

### Unit-3 INORGANIC QUALITATIVE ANALYSIS

**General introduction** :- main objective of the qualitative analysis is the detection or identification of individual elements or ions entering in to the chemical composition of a substances. The qualitative analysis may be defined as “The branch of analytical chemistry which deals with identification of number of constituents present in the given unknown sample is called as qualitative analysis.”

A variety of methods , chemical, physical and physio-chemical may be used for qualitative analysis . At this stage we are interested in chemical methods. In qualitative analysis by chemical methods the element or ion to be detected is converted in to some new compound having some characteristic properties on the bases of which one can identify the compound

Qualitative analysis can be performed by number methods depending on the amount of substances used for the analytical reactions. These are macro, micro, semi -micro and ultra-micro methods

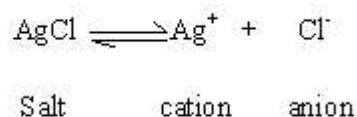
Table 3:1 Different methods of qualitative analysis

| Size of sample | Method employed | Approximate volume of sample | Approximate volume of reagent |
|----------------|-----------------|------------------------------|-------------------------------|
| 0.1 to 5.0 g.  | Macro           | 10 ml                        | 1.0to 5.0 ml                  |
| 10to100 mg.    | Semi-Micro      | 1.0 ml                       | 1 to 5 drops                  |
| 1.0to10 mg.    | Micro           | 0.1ml                        | 1drop                         |

When substance is less than 1mg, its analysis is performed under the microscope and is known as ultra-micro analysis

**Theoretical principles:-** qualitative analysis is a analytical technique which concerned with the identification of acidic (-ve ion)and basic (+ve ion) part of the inorganic material in the form of a single salt or as a mixture of two or more simple salts. When simple salt or a mixture of two or more simple salts dissolved in water, it split up in to two types of charged particles one carries positive charge called as positive ion or cation or basic radicals while the other carries a negative charge called as negative ion or anion or a acidic radical. The phenomenon of breaking

of the salts in to ions in solution is termed as dissociation. For example in silver chloride silver ion is basic radical while chloride ion is acidic radical



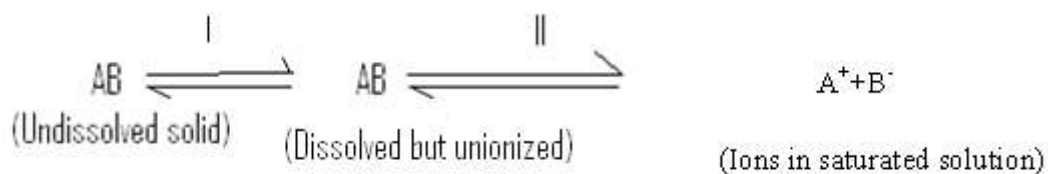
The aim of elementary qualitative analysis is to identify number of positive and negative ions present in the given inorganic salt or in a mixture for which number of experiments (called as a tests) are carried out. While carrying out the tests, we must concern with the study of formation of or disappearance of 1) Colour 2) Odour 3) Gas 4) Precipitate 5) Complex ion formation and etc.

The specific solution used to carry out specific test is called as a reagent and the chemical change observed in the test is known as the analytical or chemical reaction

### Solubility product

**Sparingly soluble salt:-**The salt or electrolyte added in water if it is having negligible solubility in water at room temperature then the salt is called as sparingly soluble salt Examples – PbSO<sub>4</sub>, BaSO<sub>4</sub> AgCl, CuS, FePO<sub>4</sub> etc.

When small amount of such a salt is added in water and thoroughly shaken then less amount of its part dissolves in water and ionizes, and gives saturated solution of the salt . Some part dissolves but remains unionized while much amount of its part remains undissolved. Two equilibriums exists when a sparingly soluble salt say AB is in contact with its saturated solution.



By applying law of mass action to equilibrium II we get

$$[\text{A}^+][\text{B}^-] / [\text{AB}] = K \text{-----(I)}$$

The undissolved and unionized part AB are in contact with the ionized part. The concentration of unionized molecule must remain constant. Hence  $[AB]$  is constant say  $K'$  hence equation (I) becomes

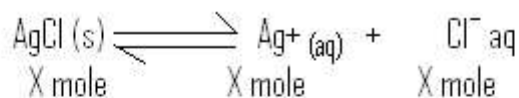
$$[A^+][B^-] = K[AB]$$

$$[A^+][B^-] = KK' = K_{SP} \text{----- (II)}$$

Where  $K_{SP}$  is another constant known as Solubility product. It may be defined as “In a saturated solution of a sparingly soluble salt or electrolyte the product of ionic concentration is constant at a given constant temperature”

The concentration of a substance in its saturated solution is known as its solubility at a given temperature expressed in unit mole per liter i.e.  $\text{mol dm}^{-3}$

Example-Solubility of a sparingly soluble salt  $\text{AgCl}$  is  $1 \times 10^{-5} \text{ mol dm}^{-3}$  at 298K. Hence its Solubility product will be



$$\begin{aligned} K_{sp} &= [\text{Ag}^+] + [\text{Cl}^-] = (1 \times 10^{-5}) (1 \times 10^{-5}) \\ &= 1 \times 10^{-10} \end{aligned}$$

**Significance or importance of Solubility product:-**The values of Solubility product explains the saturated, supersaturated and unsaturated state of solution

- 1) When ionic product is less than Solubility product i.e.  $[A^+][B^-] < K_{SP}$  then the solution produced is unsaturated solution

2) When ionic product is greater than Solubility product i.e.  $[A^+][B^-] > K_{SP}$  then the solution produced is supersaturated solution at this stage of solution precipitation takes place

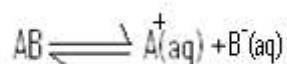
3) ) When ionic product is equal to the Solubility product i.e.  $[A^+][B^-] = K_{SP}$  then the solution produced is saturated solution

### **Common ion effect:-**

The phenomenon in which degree of dissociation or ionization of an electrolyte is suppressed by addition of another strong electrolyte containing common ion is called as Common ion effect

Consider a weak electrolyte AB whose equilibrium ionization reaction is written as

By applying law of mass action, we get mass law equation for ionization constant  $k$ .

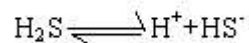
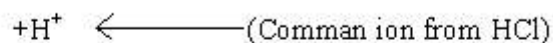


$$K = \frac{[A^+][B^-]}{[AB]}$$

Now if another strong electrolyte containing common ion either  $A^+$  or  $B^-$  is added to the solution of AB it will increase the concentration of either  $A^+$  or  $B^-$  Common ion in solution by which equilibrium of the reaction pushes to the left side hence further ionization of the electrolyte AB will be suppressed by which limited  $A^+$  or  $B^-$  ions produced in solution which are enough for the precipitation of particular group cation

Thus the degree of ionization of an electrolyte is suppressed by the addition of strong electrolyte containing common ion is known as Common ion effect.

Example:-In the precipitation of  $II^{nd}$  group radical addition of HCl will suppress the ionization of  $H_2S$  due to a Common ion effect



### Application of Solubility product and Common ion effect in separation of

**cations into groups** :-The common procedure is set for analysis of 24 cations. According to their tendency of precipitate formation with particular group reagent they are divided into six(6) groups

It should be noted that When ionic product is greater than Solubility product i.e.  $[A^+][B^-] > K_{SP}$  then the solution produced is supersaturated solution at this stage of solution precipitation takes place

Table 3:2 Separation of cations in to groups

| Group No. | Cations   | Group reagents                       | Precipitation reaction (one example)  |
|-----------|---|--------------------------------------|---|
| I         | $Ag^+, Hg^{2+}, Pb^{2+}$  | Dilute HCl                           | $Ag^+ + HCl \rightarrow AgCl \downarrow + H^+$  |
| II        | IIA- $Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}$ .<br>IIB- $Sn^{2+}, Sn^{4+}, Sb^{3+}, Sb^{5+}$<br>$As^{3+}, As^{5+}$ . | Dilute HCl + $H_2S$ gas              | HCl<br>$Cu^{2+} + H_2S \rightarrow CuS \downarrow + 2H^+$                               |
| IIIA      | $Fe^{3+}, Al^{3+}, Cr^{3+}$ .   | $NH_4Cl$ & $NH_4OH$                  | $NH_4Cl$<br>$Fe^{3+} + 3NH_4OH \rightarrow Fe(OH)_3 \downarrow + 3NH_4^+$               |
| IIIB      | $Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}$ .  | $NH_4Cl$ + $NH_4OH$ & $H_2S$ gas     | $NH_4Cl$ + $NH_4OH$<br>$Zn^{2+} + H_2S \rightarrow ZnS \downarrow + 2H^+$               |
| IV        | $Ca^{2+}, Ba^{2+}, Sr^{2+}$ .   | $NH_4Cl$ + $NH_4OH$ & $(NH_4)_2CO_3$ | $NH_4Cl$ + $NH_4OH$<br>$Ca^{2+} + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + 2NH_4^+$ |

|    |                     |                                    |   |
|----|---------------------|------------------------------------|---|
| V  | $Mg^{2+}$           | $NH_4Cl + NH_4OH$ &<br>$Na_2HPO_4$ | $NH_4Cl + NH_4OH$<br>$Mg^{2+} + Na_2HPO_4 \xrightarrow{\quad\quad\quad} MgHPO_4 \downarrow + 2Na^+$ |
| VI | $Na^+, NH_4^+, K^+$ | No particular reagent              | -----   |

**Group I :-** Cations:  $-Ag^+, Hg^{2+}, Pb^{2+}$

Group reagents :- Dilute HCl

Precipitation reaction :- 1)  $Ag^+ + HCl \rightarrow AgCl + H^+$ , 2)  $Hg^{2+} + 2HCl \rightarrow HgCl_2 + 2H^+$

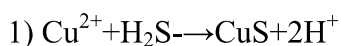
The  $AgCl, HgCl_2, PbCl_2$  precipitates of I<sup>st</sup> group cations are having lowest Solubility product ( $K_{SP}$ ) value while further group cation halides are having higher  $K_{SP}$  values hence halides of I<sup>st</sup> group get precipitated while halides of further group cations remains in solution.

**Group II:-** Cations: **Group IIA:**  $-Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}$ .

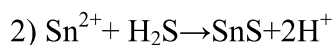
**Group IIB:**  $-Sn^{2+}, Sn^{4+}, Sb^{3+}, Sb^{5+}, As^{3+}, As^{5+}$ .

Group reagents :- Dilute HCl and  $H_2S$  gas

Precipitation reaction :- HCl



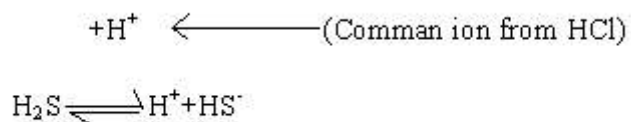
HCl



The sulphide precipitates of II<sup>nd</sup> group cations are having lower Solubility product ( $K_{SP}$ ) value while further group cation sulphides are having higher  $K_{SP}$  values hence sulphides of II<sup>nd</sup> group get precipitated while sulphides of further group cations remains in solution.

As sulphide precipitate of II<sup>nd</sup> group cation are having low Solubility product ( $K_{SP}$ ) Values, amount of sulphide ( $S^{2-}$ ) ions required for the precipitation of these cations are very less.

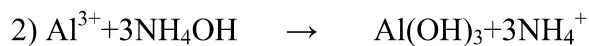
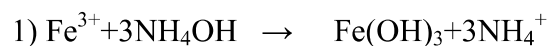
Hence ionization of  $\text{H}_2\text{S}$  is carried out in presence of dilute  $\text{HCl}$  which gives  $\text{H}^+$  common ion in solution. Due to common ion effect of  $\text{H}^+$  ion from  $\text{HCl}$  the ionization of  $\text{H}_2\text{S}$  get suppressed by which limited  $\text{S}^{2-}$  ions will be produced which will be enough for complete precipitation of  $\text{II}^{\text{nd}}$  group cations.



**Group IIIA :-** Cations:-  $\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}$ .

Group reagents :-  $\text{NH}_4\text{Cl}$  &  $\text{NH}_4\text{OH}$

Precipitation reactions:-



The hydroxide precipitates of  $\text{III}^{\text{rd}}$  A group cations are having lower Solubility product ( $K_{\text{SP}}$ ) value while further group cation hydroxides are having higher  $K_{\text{SP}}$  values hence hydroxides of  $\text{III}^{\text{rd}}$  group get precipitated while hydroxides of further group cations remains in solution.

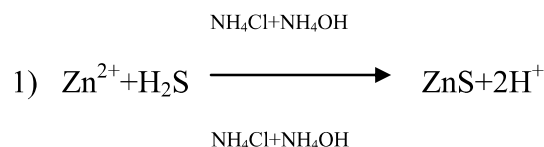
As hydroxide precipitate of  $\text{III}^{\text{rd}}$  A group cation are having low Solubility product ( $K_{\text{SP}}$ ) Values, amount of hydroxide ions required for the precipitation of these cations are very less. Hence ionization of  $\text{NH}_4\text{OH}$  is carried out in presence of  $\text{NH}_4\text{Cl}$  which gives  $\text{NH}_4^+$  common ion in solution. Due to common ion effect of  $\text{NH}_4^+$  ion from  $\text{NH}_4\text{Cl}$  the ionization of  $\text{NH}_4\text{OH}$  get suppressed by which limited  $\text{OH}^-$  ions will be produced which will be enough for complete precipitation of  $\text{III}^{\text{rd}}$  A group cations.

$\text{NH}_4^+$  (common ion from  $\text{NH}_4\text{Cl}$  suppresses ionization of  $(\text{NH}_4\text{OH})$   
 $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

**Group IIIB:-** Cations :-  $\text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$ .

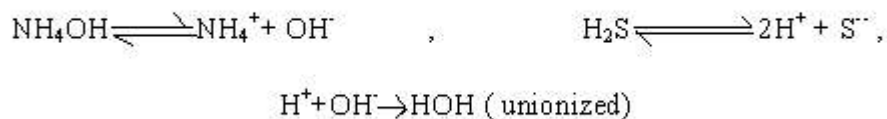
Group reagents :-  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} \ \& \ \text{H}_2\text{S}$  gas

Precipitation reactions



The cations of III<sup>rd</sup> B get precipitated as sulphide in alkaline medium. The  $K_{sp}$  values of sulphides of III<sup>rd</sup> B group cations being relatively high hence amount of sulphide ions required for precipitation of cations are very high.

If the precipitation of III<sup>rd</sup> B group is carried out with  $\text{H}_2\text{S}$  in presence of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  the  $\text{OH}^-$  ion from  $\text{NH}_4\text{OH}$  combines with  $\text{H}^+$  ion from  $\text{H}_2\text{S}$  and gives undissociated water molecule as



As  $\text{H}^+$  ions are removed from  $\text{H}_2\text{S}$ , free ionization of  $\text{H}_2\text{S}$  takes place by which excess  $\text{H}^+$  ions produces in solution which are enough for complete precipitation of III<sup>rd</sup> B group cations

In above solution  $\text{NH}_4\text{Cl}$  added suppresses ionization of  $\text{NH}_4\text{OH}$  by common ion effect due to which excess  $\text{OH}^-$  ions may not produces by which hydroxide precipitation of further group cations may be avoided

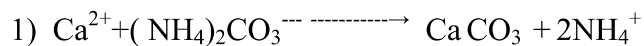
**Group IV :-** Cations :-  $\text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}$ .



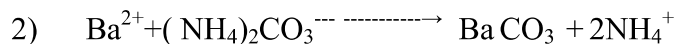
Group reagents :-NH<sub>4</sub>OH+NH<sub>4</sub>Cl and(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>

Precipitation reactions :-

NH<sub>4</sub>Cl+NH<sub>4</sub>OH



NH<sub>4</sub>Cl+NH<sub>4</sub>OH



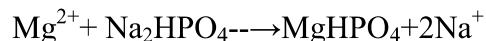
The K<sub>SP</sub> values of carbonate precipitate of IV<sup>th</sup> group cations are low. Hence for the precipitation of IV<sup>th</sup> group cation limited CO<sub>3</sub><sup>2-</sup> ions are required. If the precipitation of IV<sup>th</sup> group cations is carried out in presence of NH<sub>4</sub>OH and NH<sub>4</sub>Cl, NH<sub>4</sub><sup>+</sup> common ions of NH<sub>4</sub>OH suppresses ionization of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> by which limited CO<sub>3</sub><sup>2-</sup> ions produces which are enough for precipitation of IV<sup>th</sup> group cations. The NH<sub>4</sub>Cl added suppresses ionization of NH<sub>4</sub>OH by common ion effect unless hydroxide precipitation of V<sup>th</sup> group cation (Mg<sup>2+</sup>) takes place along with IV<sup>th</sup> group carbonate precipitate.

**Group V:-** Cation :-Mg<sup>2+</sup>

Group reagents :-NH<sub>4</sub>Cl + NH<sub>4</sub>OH and Na<sub>2</sub>HPO<sub>4</sub>

Precipitation reaction :-

NH<sub>4</sub>Cl+NH<sub>4</sub>OH



Mg<sup>2+</sup> gives white precipitate of MgHPO<sub>4</sub> with Na<sub>2</sub>HPO<sub>4</sub> in presence of NH<sub>4</sub>Cl and NH<sub>4</sub>OH. Here use of NH<sub>4</sub>Cl prevent hydroxide precipitation of Mg<sup>2+</sup> While the buffer (NH<sub>4</sub>Cl + NH<sub>4</sub>OH) provides optimum pH (pH=10) for effective precipitation of Mg<sup>2+</sup> as MgHPO<sub>4</sub>

**Group VI:-** Cations :-Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>

Group Reagents:-There is no specific reagent for this group. These cations gives their water soluble salts with the reagents. Cations of this group are detected and confirmed by their individual characteristic tests.

**Complex formation:-**

The addition product or a complex compound in which number of ligands (equal to coordination number of central metal ion) binds with central metal ion by strong coordinate bonding and produces a compound called as addition product or a complex compound. If it bears any charge then it is known as complex ion. It plays an important role in detection separation and confirmation of most of acidic and basic radicals in Inorganic semi-micro qualitative analysis. The formation of complex ion in solution experiences sudden change in colour, sudden change in solubility and dramatic change in chemical properties.

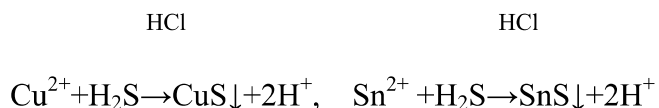
**Applications of complex formation:-**There are several applications of complex formation in qualitative analysis some of them are

- 1) Separation of II<sup>nd</sup> group in to IIA and IIB
- 2) Separation of Cu<sup>2+</sup> from Cd<sup>2+</sup> as a cyano complex
- 3) Separation of Co<sup>2+</sup> from Ni<sup>2+</sup>
- 4) Separation of Cl<sup>-</sup> from Br<sup>-</sup> and I<sup>-</sup>
- 5) Detection of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> (Brown ring test)

### 1) Separation of II<sup>nd</sup> group in to IIA and IIB:-

The IIA group or Copper group cations are Cu<sup>++</sup>, Cd<sup>++</sup>, Hg<sup>++</sup>, Pb<sup>++</sup>, Bi<sup>+3</sup>. While the IIB Group or Tin group cations are Sn<sup>+2</sup>, Sn<sup>+4</sup>, Sb<sup>+3</sup>, Sb<sup>+5</sup>, As<sup>+3</sup>, As<sup>+5</sup>. The mixture containing IIA and IIB group cations dissolved in suitable mineral acid solution or in distilled water and its solution can be prepared

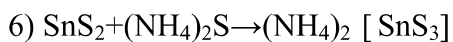
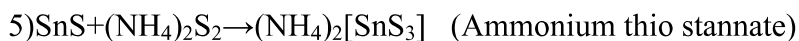
Aqueous solution of IIA and IIB group cations treated with dilute HCl and excess of H<sub>2</sub>S gas. A sulphide precipitate of IIA and IIB group cations produces .



The sulphide precipitate of IIA and IIB group cations treated with yellow ammonium sulphide ((NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>) after gentle warming IIB group precipitate dissolves

in  $(\text{NH}_4)_2\text{S}_x$  while IIA group precipitate remains as it is hence both can be separated from each other by filtration

The precipitate of IIB group cations dissolves in  $(\text{NH}_4)_2\text{S}_x$  and gives clear solution of cations by following reactions



All these thioantimonite, thioarsinite, thioantimonate, thioarsenate and thioantimonate salts are water soluble salts which gives clear solution of respective cations used for their confirmatory tests

## 2) Separation of $\text{Cu}^{2+}$ from $\text{Cd}^{2+}$ :-

Both the cations are IIA group or copper group cations Aqueous solution containing  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  cations treated with dilute HCl and excess of  $\text{H}_2\text{S}$  gas. A sulphide precipitate  $\text{CuS}$  and  $\text{CdS}$  produces as

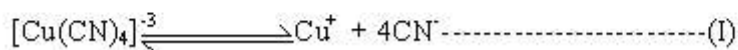
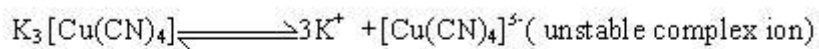
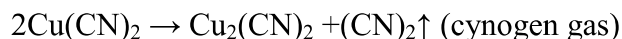
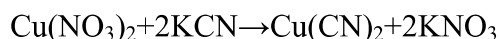


The sulphide precipitate of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  digested with concentrated Nitric acid ( $\text{HNO}_3$ ) and a clear solution of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$  produces by following reactions



When aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$  treated with excess potassium cyanide (KCN) solution  $\text{Cd}^{2+}$  ion gives precipitate of cyanide first while  $\text{Cu}^{2+}$  ion remains in solution because

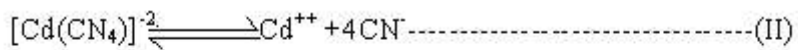
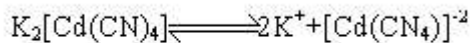
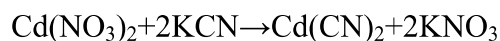
The  $\text{Cu}(\text{NO}_3)_2$  react with KCN and gives unstable  $\text{Cu}(\text{CN})_2$  as



By applying law of mass action to the above reaction (I) we get

$$K_{\text{inst}} = [\text{Cu}^+] [\text{CN}^-]^4 / [\text{Cu}(\text{CN})_4]^{3-} = 5.00 \times 10^{-28}$$

When  $\text{Cd}(\text{NO}_3)_2$  reacts with excess KCN gives very weak cyano complex



By applying law of mass action to the above reaction (II) we get

$$K_{\text{inst}} = [\text{Cd}^{++}] [\text{CN}^-]^4 / [\text{Cu}(\text{CN})_4]^{2-} = 1.4 \times 10^{-17}$$

The ionization constant value for  $[\text{Cd}(\text{CN})_4]^{2-}$  is higher than  $[\text{Cu}(\text{CN})_4]^{3-}$  due to which excess  $\text{Cd}^{++}$  ions remains free in solution than  $\text{Cu}^{++}$  ions Hence free  $\text{Cd}^{++}$

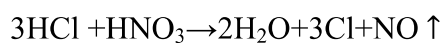
Ion from solution precipitated first with  $\text{H}_2\text{S}$  gas than  $\text{Cu}^{++}$  ions .

### 3) Separation of $\text{Co}^{2+}$ from $\text{Ni}^{2+}$ :-

Both the cations are III<sup>rd</sup>B cations. Aqueous solution containing  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  cations treated with  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  and excess of  $\text{H}_2\text{S}$  gas black precipitate of  $\text{CoS}$  and  $\text{NiS}$  produces as

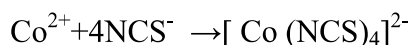


Wash the residue of  $\text{CoS}$  and  $\text{NiS}$  with distilled water and treat it with aquaria ( $\text{HCl} + \text{HNO}_3 = 1:3$ ) in an evaporating dish. Evaporate the solution to dryness, cool it, add little distilled water, stir well, and filter. Clear solution of  $\text{CoCl}_2$  and  $\text{NiCl}_2$  produces as



Divide the above solution into two parts and take test for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$

**Test for  $\text{Co}^{2+}$  :-** Treat one portion of above solution with little amyl alcohol, add few crystals of  $\text{NH}_4\text{CNS}$ , shake well. Deep blue coloured alcohol layer produces indicates presence of  $\text{Co}^{2+}$

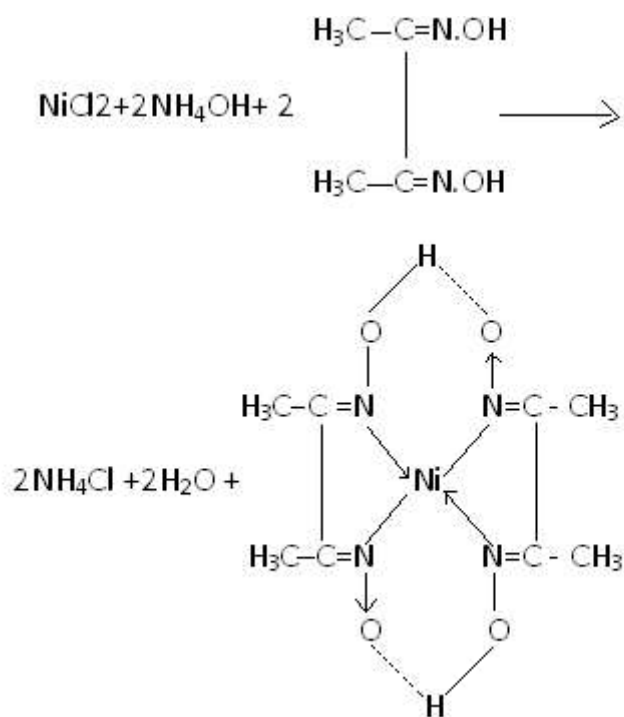


In above test use of water must be avoided because if water is used, pink colored  $[\text{Co}(\text{H}_2\text{O})_6]$  complex ion produces instead of deep blue or green  $[\text{Co}(\text{NCS})_4]^{2-}$  complex ion

$\text{Ni}^{2+}$  present in the solution does not form colored complex with  $\text{NCS}^-$  ion. Hence  $\text{Co}^{2+}$  is detected in presence of  $\text{Ni}^{2+}$

**Test for  $\text{Ni}^{2+}$  :-** To another portion of test solution add excess  $\text{NH}_4\text{OH}$  till alkaline and enough alcoholic dimethyl glyoxime solution the scarlet red colored precipitate of  $[\text{Ni}(\text{Dmg})_2]$  produces indicates confirmation of  $\text{Ni}^{2+}$

Dimethyl glyoxime is specific reagent for  $\text{Ni}^{2+}$  it gives scarlet red precipitate for  $\text{Ni}^{2+}$  in alkaline medium but it does not give such a precipitate for  $\text{Co}^{2+}$ .

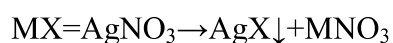


Scarlet red coloured complex of Ni(Dmg)<sub>2</sub>

## Detection and separation of acidic radicles ( byComplex formation)

### 1)Separation of Cl<sup>-</sup> from Br<sup>-</sup> and I<sup>-</sup>:-

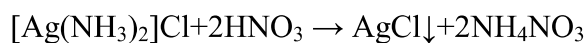
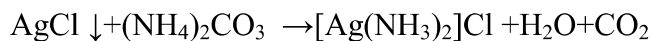
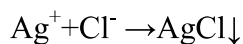
All the halides are similar in properties the group reagent for halides is silver nitrate (AgNO<sub>3</sub>) which gives halide precipitate as AgCl(white ),AgBr(pale yellow) and AgI (yellow) which all are insoluble in dilute HNO<sub>3</sub>



Where X=Cl<sup>-</sup>,Br<sup>-</sup> or I<sup>-</sup> and M=Na<sup>+</sup> or K<sup>+</sup>

Cl<sup>-</sup> can be separated from Br<sup>-</sup> and I<sup>-</sup> as, the precipitate of AgCl ,AgBr and AgI treated with aqueous ammonium carbonate solution .Silver chloride gives clear solution of amine complex while AgBr and AgI are sparingly soluble in ammonia solution hence remains

undissolved the solution is centrifuged .The centrifugate containing  $\text{Cl}^-$  acidified with dilute  $\text{HNO}_3$  . $\text{AgCl}$  get reprecipitated as a result of decomposition of ammine complex .

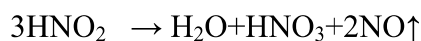
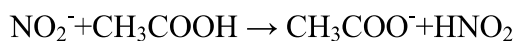


In this way  $\text{Cl}^-$  ion detected and separated from the mixture containing  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  . $\text{NH}_4\text{OH}$  is not used in the above reactions because  $\text{AgBr}$  is partially soluble in ammonia

## 2)Detection of $\text{NO}_2^-$ and $\text{NO}_3^-$ (By Brown ring test)

If the given mixture contain both  $\text{NO}_2^-$  and  $\text{NO}_3^-$  together both can be detected by Brown ring test as follows

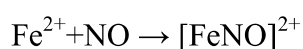
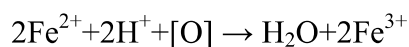
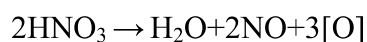
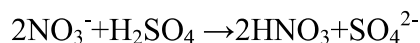
**a)Detection and confirmation of  $\text{NO}_2^-$ :**-Treat the aqueous solution of a mixture containing  $\text{NO}_2^-$  and  $\text{NO}_3^-$  with cold, fresh and saturated solution of  $\text{FeSO}_4$  in a clean test tube to it add dilute  $\text{CH}_3\text{COOH}$  solution from the side wall of test tube till solution becomes acidic, brown ring of  $[\text{FeNO}]\text{SO}_4$  complex(or brown coloured solution) produces at the junction of liquid layers indicate conformation of  $\text{NO}_2^-$  ion .The brown ring of  $[\text{FeNO}]\text{SO}_4$  produces by following reactions



For detection of  $\text{NO}_2^-$  the aqueous solution used must be free from  $\text{Br}^-$  and  $\text{I}^-$  which gives colored complexes with  $\text{Fe}^{2+}$  .

**b)Detection and confirmation of  $\text{NO}_3^-$ :**-Treat the aqueous solution of mixture containing  $\text{NO}_3^-$  ion (free from  $\text{NO}_2^-$   $\text{Br}^-$  and  $\text{I}^-$ ) with enough concentrated  $\text{H}_2\text{SO}_4$  shake well cool under tap water. To it add cold, fresh and saturated  $\text{FeSO}_4$  solution from the side wall of test tube. Brown ring at the junction of two liquid layers indicates the conformation of  $\text{NO}_3^-$  ion

The brown ring of  $[\text{FeNO}]^{2+}$  complex ion produces by following reactions



The aqueous solution used for confirmation of  $\text{NO}_3^-$  must be free from  $\text{NO}_2^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions.

### **Applications of oxidation-reduction:-**

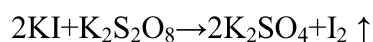
In qualitative analysis many cation and anions are detected by means of their behavior towards oxidising or reducing agents

1) Separation of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ :- The  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  are separated from each other by two probable methods

**Method –I:-Use of potassium per sulphate ( $\text{K}_2\text{S}_2\text{O}_8$ )** The oxidation potential of  $\text{K}_2\text{S}_2\text{O}_8$  is very high (2.05V) so used for separation of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$

**a) Detection , confirmation and removal of  $\text{I}^-$  :-** To the mixture of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  little ( $\text{K}_2\text{S}_2\text{O}_8$ ) is added and mixture is warmed, evolution of violet fumes indicates detection and confirmation of  $\text{I}^-$  in solution.

Heat



Add slight excess  $\text{K}_2\text{S}_2\text{O}_8$  and warm it gently till violet fumes disappears completely (avoid over heating) -  $\text{I}^-$  completely removed . Here per sulphate oxidizes  $\text{I}^-$  to  $\text{I}_2$  and itself get reduced to  $\text{SO}_4^{2-}$

**b) Detection , confirmation and removal of  $\text{Br}^-$ :-** Take solution from above test free from  $\text{I}^-$  to it add dilute  $\text{H}_2\text{SO}_4$  and warm the solution gently. Evolution of brown vapors indicates detection and confirmation of  $\text{Br}^-$ .

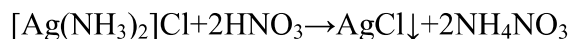
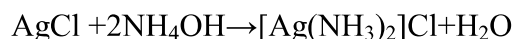
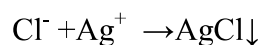


Heat



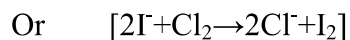
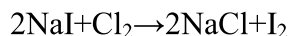
Add slight excess  $\text{K}_2\text{S}_2\text{O}_8$  and heat the solution gently till brown vapors completely removed (avoid over heating).  $\text{Br}^-$  completely removed. Here per sulphate oxidizes  $\text{Br}^-$  to  $\text{Br}_2$

**c) Detection and confirmation of  $\text{Cl}^-$ :**- Take solution from above test free from  $\text{I}^-$  and  $\text{Br}^-$  to it add enough  $\text{AgNO}_3$  white precipitate of  $\text{AgCl}$  produces which dissolves completely in ammonia and then reprecipitated with dilute  $\text{HNO}_3$  confirms presence of  $\text{Cl}^-$  ion in solution



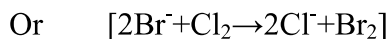
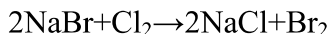
**Method II:- Use of chlorine water:-**

**a)** To the aqueous solution of a mixture containing  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  add enough chlorine water and chloroform .Shake well the solution and allow to separate two layers. Violet colour to lower organic layer indicate presence of  $\text{I}^-$  in the given solution. Take upper aqueous layer in a test tube to it add excess chlorine water and chloroform shek well repeat the same till violet colour to lower organic layer does not produces. Here  $\text{I}^-$  get removed completely in this test the  $\text{Cl}_2$  itself under goes reduction and oxidizes  $\text{I}^-$  to iodine this iodine dissolves in organic layer (chloroform ) and gives violet colour to organic layer

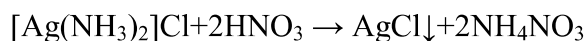
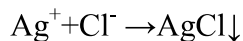


**b)** To the aqueous layer from above step(free from  $\text{I}^-$ ) add enough chlorine water and chloroform .Shake well the solution and allow to separate two layers yellow colour to lower organic layer indicate presence of  $\text{Br}^-$  in the given solution. Take upper aqueous layer to it add excess chlorine water and chloroform shake well repeat the same till yellow colour to lower organic layer does not produces. Here  $\text{Br}^-$  get removed completely

in this test the chlorine it self under goes reduction and oxidizes  $\text{Br}^-$  to  $\text{Br}_2$  which dissolves in organic layer (chloroform ) and gives yellow colour to organic layer

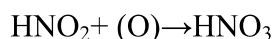
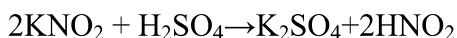


c)The aqueous layer from above step (completely free from  $\text{I}^-$ ,  $\text{Br}^-$  and organic layer) or aqueous solution containing  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  used for confirmation of  $\text{Cl}^-$  which can be treated with  $\text{AgNO}_3$  solution. A white precipitate of  $\text{AgCl}$  produces. It can be treated with aqueous ammonium carbonate solution.  $\text{AgCl}$  gives clear solution of amine complex. If the solution is treated with dilute  $\text{HNO}_3$   $\text{Cl}^-$  ion get reprecipitated as  $\text{AgCl}$ . Hence  $\text{Cl}^-$  ion detected and confirmed.



## 2) Separation of $\text{NO}_2^-$ and $\text{NO}_3^-$ :-

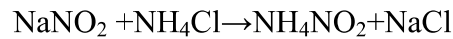
**a) Detection of  $\text{NO}_2^-$  :-** The aqueous solution containing  $\text{NO}_2^-$  and  $\text{NO}_3^-$  acidified with  $\text{H}_2\text{SO}_4$  and treated with very dilute  $\text{KMnO}_4$  solution. Decolouration of  $\text{KMnO}_4$  solution confirms the presence of  $\text{NO}_2^-$  here  $\text{KMnO}_4$  is reduced by  $\text{HNO}_2$  to  $\text{MnSO}_4$  where as  $\text{HNO}_2$  is oxidized to  $\text{HNO}_3$



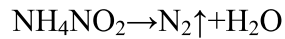
Nitrate present in the solution does not interferes in the above test.

**b) Removal of  $\text{NO}_2^-$  :-** Under specific conditions nitrite can be reduced to nitrogen and separated from nitrate. To the solution containing  $\text{NO}_2^-$  an excess of solid  $\text{NH}_4\text{Cl}$  is added and the solution is boiled to expel out  $\text{NO}_2^-$  as  $\text{N}_2$  gas.

Boil

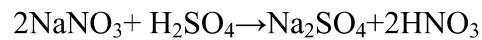


Boil



**c) Detection of  $\text{NO}_3^-$ :**-After the removal of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  can be tested by following tests :-

1) Solution is warmed with Cu foil and conc.  $\text{H}_2\text{SO}_4$ . Brown gas evolves that turns starch iodide paper black indicates confirmation of  $\text{NO}_3^-$ .



2) Brown ring test:-[Please refer the brown ring test for  $\text{NO}_3^-$ ]

### Spot tests

Scientist F. Fiegl and his colleagues developed an advanced analytical technique in 1918 for detection and confirmation of basic radicals called as Spot tests analysis. The technique is the most superior technique than Inorganic semi micro qualitative analysis because of the following advantages

Advantages

- 1) Very simple equipments are required .
- 2) Very less space is required.
- 3) Less number of labors are required.
- 4) Very very small quantity of sample and reagents are required .
- 5) Very fast technique, less time can be consumed.
- 6) It is more economical.
- 7) Simple to operate.
- 8) Pollution free technique.
- 9) Carried out even at micro level.

The spot test analysis is a simple technique for which one or two drops of sample solution of a high purity material is required. One drop of reagent solution is

required. The equipments required are filter paper strips or a spot plate, reagent bottles, sample solution containers, dryer and etc.

**Experimental procedure for spot test analysis :-** Take a drop of sample solution on a paper strip, dry it with the dryer apply a drop of a reagent on it , intense colour develops on a paper strip indicates confirmation of the cation. Spot tests also may be carried on spot plate.

Requirements:- The basic requirements of spot test analysis are, High purity (A.R. Grade) inorganic salts and reagents, suitable experimental conditions and cleanliness of equipments and working place are required

The technique has some limitations like the reagents required for the analysis must be of higher quality, which are costly. The sample solution must be free from quantamination, prepared by using A.R.grade inorganic salts. The organometallic complex formation or chelation reactions which proceeds in spot test analysis may not be clearly understood .

**Table 3:3 Detection of some cations by spot test analysis**

| Test  | Observation<br>Colour of the spot  | Inference  |
|---|------------------------------------|--|
| 1)Rubeanic acid test:-take a drop of original solution(O.S.) on a paper strip +a drop of reagent-expose toNH <sub>3</sub> gas | a)Olive green<br>b)Blue<br>c)Brown | Cu <sup>2+</sup> present<br>Ni <sup>2+</sup> present<br>Co <sup>2+</sup> present |
| 2)Dimethyl glyoxime test:-take a drop of O.S. on a paper strip+adropof reagent-expose toNH <sub>3</sub> gas                   | Scarlet red colour                 | Ni <sup>2+</sup> present and confirmed   |
| 3)Potassium ferrocyanide test:- take a drop of O.S. on a spot plate+a drop of reagent   | Intence blue colour                | Fe <sup>3+</sup> present and confirmed   |