

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

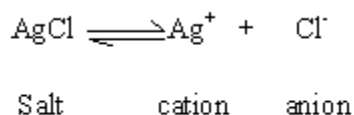
Table 3:1 Different methods of qualitative analysis

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



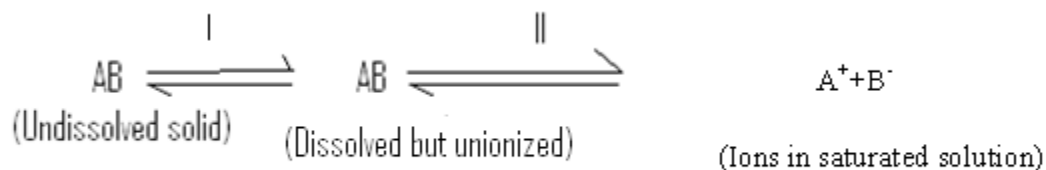
The aim of elementary qualitative analysis is to identify number of positive and negative ions present in the given inorganic salt or in a mixture for which number of experiments (called as a tests) are carried out. While carrying out the tests, we must concern with the study of formation of or disappearance 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 – PbSO₄, BaSO₄ AgCl, CuS, FePO₄ 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

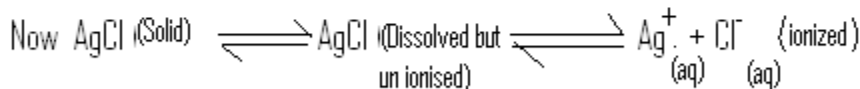
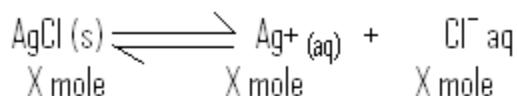
$$[A^+][B^-] = K[AB]$$

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

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. mol dm^{-3}

Example-Solubility of a sparingly soluble salt 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

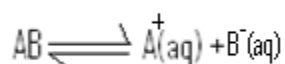
3)) When ionic product is equal to the Solubility product i.e. $[A^+][B^-] = K_{SP}$ then the solution produced is saturated solution

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 .

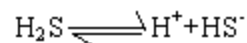


$$K = \frac{[A^+][B^-]}{[AB]}$$

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- $Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}$. IIB- $Sn^{2+}, Sn^{4+}, Sb^{3+}, Sb^{5+}$ As^{3+}, As^{5+} .	Dilute HCl + H_2S gas	HCl $Cu^{2+} + H_2S \rightarrow CuS \downarrow + 2H^+$
IIIA	$Fe^{3+}, Al^{3+}, Cr^{3+}$.	NH_4Cl & NH_4OH	NH_4Cl $Fe^{3+} + 3NH_4OH \rightarrow Fe(OH)_3 \downarrow + 3NH_4^+$
IIIB	$Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}$.	NH_4Cl + NH_4OH & H_2S gas	NH_4Cl + NH_4OH $Zn^{2+} + H_2S \rightarrow ZnS \downarrow + 2H^+$
IV	$Ca^{2+}, Ba^{2+}, Sr^{2+}$.	NH_4Cl + NH_4OH & $(NH_4)_2CO_3$	NH_4Cl + NH_4OH $Ca^{2+} + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + 2NH_4^+$

V	Mg^{2+}	$NH_4Cl + NH_4OH$ & Na_2HPO_4	$NH_4Cl + NH_4OH$ $Mg^{2+} + Na_2HPO_4 \xrightarrow{\quad\quad\quad} MgHPO_4 \downarrow + 2Na^+$
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) $Hg^{2+} + 2HCl \rightarrow HgCl_2 + 2H^+$

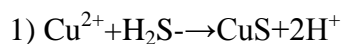
The $AgCl, HgCl_2, PbCl_2$ precipitates of Ist group cations are having lowest Solubility product (K_{SP}) value while further group cation halides are having higher K_{SP} values hence halides of Ist group get precipitated while halides of further group cations remains in solution.

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

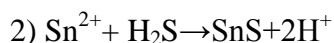
Group IIB:- $Sn^{2+}, Sn^{4+}, Sb^{3+}, Sb^{5+}, As^{3+}, As^{5+}$.

Group reagents :- Dilute HCl and H_2S gas

Precipitation reaction :- HCl



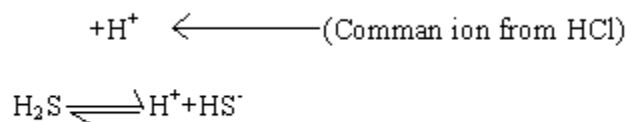
HCl



The sulphide precipitates of IInd group cations are having lower Solubility product (K_{SP}) value while further group cation sulphides are having higher K_{SP} values hence sulphides of IInd group get precipitated while sulphides of further group cations remains in solution.

As sulphide precipitate of IInd 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.

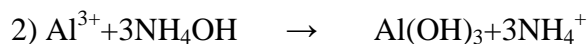
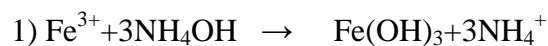
Hence ionization of H_2S is carried out in presence of dilute HCl which gives H^+ common ion in solution. Due to common ion effect of H^+ ion from HCl the ionization of H_2S get suppressed by which limited S^{2-} ions will be produced which will be enough for complete precipitation of II^{nd} group cations.



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

Group reagents :- NH_4Cl & NH_4OH

Precipitation reactions:-



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

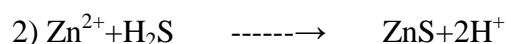
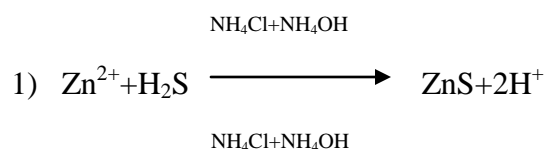
As hydroxide precipitate of III^{rd} A group cation are having low Solubility product (K_{SP}) Values, amount of hydroxide ions required for the precipitation of these cations are very less. Hence ionization of NH_4OH is carried out in presence of NH_4Cl which gives NH_4^+ common ion in solution. Due to common ion effect of NH_4^+ ion from NH_4Cl the ionization of NH_4OH get suppressed by which limited OH^- ions will be produced which will be enough for complete precipitation of III^{rd} A group cations.

NH_4^+ (common ion from NH_4Cl suppresses ionization of (NH_4OH)
 $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

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

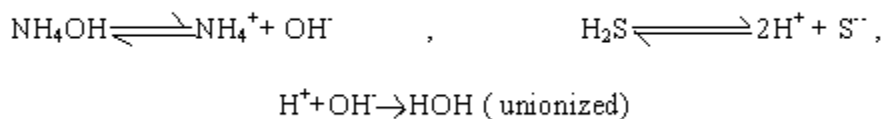
Group reagents :- $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ & H_2S gas

Precipitation reactions



The cations of IIIrd B get precipitated as sulphide in alkaline medium. The K_{sp} values of sulphides of IIIrd B group cations being relatively high hence amount of sulphide ions required for precipitation of cations are very high.

If the precipitation of IIIrd B group is carried out with H_2S in presence of NH_4Cl and NH_4OH the OH^- ion from NH_4OH combines with H^+ ion from H_2S and gives undissociated water molecule as



As H^+ ions are removed from H_2S , free ionization of H_2S takes place by which excess H^+ ions produces in solution which are enough for complete precipitation of IIIrd B group cations

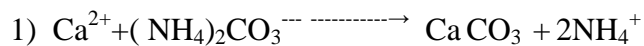
In above solution NH_4Cl added suppresses ionization of NH_4OH by common ion effect due to which excess OH^- ions may not produces by which hydroxide precipitation of further group cations may be avoided

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

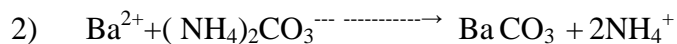
Group reagents :-NH₄OH+NH₄Cl and(NH₄)₂CO₃

Precipitation reactions :-

NH₄Cl+NH₄OH



NH₄Cl+NH₄OH



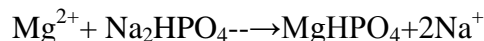
The K_{SP} values of carbonate precipitate of IVth group cations are low. Hence for the precipitation of IVth group cation limited CO₃²⁻ ions are required. If the precipitation of IVth group cations is carried out in presence of NH₄OH and NH₄Cl, NH₄⁺ common ions of NH₄OH suppresses ionization of (NH₄)₂CO₃ by which limited CO₃²⁻ ions produces which are enough for precipitation of IVth group cations. The NH₄Cl added suppresses ionization of NH₄OH by common ion effect unless hydroxide precipitation of Vth group cation (Mg²⁺) takes place along with IVth group carbonate precipitate.

Group V:- Cation :-Mg²⁺

Group reagents :-NH₄Cl + NH₄OH and Na₂HPO₄

Precipitation reaction :-

NH₄Cl+NH₄OH



Mg²⁺ gives white precipitate of MgHPO₄ with Na₂HPO₄ in presence of NH₄Cl and NH₄OH. Here use of NH₄Cl prevent hydroxide precipitation of Mg²⁺ While the buffer (NH₄Cl + NH₄OH) provides optimum pH (pH=10) for effective precipitation of Mg²⁺ as MgHPO₄

Group VI:- Cations :-Na⁺,NH₄⁺,K⁺

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.

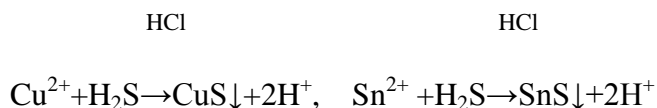
Applications of complex formation:-There are several applications of complex formation in qualitative analysis some of them are

- 1) Separation of IInd group in to IIA and IIB
- 2) Separation of Cu²⁺ from Cd²⁺ as a cyano complex
- 3) Separation of Co²⁺ from Ni²⁺
- 4) Separation of Cl⁻ from Br⁻ and I⁻
- 5) Detection of NO₂⁻ and NO₃⁻ (Brown ring test)

1) Separation of IInd group in to IIA and IIB:-

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

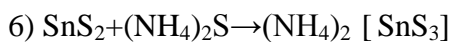
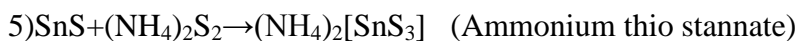
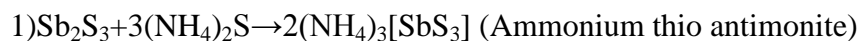
Aqueous solution of IIA and IIB group cations treated with dilute HCl and excess of H₂S gas. A sulphide precipitate of IIA and IIB group cations produces .



The sulphide precipitate of IIA and IIB group cations treated with yellow ammonium sulphide ((NH₄)₂S_x) 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 Cu^{2+} from Cd^{2+} :-

Both the cations are IIA group or copper group cations Aqueous solution containing Cu^{2+} and Cd^{2+} cations treated with dilute HCl and excess of H_2S gas. A sulphide precipitate CuS and CdS produces as

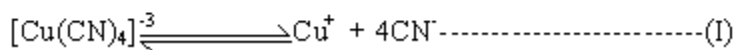
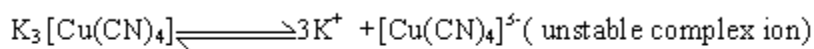
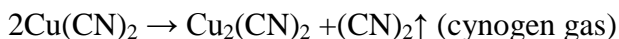
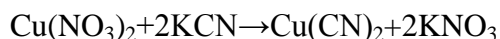


The sulphide precipitate of Cu^{2+} and Cd^{2+} digested with concentrated Nitric acid (HNO_3) and a clear solution of $\text{Cu}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ produces by following reactions



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

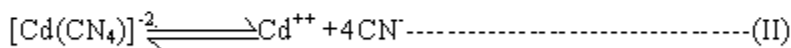
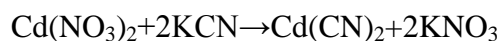
The $\text{Cu}(\text{NO}_3)_2$ react with KCN and gives unstable $\text{Cu}(\text{CN})_2$ as



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

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

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

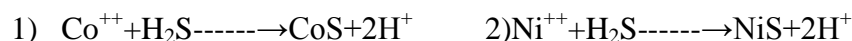
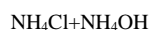
$$K_{\text{inst}} = \frac{[\text{Cd}^{++}][\text{CN}^-]^4}{[\text{Cd}(\text{CN})_4]^{2-}} = 1.4 \times 10^{-17}$$

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

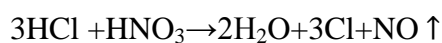
Ion from solution precipitated first with H_2S gas than Cu^{++} ions .

3) Separation of Co^{2+} from Ni^{2+} :-

Both the cations are IIIrdB cations. Aqueous solution containing Co^{2+} and Ni^{2+} cations treated with NH_4OH and NH_4Cl and excess of H_2S gas black precipitate of CoS and NiS produces as

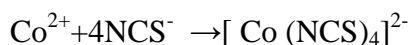


Wash the residue of CoS and NiS with distilled water and treat it with aquaria ($\text{HCl} + \text{HNO}_3 = 1:3$) in an evaporating dish. Evaporate the solution to dryness, cool it, add little distilled water, stir well, and filter. Clear solution of CoCl_2 and NiCl_2 produces as



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

Test for Co^{2+} :- Treat one portion of above solution with little amyl alcohol, add few crystals of NH_4CNS , shake well. Deep blue coloured alcohol layer produces indicates presence of Co^{2+}

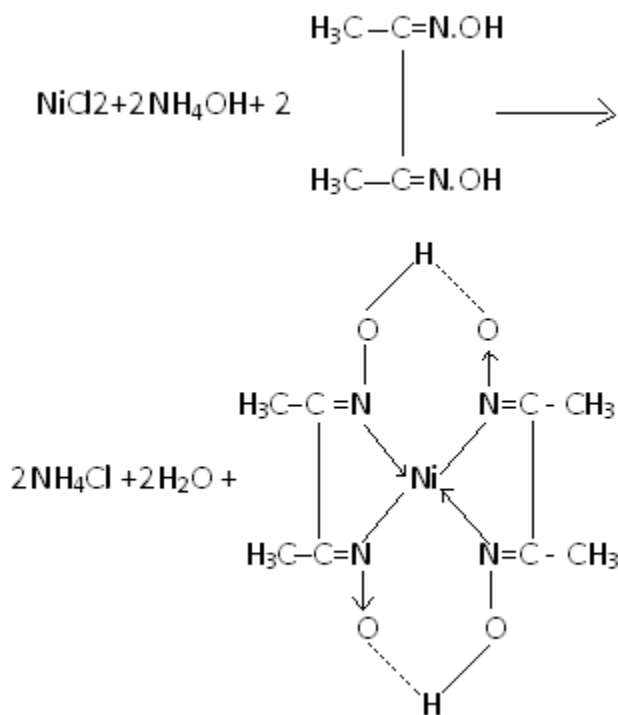


In above test use of water must be avoided because if water is used, pink colored $[\text{Co}(\text{H}_2\text{O})_6]$ complex ion produces instead of deep blue or green $[\text{Co}(\text{NCS})_4]^{2-}$ complex ion

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

Test for Ni^{2+} :- To another portion of test solution add excess NH_4OH till alkaline and enough alcoholic dimethyl glyoxime solution the scarlet red colored precipitate of $[\text{Ni}(\text{Dmg})_2]$ produces indicates confirmation of Ni^{2+}

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

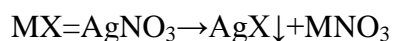


Scarlet red coloured complex of Ni(Dmg)₂

Detection and separation of acidic radicles (byComplex formation)

1)Separation of Cl⁻ from Br⁻ and I⁻:-

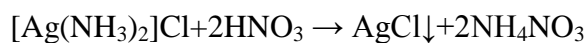
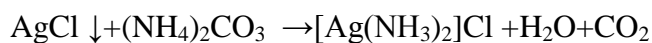
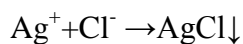
All the halides are similar in properties the group reagent for halides is silver nitrate (AgNO₃) which gives halide precipitate as AgCl(white),AgBr(pale yellow) and AgI (yellow) which all are insoluble in dilute HNO₃



Where X=Cl⁻,Br⁻ or I⁻ and M=Na⁺ or K⁺

Cl⁻ can be separated from Br⁻ and I⁻ 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 Cl^- acidified with dilute HNO_3 . AgCl get reprecipitated as a result of decomposition of ammine complex .

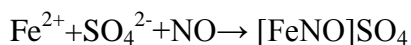
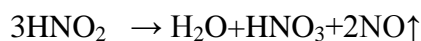
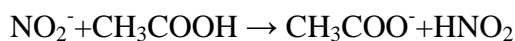


In this way Cl^- ion detected and separated from the mixture containing Cl^- , Br^- and I^- . NH_4OH is not used in the above reactions because AgBr is partially soluble in ammonia

2)Detection of NO_2^- and NO_3^- (By Brown ring test)

If the given mixture contain both NO_2^- and NO_3^- together both can be detected by Brown ring test as follows

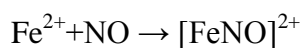
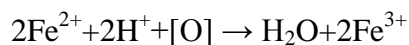
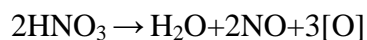
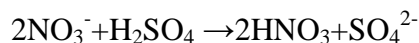
a)Detection and confirmation of NO_2^- :-Treat the aqueous solution of a mixture containing NO_2^- and NO_3^- with cold, fresh and saturated solution of FeSO_4 in a clean test tube to it add dilute CH_3COOH solution from the side wall of test tube till solution becomes acidic, brown ring of $[\text{FeNO}]\text{SO}_4$ complex (or brown coloured solution) produces at the junction of liquid layers indicate conformation of NO_2^- ion .The brown ring of $[\text{FeNO}]\text{SO}_4$ produces by following reactions



For detection of NO_2^- the aqueous solution used must be free from Br^- and I^- which gives colored complexes with Fe^{2+} .

b)Detection and confirmation of NO_3^- :-Treat the aqueous solution of mixture containing NO_3^- ion (free from NO_2^- , Br^- and I^-) with enough concentrated H_2SO_4 shake well cool under tap water. To it add cold, fresh and saturated FeSO_4 solution from the side wall of test tube. Brown ring at the junction of two liquid layers indicates the conformation of NO_3^- ion

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



The aqueous solution used for confirmation of NO_3^- must be free from NO_2^- , Br^- and I^- ions.

Applications of oxidation-reduction:-

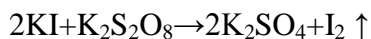
In qualitative analysis many cation and anions are detected by means of their behavior towards oxidising or reducing agents

1) Separation of Cl^- , Br^- and I^- :- The Cl^- , Br^- and 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 Cl^- , Br^- and I^-

a) Detection , confirmation and removal of I^- :- To the mixture of Cl^- , Br^- and 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 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) - I^- completely removed . Here per sulphate oxidizes I^- to I_2 and itself get reduced to SO_4^{2-}

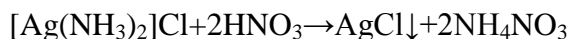
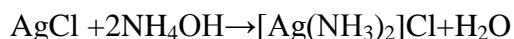
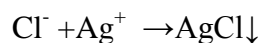
b) Detection , confirmation and removal of Br^- :- Take solution from above test free from I^- to it add dilute H_2SO_4 and warm the solution gently. Evolution of brown vapors indicates detection and confirmation of Br^- .

Heat



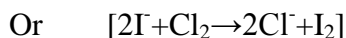
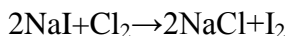
Add slight excess $\text{K}_2\text{S}_2\text{O}_8$ and heat the solution gently till brown vapors completely removed (avoid over heating). Br^- completely removed. Here per sulphate oxidizes Br^- to Br_2

c) Detection and confirmation of Cl^- :- Take solution from above test free from I^- and Br^- to it add enough AgNO_3 white precipitate of AgCl produces which dissolves completely in ammonia and then reprecipitated with dilute HNO_3 confirms presence of Cl^- ion in solution



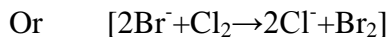
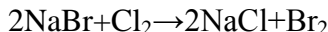
Method II:- Use of chlorine water:-

a) To the aqueous solution of a mixture containing Cl^- , Br^- and 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 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 I^- get removed completely in this test the Cl_2 itself under goes reduction and oxidizes I^- to iodine this iodine dissolves in organic layer (chloroform) and gives violet colour to organic layer

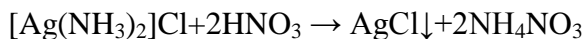
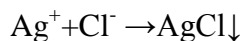


b) To the aqueous layer from above step(free from I^-) add enough chlorine water and chloroform .Shake well the solution and allow to separate two layers yellow colour to lower organic layer indicate presence of Br^- in the given solution. Take upper aqueous layer to it add excess chlorine water and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

in this test the chlorine it self under goes reduction and oxidizes Br^- to Br_2 which dissolves in organic layer (chloroform) and gives yellow colour to organic layer

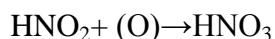
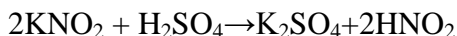


c)The aqueous layer from above step (completely free from I^- , Br^- and organic layer) or aqueous solution containing Cl^- , Br^- and I^- used for confirmation of Cl^- which can be treated with AgNO_3 solution. A white precipitate of AgCl produces. It can be treated with aqueous ammonium carbonate solution. AgCl gives clear solution of amine complex. If the solution is treated with dilute HNO_3 Cl^- ion get reprecipitated as AgCl . Hence Cl^- ion detected and confirmed.



2) Separation of NO_2^- and NO_3^- :-

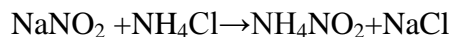
a) Detection of NO_2^- :- The aqueous solution containing NO_2^- and NO_3^- acidified with H_2SO_4 and treated with very dilute KMnO_4 solution. Decolouration of KMnO_4 solution confirms the presence of NO_2^- here KMnO_4 is reduced by HNO_2 to MnSO_4 where as HNO_2 is oxidized to HNO_3



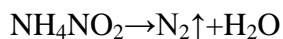
Nitrate present in the solution does not interferes in the above test.

b) Removal of NO_2^- :- Under specific conditions nitrite can be reduced to nitrogen and separated from nitrate. To the solution containing NO_2^- an excess of solid NH_4Cl is added and the solution is boiled to expel out NO_2^- as N_2 gas.

Boil

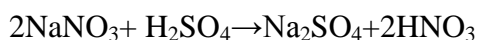


Boil



c) Detection of NO_3^- :-After the removal of NO_2^- , NO_3^- can be tested by following tests :-

1) Solution is warmed with Cu foil and conc. H_2SO_4 . Brown gas evolves that turns starch iodide paper black indicates confirmation of NO_3^- .



2) Brown ring test:-[Please refer the brown ring test for 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 most superior than Inorganic semi micro qualitative analysis because of 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 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 ₃ gas	a)Olive green b)Blue c)Brown	Cu ²⁺ present Ni ²⁺ present Co ²⁺ present
2)Dimethyl glyoxime test:-take a drop of O.S. on a paper strip+adropof reagent-expose toNH ₃ gas	Scarlet red colour	Ni ²⁺ 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 ³⁺ present and confirmed

EXERCISE

1.) Select the most correct alternative and rewrite the sentence again.

A. If ionic product-----the solubility product then the state of solution is saturated state

a) $>$ b) $<$ c) $=$ d) \leq

B) When ionic product----- the solubility product precipitation occurs

a) $>$ b) $<$ c) $=$ d) \leq

C) Degree of dissociation of H_2S is suppressed by addition of -----strong electrolyte

a) KCl b) HCl c) NH_4Cl d) Na_2CO_3

D) The group reagent for Vth group is-----

a) H_2S b) NH_4OH c) $(\text{NH}_4)_2\text{CO}_3$ d) Na_2HPO_4

E) The quantity of sample required for semi-micro qualitative analysis is-----

a) 10 to 100 mg. b) 1 to 10 mg. c) 0.1 to 5.0 mg. d) 100 mg to 1 gm

F) Due to common ion effect weak electrolyte becomes-----

a) more weak b) more strong c) remains as it is d) either weak or strong

G) Yellow ammonium sulphate is used for separation of group -----

a) IIIArd to IIIBrd b) IInd A to IInd B c) IVth to Vth d) Ist to IInd

H) H_2S in presence of HCl is a group reagent for

- a) IIIArd b) IIIBrd c) IInd d) Vth

I) In-----group there is only one Mg²⁺ basic radical

- a) IIIArd b) IIIBrd c) IInd d) Vth

J) the chemical composition of brown ring produced in the test of NO₂ is-----

- a) [FeNO]SO₄ b) [FeNO]Cl₂ c) [FeSO₄]NO₂ d) [FeCl₂]NO

K) The spot test analysis technique was developed by scientist-----and his coworkers

- a) C. V. Raman b) A.I. Vogel c) F. iegl d) P. Waage

L)-----gives blood red colouration to ferric ion

- a) K₃ [Fe(CN)₆] b) K₄ [Fe(CN)₆] c) NH₄CNS d) (NH₄)₂ [Hg(SCN)₄]

M) Dimethyl glyoxime is a specific reagent for-----

- a) Ni²⁺ b) Co²⁺ c) Cu²⁺ d) Fe³⁺

N) IInd A group cations are called as----- group cations

- a) tin b) cadmium c) arsenic d) Copper

O) The basic radicals are classified in to different groups according to their tendency to give-----
---with specific group reagent

- a) precipitate b) complex ion c) double salt d) clear solution

P)-----group basic radicals are not having specific group reagent

- a) Vth b) IVth c) VIth d) IInd

ANSWERS:-A-c, B-a, C-b, D-d, E-a, F-a, G-b, H-c, I-d, J-a, K-c, L-c, M-a,

N-d, O-a, P-c

2. Write precise note on the following.

i) Solubility product

ii) Common ion effect

iii) complex formation

vi) Separation of Cu^{2+} and Cd^{2+}

vii) Separation of Co^{2+} and Ni^{2+}

viii) Separation of NO_2^- and NO_3^-

.ix) Separation of Cl^- from Br^- and I^-

X) Separation of Cl^- , Br^- and I^- by oxidation and reduction

xi) Brown ring test for NO_2^- and NO_3^-

3. Discuss the basic principles involved in the semi-micro qualitative analysis.

4. How Cu^{2+} is separated from Cd^{2+} by complex ion formation ?

5. How Cl^- is separated from Br^- and I^- by complex ion formation?

6. How NO_2^- and NO_3^- are detected by complex formation?

7. Explain in brief separation of Cl^- , Br^- and I^- by oxidation and reduction.

8. Explain in brief application of Solubility product and Common ion effect in the separation of II^{nd} group cations.

9. Explain in brief application of Solubility product and Common ion effect in the separation of III^{rd} group cations.

10. How Co^{2+} is separated from Ni^{2+} by complex ion formation?

11. Explain the role of oxidation and reduction in the separation of NO_2^- and NO_3^- .