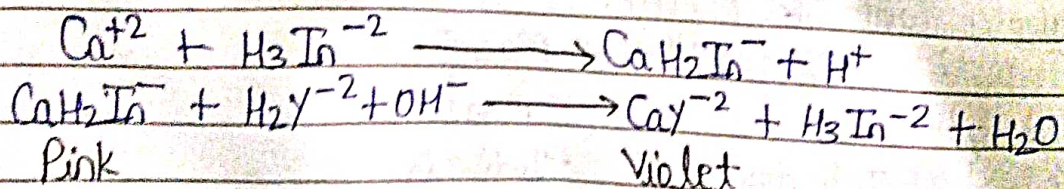


\* Murexide is used for the direct titration of calcium at pH = 12, the end point changes from red to blue violet.

\* At pH = 12, Mg-murexide is less stable than the Ca-complex, so  $Ca^{+2}$  ion can be titrated in the presence of Mg at this pH.

\* Murexide gives yellow chelates with Cu, Co, Ni metal ions.

\* It is used for the determination of  $Ca^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$  &  $Cu^{+2}$  salts at pH 9-11.



## # Masking and Demasking Agents :-

Masking Agents :- A reagent added to prevent reaction of some metal ion with EDTA (block metal ions).

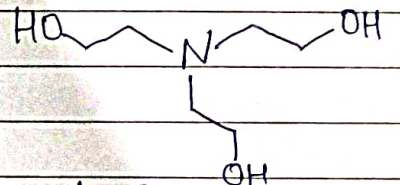
→ These reagent form complexes with interfering ions which are more stable than complexes formed with indicator & EDTA.

### Masking & Demasking agents :-

(A) Cyanide (KCN) :- Used as a masking agent for  $\text{Ag}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Zn}^{+2}$ .

$$M^+ + 4\text{CN}^- \longrightarrow [M(\text{CN})_4]^{-2}$$

(B) Triethanolamine :- Used as a masking agent for  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$  &  $\text{Sn}^{+2}$ .



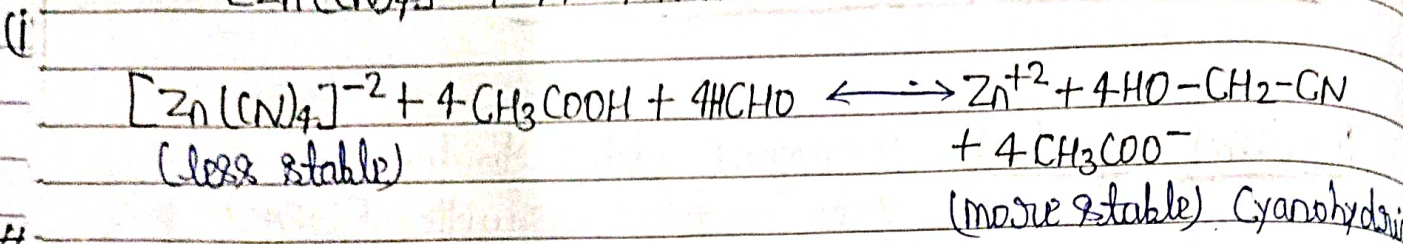
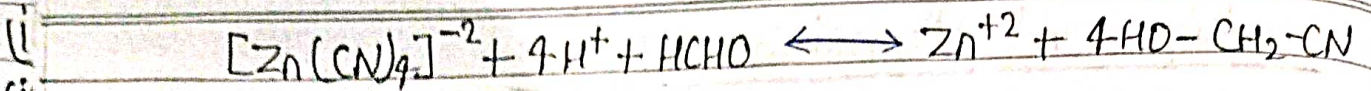
(C) Fluoride (NH<sub>4</sub>F) :- Used as a masking agent for  $\text{Fe}^{+3}$  &  $\text{Al}^{+3}$  to give hexafluoro complex  $[\text{FeF}_6]^{-3}$  &  $[\text{AlF}_6]^{-3}$ .

(D) Iodide (KI) :- Used as a masking agent for  $\text{Hg}^{+2}$  to give tetraiodo complex ( $\text{HgI}_4$ ).

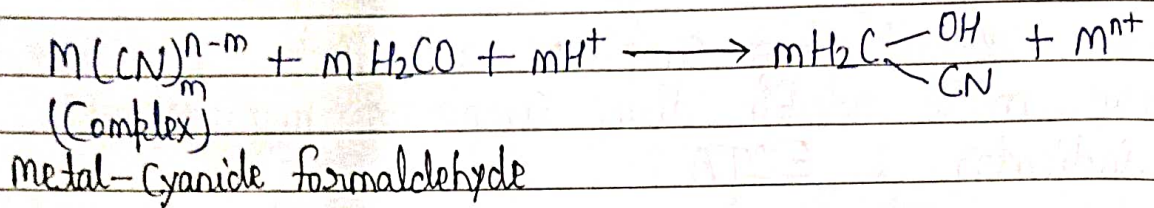
Demasking Agent :- Reagents that release of a metal ion from a masking agent.

Example :-

→ The masking by  $\text{CN}^-$  can be removed by (mixture of formaldehyde - acetic acid) - on addition of demasking agent to  $[\text{Zn}(\text{CN})_4]^{-2}$ , Zn is liberated & titrated.



#

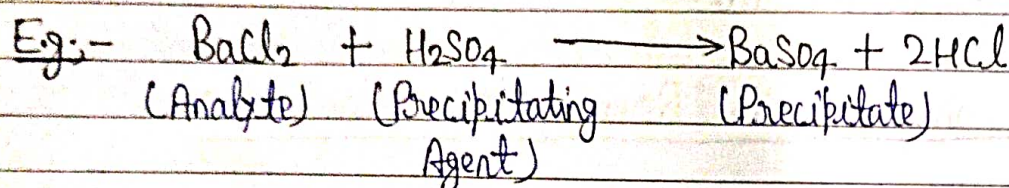


→ Oxidation with  $H_2O_2$  releases  $Cu^{+2}$  from  $Cu^+$ -Thiourea Complex.

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# Gravimetric Analysis

Gravimetric Analysis is based on conversion of ion/elements/Analyte/Radical into precipitate a pure & stable compound after a precipitation reaction, which can be directly weighed & quantified.



## Basics :-

- Analyte is taken & precipitated by titrating with suitable precipitating agent.
- Precipitate is pure & stable compound.
- Precipitated compound is filtered, dried & weighed accurately.

$$\% \text{ of analyte} = \frac{\text{wt. of precipitate} \times \text{Gravimetric factor} \times 10}{\text{Weight of Sample}}$$

## Gravimetric Factor :-

Atomic mass of  $\text{BaSO}_4 = 233.42 \text{ g/mol}$ .

Atomic mass of  $\text{Ba}^{2+}$  ion =  $137.36 \text{ g/mol}$ .

$$\text{Gravimetric factor} = \frac{137.36 \text{ g/mol}}{233.42 \text{ g/mol}}$$

## # Advantages :-

- Analysis can be done precisely and accurately by using sensitive & modern analytical balance.



(i) → Mother liquor can be analysed for completion of the precipitation reaction & errors can be reduced to great extent.

(ii) → Direct measurement (weighing) of the compound is done in gravimetric analysis, so calibration is not required & it's an absolute method.

#

→ It is less expensive as compared to other analytical methods.

### # Steps involved in Gravimetric Analysis :-

(i) Preparation of sample solution :- Generally dilute solution is preferred.

(ii) Precipitation :- Precipitating agent (titrant) is added in the sample solution & preparation takes place.

#

→ After addition of precipitating agent supersaturation occurs  
→ Nucleation starts after supersaturation and nuclei will grow further as precipitate.

(iii) Digestion :- The precipitate is left hot (below boiling point) for 30-60 min. in order to digest the particles.

→ This digestion involves dissolution of small particles & re-precipitation of larger, once when cooling slowly.  
→ This process is known as Ostwald Ripening.  
→ Digestion is highly useful for colloidal precipitation.

(iv) Filtration & Washing :- Take filter paper & filter the supernatant (mother liquor) liquid & precipitate.

→ After filtration, washing is done by hot water / electrolyte solution.

→ Impurities are removed after washing.

→ Colloidal solution should not be washed by using water because it leads to peptization (conversion of ppt. into colloid)

(v) Drying or ignition :- After drying or ignition, we can get exactly known amount of the analyte.

### # Purity of the Precipitate :-

\* When the precipitate is separated out from solution, it is always not preferably pure & may be contaminated after washing.

\* The amount of impurity depends on nature of precipitate & condition of precipitation.

\* It may be due to :-

# Co-precipitation :- when two or more ions are simultaneously precipitated out in the same solution, then the condition is known as Co-precipitation.

### Inclusion :-

• An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier resulting in crystallographic defect.

• This can happen when the ionic radius & charge of the impurity are similar to those of the carrier.

For e.g. :-

Ammonium Magnesium Phosphate  
 $\text{NH}_4\text{MgPO}_4$  (Analyte Precipitate)

If  $\text{K}^+$  is solution,

Then,  $\text{KMgPO}_4$  (Impurity)

Formula wt. of  $\text{NH}_4^+$  (18) &  $\text{K}^+$  (39)

Formula wt. of Impurity is more i.e., positive error occur.

Occlusion :-

- Occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.
- Occlusion are minimized by maintaining the precipitate in equilibrium with its supernatant solution for an extended time. This process is called digestion & may be carried out at room temperature or at an elevated temperature.

The problem of co-precipitation can be minimized by digestion (waiting for the precipitate to equilibrate & form larger & purer particles) or by dissolving the sample & precipitating it again.

# Post - Precipitation :-

- \* Post precipitation is a kind of precipitation ~~can be minimized by digestion~~ (waiting for the precipitate where the precipitation of the undesirable compound occurs after the formation of the precipitate of the desired compound.
- \* Rate of reaction is slower in post precipitation & it occurs generally during digestion process.
- \* Post - precipitation always given positive errors.

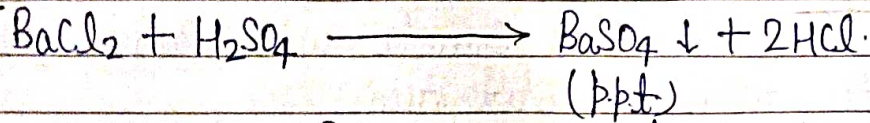
Example :-

$\text{CuS}$  (Analyte precipitate)  
 $\text{Cu}^{+2}$  (Analyte)

$\text{ZnS}$  (Zinc Sulphate)  
 $\text{Zn}^{+2}$  (Present in the solution).

## Estimation of Barium Sulphate :-

Principle :-



$\text{BaSO}_4$  precipitate is filtered, washed, dried, ignited & weighed to estimate Barium.

## # Preparation of Sample & Reagent :-

Sample preparation :- 20.8g of  $\text{BaCl}_2$  is dissolved in 100ml of distilled water.

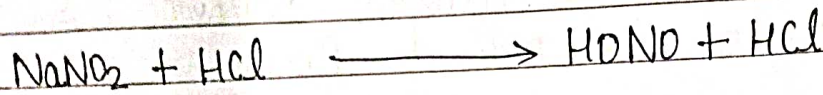
Dilute  $\text{H}_2\text{SO}_4$  :- Dissolve 3ml of conc.  $\text{H}_2\text{SO}_4$  in 100ml of distilled water.

## Methodology :-

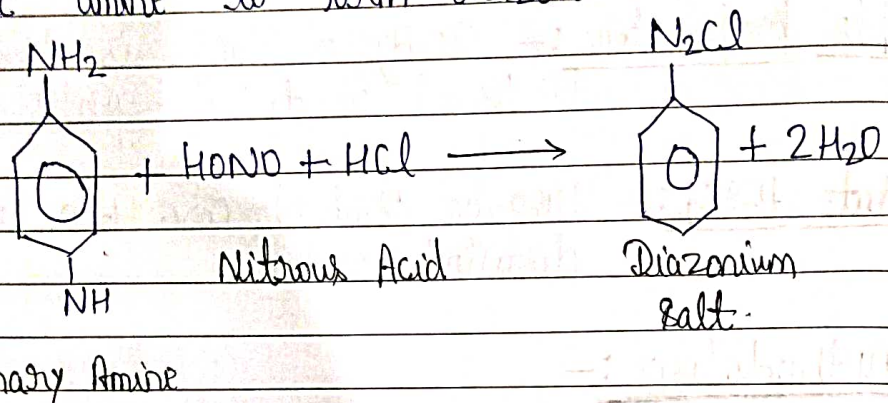
- (i) Pipette out 25ml of  $\text{BaCl}_2$  solution & transfer into a 500ml beaker.
- (ii) Add 0.5ml of conc.  $\text{H}_2\text{SO}_4$  & makeup the volume upto 100ml by distilled water.
- (iii) Heat the solution till boiling & solution become hot.
- (iv) Dilute  $\text{H}_2\text{SO}_4$  is added dropwise with constant stirring in the hot solution till the completion of precipitation reaction.
- (v) Allow the precipitate to settle down & but the supernatant liquid for complete precipitate.
- (vi) Completion of precipitation reaction is checked by adding 2-3 drops of dilute  $\text{H}_2\text{SO}_4$ .
- (vii) Filter the precipitate by using filter paper.
- (viii) Wash the ppt. 3-4 times by hot water, transfer the ppt. into hot air oven at  $110^\circ\text{C}$  for drying the ppt. along with filter paper.
- (ix) After drying transfer the filter paper.
- (x) Cool & weight crucible accurately.

## # Diazotization Titration :-

Principle :- Primary aromatic amines in the presence of HCl acid reacts with Sodium Nitrate ( $\text{NaNO}_2$ ) to form diazotisation.



→ The obtained Nitrous acid react with the primary aromatic amine to form diazonium salt.



→ This method is also known as Nitric titration. Starch Iodine paper is used to detect end point.

→ Diazotization titration method is used to determine Sulphonamide, Sulphanilamide & other Sulpha drug.

## # Method of Diazotization titration :-

There are mainly three methods based on titration procedure.

(i) Direct Method :- The main principle involved in this method is to treat the amino group containing drug, with the acid solution.

→ The resulting solution is immersed in the cold water bath or ice water bath by maintaining the temperature at  $0-5^\circ\text{C}$ .

→ The end point is determined by the above mentioned method.

(ii) Indirect Method:- The principle involved in this method is that, the excess nitrous acid is added to titration with the other appropriate titrant.

→ This method is mainly used for the titration of insoluble diazonium salts.

(iii) Other Method:- The main principle involved in this method is the formation of diazo oxide which is more stable than diazo compound.

### # Application of Diazotization titration:-

→ Used in the determination of the Sulphonamide.

→ Used in the determination of the dopamine.

→ Used in the determination of the procaine.

→ Used in the determination of amphetamine.

→ Used in the determination of chlorphenamide.

→ Used in the determination of Vitamin B<sub>4</sub>.