SALT ANALYSIS/QUALITATIVE ANALYSIS

INTRODUCTION

It is extremely useful to know how to detect the presence of specific ions in an aqueous solution. This type of analysis falls under the general category of analytical chemistry called **qualitative analysis**, which addresses the question "What is in a sample ?" The basis of a qualitative analysis is the fact that ions will undergo specific chemical reactions with certain reagents to yield observable products. For example, silver ion can be precipitated with hydrochloric acid to yield solid silver chloride. Because many cations will not react with hydrochloric acid in this way, this simple reaction can be used to separate ions that form insoluble chlorides from those that do not. In fact, the qualitative detection of ions in a mixture is commonly accomplished by a system of analysis in which precipitation reactions play a major role. In addition, acid-base reactions, oxidation-reduction reactions, and the formation of complex ions are often used in a systematic way for either separating ions or for determining the presence of specific ions.

The qualitative analysis of ions in a mixture must follow a scheme that can be summarized as follows :

(1) Add reagents that exploit the more general properties of ions to separate major groups of ions ;

(2) Separate major groups into subgroups with reactions that will distinguish less general properties; and

(3) Add reagents that will specifically confirm the presence of individual ions.

Following this general three-step plan, several different analytical schemes have been devised that are based on various ways of defining major groups.

Salt Analysis

(A)
Analysis of Anion
- by Wet Test

(B)
Analysis of Cation
- by Dry Test
- by Flame Test
- by Wet Test

Preliminary tests

— Physical appearance (colour and smell).
— Dry heating test.
— Charcoal cavity test.
— Charcoal cavity and cobalt nitrate test.
— Flame test.
— Borax bead test.
— Dilute sulphuric acid test.
— Potassium permanganate test.
— Concentrated sulphuric acid test.
— Tests for sulphate, phosphate and borate.

Wet tests for acid radicals

Wet tests (group analysis) for basic radicals

Physical appearance (smell).

Physical Examination

Take a pinch of the salt between your fingers and rub with a drop of water	
Smell	**Inference**
Ammonical smell	NH_4^+
Vinegar like smell	CH_3COO^-
Smell like that of rotten eggs	S^{2-}

DRY HEATING TEST :

This test is performed by heating a small amount of mixture in a dry test tube. Quite valuable information can be generated by carefully performing and noting the observations here. On heating some salts undergo decomposition thus evolving the gases or may undergo characteristic changes in the colour of residue. These observations are tabulated below along with the inferences that you can draw.

S.No.	Observation	Inference
1	**Gas evolved**	
(a)	**Colourless and odourless gas** CO_2 gas – turns lime water milky	CO_3^{2-}
(b)	**Colourless gas with odour**	
(i)	H_2S gas–Smells like rotten eggs, turns lead acetate paper black.	Hydrated S^{2-}
(ii)	SO_2 gas–Characteristic suffocating smell, turns acidified potassium dichromate solution or paper green.	SO_3^{2-}
(iii)	HCl gas – Pungent smell, white fumes with ammonia, white precipitate with silver nitrate solution.	Cl^-
(iv)	Acetic acid vapours–Characteristic vinegar like smell.	CH_3COO^-
(v)	NH_3 gas– Characteristic smell, turns Nessler's solution brown.	NH^{4+}
(c)	**Coloured gases – Pungent smell**	
(i)	NO_2 gas – Reddish brown, turns ferrous sulphate solution black.	NO^{2-} or NO^{3-}
(ii)	Cl_2 gas – Greenish yellow, turns starch iodide paper blue.	Cl^-
(iii)	Br_2 vapours – Reddish brown, turns starch paper orange red.	Br^-
(iv)	I_2 vapours – Dark violet, turns starch paper blue.	I^-
2	**Sublimate formed**	
(a)	**White sublimate**	NH^{4+}
(b)	**Black sublimate accompanied by violet vapours.**	I^-
3	**Fusion**	
	The mixture fuses	Alkali metal salts or salt containing water of crystallisation.
4	**Swelling**	
	The mixture swells up into voluminous mass.	PO_4^{3-}, BO_3^{3-} indicated
5	**Residue**	
(i)	Yellow when hot, white when cold.	Zn^{2+}
(ii)	Brown when hot and yellow when cold	Pb^{2+}
(iii)	Original salt blue becomes white on heating	Hydrated CuSO4 indicated
(iv)	Coloured salt becomes brown or black on heating.	Co^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+} indicated

EDUBULL KEY POINTS

(i) Use a perfectly dry test–tube for performing this test. While drying a test–tube, keeps it in slanting position with its mouth slightly downwards so that the drops of water which condense on the upper cooler parts, do not fall back on the hot bottom, as this may break the tube.

(ii) For testing a gas, a filter paper strip dipped in the appropriate reagent is brought near the mouth of the test tube or alternatively the reagent is taken in a gas–detector and the gas is passed through it.

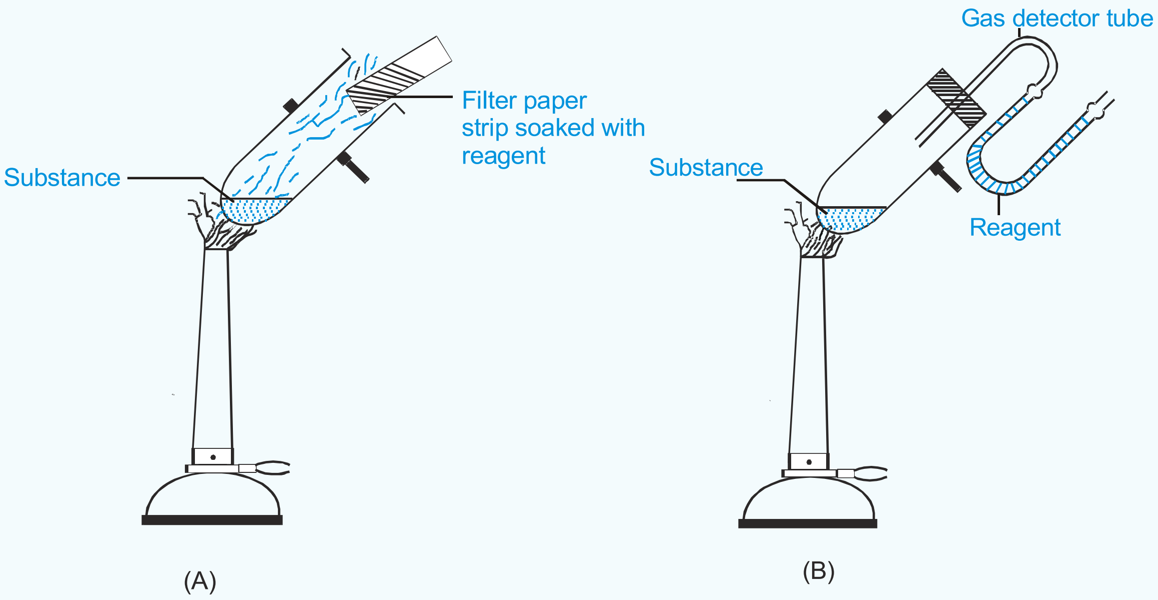


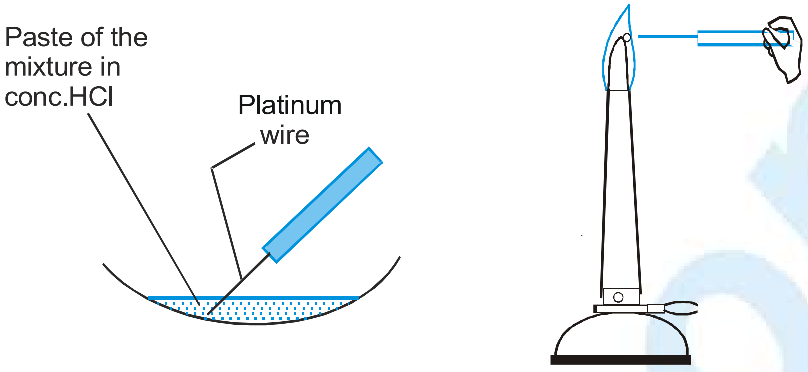
Figure : Detection of gas evolved.

(iii) Do not heat the tube strongly at one point as it may break.

Flame test :

The chlorides of the metals are more volatile as compared to other salts and these are prepared in situ by mixing the compounds with a little concentrated hydrochloric acid. On heating in a non-luminous Bunsen flame they are volatilized and impart a characteristic colour to the flame as these absorb energy from the flame and transmit the same as light as characteristic colour .

Colour of Flame	Inference
Crimson Red / Carmine Red	Lithium
Golden yellow	Sodium
Violet/Lilac	Potassium
Brick red	Calcium
Crimson	Strontium
Apple Green/Yellowish Green	Barium
Green with a Blue centre/Greenish Blue	Copper



(A) Dipping the platinum wire in the paste of salt and HCl.

(B) Introducing the wire in the flame

Figure : Flame test

SOLUBILITY CHART

S.No.	Anion	Solubility / Exception
1	CO_3^{2-}	Except carbonates of alkali metals and of ammonium, all other normal carbonates are insoluble.
2	SO_3^{2-}	Only the sulphites of the alkali metals and of ammonium are water soluble. The sulphite of other metals are either sparingly soluble or insoluble.
3	S^{2-}	The acid, normal and polysulphide of alkali metals are soluble in water. The normal sulphides of most other metals are insoluble; those of the alkaline earths are sparingly soluble, but are gradually changed by contact with water into soluble hydrogen sulphides.
4	NO^{2-} , NO^{3-}	Almost all nitrites and nitrates are soluble in water. AgNO2 is sparingly soluble. Nitrates of mercury and bismuth give basic salts on treatment with water. These are soluble in dilute nitric acid.
5	CH_3COO^-	Acetates are water soluble except Ag(I) and Hg(II) acetates which are sparingly soluble.
6	Cl^-	Most chlorides are soluble in water. PbCl2 (sparingly soluble in cold but readily soluble in boiling water), Hg2Cl2, AgCl, CuCl, BiOCl, SbOCl and Hg2OCl2 are insoluble in water.
7	Br^-	Silver, mercury(I) and copper(I), bromides are insoluble. Lead bromide is sparingly soluble in cold but more soluble in boiling water. All other bromides are soluble in water.
8	I^-	Silver, mercury(I), mercury(II), copper(I), lead and bismuth(III) iodides are the least soluble salts. All other iodides are water soluble.
9	SO_4^{2-}	The sulphates of barium, strontium and lead are insoluble in water, those of calcium and mercury(II) are slightly soluble. Some basic sulphates of mercury, bismuth and chromium are also insoluble, but these dissolves in dilute hydrochloric or nitric acid.
10	PO_4^{3-}	The phosphate of the alkali metals, with the exception of lithium and ammonium, are soluble in water ; the primary phosphate of the alkaline earth metals are soluble. All the phosphates of the other metals and also the secondary and tertiary phosphate of the alkaline earth metals are sparingly soluble or insoluble in water.

ANALYSIS OF ANIONS (ACIDIC RADICALS) –

Analysis of anions can be divided into two groups

GROUP 'A' RADICALS :

Group 'A' contains anions, which are characterised by volatile products obtained on treatment with acids. It is further divided into two sub groups.

(1) Gases liberated with dilute HCl/dilute H_2SO_4 :

Carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulphide (S^{2-}), Sulphite (SO_3^{2-}) and nitrite (NO_2^-)

(2) Gases or acid vapours evolved with concentrated H2SO4 :

Fluoride (F^-), Chloride (Cl^-), Bromide (Br^-), Iodide (I^-), Nitrate (NO_3^-), Acetate (CH_3COO^-), Borate (BO_3^{3-}), Oxalate ($C_2O_4^{2-}$), Permanganate (MnO_4^-) and all anions of (1).

GROUP 'B' RADICALS :

Group 'B' includes anions that are characterised by their specific reactions in solutions. These reactions may be:

(1) Precipitation reactions : SO_4^{2-}, PO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$ etc.

(2) Oxidation and reduction in solution : CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, MnO_4^{-2} etc.

GROUP 'A' RADICALS :

(1) RADICALS DETECTED WITH DILUTE HCl/DILUTE H_2SO_4

(I) CARBONATE (CO_3^{2-})

All carbonates except those of alkali metals and ammonium are insoluble in H_2O.

(i) Dilute HCl

With dilute HCl, it decomposes with effervescences due to the evolution of carbon dioxide.

$$CO_3^{2-} + 2H^+ \longrightarrow CO_2\uparrow + H_2O$$

The gas produces white turbidity with lime water, $Ca(OH)_2$ or baryta water, $Ba(OH)_2$.

$$CO_2\uparrow + Ca^{2+} + 2OH^- \longrightarrow \underset{\text{White turbidity}}{CaCO_3\downarrow} + H_2O$$

$$CO_2\uparrow + Ba^{2+} + 2OH^- \longrightarrow \underset{\text{White turbidity}}{BaCO_3\downarrow} + H_2O$$

It must be remembered that with prolonged passage of carbon dioxide, the turbidity slowly disappears due to the formation of soluble bicarbonate.

$$CaCO_3\downarrow + CO_2\uparrow + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

(ii) Barium Chloride or Calcium Chloride Solution

Carbonates on treatment with $BaCl_2$ or $CaCl_2$ gives white precipitate of barium or calciumcarbonate, which is soluble in mineral acids and carbonic acid.

$$CO_3^{2-} + Ba^{2+} \longrightarrow \underset{\text{White ppt}}{BaCO_3\downarrow}$$

$$CO_3^{2-} + Ca^{2+} \longrightarrow \underset{\text{White ppt}}{CaCO_3\downarrow}$$

(iii) Silver Nitrate Solution

Carbonates give a white precipitate of silver carbonate with $AgNO_3$ solution.

$$CO_3^{2-} + 2Ag^+ \longrightarrow \underset{\text{White ppt}}{Ag_2CO_3\downarrow}$$

The precipitate is soluble in nitric acid and in ammonia. The precipitate becomes yellow brown on addition of excess reagent owing to the formation of silver oxide. The same happens if the mixture is boiled.

$$Ag_2CO_3\downarrow \longrightarrow \underset{\text{Yellow ppt}}{Ag_2O\downarrow} + CO_2\uparrow$$

(II) BICARBONATE (HCO^{3-})

(i) Dilute HCl

With dilute HCl, all bicarbonates gives effervescences due to the evolution of CO_2.

$$HCO_3^- + H^+ \longrightarrow CO_2\uparrow + H_2O$$

The gas gives white turbidity with lime water or baryta water.

$$CO_2\uparrow + Ca(OH)_2 \longrightarrow \underset{\text{White turbidity}}{CaCO_3\downarrow} + H_2O$$

(ii) On boiling

When boiled, all bicarbonates decompose to give corresponding carbonates and carbondioxide, which turns lime water milky.

$$2HCO_3^- \longrightarrow CO_3^{2-} + H_2O + CO_2\uparrow$$

(iii) Test for Carbonate in the Presence of Bicarbonate

Adding an excess of calcium chloride to a mixture of carbonate and bicarbonate, the former is precipitated quantitively.

$$CO_3^{2-} + Ca^{2+} \longrightarrow \underset{\text{White ppt / turbidity}}{CaCO_3\downarrow}$$

On filtering the solution rapidly, bicarbonate ions pass into the filtrate. On adding ammonia to the filtrate, a white precipitate or cloudiness is obtained.

$$2HCO_3^- + 2Ca^{2+} + 2NH_3 \longrightarrow \underset{\text{White ppt/turbidity}}{2CaCO_3\downarrow} + 2NH_4^+$$

(III) SULPHIDE (S^{2-})

(i) Dilute HCl or Dilute H_2SO_4

Sulphide on treatment with dilute HCl or dilute H_2SO_4 gives a pungent smelling gas, H_2S (smell of rotten eggs).

$$S^{2-} + 2H^+ \longrightarrow H_2S\uparrow$$

The blackening of filter paper moistened with lead acetate solution may identify the gas.

$$(CH_3COO)_2Pb + H_2S\uparrow \longrightarrow \underset{\text{Shining black}}{PbS\downarrow} + 2CH_3COOH$$

Alternatively, a filter paper moistened with cadmium acetate solution turns yellow.

$$H_2S\uparrow + Cd^{2+} \longrightarrow \underset{\text{Yellow ppt}}{CdS\downarrow} + 2H^+$$

(ii) Silver Nitrate Solution

With $AgNO_3$ solution, sulphides gives a black precipitate of silver sulphide which is insoluble in cold but soluble in hot dilute nitric acid.

$$S^{2-} + 2Ag^{+} \longrightarrow \underset{\text{Black ppt}}{Ag_2S\downarrow}$$

(iii) Sodium Nitroprusside Solution

With sodium nitroprusside solution, ionic sulphide gives a purple colour in alkaline medium.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{Purple colour}}{Na_4[Fe(CN)_5NOS]}$$

No reaction occurs with solutions of hydrogen sulphide or free gas. If however, filter paper moistened with a solution of the reagent is made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide also.

(iv) Catalysis of Iodine-Azide Reaction Test

Solution of sodium azide, NaN_3 and iodine as I_3^- do not react, but on addition of traces of sulphide, (which acts as a catalyst) nitrogen gas is evolved immediately.

$$\underset{\text{colourless}}{2N_3^-} + \underset{\text{dark brown}}{I_3^-} \xrightarrow{\text{In presence of } S^{2-}} 3I^- + \underset{\text{colourless gas}}{3N_2\uparrow}$$

Thiosulphates and thiocyanates behave similarly and hence must be absent for this test.

(IV) SULPHITE (SO_3^{2-})

Only the sulphites of alkali metals and ammonium are soluble in water.

(i) Dilute HCl or Dilute H_2SO_4

Dilute HCl or H_2SO_4 decomposes sulphites with the evolution of sulphur dioxide.

$$SO_3^{2-} + 2H^{+} \longrightarrow SO_2\uparrow + H_2O$$

The gas can be identified

(a) By suffocating odour of burning sulphur.

(b) By green colour formation, when passed through acidified $K_2Cr_2O_7$ solution.

$$3SO_2\uparrow + \underset{\text{orange}}{Cr_2O_7^{2-}} + 2H^{+} \longrightarrow 3SO_4^{2-} + \underset{\text{Green colour}}{2Cr^{3+}} + H_2O$$

(c) Lime water test

On passing SO_2 gas through lime water, a milky precipitate of calcium sulphite is formed.

$$SO_2\uparrow + Ca(OH)_2 \longrightarrow \underset{\text{Milky ppt}}{CaSO_3\downarrow} + H_2O$$

Precipitate dissolves on prolonged passage of the gas, due to the formation of calcium bisulphite.

$$SO_3\downarrow + SO_2\uparrow + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(HSO_3)_2}$$

(d) Potassium Iodate–Starch Paper

When the evolved gas (SO_2) comes in contact with filter paper moistened with KIO_3 and starch solution, the paper turns blue due to iodine–starch complex.

$$2KIO_3 + 5SO_2\uparrow + 4H_2O \longrightarrow 2KHSO_4 + I_2 + 3H_2SO_4$$

(ii) Barium Chloride or Strontium Chloride Solution

With $BaCl_2$ or $SrCl_2$ solution, sulphites gives a white precipitate of barium sulphite or strontium sulphite.

$$SO_3^{2-} + Ba^{2+} \longrightarrow \underset{\text{White ppt}}{BaSO_3\downarrow}$$

$$SO_3^{2-} + Sr^{2+} \longrightarrow \underset{\text{White ppt}}{SrSO_3\downarrow}$$

The precipitate dissolves in dilute hydrochloric acid, when sulphur dioxide is liberated.

$$BaSO_3\downarrow + 2H^+ \longrightarrow Ba^{2+} + SO_2\uparrow + H_2O$$

On standing, the precipitate is slowly oxidised to sulphate and is then insoluble in dilute mineral acids.

(V) NITRITE (NO^{2-})

All other nitrites except $AgNO_2$ (sparingly soluble) are soluble in H_2O.

(i) Dilute HCl

On adding dilute HCl to solid nitrite in cold produces a pale blue liquid first (due to the presence of free nitrous acid, HNO_2 or its anhydride N_2O_3) and then evolution of reddish-brown fumes of nitrogen dioxide (NO_2) takes place. The NO_2 is produced by the combination of nitric oxide (NO) with oxygen of the air.

$$\begin{aligned}
NO_2^- + H^+ &\longrightarrow HNO_2 \\
2HNO_2 &\longrightarrow H_2O + N_2O_3 \\
3HNO_2 &\longrightarrow HNO_3 + 2NO\uparrow + H_2O \\
2NO\uparrow + O_2\uparrow &\longrightarrow \underset{\text{Raddish-brown}}{2NO_2\uparrow}
\end{aligned}$$

(ii) Silver Nitrate Solution

With silver nitrate solution, a white crystalline precipitate of $AgNO_2$ is obtained.

$$NO_2^- + Ag^+ \longrightarrow \underset{\text{White ppt}}{AgNO_2\downarrow}$$

(iii) Potassium Iodide Solution

Addition of a nitrite solution to that of KI followed by acidification with CH_3COOH or dilute H_2SO_4 produces iodine, which turns starch–iodine complex blue.

$$2NO_2^- + 3I^- + 4CH_3COOH \longrightarrow I_2 + 2NO\uparrow + 4CH_3CO_2^- + 2H_2O$$

$$I_2 + \text{Starch} \longrightarrow \text{Deep blue colour}$$

$$I_2 + \text{Excess KI} \longrightarrow K^+I_3^- \text{ (Dark brown)}$$

(iv) Brown ring test

When the nitrite solution is added carefully to a concentrated solution of iron **(II)** sulphate acidified with dilute acetic or dilute sulphuric acid, a brown ring appears due to the formation of $[Fe(H_2O)_5NO]SO_4$ at the junction of the two liquids. If the addition has not been made slowly and caustiously, a brown colouration results.

$$NO_2^- + CH_3COOH \longrightarrow HNO_2 + CH_3COO^-$$

$$3HNO_2 \longrightarrow H_2O + HNO_3 + 2NO\uparrow$$

$$FeSO_4 + 6H_2O \longrightarrow [Fe(H_2O)_6]SO_4$$

$$[Fe(H_2O)_6]SO_4 + NO\uparrow \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + H_2O$$

(v) Sulphamic Acid ($HO–SO_2–NH_2$) Test

When a solution of a nitrite is treated with solid sulphamic acid, it is completely decomposed.

$$HO–SO_2–NH_2 + NO_2^- \longrightarrow N_2\uparrow + H^+ + SO_4^{2-} + H_2O$$

Since no nitrate is formed in this reaction, this is an excellent method for the complete removal of nitrite.

(2) RADICALS DETECTED WITH CONCENTRATED H_2SO_4

(I) FLUORIDE (F–)

(i) Silica and Concentrated Sulphuric acid

Fluorides on warming with concentrated H_2SO_4 gives a colourless, corrosive gas, hydrogen fluoride (H_2F_2). The gas fumes in moist air and the test tube acquires a greasy appearance as a result of the corrosive action of the vapour on the silica in the glass, which liberates the gas, silicon tetrafluoride, SiF_4. By holding a moistened glass rod in the vapour, gelatinous silicic acid (H_2SiO_3) is deposited on the rod, which is a product of the decomposition of the silicon tetrafluoride.

$$2F^- + H_2SO_4 \longrightarrow H_2F_2\uparrow + SO_4^{2-}$$

$$SiO_2 + 2H_2F_2 \longrightarrow SiF_4\uparrow + 2H_2O$$

$$3SiF_4\uparrow + 3H_2O \longrightarrow 2[SiF_6]^{2-} + H_2SiO_3\downarrow + 4H^+$$

Note that at room temperature hydrogen fluoride gas is almost completely dimerized, therefore its formula has been written as H_2F_2. At elevated temperatures (say 90°C), it dissociates completely to monomeric hydrogen fluoride.

$$H_2F_2(g) \xrightarrow[90°C]{above} 2HF(g)$$

(ii) The etching test

A clean watch glass coated on the convex side with paraffin wax and scratching a design on the wax with a dail exposes part of the glass. A mixture of fluoride salt and concentrated sulphuric acid is placed in a small lead or platinum crucible and the latter immeadiately covered with the watch glass, convex side down. A little water should be poured in the upper (concave) side of the watch glass to prevent the wax from melting. The crucible is very gently warmed. After 5–10 minutes, the hydrogen fluoride would etch the glass.

(iii) Silver Nitrate Solution

With silver nitrate solution, no precipitate is obtained, as silver fluoride is soluble in water.

(iv) Calcium Chloride Solution

With calcium chloride solution, a white, slimy precipitate of calcium fluoride (CaF_2), sparingly soluble in acetic acid but slightly more soluble in dilute hydrochloric acid is formed.

$$2F^- + Ca^{2+} \longrightarrow \underset{\text{White slimy ppt}}{CaF_2\downarrow}$$

(II) CHLORIDE (Cl^-)

Most chlorides are soluble in water except Hg_2Cl_2, $CuCl$, $AgCl$, $PbCl_2$, $BiOCl$ and $SbOCl$, $PbCl_2$ is soluble in hot water

(i) Concentrated H_2SO_4

With concentrated H_2SO_4, chlorides gives vapours of HCl.

$$Cl^- + H_2SO_4 \longrightarrow HCl\uparrow + HSO_4^-$$

Vapour evolved

(a) Turns blue litmus paper red

(b) Gives white fumes of NH_4Cl when a glass rod moistened with aqueous ammonia solution is brought close to the mouth of test tube.

(ii) Manganese Dioxide and Concentrated Sulphuric Acid

When a solid chloride is treated with MnO_2 and concentrated H_2SO_4, yellow-green coloured gas (Cl_2) is evolved.

$$MnO_2 + 2H_2SO_4 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2\uparrow + 2SO_4^{2-} + 2H_2O$$

Yellow-green

(iii) Silver Nitrate Solution

Chlorides on treatment with $AgNO_3$ solution gives a white curdy precipitate of AgCl insoluble in water and in dilute nitric acid but soluble in dilute ammonia solution due to the formation of soluble complex.

$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

White curdy ppt

$$AgCl\downarrow + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$$

Soluble

(iv) Lead Acetate Solution

With $(CH_3CO_2)_2Pb$ solution, chlorides gives a white precipitate of lead chloride.

$$2Cl^- + Pb^{2+} \longrightarrow PbCl_2\downarrow$$

White ppt

(v) Chromyl Chloride Test

When a mixture containing chloride ion is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, deep orange-red fumes of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2\uparrow + 3H_2O$$

Orange-red
fumes

When chromyl chloride vapours are passed into sodium hydroxide solution, a yellow solution of sodium chromate is formed, which when treated with lead acetate gives yellow precipitate of lead chromate.

$$CrO_2Cl_2\uparrow + 2NaOH \longrightarrow Na_2CrO_4 + 2HCl$$

Yellow solution

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + PbCrO_4\downarrow$$

Yellow ppt

This test is given by ionic chlorides only. Chlorides of Hg^{2+}, Pb^{2+}, Ag^+, Sn^{2+} and Sb^{3+} do not respond to chromyl chloride test due to their covalent character, which allows them to ionise only slightly.

(III) BROMIDE (Br^-)

All bromides are soluble in water except AgBr, Hg_2Br_2, CuBr and $PbBr_2$ (soluble in boiling water)

(i) Concentrated H_2SO_4

If concentrated sulphuric acid is poured in a bromide solution, first a reddish-brown solution is formed, later reddish-brown vapours of bromine accompany the hydrogen bromide.

$$2KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2HBr\uparrow$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2\uparrow + Br_2\uparrow$$

Reddish-brown

If concentrated H_3PO_4 is used instead of H_2SO_4 and the mixture is warmed, only hydrogen bromide is formed.

$$KBr + H_3PO_4 \longrightarrow HBr\uparrow + KH_2PO_4$$

(ii) Manganese dioxide and Concentrated Sulphuric Acid

When a mixture of solid bromide, MnO_2 and concentrated H_2SO_4 is heated, reddish-browm vapour of bromine are evolved.

$$2KBr + MnO_2 + 2H_2SO_4 \longrightarrow Br_2\uparrow + K_2SO_4 + MnSO_4 + 2H_2O$$

Reddish-brown

(iii) Silver Nitrate Solution

With $AgNO_3$ solution, bromide gives a curdy pale yellow precipitate of silver bromide. This precipitate is sparingly soluble in dilute ammonia but readily soluble in concentrated ammonia solution and insoluble in dilute HNO_3.

$$Br^- + Ag^+ \longrightarrow AgBr\downarrow$$

Pale yellow ppt

(iv) Lead Acetate Solution

Bromides on treatment with lead acetate solution, gives a white crystalline precipitate of lead bromide, which is soluble in boiling water.

$$2Br^- + Pb^{2+} \longrightarrow PbBr_2\downarrow \xrightarrow{\text{on boiling}} \text{Clear solution} \xrightarrow{\text{cooled}} \text{white ppt.}$$

White ppt

(v) Chlorine Water

When chlorine water is added to a solution of bromide, free bromine is liberated which colours the solution orange-red. If CS_2, $CHCl_3$ or CCl_4 is added to the solution and the liquid shaken, the bromine dissolves in the organic solvent and after allowing to stand forms a reddish-brown solution below the colourless aqueous layer.

$$2KBr + Cl_2(\text{water}) \longrightarrow 2KCl + Br_2$$

$$Br_2 + \text{Chloroform} \longrightarrow \text{Reddish-brown solution}$$

With excess of chlorine water, the bromine is converted into yellow bromine monochloride and a pale yellow solution results.

$$Br_2\uparrow + Cl_2\uparrow \longrightarrow 2BrCl$$

Pale yellow solution

(vi) Potassium Dichromate and Concentrated H_2SO_4

When a mixture of solid bromide, $K_2Cr_2O_7$ and concentrated H_2SO_4 is heated and passing the evolved vapours into water, a orange-red solution is obtained.

$$6KBr + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow \underset{\text{Orange-red solution}}{3Br_2\uparrow} + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O$$

(IV) IODIDE (I^-)

Iodides are generally soluble in water except AgI, Hg_2I_2, HgI_2, CuI and PbI_2.

(i) Concentrated H_2SO_4

With concentrated H_2SO_4 iodides gives violet vapours of iodine on warming.

$$2I^- + \underset{\text{oxidising agent}}{2H_2SO_4} \longrightarrow \underset{\text{Violet vapours}}{I_2\uparrow} + SO_4^{2-} + 2H_2O + SO_2\uparrow$$

(ii) Silver Nitrate Solution

With $AgNO_3$ solution, iodides form a yellow curdy precipitate of silver iodide, which is very slightly soluble in concentrated ammonia solution, but is completely insoluble in dilute HNO_3.

$$I^- + Ag^+ \longrightarrow \underset{\text{Yellow curdy ppt}}{AgI\downarrow}$$

(iii) Lead Acetate Solution

With $(CH_3CO_2)_2Pb$ solution, a yellow precipitate of lead iodide (PbI_2) is formed, which is soluble in hot water forming a colourless solution and yielding golden-yellow plates on cooling.

$$2I^- + Pb^{2+} \longrightarrow \underset{\text{Yellow ppt}}{PbI_2\downarrow}$$

(iv) Potassium Dichromate and Concentrated Sulphuric Acid

When iodides are warmed with $K_2Cr_2O_7$ and concentrated H_2SO_4, iodine is liberated.

$$6I^- + Cr_2O_7^{2-} + 7H_2SO_4 \longrightarrow \underset{\text{Violet vapours}}{3I_2\uparrow} + 2Cr^{3+} + 7SO_4^{2-} + 7H_2O$$

(v) Chlorine Water

When this reagent is added dropwise to a solution of an iodide, free iodine is liberated, which colours the solution brown and on shaking with CS_2, $CHCl_3$ or CCl_4 it dissolves in organic layer forming a violet solution, which settles below the aqueous layer.

$$2KI + Cl_2 \longrightarrow I_2 + 2KCl$$

$$I_2 + \text{Chloroform} \longrightarrow \text{Violet solution}$$

(vi) Copper Sulphate Solution

With $CuSO_4$ solution, iodide produces a brown precipitate consisting of a mixture of copper **(I)** iodide and iodine. On addition of hypo ($Na_2S_2O_3$) to the solution, brown precipitate changes to white (colourless).

$$4I^- + 2Cu^{2+} \longrightarrow \underset{\text{Brown ppt}}{Cu_2I_2\downarrow} + I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

(vii) Mercury (II) Chloride Solution

With $HgCl_2$ solution, iodide gives a scarlet precipitate of HgI_2.

$$2I^- + HgCl_2 \longrightarrow \underset{\text{Scarlet ppt}}{HgI_2\downarrow} + 2Cl^-$$

The preceipitate dissolves in excess of KI, forming tetraiodomercurate **(II)** complex.

$$HgI_2 + 2I^- \longrightarrow \underset{\text{Soluble}}{[HgI_4]^{2-}}$$

(V) NITRATE (NO^{3-})

All nitrates are soluble in water. The nitrates of mercury and bismuth give basic salts on treatment with H_2O but are soluble in dilute nitric acid.

(i) Concentrated H_2SO_4

Nitrates produces reddish-brown vapours of nitrogen dioxide on treatment with concentrated H_2SO_4.

$$4NO_3^- + 2H_2SO_4 \longrightarrow \underset{\text{Reddish-brown vapours}}{4NO_2} - + 2SO_4^{2-} + 2H_2O + O_2\uparrow$$

(ii) Brown Ring Test

When a freshly prepared saturated solution of iron **(II)** sulphate is added to nitrate solution and then concentrated H_2SO_4 is added slowly from the side of the test tube, a brown ring is obtained at the junction of two layers.

$$2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO\uparrow + 4SO_4^{2-} + 4H_2O$$

$$FeSO_4 + 6H_2O \longrightarrow [Fe(H_2O)_6]SO_4$$

$$[Fe(H_2O)_6]SO_4 + NO\uparrow \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + H_2O$$

On shaking and warming the mixture the brown colour disappears, nitric oxide is evolved and yellow solution of iron**(III)** ions remains.

Bromides and iodides interfere because of the liberated halogen. This test is not trustworthy in the presence of chromates, sulphites, thiosulphates and iodates. All of these anions can be removed by adding an excess of nitrate-free Ag_2SO_4 and filtering the insoluble silver salts.

(VI) ACETATE (CH_3CO^{2-})

(i) Dilute Sulphuric Acid

On adding a small quantity of dilute H_2SO_4 to the acetate salt, acetic acid is produced, which can be easily recognized by its vinegar–like odour

$$CH_3COO^- + H^+ \longrightarrow \underset{\text{Vinegar like odour}}{CH_3COOH}$$

(ii) Iron (III) Chloride Solution

With $FeCl_3$ solution, acetates give a deep red colouration due to the formation of ferric acetate.

$$3CH_3COONa + FeCl_3 \xrightarrow{\text{on boiling}} \underset{\text{Blood red colouration}}{[Fe(OH)_2(CH_3COO)]} + 3NaCl$$

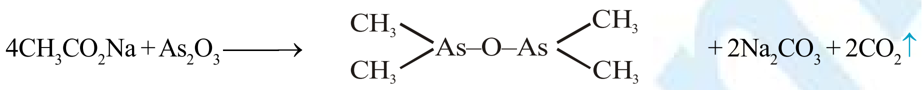
(iii) Silver Nitrate Solution

Acetates on treatment with $AgNO_3$ solution give a white crystalline precipitate of silver acetate.

$$CH_3COO^- + Ag^+ \longrightarrow \underset{\text{White ppt}}{CH_3COOAg\downarrow} \xrightarrow{\Delta} \text{Clear solution}$$

(iv) Cacodyl Oxide Reaction

Acetate salt on heating with solid As_2O_3 gives cacodyl oxide, which have an extremely nauseating odour. The cacodyl oxide is poisonous also.



$$4CH_3CO_2Na + As_2O_3 \longrightarrow (CH_3)_2As{-}O{-}As(CH_3)_2 + 2Na_2CO_3 + 2CO_2\uparrow$$

Cacodyl oxide (nauseating odour)

(VII) BORATE (BO_3^-)

(i) Concentrated H_2SO_4

On heating BO_3^{3-} salts with concentrated sulphuric acid, white fumes of boric acid are evolved. If concentrated hydrochloric acid is added to a concentrated solution of borax, boric acid is precipitate.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow \underset{\text{White fumes}}{4H_3BO_3\uparrow} + 2Na^+ + SO_4^{2-}$$

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3\uparrow + 2Na^+ + SCl$$

(ii) Concentrated Sulphuric Acid and Alcohol (Flame Test)

When some concentrated sulphuric acid is added to solution of borate ion in presence of methanol or ethanol colourless fumes evolved which burn with a green-edged flame, due to the formation of methyl borate, $B(OCH_3)_3$ or of ethyl borate $B(OC_2H_5)_3$.

$$H_2SO_4\,(\text{conc.}) + H_3BO_3 + 3CH_3OH \longrightarrow \underset{\text{(Burn with Green–edged flame)}}{B(OCH_3)_3\uparrow} + 3H_2O$$

$$H_2SO_4\,(\text{conc.}) + H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{(Burn with Green–edged flame)}}{B(OC_2H_5)_3\uparrow} + 3H_2O$$

(VIII) OXALATE ($C_2O_4^{2-}$)

Alkali metal oxalates are solulbe in water.

(i) Silver Nitrate Solution

With silver nitrate solution, a white curdy precipitate of silver oxalate is obtained which is sparingly soluble in water, soluble in ammonia solution and in dilute nitric acid.

$$(C_2O_4)^{2-} + 2Ag^+ \longrightarrow \underset{\text{White curdy ppt}}{Ag_2C_2O_4} \xrightarrow{\Delta} \text{No change}$$

$$Ag_2C_2O_4 + 4NH_3 \longrightarrow 2[Ag(NH_3)_2]^+ + (C_2O_4)^{2-}$$

$$Ag_2C_2O_4 + 2H^+ \longrightarrow 2Ag^+ + (C_2O_4)^{2-} + 2H^+$$

(ii) Calcium Chloride Solution

With calcium chloride solution, a white crystaline precipitate of calcium oxalate from neutral solutions is obtained, which is insoluble in dilute acetic acid and oxalic acid but soluble dilute hydrochloric acid and in dilute nitric acid.

$$(C_2O_4)^{2-} + Ca^{2+} \longrightarrow \underset{\text{White ppt}}{CaC_2O_4}$$

(iii) Potassium Permanganate Solution

Potassium permanganate solution gets decolourized when warmed in acid solution with an oxalate salt to 60°C. Many other organic compounds also effect the bleaching of permanganate but if the evolved carbon dioxide is tested by the lime water reaction, the test becomes specific for oxalates.

$$5(C_2O_4)^{2-} + \underset{\text{(purple)}}{2MnO_4^-} + 16H^+ \longrightarrow 10CO_2\uparrow + \underset{\text{(colourless)}}{2Mn^{2+}} + 8H_2O$$

GROUP 'B' RADICALS

(I) SULPHATE (SO_4^{2-})

Sulphates of barium, strontium and lead are practically insoluble in water, those of calcium and mercury**(II)** are slightly soluble and most of the remaining metallic sulphates are soluble.

(i) Barium Chloride Solution

On adding $BaCl_2$ solution to a sulphate salt solution, a white precipitate of barium sulphate ($BaSO_4$) insoluble in warm dilute hydrochloric acid and in dilute nitric acid but moderately soluble in boiling concentrated hydrochloric acid is formed.

$$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4\downarrow$$

White ppt

(ii) Mercury(II) Nitrate Solution

With $Hg(NO_3)_2$ solution, sulphates form a yellow precipitate of basic mercury**(II)** sulphate.

$$SO_4^{2-} + 3Hg^{2+} + 2H_2O \longrightarrow HgSO_4.2HgO\downarrow + 4H^+$$

Yellow ppt

(II) PHOSPHATE (PO_4^{3-})

(i) Barium Chloride Solution

With barium chloride solution, white amorphous precipitate of barium phosphate, $Ba_3(PO_4)_2$ is formed from neutral solutions, soluble in dilute mineral acids and in acetic acid.

$$2PO_4^{3-} + 3Ba^{2+} \longrightarrow Ba_3(PO_4)_2\downarrow$$

White ppt

(ii) Silver Nitrate Solution

With silver nitrate solution, a yellow precipitate of silver orthophosphate, Ag_3PO_4 is formed which is soluble in dilute ammonia solution and in dilute nitric acid.

$$PO_4^{3-} + 3Ag^+ \longrightarrow Ag_3PO_4\downarrow$$

Yellow ppt

$$Ag_3PO_4\downarrow + 6NH_3 \longrightarrow 3[Ag(NH_3)_2]^+ + PO_4^{3-}$$

$$Ag_3PO_4\downarrow + 2H^+ \longrightarrow H_2PO_4^- + 3Ag^+$$

(iii) Ammonium Molybdate Reagent

When ammonium molybdate is treated with a solution containing phosphate a canary yellow crystalline precipitate of ammonium phosphomolybdate (ammonium dodecamolybdatophosphate), $(NH_4)_3[PMo_{12}O_{40}]$ or $(NH_4)_3[P(Mo_3O_{10})_4]$ is formed. In the compound formed, the Mo_3O_{10} group replaces each oxygen atom in phosphate.

$$PO_4^{3-} + 3NH_4^+ + 12MoO_4^{2-} + 24H^+ \longrightarrow (NH_4)_3[P(Mo_3O_{10})_4]\downarrow + 12H_2O$$

Canary-Yellow ppt

(III) CHROMATE (CrO_4^{2-}) & DICHROMATE ($Cr_2O_7^{2-}$)

The chromates of the alkali metals, calcium and magnesium are soluble in water. $SrCrO_4$ is sparingly soluble. Most other metallic chromates are insoluble in H_2O.

Metallic chromates give yellow solution which dissolved in water. In the presence of H^+ ion, chromates are converted into dichromates (orange–red solution). On adding alkalies i.e., hydroxyl ions, the colour again becomes yellow due to the formation of CrO_4^{2-} back.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Yellow Orange

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$$

The reaction may also be expressed as

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

(i) Barium Chloride Solution

With $BaCl_2$ solution, CrO_4^{2-} gives a pale yellow precipitate of barium chromate, soluble in dilute mineral acids but insoluble in water and acetic acid.

$$CrO_4^{2-} + Ba^{2+} \rightleftharpoons BaCrO_4\downarrow$$

Pale yellow ppt

Dichromate ion also gives the same precipitate but as a strong acidic solution is formed and precipitation is only paratial.

$$Cr_2O_7^{2-} + 2Ba^{2+} + H_2O \rightleftharpoons 2BaCrO_4\downarrow + 2H^+$$

Pale yellow ppt

If sodium hydroxide or sodium acetate is added, precipitation becomes quantitative.

(ii) Silver Nitrate Solution

CrO_4^{2-} on treatment with silver nitrate solution gives a brownish–red precipitate of silver chromate, which is soluble in dilute nitric acid and in ammonia solution but is insoluble in acetic acid. HCl converts the precipitate into silver chloride.

$$CrO_4^{2-} + 2Ag^+ \rightleftharpoons Ag_2CrO_4\downarrow$$

Brick–red ppt

$$2Ag_2CrO_4\downarrow + 2H^+ \xrightarrow{\Delta} 4Ag^+ + Cr_2O_7^{2-} + H_2O$$

$$Ag_2CrO_4\downarrow + 4NH_3 \longrightarrow 2Ag[(NH_3)_2]^+ + CrO_4^{2-}$$

$$Ag_2CrO_4\downarrow + 2Cl^- \longrightarrow 2AgCl\downarrow + CrO_4^{2-}$$

White ppt

A reddish–brown precipitate of silver dichromate, $Ag_2Cr_2O_7$ is formed with a concentrated solution of a dichromate, which on boiling with water gets converted into less soluble silver chromate.

$$Cr_2O_7^{2-} + 2Ag^+ \longrightarrow Ag_2Cr_2O_7\downarrow$$

Reddish-brown ppt

$$Ag_2Cr_2O_7\downarrow + H_2O \xrightarrow{\Delta} Ag_2CrO_4\downarrow + CrO_4^{2-} + 2H^+$$

Brick red

(iii) Lead acetate Solution

With lead acetate solution, CrO_4^{2-} gives a yellow precipitate of lead chromate ($PbCrO_4$), insoluble in acetic acid but soluble in dilute nitric acid.

$$CrO_4^{2-} + Pb^{2+} \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4\downarrow}$$

$$2PbCrO_4\downarrow + 2H^+ \rightleftharpoons 2Pb^{+2} + Cr_2O_7^{2-} + H_2O$$

The precipitate is soluble in sodium hydroxide solution and acetic acid reprecipitates lead chromate.

(iv) Hydrogen Peroxide

If an acidic solution of a chromate is treated with H_2O_2 in the presence of ether / amyl alcohol, a deep–blue solution of chromium pentoxide or chromic peroxide is obtained in ethereal layer.

$$CrO_4^{2-} + 2H^+ + 2H_2O_2 \longrightarrow \underset{\substack{\text{Deep blue}\\\text{colouration}}}{CrO_5} + 3H_2O$$

CrO_5 is unstable and it decomposes yielding oxygen and a green solution of Cr^{3+} in the absence of ether / amyl alcohol. In presence of organic solvents such as diethyle ether, amyle alcohol or pyridine, permanent blue colour is obtained.

(IV) PERMANGANATE (MnO^{4-})

All permanganates are soluble in water forming purple solutions.

(i) Hydrogen Peroxide

H_2O_2 decolourises acidfied permanganate solution, H_2O_2 act as a reducing agent.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 5O_2\uparrow + 2Mn^{2+} + 8H_2O$$

(ii) Iron(II) Sulphate Solution

Iron**(II)** sulphate solution in the presence of sulphuric acid, reduces permanganate to manganese**(II)**. The solution becomes yellow because of the formation of iron**(III)** ions.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow \underset{\text{Yellow solution}}{5Fe^{3+}} + Mn^{2+} + 4H_2O$$

ANALYSIS OF CATIONS

(1) Dry Tests

Borax Bead Test :

If borax, $Na_2B_4O_7.10H_2O$ is heated on the platinum loop, a transparent colourless glass like bead of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3) is formed.

$$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

Characteristics coloured beads are produced with salts of copper, iron, chromium, manganese, cobalt and nickel.

$$CuO + B_2O_3 \longrightarrow \underset{\text{Copper (II) metaborate}}{Cu(BO_2)_2}$$

Results have been summarised in Table.

Oxidising Flame		Reducing Flame		Metal
Hot	Cold	Hot	Cold	
Green	Blue	Colourless	Opaque red-brown	Copper
Yellowwish-brown	Yellow	Green	Green	Iron
Yellow	Green	Green	Green	Chromium
Violet (amethyst)	Amethyst	Colourless	Colourless	Mangenese
Blue	Blue	Blue	Blue	Cobalt
Violet	Reddish–brown	Grey	Grey	Nickel
Yellow	Colourless	Brown	Brown	Molybdenum
Rose–violet	Rose–violet	Red	Violet	Gold
Yellow	Colourless	Yellow	Yellowish–brown	Tungsten
Yellow	Pale–yellow	Green	Bottle–green	Uranium
Yellow	Greenish–yellow	Brownish	Emerald–green	Vanadium
Yellow	Colourless	Grey	Pale violet	Titanium
Orange–red	Colourless	Colourless	Colourless	Cerium

Note : This test is performed only for coloured salt samples.

Microcosmic Salt Bead Test

A test similar of Borax Bead test is used for identification of coloured cations if microcosmic salt, $Na(NH_4)HPO_4.4H_2O$, is used.

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} \underset{\text{transparent beat}}{NaPO_3} + H_2O\uparrow + NH_3\uparrow$$

$$NaPO_3 + CaO \longrightarrow \underset{\text{(blue bead)}}{NaCoPO_4}$$

Results have been summarised in table.

Oxidising Flame	Reducing Flame	Metal
Green when hot, blue when cold	Colourles when hot, red when cold	Copper
Yellowish–or reddish–brown when hot, yellow when cold	Yellow when hot, colourless to green when cold	Iron
Green, hot and cold	Green, hot and cold	Chromium
Violet, hot and cold	Colourless, hot and cold	Manganese
Blue, hot and cold	Blue, hot and cold	Cobalt
Brown, hot and cold	Grey when cold	Nickel
Yellow, hot and cold	Green when cold	Vanadium
Yellow when hot, yellow-green when cold	Green, hot and cold	Uranium
Pale yellow when hot, colourless when cold	Green when hot, blue when cold	Tungsten
Colourless, hot and cold	Yellow when hot, violet when cold	Titanium

Sodium Carbonate Bead Test

The sodium carbonate bead is prepared by fusing a small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame; a white, opaque bead is produced. If this is moistened, dipped into a little KNO_3 and then into a small quantity of a manganese salt (for example) and the whole heated in the oxidising flame, a green bead of sodium manganate (Na_2MnO_4) is formed.

$$MnO + Na_2CO_3 + O_2 \xrightarrow{\Delta} Na_2MnO_4 + CO_2$$

A yellow bead is obtained with chromium salt due to formation of sodium chromate (Na_2CrO_4)

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \longrightarrow 4Na_2CrO_4 + 4CO_2$$

(2) Flame Tests

Paste of the salt and con. HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed; salts, particularly of group V(Ba^{2+}, Ca^{2+}, Sr^{2+}), are identified by colours of the flame and summariesed in table.

Colour	Cation
Golden yellow	Na^+
Violet (Lilac)	K^+
Carmine–red	Li^+
Brick–red	Ca2+
Apple–green	Ba^{2+}, Mo^{2+}
Green	Cu^{2+}, ($BO3^{3-}$), Tl^{3+}
Crimson–red	Sr^{2+}

When both Na^+ and K^+ are present the yellow coloration of sodium flame masks that of potassium. In such cases view the flame through cobalt glass, the yellow sodium colour is absorbed and the potassiuim flame appears crimision,

Potassium chloride is much more volatile than the chlorides of the alkaline earth metals. It is therefore possible to detect potassium in lower oxidising flame and calcium strontium and barium in the fusion zone.

Flame coloration	Flame coloration through cobalt glass	Caused by
Golden–Yellow	Nil	Sodium
Voliet	Crimson	Potassium
Brick–Red	Light–green	Calcium
Crimson	Purple	Strontium
Yellowish–green	Bluish–green	Barium
Golden yellow	Crimson red	$Na^+ + K^+$ (both)

(3) Qualitative Analysis of Cation mixtures :

The identification of individual species of cations present in an unknown mixture of electrolytes involves a preliminary segregation of the cations into selected classifiable groups.

A simple system devised for the purpose is based on the selective precipitation of sapringly soluble compounds of the cations from an orignal solution (O.S.) of the electrolyte mixture.

In its most simplified form, for the more common cations only, these compounds fall into five groups. Within each group the anion is the same for the different cations and the solubility products are small and do not differ too greatly from one another.

Group I

The sparingly soluble chlorides derived from Pb^{2+}, Hg_2^{2+} and Ag^+ ions are precipitated by the addition of dilute HCl. Other cations do not get precipitated as chloride because their K_{sp} is quite high.

Chloride	Ksp at 25°C
$PbCl_2$	1.6×10^{-5}
Hg_2Cl_2	1.3×10^{-18}
AgCl	1.8×10^{-10}

Group II

The sparingly soluble sulphides derived from Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+} and Bi^{3+} ions (and in addition the sparingly soluble covalent sulphides As_2S_3, Sb_2S_3 and SnS) are precipitated by the passage of hydrogen sulphide (H_2S) through an acidic solution whose concentration of hydrogen ions is small.

Sulphide	Ksp at 25°C
HgS	3×10^{-52}
PbS	8×10^{-28}
CuS	8×10^{-36}
CdS	1×10^{-27}
Bi_2S_3	1×10^{-96}

The K_{sp} value of group II sulphide is quite low in comparison to K_{sp} values of group IV sulphides, hence they do not get precipitated in acidic medium, where S^{2-} ion concentration is quite low.

Group III

The sparingly soluble hydroxides derived from Fe^{3+}, Cr^{3+} and Al^{3+} ions are precipitated by the addition of ammonium hydroxide, (NH_4OH) solution in the presence of excess ammonium chloride, NH_4Cl and NH_4OH helps in maintaining the pH, that does not allow dissolving of amphoteric hydroxide Al_2O_3 and Cr_2O_3.

Hydroxide	Ksp at 25°C
$Fe(OH)_3$	6×10^{-38}
$Cr(OH)_3$	7×10^{-31}
$Al(OH)_3$	1.4×10^{-34}

Group IV

A further group of sparingly soluble sulphides, those derived from Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} ions, are precipitated by the passage of H_2S through a basic solution. In basic solution H_2S is fully ionised to give sufficient sulphide ion concentrations to precipitate group IV sulphides.

Sulphide	Ksp at 25°C
CoS	8×10^{-23}
NiS	2×10^{-21}
MnS	1×10^{-11}
ZnS	8×10^{-25}

Group V

The sparingly soluble carbonates derived from Ca^{2+}, Sr^{2+} and Ba^{2+} ions are precipitated by the addition of ammonium carbonate, $(NH_4)_2CO_3$, solution in the presence of NH_4OH and NH_4Cl.

Carbonate	KSP at 25°C
$CaCO_3$	4.7×10^{-9}
$SrCO_3$	7×10^{-10}
$BaCO_3$	1.6×10^{-9}

The most common cations remaining in solution after the precipitation of group V are Na^+, K^+ (all the simple salts of the alkali metals are water soluble) and Mg^{2+} ions. Role of NH_4Cl is protonation of CO_3^{-2} ions produce by dissociation of $(NH_4)_2CO_3$ to give limited concentration of CO_3^{2-}, so that Mg^{2+} do not get precipitated. Also, buffer solution ($NH_4Cl + NH_4OH$) help in maintaining pH to go too high that avoids precipitation of cations including Mg^{2+} as hydroxydes.

Identification of the cations within each of the groups is based on specific and characteristic reactions of each cation. These may be found in any treatise on qualitative inorganic analysis.

The order of group precipitation is such that precipitating reagents for later groups also precipitate in most cases completely removed in the above prescribed order it they are not to interfere

Ex.

(1) K_{sp} of Ag_2S at 25°C = 7×10^{-50}

Hence, Ag_2S will be precipitated in group II unless it has been completely removed as AgCl in group I.

(2) Any of the cations normally precipitated as their sulphides in group II, will reappear in the group IV precipitate, unless completely removed in group II.

(3) $K_{sp}(ZnCO_3)$ at 25°C = 2.1×10^{-11}

Hence, $ZnCO_3$ will be precipitated in group V unless it has been completely removed as ZnS in group IV.

Precipitation of Fe^{+3} in III group hydroxide :

If Fe^{2+} ions are present in the electrolyte mixutre under analysis, they must be oxidised to Fe^{3+} ions (with concentrated HNO_3) prior to the precipitation of the group III hydroxides. FeS will then interfere with the further analysis of these sulphides.

Group V radicals are precipitated as insoluble carbonates in ammonical solution containing ammonium chloride. The carbonates of Ba^{2+}, Sr^{2+} and Ca^{2+} are precipitated while $MgCO_3$ does not.

This is due to following equation in which protonation of CO_3^{-2} by NH_4^+ ion.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$CO_3^{-2} + NH_4^+ \rightleftharpoons NH_3 + HCO_3^-$$

The low concentration of CO_3^{-2} + ions is sufficient to exceed the solubility products of the carbonates of calcium, strontium and barium, while magnesium remains in solution, because the solubility product of magnesium carbonate is comparatively high.

Why is Mg^{2+} not precipitated in group V ?

Magnesium is not precipitated as $MgCO_3$ in V group, because the concentration of CO_3^{2-} ions is such that the solubility product of the $MgCO_3$ is not reached, while Ca**(II)**, Sr**(II)** and Ba**(II)** can be easily precipitated with such a low concentration of CO_3^{2-} ions.

Explanation for lead coming in group I as well as group II

Lead is precipitated in Group I as $PbCl_2$. Since it is partly soluble in water, a part of its goes into the filtrate which is to be tested for group II radicals. Thus, on passing H_2S gas, it gives a black ppt. of PbS.

$$Pb^{+2} + H_2S \longrightarrow PbS + 2H^+$$

Difficulty caused by presence of large excess of HCl in precipitation of group I and II cations

In presence of large excess of HCl, the chloride's of barium, strontium and calcium may also get precipitated in I and II group. In II group too due to presence of large excess of HCl cadmium sulphide may not be precipitated. It is due to the fact that with greater concentration of H^+ ions the dissociation of H_2S is suppressed. With this small concentration of S^{2-} ions the solubility product of CdS is not exceeded and hence is not precipitated.

Reason for the formation of a white ppt. in II group in few cases even in the absence of members of the group

It is due to precipitation of sulphur owing to the presence of oxidising radicals like nitride, sulphite or ferric in the mixture. These oxides give a precipitate of sulphur with H_2S .

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$2HNO_2 + H_2S \longrightarrow 2NO + 2H_2O + S$$

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

Moreover, if the original solution of the mixture has been prepared in HNO_3 even then sulphur is precipitated.

$$2HNO_3 + 3H_2S \longrightarrow 4H_2O + 2NO + 3S$$

Role of Addition of Nitric Acid before the Precipitation of Group III

Nitric acid is added to oxidise ferrous ion into ferric ion.

$$3FeSO_4 + 4HNO_3 \longrightarrow Fe_2(SO_4)_3 + 4NO + 2H_2O$$

The oxidation of ferrous ion into ferric ion is essential due to the following reasons.

(a) Fe^{2+} is not completely precipitated as $Fe(OH)_2$ in presence of NH_4Cl by addition of NH_4OH whereas Fe^{3+} is completely precipitated as $Fe(OH)_3$ under the same conditions.

(b) Further $Fe(OH)_2$ is oxidised slowly to ferric hydroxide. Instead of getting a precipitate of a definite colour, the precipitate is differently coloured. Moreover, $Fe(OH)_2$ is green in colour like $Cr(OH)_3$ whereas $Fe(OH)_3$ is brown in colour. Thus the colour of the precipitate of $Fe(OH)_3$ helps to distinguish it for , $Cr(OH)_3$.

Reason for boiling of H_2S from the filtrate of II group before proceeding to III group

If H_2S is not boiling off from the filtrate of II group.

(a) Then sulphur will be precipitated on boiling with conc. HNO_3, which is essential to oxidise ferrous into ferric salts.

(b) Fe^{2+} is also present in the mixture will be precipitated as black FeS.

The sulphide of IV group radicals Co, Ni, Mn and Zn will be precipitated in III group on addition of NH_4Cl and NH_4OH due to presence of disolve H_2S.

Reason for the formation of a ppt. in group III in the absence of cations of that group

If a mixture contains radicals like oxalate, phosphate, fluoride, borate, called interfering acid radicals the elements of IV, V and VI group basic radicals are precipitated in III group as salts of these acid radicals. The salts of such radicals are soluble in dil HCl but when NH_4Cl and NH_4OH are added to test for the presence of III group, these fluorides, oxalates, phosphates of IV, V, VI group radicals get precipitated.

More ever, magnanese which is in IV group of qualitative analysis is also sometimes precipitated in III group as hydroxide which gets oxidised by atmospheric oxygen into brown coloured hydrated manganese oxide or magnanic hydoxide or magnanous acid H_2MnO_3.

$$2Mn(OH)_2 + O \longrightarrow Mn_2O_3 + 2H_2O$$

$$2Mn(OH)_2 + H_2O + O \longrightarrow 2Mn(OH)_3$$

Reason for not using NaCl and NaOH as III group reagents in place of NH_4Cl and NH_4OH in III group of qualitative analysis.

NaOH is highly ionised electrolyte which produces very high concentration of OH^- ions. The latter cannot be decreased by common Na^+ ions produced from NaCl as the case in NH_4Cl and NH_4OH. Thus with this greater concentration of OH^- ions the solubility product of not only the hydroxides of III group metals but also those of IV, V and VI group metals is exceeded. Hence, the latter also precipitate out in III group.

Flame colouration comes with difficulty and sometimes not at all in case of phosphates of metals.

The flame test is based on the fact that the chlorides of metals vapourise at high temperature producing metallic ions which impart characteristics colour to the flame. The phosphates on the other hand, are non-volatile and moreover are converted with difficulty into chloride with HCl. Secondly, if they are partly converted into chlorides at high temperatures of the flame, metallic ions produced from latter recombine with phosphate ions to give back non-volatile phosphates of the metals. Thus in such a case no flame test is given.

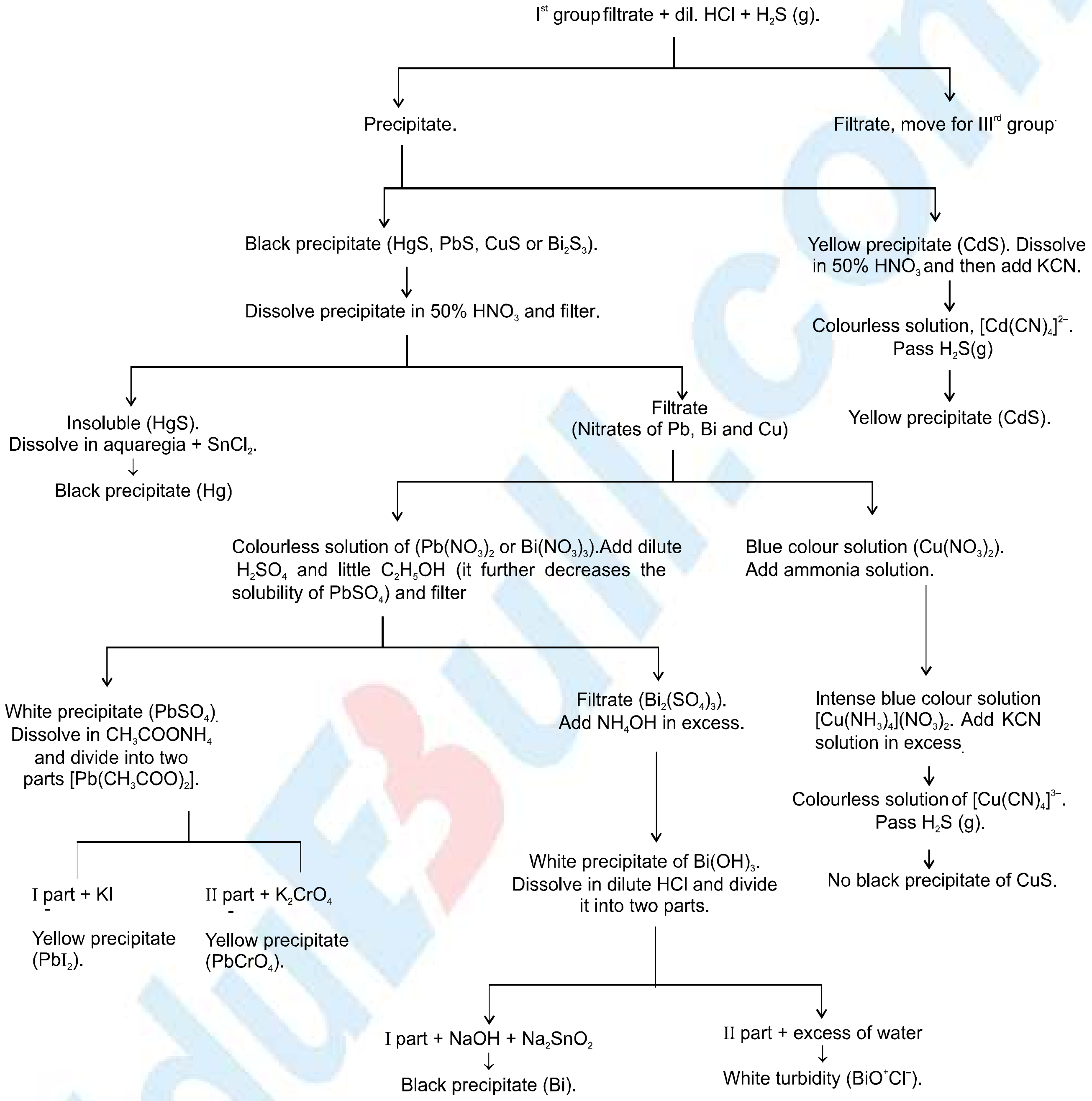
Reason for removing fluoride, borates and oxalate before carrying out analysis of III group and onwards.

The fluorides, borates and oxalates of metals are soluble in HCl, but when NH_4Cl and NH_4OH are added to detect the presence of III group, the fluorides, etc., of IV, V and VI group radicals are also precipitated in III group. Thus these radicals interfere in the systematic analysis of basic radicals and their removal becomes essential prior to addition of NH_4OH for III group.

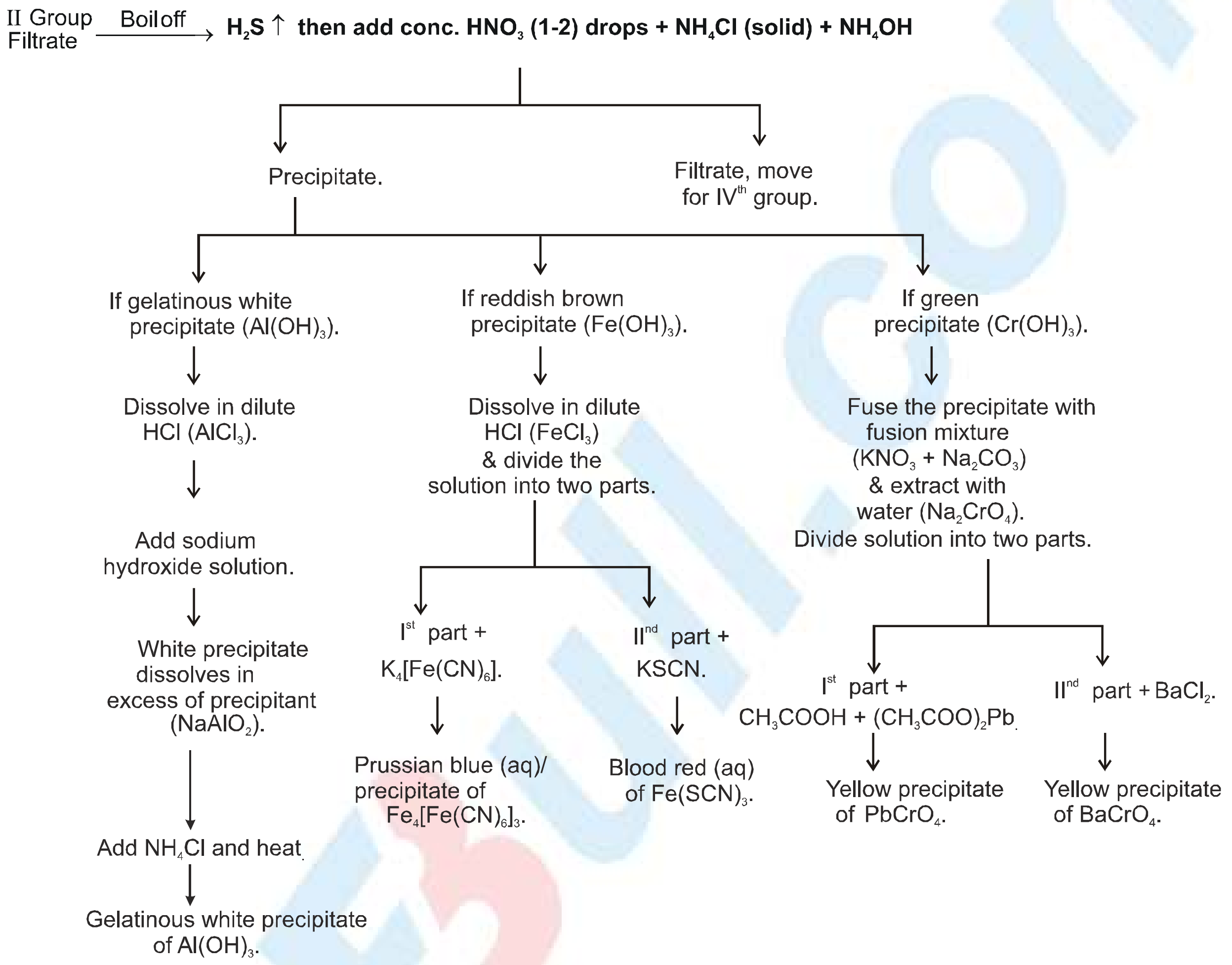
Qualitative Analysis of Cation mixtures

S.N.	Group	Group Reagent	Cations	ppt/colour
1	I	Dil. HCl	Ag^+, Hg_2^{2+}, Pb^{2+}	$AgCl$ Hg_2Cl_2 White $PbCl_2$
2	IIA	H_2S /dil. HCl	Cu^{2+}, Bi^{3+}, Hg^{2+}, Pb^{+2}, Cd^{2+}	CuS, Bi_2S_3, HgS, PbS, CdS ↓ ↓ ↓ ↓ ↓ Black Brown Black Black Yellow
3	IIB	H_2S /dil. HCl	Sn2+, Sn4+, As3+, As5+, Sb3+, Sb5+	SnS SnS_2 As_2S_3 As_2S_5 Sb_2S_3 Sb_2S_5 ↓ ↓ ↓ ↓ ↓ ↓ Brown Yellow Yellow Yellow Orange Orange
4	III	NH_4OH/NH_4Cl	Fe^{3+}, Al^{3+}, Cr^{3+}	Fe(OH)3 Al(OH)3 Cr(OH)3 ↓ ↓ ↓ Brown White Green
5	IV	$H_2S/NH_4OH/NH_4Cl$	Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}	NiS CoS MnS ZnS ↓ ↓ ↓ ↓ Black Black Pink/Buff/Skin Dirty white
6	V	$(NH_4)_2CO_3$/ NH_4OH/NH_4Cl	Ba^{2+}, Sr^{2+}, Ca^{2+}	$BaCO_3$ $SrCO_3$ $CaCO_3$ ↓ ↓ ↓ White White White
7	VI	No common group reagent	K^+, Na^+, Mg2+	No common ppt
8	Zero	No common group reagent	$\overset{\oplus}{NH_4}$	No common ppt (Generally identify by Nessler's reagent)

IIA Group (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, *Cd^{2+})

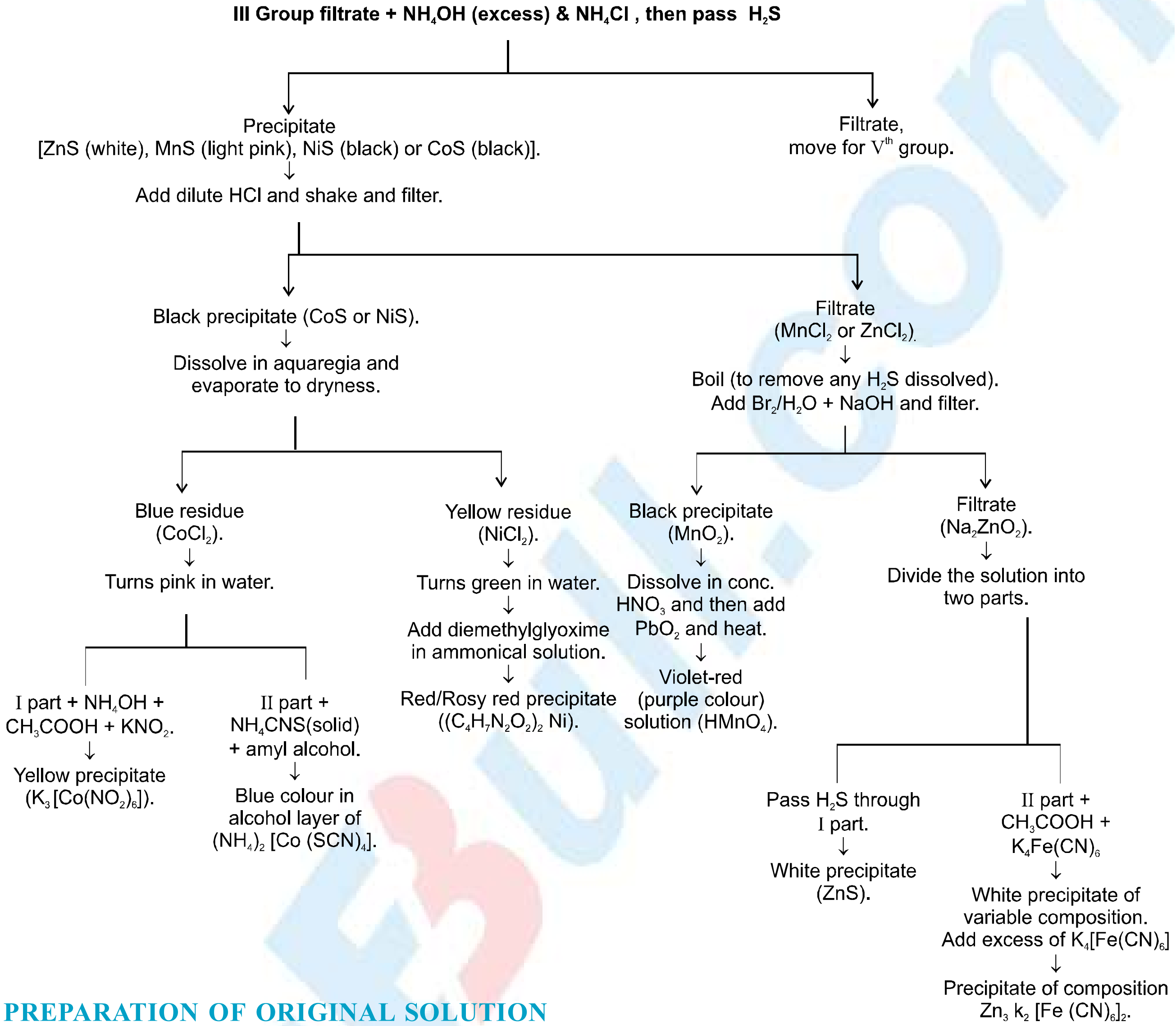


IIIrd Group (Al^{3+}, Cr^{3+}, Fe^{3+})



- Concentrated HNO_3 is added to oxidise Fe^{2+} to Fe^{3+} if present.
- Solid NH_4Cl should be added in excess other wise cations like Zn, Mn, Mg may be precipitated here. To much excess of NH_4Cl should be avoided other wise Cr is not precipitated and Al may form a colloidal solution.

IVth GROUP (Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}) :



III Group filtrate + NH_4OH (excess) & NH_4Cl , then pass H_2S

Precipitate
[ZnS (white), MnS (light pink), NiS (black) or CoS (black)].
↓
Add dilute HCl and shake and filter.

Filtrate,
move for Vth group.

Black precipitate (CoS or NiS).
↓
Dissolve in aquaregia and evaporate to dryness.

Blue residue ($CoCl_2$).
↓
Turns pink in water.

I part + NH_4OH + CH_3COOH + KNO_2.
↓
Yellow precipitate ($K_3[Co(NO_2)_6]$).

II part + NH_4CNS(solid) + amyl alcohol.
↓
Blue colour in alcohol layer of $(NH_4)_2$ [Co $(SCN)_4$].

Yellow residue ($NiCl_2$).
↓
Turns green in water.
↓
Add diemethylglyoxime in ammonical solution.
↓
Red/Rosy red precipitate ($(C_4H_7N_2O_2)_2$ Ni).

Filtrate
($MnCl_2$ or $ZnCl_2$).
↓
Boil (to remove any H_2S dissolved).
Add Br_2/H_2O + NaOH and filter.

Black precipitate (MnO_2).
↓
Dissolve in conc. HNO_3 and then add PbO_2 and heat.
↓
Violet-red (purple colour) solution ($HMnO_4$).

Filtrate (Na_2ZnO_2).
↓
Divide the solution into two parts.

Pass H_2S through I part.
↓
White precipitate (ZnS).

II part + CH_3COOH + $K_4Fe(CN)_6$
↓
White precipitate of variable composition.
Add excess of $K_4[Fe(CN)_6]$
↓
Precipitate of composition Zn_3 k_2 [Fe $(CN)_6]_2$.

PREPARATION OF ORIGINAL SOLUTION

Transparent, aqueous solution of salt is known as original solution and it is prepared by dissolving salt/mixture in suitable solvent. To prepare original solution, following solvents are used strictly in the order given below:

(i) Cold Water
(ii) Hot water
(iii) Dilute HCl
(iv) Conc. HCl

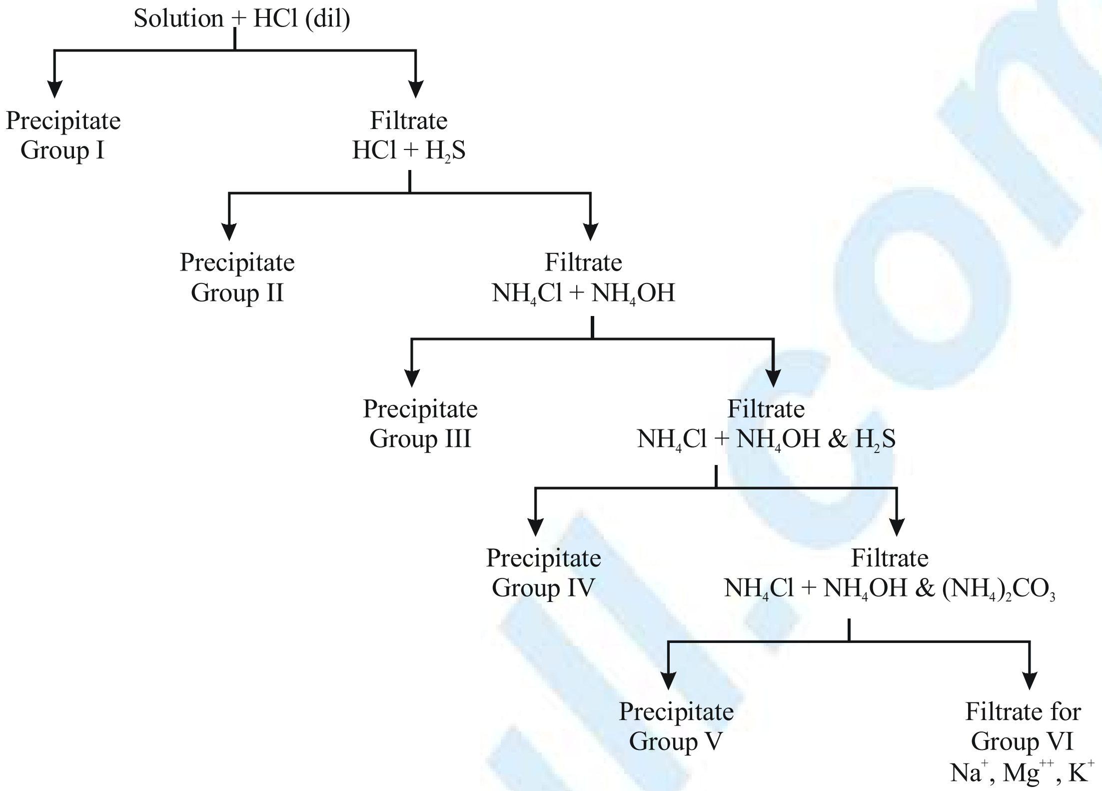
To prepare original solution small quantity of substance is shaken with cold, distilled water. It substance dissolves, whole substance is dissolved in water to prepare original solution. If substance remains insoluble then, mixture is heated and solubility is tested.

If substance is insoluble in hot water also then a few drops of dil HCl are added.

If substance remains insoluble in dil. HCl also, then we try to dissolve in dil. HNO_3.

If substance does not dissolve in the solvents used in above steps, then it is dissolved in conc. HCl. If it remains insoluble even in concentrate HCl, then a paste of substance and concentrate HCl is made in a porcelein dish and this mixture is heated till it becomes semi-solid. Again concentrate HCl is added to make paste and is heated again to get a semi-solid. The procedure is repeated twice or thrice and semi-solid thus obtained is dissolved in distil water. The solution is filtered and filtrate is as original solution. If some insoluble part is obtained that is neglected and is not used. The filtrate obtained as original solution is necessarily diluted with water.

Method of Analysis :



(A) Group I (Pb^{2+}, Ag^+, Hg^{2+}) RADICALS :

On adding dilute HCl to the salt solution if white precipitate is obtained, it indicates the presence of Pb^{2+}, Ag^+ or Hg_2^{2+} ion in the solution.

$$Ag^+ \xrightarrow{\text{dil. HCL}} AgCl\downarrow \quad \text{white ppt.}$$

$$Pb^{+2} \xrightarrow{\text{dil. HCL}} PbCl_2\downarrow \quad \text{white ppt.}$$

$$Hg_2^{+2} \xrightarrow{\text{dil. HCL}} Hg_2Cl_2\downarrow \quad \text{white ppt.}$$

Reaction of :-

(1) LEAD (II)

(i) Sodium Hydroxide Solution

With NaOH, Pb^{2+} forms a white precipitate of lead hydroxide. The precipitate dissolves in excess of the reagent (NaOH) when tetrahydroxyplumbate**(II)** ions are formed.

$$Pb^{2+} + 2OH^- \longrightarrow \underset{\text{White ppt}}{Pb(OH)_2\downarrow}$$

$$Pb(OH)_2\downarrow + 2OH^- \longrightarrow \underset{\text{Soluble}}{[Pb(OH)_4]^{2-}}$$

(ii) Ammonia Solution

With ammonia solution, Pb^{2+} gives a white precipitate of lead hydroxide.

$$Pb^{+2} + 2NH_4OH \longrightarrow Pb(OH)_2 + 2NH_4^+$$

White ppt

The precipitate is insoluble in excess reagent (NH_4OH).

(iii) Potassium Chromate Solution

$PbCl_2$ is soluble in hot water and gives a yellow precipitate with K_2CrO_4. The precipitate obtained is insoluble in acetic acid but soluble in NaOH and nitric acid.

$$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2KCl$$

Yellow ppt

$$PbCrO_4\downarrow + 4NaOH \longrightarrow Na_2[Pb(OH)_4] + Na_2CrO_4$$

$$2PbCrO_4\downarrow + 2H^+ \longrightarrow 2Pb^{2+} + Cr_2O_7^{2-} + H_2O$$

(iv) Potassium Iodide Solution

$PbCl_2$ on addition of KI solution gives bright yellow precipitate of PbI_2.

$$PbCl_2 + 2KI \longrightarrow PbI_2\downarrow + 2KCl$$

Yellow ppt

The precipitate is moderately soluble in boiling water to yield a colourless solution, from which it separates as golden yellow plates on cooling.

Yellow precipitate dissolves on adding excess of potassium iodide solution.

$$PbI_2 + 2KI\ (excess) \rightleftharpoons K_2[PbI_4]$$

colourless soluble complex

The reaction is reversible and on diluting with H_2O, the precipitate reappears.

(v) Reaction with KCN

$$Pb^{+2} + KCN \longrightarrow Pb(CN)_2\downarrow \xrightarrow{\text{excess KCN}} \text{Insoluble}$$

white

2. SILVER (I)

(i) Dilute Hydrochloric Acid

With dilute hydrochloric acid (or soluble chlorides), a white precipitate of silver chloride is formed.

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

White ppt

With concentrated hydrochloric acid precipitation does not occur. After decanting the liquid from over the precipitate. It can be dissolved in concentrated hydrochloric acid, when a dichloroargentate complex is formed.

$$AgCl + Cl^- \rightleftharpoons [AgCl_2]^-$$

Soluble

On dilution with water, the equilibrium shifts back to the left and the precipitate reappears. Dilute ammonia solution dissolves the precipitate to form the diammineargentate(I) ion, (complex ion).

$$AgCl\downarrow + 2NH_3 \rightleftharpoons \underset{\text{Soluble}}{[Ag(NH_3)_2]^+} + Cl^-$$

Dilute nitric acid or hydrochloric acid neutralizes the excess ammonia and the precipitate reappears because the equilibrium is shifted backwards.

(ii) Ammonia solution

Ag^+ give brown precipitate of silver oxide with NH_3 solution.

$$2Ag^+ + 2NH_3 + H_2O \rightleftharpoons \underset{\text{Brown ppt}}{Ag_2O\downarrow} + 2NH_4^+$$

The reaction reaches equilibrium, thus the precipitation is incomplete at any stage. The precipitate dissolves in excess of the reagent forming diamineargentate(I) ion.

$$Ag_2O\downarrow + 4NH_3 + H_2O \longrightarrow \underset{\text{Soluble}}{2[Ag(NH_3)_2]^+} + 2OH^-$$

(iii) Potassium Iodide Solution

Ag^+ give yellow precipitate of silver iodide on reaction with KI solution.

$$Ag^+ + I^- \longrightarrow \underset{\text{Yellow ppt}}{AgI\downarrow} \xrightarrow{\text{excess KI}} \text{No change}$$

The precipitate is insoluble in dilute or concentrated ammonia but dissolves in KCN and in sodium thiosulphate.

$$AgI\downarrow + 2CN^- \longrightarrow [Ag(CN)_2]^- + I^-$$

$$AgI\downarrow + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + I^-$$

(iv) Disodium Hydrogen Phosphate Solution

With disodium hydrogen phosphate in neutral solution, a yellow precipitate of silver phosphate is obtained.

$$3Ag^+ + HPO_4^{2-} \longrightarrow \underset{\text{Yellow ppt}}{Ag_3PO_4\downarrow} + H^+ + \xrightarrow[\text{Solution}]{NH_3} \underset{\text{soluble complex}}{[Ag(NH_3)_2]^+}$$

Nitric acid and ammonia solution dissolves the precipitate.

(v) Hydrazine sulphate (Saturated)

When hydrazine sulphate is added to a solution of diamineargenatate ions, it forms finely divided silver metal and gaseous nitrogen is evolved.

$$4[Ag(NH_3)_2]^+ + H_2N\text{–}NH_2.H_2SO_4 \longrightarrow \underset{\text{Silver mirror}}{4Ag\downarrow} + N_2\uparrow + 6NH_4^+ + 2NH_3 + SO_4^{2-}$$

If the vessel in which the reaction is carried out is clean, silver adheres to the glass walls forming an attractive mirror.

(vi) Reaction with NaOH

$$Ag^+ + NaOH \longrightarrow \quad \underset{\text{Brownish black}}{Ag_2O\downarrow} \xrightarrow[\text{NaOH}]{\text{excess}} \text{Insoluble}$$

3. MERCURY (I)

(i) Sodium Hydroxide Solution

With NaOH, Hg_2^+ forms a black precipitate of mercury(I) oxide.

$$Hg_2^{2+} + 2OH^- \longrightarrow \underset{\text{Black ppt}}{Hg_2O\downarrow} + H_2O \xrightarrow[\text{NaOH}]{\text{excess}} \text{Insoluble}$$

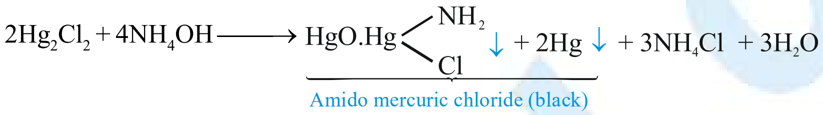
The precipitate is insoluble in excess reagent but dissolves in dilute nitric acid.

When the solution is boiled, the colour of precipitate changes to grey owing to the disproportionation, when mercury(II) oxide and mercury metal are formed.

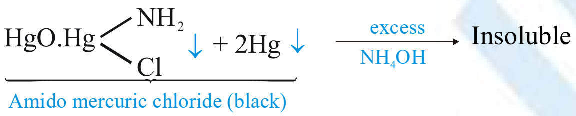
$$Hg_2O\downarrow \longrightarrow HgO\downarrow + Hg\downarrow$$

(ii) Ammonia Solution

$HgCl_2$ on treatment with NH_4OH results in giving black precipitate, which is a mixture of mercury metal and basic mercury(II) amido chloride (white precipitate)



$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow \underbrace{HgO.Hg\begin{matrix}NH_2\\ Cl\end{matrix}\downarrow + 2Hg\downarrow}_{\text{Amido mercuric chloride (black)}} + 3NH_4Cl + 3H_2O$$



$$\underbrace{HgO.Hg\begin{matrix}NH_2\\ Cl\end{matrix}\downarrow + 2Hg\downarrow}_{\text{Amido mercuric chloride (black)}} \xrightarrow[NH_4OH]{\text{excess}} \text{Insoluble}$$

(iii) Potassium Iodide Solution

Hg_2^{2+} give a green precipitate of mercury(I) iodide on reaction with KI solution.

$$Hg_2^{2+} + 2I^- \longrightarrow \underset{\text{Green ppt}}{Hg_2I_2}$$

If excess reagent is added, a disproportionation reaction takes place and a soluble tetraiodomercurate(II) ions and black precipitate of mercury is formed.

$$Hg_2I_2\downarrow + 2I^- \longrightarrow \underset{\text{soluble complex}}{[HgI_4]^{2-}} + \underset{\text{Black ppt}}{Hg\downarrow}$$

Boiling the mercury(I) iodide precipitate with water, disproportionation again takes place and a mixture of red mercury(II) iodide precipitate and black mercury is formed.

$$Hg_2I_2\downarrow \longrightarrow \underset{\text{scarlet red ppt}}{HgI_2\downarrow} + \underset{\text{Black ppt}}{Hg\downarrow}$$

(iv) Potassium Chromate Solution

Hg_2^{2+} give a red crystalline precipitate of mercury(I) chromate with potassium chromate solution in hot.

$$Hg_2^{2+} + CrO_4^{2-} \longrightarrow \underset{\text{Brick Red ppt}}{Hg_2CrO_4\downarrow} \xrightarrow[\text{Solution}]{NH_3} \underbrace{Hg\downarrow\ Hg(NH_2)X\downarrow}_{\text{over all Black ppt.}}$$

Addition of sodium hydroxide turns the precipitate into black mercury(I) oxide.

$$Hg_2CrO_4\downarrow + 2OH^- \longrightarrow \underset{\text{Black ppt}}{Hg_2O\downarrow} + CrO_4^{2-} + H_2O$$

(B) GROUP II A (Pb^{2+}, Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}) RADICALS :

The precipitates of group IIA are insoluble in yellow ammonium sulphide.

1. MERCURY (II)

HgS precipitated dissolves in aqua regia (3HCl : HNO_3) forming undissociated $HgCl_2$.

$$3HgS\downarrow + 6HCl + 2HNO_3 \longrightarrow 3HgCl_2 + 3S\downarrow + 2NO\uparrow + 4H_2O$$

(i) Potassium Iodide Solution

Potassium iodide when added slowly to the solution of Hg^{2+}, a scarlet red precipitate mercury(II) iodide is formed.

$$Hg^{2+} + 2I^- \longrightarrow \underset{\text{Scarlet red ppt}}{HgI_2\downarrow}$$

The precipitate dissolves in excess reagent, when colourless tetraiodomecurate(II) ions are formed.

$$HgI_2 + 2I^- \longrightarrow \underset{\text{Soluble}}{[HgI_4]^{2-}} \text{ or } HgI_2 + 2KI \longrightarrow K_2[HgI_4]$$

An alkaline solution of potassium tetraiodomercurate(II) serves as a selective and sensitive reagent for ammonium ions (Nessler's reagent)

(ii) Tin(II) Chloride Solution

When $SnCl_2$ solution is added to a solution of Hg^{2+}, a white silky precipitate of mercury(I) chloride(calomel) is obtained.

$$2Hg^{2+} + SnCl_2 \longrightarrow \underset{\text{White Silky ppt}}{Hg_2Cl_2\downarrow} + Sn^{4+}$$

If more reagent is added, mercury(I) chloride is further reduced and black precipitate of mercury is formed.

$$Hg_2Cl_2\downarrow + SnCl_2 \longrightarrow \underset{\text{Black ppt}}{2Hg\downarrow} + SnCl_4$$

(iii) Cobalt(II) Thiocyanate Test

When $[Co(SCN)_4]^{2-}$ is added to the solution of Hg^{2+} and walls of the vessel are stirred with a glass rod, a deep-blue crystalline precipitate of cobalt tetrathiocyanatomercurate(II) is formed.

$$Hg^{2+} + Co^{2+} + 4SCN^- \longrightarrow \underset{\text{Deep-blue ppt}}{Co[Hg(SCN)_4]\downarrow}$$

2. COPPER (II)

Hot, concentrated nitric acid dissolves copper(II) sulphide, leaving behind sulphur as a white precipitate.

$$3CuS\downarrow + 8HNO_3 \longrightarrow 3Cu^{2+} + 6NO_3^- + \underset{\text{White ppt}}{3S\downarrow} + 2NO\uparrow + 4H_2O$$

When boiled for long sulphur is oxidised to H_2SO_4 and a clear blue solution is obtained.

$$S\downarrow + 2HNO_3 \longrightarrow 2H^+ + SO_4^{2-} + 2NO\uparrow$$

(i) Ammonia Solution

When ammonia solution is added to solution of Cu^{2+}, a blue precipitate of a basic copper sulphate is obtained, which is soluble in excess reagent giving deep-blue colouration of tetreamminecopper(II) sulphate.

$$2Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \longrightarrow \underset{\text{Blue ppt}}{Cu(OH)_2.CuSO_4\downarrow} + 2NH_4^+$$

$$Cu(OH)_2.CuSO_4\downarrow + 8NH_3 \longrightarrow \underset{\text{Deep-blue colouration}}{2[Cu(NH_3)_4]^{2+}} + SO_4^{2-} + 2OH^-$$

(ii) Potassium Iodide

Potassium iodide with Cu^{2+} gives a white precipitate of copper(I) iodide but the solution is intensely brown because of the formation of tri–iodide ions(or iodine)

$$2Cu^{2+} + 5I^- \longrightarrow \underset{\text{White ppt}}{Cu_2I_2\downarrow} + I_3^-$$

Adding an excess of sodiuim thiosulphate (hypo) to the solution, tri-iodide ions reduced to colourless iodide ions and the white colour of the precipitate becomes visible. The reduction with thiosulphate yields tetrathionate ions.

$$I_3^- + 2S_2O_3^{2-} \longrightarrow \underbrace{3I^- + S_4O_6^{2-}}_{\text{overall colourless}}$$

These reactions are used in quantitative analysis for the iodometric determination of copper.

(iii) Potassium Hexacyanoferrate(II) solution

Cu^{2+} ions give chocolate–brown precipitate with $K_4[Fe(CN)_6]$ solution.

$$2Cu^{2+} + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate–brown ppt}}{Cu_2[Fe(CN)_6]\downarrow} + 4K^+$$

(iv) Potassium Thiocyanate Solution

With potassium thiocyanate, a black precipitate of copper(II) thiocyanate is obtained.

$$Cu^{2+} + 2SCN^- \longrightarrow \underset{\text{Black ppt}}{Cu(SCN)_2\downarrow}$$

The precipitate decomposes slowly to form white copper(I) thiocyanate and thiocyanogen is formed.

$$2Cu(SCN)_2\downarrow \longrightarrow \underset{\text{White ppt}}{2CuSCN\downarrow} + (SCN)_2\uparrow$$

Thiocyanogen decomposes rapidly in aqueous solutions.

Copper(II) thiocyanate can be transformed to copper(I) thiocyanate immediately by adding a suitable reducing agent like saturated solution of sulphur dioxide.

$$2Cu(SCN)_2\downarrow + SO_2 + 2H_2O \longrightarrow \underset{\text{White ppt}}{2CuSCN\downarrow} + 2SCN^- + SO_4^{2-} + 4H^+$$

(v) Test by NaCN & KCN

Addition of KCN to $CuSO_4$ solution first causes reduction and then precipitates CuCN (cuprous cyanide). This reacts with excess CN^-, forming a soluble four co-ordinate compledx $[Cu(CN)_4]^{3-}$ which is tetrahedral in shape :

$$2Cu^{2+} + 4CN^- \longrightarrow 2Cu^{I}CN + (CN)_2$$

Cyanogen

$$CuCN + 3CN^- \longrightarrow [Cu^{I}(CN)_4]^{3-}$$

colourless complex

Note : $[Cu(CN)_4]^{3-}$ is a stable complex. Cd^{2+} also forms complex $[Cd(CN)_4]^{2-}$ but unstable, which ionises to form Cd^{2+} and CN^-. Thus if Cd^{2+} and Cu^{2+} both are present, Cu^{2+} and Cd^{2+} both are complexed by CN^-. If H_2S gas is passed, Cd^{2+} (in unstable $[Cd(CN)_4)^{2-}]$) gives yellow precipitate of CdS.

3. BISMUTH (III)

Black precipitate of Bi_2S_3 is obtained dissolves in hot dilute nitric acid, leaving behind sulphur in the form of a white precipitate.

$$Bi_2S_3\downarrow + 8H^+ + 2NO_3^- \longrightarrow 2Bi^{3+} + 3S\downarrow + 2NO\uparrow + 4H_2O$$

White ppt

(i) Sodium Hydroxide

With NaOH solution, Bi^{3+} give a white precipitate of bismuth**(III)** hydroxide.

$$Bi^{3+} + 3OH^- \longrightarrow Bi(OH)_3\downarrow$$

White ppt

The precipitate is soluble in acids.

$$Bi(OH)_3\downarrow + 3H^+ \longrightarrow Bi^{3+} + 3H_2O$$

When boiled, the precipitate loses water and turns yellowish-white.

$$Bi(OH)_3\downarrow \longrightarrow BiO.OH\downarrow + H_2O$$

Yellowish-white ppt

$Bi(OH)_3$ when reduced by tetrahydroxostannate**(II)** ions give black precipitate of bismuth metal.

$$2Bi(OH)_3\downarrow + 3[Sn(OH)_4]^{2-} \longrightarrow 2Bi\downarrow + 3[Sn(OH)_6]^{2-}$$

(ii) Potassium Iodide

When KI solution is added dropwise to Bi^{3+} solution, a black precipitate of bismuth**(III)** iodide is obtained.

$$Bi^{3+} + 3I^- \longrightarrow BiI_3\downarrow$$

Brownish black ppt

The precipitate dissolves readily in excess reagent, when orange–coloured tetraiodobismuthate ions are formed.

$BiI_3\downarrow + I^-$ ‡ ˆ† $[BiI_4]^-$

Heating the precipitate of BiI_3 with water, it turns orange due to the formation of bismuthyl iodide.

$$BiI_3\downarrow + H_2O \longrightarrow BiOI\downarrow + 2H^+ + 2I^-$$

Orange ppt

(iii) Water

When a solution of a bismuth salt is poured into a large volume of water, a white precipitate of the corresponding basic salt is produced. This is soluble in dilute mineral acids but is insoluble in alkali hydroxides.

$$Bi^{3+} + NO_3^- + H_2O \longrightarrow BiO(NO_3)\downarrow + 2H^+$$

White ppt

$$Bi^{3+} + Cl^- + H_2O \longrightarrow BiOCl\downarrow + 2H^+$$

White ppt

4. CADMIUM (II)

Yellow precipitate of CdS dissolves in hot dilute nitric and giving Cd^{+2} ions.

(i) Ammoniaum Hydroxide

With NH_4OH solution, Cd^{2+} give a white precipitate of cadmium hydroxide.

$$Cd^{2+} + 2NH_4OH \rightleftharpoons Cd(OH)_2\downarrow + 2NH_4^+$$

White ppt

The precipitate dissolves in acid when the equilibrium shifts towards the left.

An excess of reagent dissolves the precipitate, when tetramminecadmiate**(II)** ions are formed.

$$Cd(OH)_2\downarrow + 4NH_3 \longrightarrow [Cd(NH_3)_4]^{2+} + 2OH^-$$

(ii) Potassium Cyanide

With KCN solution, Cd^{2+} forms a white precipitate of cadmium cyanide.

$$Cd^{2+} + 2CN^- \longrightarrow Cd(CN)_2\downarrow$$

White ppt

An excess of reagent dissolves the precipitate due to the formation of tetracyanocadmiate**(II)** ions.

$$Cd(CN)_2\downarrow + 2CN^- \longrightarrow [Cd(CN)_4]^{2-}$$

The colourless complex is not too stable. Thus, when hydrogen sulphide gas is passed, cadmium sulphide is precipitated.

$$[Cd(CN)_4]^{2-} + H_2S \longrightarrow CdS\downarrow + 2H^+ + 4CN^-$$

The marked difference in the stabilities of the copper and cadmium tetracyanato complexes serves as the basis for the separation of Cu^{2+} and Cd^{2+} ions.

(iii) Potassium Iodide

With KI solution, no precipitate is formed (distinction from copper).

(C) GROUP II B RADICALS :

1. TIN (II) & TIN (V)

SnS (brown precipitate) and SnS_2 (yellow precipitate), both are soluble in concentrated HCl and yellow ammonium sulphide.

$$SnS\downarrow + S_2^{2-} \longrightarrow SnS_3^{2-}$$

$$SnS_2\downarrow + 2S_2^{2-} \longrightarrow SnS_3^{2-} + S_3^{2-}$$

(i) Sodium Hydroxide Solution

With NaOH, Sn^{2+} gives a white precipitate of tin**(II)** hydroxide, which is soluble in excess alkali.

$$Sn^{2+} + 2OH^- \longrightarrow Sn(OH)_2\downarrow$$

White ppt

$$Sn(OH)_2\downarrow + 2OH^- \longrightarrow [Sn(OH)_4]^{2-}$$

With NaOH solution, Sn^{4+} give a gelatinous white precipitate of tin**(IV)** hydroxide, which is soluble in excess of precipitant forming hexahydrostannate**(IV)**.

$$Sn^{4+} + 4OH^- \longrightarrow Sn(OH)_4\downarrow$$

White ppt

$$Sn(OH)_4\downarrow + 2OH^- \rightleftharpoons [Sn(OH)_6]^{2-}$$

(ii) Ammonia Solution

With NH_4OH, Sn^{2+} forms a white precipitate of $Sn(OH)_2$ but the precipitate is insoluble in excess of NH_4OH.

$$Sn^{2+} + 2OH^- \longrightarrow Sn(OH)_2\downarrow$$

White ppt

With NH_4OH, Sn^{4+} gives white precipitate of $Sn(OH)_4$, which is insoluble in excess of NH_4OH.

$$Sn^{4+} + 4OH^- \longrightarrow Sn(OH)_4\downarrow$$

White ppt

(iii) Mercury(II) Chloride Solution

With mercury(II) chloride solution, a white precipitate of mercury(I) chloride (calomel) is formed if a large amount of the reagent is added quickely.

$$Sn^{2+} + 2HgCl_2 \longrightarrow Hg_2Cl_2\downarrow + Sn^{4+} + 2Cl^-$$

White ppt

If however, tin(II) ions are in excess, the precipitate turns grey, especially on warming, owing to further reduction to mercury metal.

$$Sn^{2+} + Hg_2Cl_2\downarrow \longrightarrow 2Hg\downarrow + Sn^{4+} + 2Cl^-$$

Grey ppt

Sn^{4+} gives no precipitate with mercury(II) chloride solution.

(D) GROUP III (Fe^{3+}, Al^{3+}, Cr^{3+})

1. IRON (III)

(i) Ammonium Sulphide Solution

With ammonium sulphide solution, Fe^{3+} gives a black precipitate of iron(II) sulphide and sulphur.

$$2Fe^{3+} + 3S^{2-} \longrightarrow 2FeS\downarrow + S\downarrow$$

Black ppt

In hydrochloric acid, the black iron(II) sulphide precipitate dissolves and the white colour of sulphur becomes visible.

$$FeS\downarrow + 2H^+ \longrightarrow S\downarrow + Fe^{2+}$$

white ppt.

The damp iron(II) sulphide precipitate, when exposed to air, is slowly oxidized to brown iron(III) hydroxide.

$$4FeS\downarrow + 6H_2O + 3O_2 \longrightarrow 4Fe(OH)_3\downarrow + 4S\downarrow$$

From alkaline solutions of ammonium sulphide, black iron(III) sulphide is obtained.

$$2Fe^{3+} + 3S^{2-} \longrightarrow Fe_2S_3\downarrow$$

On acidification with hydrochloric acid, iron(III) ions are reduced to iron(II) ions and sulphur is formed.

$$Fe_2S_3\downarrow + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2S\uparrow + S\downarrow$$

(ii) Sodium Hydroxide Solution

With sodium hydroxide solution, a reddish-brown precipitate of iron(III) hydroxide, insoluble in excess of the reagent (distinction from aluminium and chromium) is obtained.

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

Reddish-brown ppt

(iii) Potassium Hexacyanoferrate(II)

With potassium hexacyanoferrate(II) solution, Fe^{3+} gives intense blue precipitate of iron(III) hexacyanoferrate (Prussian blue)

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3\downarrow$$

Prussian blue

The precipitate is insoluble in dilute acids but decomposes in concentrated hydrochloric acid. A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained. Sodium hydroxide turns the precipitate red as iron(III) oxide and hexacyanoferrate(II) ions are formed.

$$Fe_4[Fe(CN)_6]_3\downarrow + 12OH^- \longrightarrow 4Fe(OH)_3\downarrow + 3[Fe(CN)_6]^{4-}$$

Raddish-brown ppt

Oxalic acid also dissolves Prussian blue forming a blue solution. This process was once used to manufacutre blue writing inks.

If iron**(III)** chloride is added to an excess of potassium hexacyanoferrate**(II)**, a product with the composition $KFe[Fe(CN)_6]$ is formed. This tends to form colloidal solutions ("Soluble Prussian Blue) and cannot be filtered.

(iv) Potassium Hexacyanoferrate(III)

With potassium hexacyanoferrate**(III)**, a brown colouration is produced, due to the formation of an undissociated complex, iron**(III)** hexacyanoferrate**(III)**.

$$Fe^{3+} + [Fe(CN)_6]^{3-} \longrightarrow Fe[Fe(CN)_6] \xrightarrow[\text{or } SnCl_2 \text{ solution}]{H_2O_2 \text{ solution}} Fe_4[Fe(CN)_6]_3$$

Brown colouration prussian blue

Upon adding hydrogen peroxide or some tin**(II)** chloride solution, the hexacyanoferrate**(III)** part of the compound is reduced and Prussian blue is precipitated.

(v) Disodium Hydrogen Phosphate Solution

With disodium hydrogen phosphate solution a yellowish-white precipitate of iron**(III)** phosphate is formed.

$$Fe^{3+} + HPO_4^{2-} \longrightarrow FePO_4\downarrow + H^+$$

Yellowish-white ppt

The reaction is reversible, because a strong acid is formed which dissolves the precipitate. It is advisable to add small amounts of sodium acetate, which acts as a buffer.

(vi) Sodium Acetate Solution

With sodium acetate solution, a reddish-brown colouration is obtained, attributed to the formation of a complex ion with the composition. $[Fe_3(OH)_2(CH_3COO)_6]^+$. The reaction

$$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4H_2O \longrightarrow 3Fe(OH)_2CH_3COO\downarrow + 3CH_3COOH + H^+$$

Reddish-brown ppt

The excess of acetate ion acts as a buffer and the reaction goes to completion.

(vii) Ammonium Thiocyanate Solution

With ammonium thiocyanate solution in slightly acidic medium, a deep-red colouration is produced (difference from iron**(II)** ions), due to the formation of a non-dissociated iron**(III)** thiocyanate complex.

$$Fe^{3+} + 3SCN^- \longrightarrow Fe(SCN)_3 \xrightarrow[\text{or } HgCl_2]{NaF} \text{colour becomes faded}$$

Deep-red colouration

This neutral molecule can be extracted by ether or amyl alcohol.

2. ALUMINIUM (III)

Halides, nitrates, sulphates of Al are water soluble and the aqueous solutions display acidic character owing to hydrolysis.

(i) Sodium Hydroxide Solution

With sodium hydroxide solution, Al^{3+} gives a white precipitate of aluminum hydroxide.

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3\downarrow$$

White ppt

The precipitate dissolves in excess reagent, forming tetrahydroxoaluminate ions.

$$Al(OH)_3 + OH^- \rightleftharpoons \underset{\text{Soluble}}{[Al(OH)_4]^-}$$

The reaction is reversible and any reagent, which will reduce the hydroxyl ion concentration sufficiently should cause the reaction to proceed from right to left with the consequent precipitation of aluminium hydroxide. This may be effected with a solution of ammonium chloride (the hydroxyl ion concentration is reduced owing to the formation of the weak base ammonia, which can be readily removed as ammonia gas by heating) or by the adding of acid; in the latter case, a large excess of acid causes the precipitated hydroxide to redissolve.

$$[Al(OH)_4]^- + NH_4^+ \longrightarrow Al(OH)_3\downarrow + NH_3\uparrow + H_2O$$

$$[Al(OH)_4]^- + H^+ \rightleftharpoons Al(OH)_3\downarrow + H_2O$$

$$Al(OH)_3 + 3H^+\downarrow \rightleftharpoons Al^{3+} + 3H_2O$$

(ii) Disodium Hydrogen Phosphate Solution

With disodium hydrogen phosphate solution, a white gelatinous precipitate of aluminium phosphate is obtained.

$$Al^{3+} + HPO_4^{2-} \rightleftharpoons \underset{\text{White ppt}}{AlPO_4\downarrow} + H^+$$

The reaction is reversible; strong acids dissolve the precipitate. However, the precipitate is insoluble in acetic acid (difference from phosphates of alkaline earth, which are soluble). The precipitate can also be dissolved in sodium hydroxide.

(iii) Cobalt nitrate Solution

Aluminium compounds, when heated with sodium carbonate upon charcoal gives a white infusible solid, which glows when hot. If the residue is moistened with a little cobalt nitrate solution and again heated, a blue infusible mass is obtained.

$$2Al_2O_3 + 2Co^{2+} + 4NO_3^- \longrightarrow 2CoAl_2O_4 + 4NO_2\uparrow + O_2\uparrow$$

Use of excess cobalt nitrate solution should be avoided since this will produce black cobalt oxide (Co_3O_4) upon ignition, which will mask the blue colour.

3. CHROMIUM (III)

(i) Sodium Hydroxide Solution

With sodium hydroxide solution, a green precipitate of chromium**(III)** hydroxide is formed

$$Cr^{3+} + 3OH^- \longrightarrow \underset{\text{Green ppt}}{Cr(OH)_3\downarrow}$$

The reaction is reversible; on the addition of acids the precipitate dissolves. In excess reagent, the precipitate dissolves readily, tetrahydroxochromate**(III)** ions (or chromite ions) are formed.

$$Cr(OH)_3 + OH^- \rightleftharpoons \underset{\text{Soluble}}{[Cr(OH)_4]^-}$$

The solution is green. The reaction is reversible; on (slight) acidification and also on boiling chromium**(III)** hydroxide precipitates again.

(ii) Ammonia Solution

Bluish-green gelatinous precipitate of $Cr(OH)_3$ is obtained when treated with ammonia solution but dissolves in excess of ammonia due to the formation of a soluble complex.

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{Bluish-green ppt}}{Cr(OH)_3\downarrow} + 3NH_4Cl$$

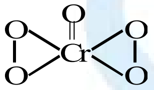
$$Cr(OH)_3\downarrow + \underset{\text{Excess}}{6NH_3} \longrightarrow \underset{\text{Pink colouration}}{[Cr(NH_3)_6]^{3+}} + 3OH^-$$

(iii) Chromium Pentoxide (Chromium Peroxide, Peroxochromic Acid) Test

On acidifying the solution with dilute sulphuric acid, adding few drops of ether or amyl alcohol to the mixture and finally adding some hydrogen peroxide, blue colouration is formed, which can be extracted into the organic phase by gently shaking. During the reaction, chromium pentoxide is formed.

$$CrO_4^{2-} + 2H^+ + 2H_2O_2 \longrightarrow \underset{\substack{\text{Blue colouration}\\ \text{in ether layer}}}{CrO_5} + 3H_2O$$

Chromium pentoxide has the following structure :

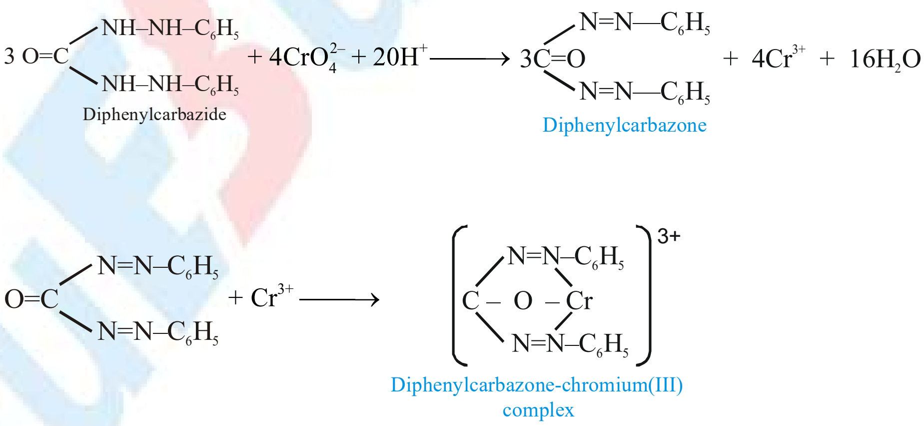


Because of the two peroxide groups, the compound is often called chromium peroxide. The name peroxochromic acid is less appropriate, because the compound does not contain hydrogen at all. In aqueous solution, the blue colour fades rapidly, because chromium pentoxide decomposes to chromium**(III)** and oxygen.

$$4CrO_5 + 12H^+ \longrightarrow 4Cr^{3+} + 7O_2\uparrow + 6H_2O$$

(iv) 1,5–Diphenylcarbazide Test

In dilute mineral acid solution, diphenylcarbazide produces a soluble violet colour, which is a characterstic test for chromium. During the reaction, chromate is reduced to chromium**(III)** and diphenylcarbazone is formed. These reaction products in turn produce a complex with the characteristic colour.



Diphenylcarbazide

Diphenylcarbazone

Diphenylcarbazone-chromium(III) complex

(E) GROUP IV (Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+})

1. ZINC (II)

(i) Sodium Hydroxide Solution

With sodium hydroxide solution, a white gelatinous precipitate of zinc hydroxide is formed

$$Zn^{2+} + 2OH^- \longrightarrow \underset{\text{White gelatinous ppt}}{Zn(OH)_2\downarrow}$$

The precipitate is soluble in acids.

$$Zn(OH)_2\downarrow + 2H^+ \longrightarrow Zn^{2+} + 2H_2O$$

and also in the excess of the reagent

$$Zn(OH)_2\downarrow + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$$

Zinc hydroxide is thus an amphoteric compound.

(ii) Ammonia Solution

With ammonia solution, Zn^{2+} forms a white gelatinous precipitate of $Zn(OH)_2$, which is readily soluble in excess reagent.

$$Zn^{2+} + 2NH_3 + 2H_2O \longrightarrow \underset{\text{White gelatinous ppt}}{Zn(OH)_2\downarrow} + 2NH_4^+$$

$$Zn(OH)_2\downarrow + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + 2OH^-$$

(iii) Disodium Hydrogen Phosphate Solution

With disodium hydrogen phosphate solution, a white precipitate of zinc phosphate is formed.

$$3Zn^{2+} + 2HPO_4^{2-} \rightleftharpoons \underset{\text{White ppt}}{Zn_3(PO_4)_2\downarrow} + 2H^+$$

In the presence of ammonia ions, zinc ammonium phosphate is formed.

$$Zn^{2+} + NH_4^+ + HPO_4^{2-} \rightleftharpoons Zn(NH_4)PO_4\downarrow + H^+$$

Both precipitates are soluble in dilute acids, when the reactions are reversed. Also, both precipitates are soluble in ammonia.

$$Zn_3(PO_4)_2 + 12NH_3 \longrightarrow 3[Zn(NH_3)_4]^{2+} + 2PO_4^{3-}$$

$$Zn(NH_4)PO_4 + 3NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + HPO_4^{2-}$$

(iv) Potassium Hexacyanoferrate(II)

With potassium hexacyanoferrate(II) solution, a white precipitate of variable composition is obtained. If the reagent is added in some excess, the composition of the precipitate is $K_2Zn_3[Fe(CN)_6]_2$.

$$3Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \longrightarrow \underset{\text{White ppt}}{K_2Zn_3[Fe(CN)_6]_2\downarrow}$$

The precipitate is insoluble in dilute acids but dissolves readily in sodium hydroxide.

$$K_2Zn_3[Fe(CN)_6]_2 + 12OH^- \longrightarrow 2[Fe(CN)_6]^{4-} + 3[Zn(OH)_4]^{2-} + 2K^+$$

This reaction can be used to distinguish zinc from aluminium.

(v) Ammonium tetrathiocyanatomercurate(II)

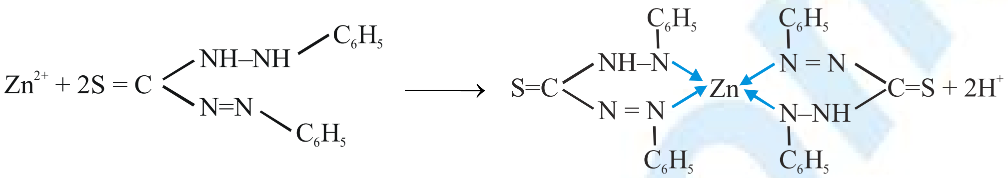
Copper salts alone do not form a precipitate with the ammonium tetrathiocyanatomercurate(II) reagent while zinc ions, if present alone from a white precipitate.

$$Zn^{2+} + [Hg(SCN)_4]^{2-} \longrightarrow \underset{\text{White ppt}}{Zn[Hg(SCN)_4]\downarrow}$$

In the presence of copper ions, the copper complex coprecipitates with that of zinc and the violet (or blackish-purple) precipitate consisting of mixed crystals of $Zn(Hg(SCN)_4] + Cu[Hg(SCN)_4]$ is obtained.

(vi) Diphenylthiocarbazone (dithizone) test

Dithizone forms complexes with a number of metal ions, which can be extracted with chloroform. The zinc complex, formed in neutral, alkaline or acetic acid solutions, is red in colour.



Red ppt

2. MANGANESE (II)

(i) Sodium Hydroxide Solution

With sodium hydroxide solution, an initially white precipitate of manganese**(II)** hydroxide is obtained.

$$Mn^{2+} + 2OH^{-} \longrightarrow \underset{\text{White ppt}}{Mn(OH)_2\downarrow}$$

The precipitate is insoluble in excess reagent. It rapidly oxidizes on exposure to air, becoming brown, when hydrated manganese dioxide, $MnO(OH)_2$, is formed.

$$2Mn(OH)_2\downarrow + O_2 \longrightarrow \underset{\text{Brown ppt}}{2MnO(OH)_2\downarrow}$$

(ii) Ammonia Solution

With NH_3 solution, Mn^{2+} gives a white precipitate of manganese **(II)** hydroxide.

$$Mn^{2+} + 2NH_3 + 2H_2O \rightleftharpoons \underset{\text{pinkish white ppt}}{Mn(OH)_2\downarrow} + 2NH_4^+$$

The precipitate is soluble in ammonium salts, when the reaction proceeds towards the left.

(iii) Disodium Hydrogen Phosphate Solution

With disodium hydrogen phosphate solution, a pink precipitate of manganese ammonium phosphate $Mn(NH_4)PO_4.7H_2O$, in the presence of ammonia (or ammonium ions) is obtained.

$$Mn^{2+} + NH_3 + HPO_4^{2-} \longrightarrow \underset{\text{pink ppt}}{Mn(NH_4)PO_4\downarrow}$$

If ammonium slats are absent, pink precipitate manganese**(II)** phosphate is formed.

$$3Mn^{2+} + 2HPO_4^{2-} \longrightarrow \underset{\text{Pink ppt}}{Mn_3(PO_4)_2\downarrow} + 2H^+$$

Both precipitates are soluble in acids.

(iv) Lead dioxide and Concentrated Nitric Acid

On boiling a dilute solution of manganese**(II)** ions with lead dioxide and a little concentrated nitric acid and allowing the suspended solid containing unattacked lead dioxide to settle, the supermatant liquid acquires a violet-red (or purple) colour due to permagnate acid.

$$5PbO_2 + 2Mn^{2+} + 4H^+ \longrightarrow \underset{\text{Purple colour}}{2MnO_4^-} + 5Pb^{2+} + 2H_2O$$

(v) Sodium Bismuthate ($NaBiO_3$) Solution

When sodium bismuthate ($NaBiO_3$) is added to a cold solution of manganese(II) ions in dilute nitric acid or in dilute sulphuric acid, the mixture stirred and excess reagent filtered off, a violet red (or purple) solution of permanganate is produced.

$$2Mn^{2+} + 5NaBiO_3 + 14H^+ \longrightarrow \underset{\text{Purple colour}}{2MnO_4^-} + 5Bi^{3+} + 5Na^+ + 7H_2O$$

3. NICKEL (II)

The black precipitate of NiC(II) is insoluble in cold dilute HCl and in acetic acid but dissolves in hot concentrated nitric acid and in aqua regia with the separation of sulphur.

$$NiS\downarrow + 2HNO_3 + 6H^+ \longrightarrow 3Ni^{2+} + 3S\downarrow + 2NO\uparrow + 4H_2O$$

$$NiS\downarrow + HNO_3 + 3HCl \longrightarrow Ni^{2+} + S\downarrow + NOCl\uparrow + 2Cl^- + 2H_2O$$

(i) Sodium Hydroxide Solution

With Ni^{2+}, NaOH gives a green precipitate of $Ni(OH)_2$.

$$Ni^{2+} + 2OH^- \longrightarrow \underset{\text{Green ppt}}{Ni(OH)_2\downarrow}$$

The precipitate is insoluble in excess reagent. The precipitate dissolves in ammonia and excess alkali hydroxide.

$$Ni(OH)_2\downarrow + 6NH_3 \longrightarrow \underset{\text{Deep–blue colouration}}{[Ni(NH_3)_6]^{2+}} + 2OH^-$$

$$Ni(OH)_2\downarrow + 6NH_4^+ + 4OH^- \longrightarrow \underset{\text{Deep–blue colouration}}{[Ni(NH_3)_6]^{2+}} + 6H_2O$$

(ii) Ammonia Solution

With ammonia solution, Ni^{2+} gives a green precipitate of nickel (II) hydroxide.

$$Ni^{2+} + 2NH_3 + 2H_2O \longrightarrow \underset{\text{Green ppt}}{Ni(OH)_2\downarrow} + 2NH_4^+$$

The precipitate dissolves in excess reagent and the solution turns deep blue.

$$Ni(OH)_2\downarrow + 6NH_3 \longrightarrow \underset{\text{Deep-blue colouration}}{[Ni(NH_3)_6]^{2+}} + 2OH^-$$

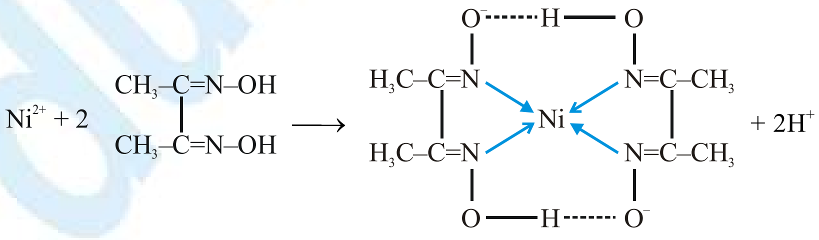
If ammonium salts are present, no precipitation occurs, but the complex is formed immediately.

(iii) Potassium Nitrite Solution

No precipitate is produced in the presence of acetic acid (difference from cobalt)

(iv) Dimethylglyoxime Reagent ($C_4H_8O_2N_2$)

Ni^{2+} in presence of ammonia gives a rosy red precipitate of bis(dimethylglyoximato) nickel(II).



Bis(dimethylglyoximato)nickel(II)
Rosy red ppt

Iron(II) (red colouration), bismuth (yellow precipitate) and larger amounts of cobalt (brown colouration) interfere in ammoniacal solution.

(v) $KHCO_3$, NaOH and Br_2 Water

On addition of $KHCO_3$, NaOH and Br_2 water to solution of Ni^{2+}, a black precipitate of Ni_2O_3 is formed.

$$NiCl_2 + 2KHCO_3 \longrightarrow NiCO_3 + 2KCl + H_2O + CO_2\uparrow$$

$$2NiCO_3 + 4NaOH + [O] \longrightarrow \underset{\text{Black ppt}}{Ni_2O_3\downarrow} + 2Na_2CO_3 + 2H_2O$$

(F) GROUP V (Ba^{2+}, Sr^{2+}, Ca^{2+})

1. BARIUM (II)

(i) Potassium Chromate Solution

Ba^{2+} ion in solution produces a yellow precipitate with K_2CrO_4 solution.

$$Ba^{2+} + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt}}{BaCrO_4\downarrow} + 2K^+$$

The precipitate is insoluble in dilute acetic acid but readily soluble in mineral acids. Addition of acid to K_2CrO_4 solution causes the yellow colour of the solution to change to reddish–orange due to formation of $Cr_2O_7^{2-}$.

$$\underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+ \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$$

(ii) Ammonium Sulphate Solution

Ba^{2+} ions in solution produces a white precipitate with $(NH_4)_2SO_4$ solution.

$$Ba^{2+} + (NH_4)_2SO_4 \longrightarrow \underset{\text{White ppt}}{BaSO_4\downarrow} + 2NH_4^+$$

The percipitate is insoluble in dilute acids and in ammonium sulphate solution but appreciably soluble in boiling concentrated H_2SO_4.

$$BaSO_4\downarrow + H_2SO_4(conc.) \longrightarrow Ba^{2+} + 2HSO_4^-$$

(iii) Ammonium Oxalate Solution

Ba^{2+} ions in solution produces a white precipitate with $(NH_4)_2C_2O_4$ solution

$$Ba^{2+} + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White ppt}}{BaC_2O_4\downarrow} + 2NH_4^+$$

The precipitate readily dissolves in hot dilute acetic acid and in mineral acids.

2. STRONTIUM (II)

(i) Ammonium Sulphate Solution

Sr^{2+} ions give a white precipitate with $(NH_4)_2SO_4$ solution.

$$Sr^{2+} + (NH_4)_2SO_4 \longrightarrow \underset{\text{White ppt}}{SrSO_4\downarrow} + 2NH_4^+$$

The precipitate is slightly soluble in boiling hydrochloric acid.

(ii) Ammonium Oxalate Solution

Sr^{2+} ions give a white precipitate with $(NH_4)_2C_2O_4$ solution.

$$Sr^{2+} + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White ppt}}{SrC_2O_4\downarrow} + 2NH_4^+$$

The precipitate is insoluble in acetic acid but soluble in mineral acids.

3. CALCIUM (II)

(i) Ammonium Oxalate Solution

Ca^{2+} ions give a white precipitae with concentrated $(NH_4)_2C_2O_4$ solution immediately.

$$Ca^{2+} + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White ppt}}{CaC_2O_4\downarrow} + 2NH_4^+$$

The precipitate is insoluble in acetic acid but soluble in mineral acids.

(ii) Potassium Hexacyanoferrate(II) Solution

With potassium hexacyanoferrate(II) solution, Ca^{2+} ions give a white precipitate of a mixed salt.

$$Ca^{2+} + K_4[Fe(CN)_6] \longrightarrow K_2Ca[Fe(CN)_6]\downarrow + 2K^+$$

The test can be used to distinguish calcium ion from strontium and barium ions.

(G) GROUP VI (Na^+, K^+, Mg^{2+})

1. MAGNESIUM (II)

(i) Ammonia Solution

Mg^{2+} gives white gelationous precipitate of magnesium hydroxide on reaction with ammonium hydroxide.

$$Mg^{2+} + 2NH_4OH \longrightarrow \underset{\text{White ppt}}{Mg(OH)_2\downarrow} + 2NH_4^+$$

The precipitate obtained is sparingly soluble in water but readily soluble in ammonium salts.

(ii) Ammonium Carbonate Solution

Mg^{2+} reacts with ammonium carbonate solution in the absence of NH_4^+ salts to give a white precipitate of basic magnesium carbonate.

$$5Mg^{2+} + 6CO_3^{2-} + 7H_2O \longrightarrow \underset{\text{White ppt}}{4MgCO_3.Mg(OH)_2.5H_2O\downarrow} + 2HCO_3^-$$

In the presence of NH_4^+ salts no precipitation occurs, because the equilibrium

$$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCOO_3^-$$

is shifted towards the formation of HCO_3^- ions.

(iii) Disodium hydrogen phosphate Solution

With disodium hydrogen phosphate solution, Mg^{2+} gives a white crystalline precipitate magnesium ammonium phosphate in the absence of NH_4Cl and ammonia solution.

$$Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow \underset{\text{White ppt}}{Mg(NH_4)PO_4\downarrow}$$

A white flocculent precipitate of magnesium hydrogen phosphate ($MgHPO_4$) is obtained in neutral solutions.

$$Mg^{2+} + HPO_4^{2-} \longrightarrow \underset{\text{White ppt}}{MgHPO_4\downarrow}$$

(H) GROUP ZERO (NH^+_4)

1. AMMONIUM (NH^+_4)

(i) Sodium Hydroxide Solution

All ammonium salts on heating with alkali (NaOH) gives smell of NH_3.

$$NH_4^+ + OH^- \longrightarrow NH_3\uparrow + H_2O$$

(a) The gas evolved can be detected by its smell.

(b) Gas evolved gives white fumes of NH_4Cl with HCl.

$$NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow}$$

(c) Paper soaked in $CuSO_4$ solution, becomes deep-blue by NH_3 due to the complex formation.

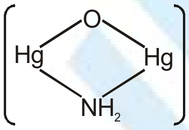
$$CuSO_4 + 4NH_3 \longrightarrow \underset{\text{Deep-blue colouration}}{[Cu(NH_3)_4]SO_4}$$

(d) Gas can be identified by its ability to turn filter paper moistened with mercury**(I)** nitrate solution black.

$$2NH_3 + Hg_2^{2+} + NO_3^- \longrightarrow \underset{\substack{\text{Mercury(II) amidonitrate}\\ \text{white ppt}}}{Hg(NH_2)NO_3\downarrow} + \underset{\text{Black ppt}}{Hg\downarrow} + NH_4^+$$

(ii) Nessler's Reagent

With Nesseler's reagent (an alkaline solution of potassium tetraiodomercurate**(II)**, ammonium salts form a brown precipitate or brown or yellow colouration is produced depending on the amount of NH_4^+ ions present in the solution. The precipitate is a basic mercury**(II)** amido–iodine.

$NH_4Cl + 2K_2HgI_4 + 3KOH \longrightarrow$  $I^{\ominus} + 4KI + 2H_2O + 3NaI$

Iodide of Millon's base
Brown ppt

This test can detect even traces of NH_3 present in a sample.

(iii) Sodium Hexanitritocobaltate(III) Solution

With NH_4^+ ions, sodium hexanitritocobaltate**(III)** solution gives a yellow precipitate of ammonium hexanitritocobaltate**(III)**.

$$3NH_4^+ + [Co(NO_2)_6]^{3} \longrightarrow \underset{\text{Yellow ppt}}{(NH_4)_3[Co(NO_2)_6]\downarrow}$$

2. IRON (II)

(i) Sodium Hydroxide Solution

With sodium hydroxide, Fe^{2+} forms a white precipitate or iron**(II)** hydroxide, $[Fe(OH)_2]$ in the complete absence of air, insoluble in excess but soluble in acids. Upon exposure to air, iron**(I)** hydroxide is rapidly oxidized, yielding ultimately reddish–brown iron**(III)** hydroxide. Under ordinary conditions, it appears as a dirty–green precipitate. The addition of hydrogen peroxide to $Fe(OH)_2$ immediately oxidizes it to iron**(III)** hydroxide.

$$Fe^{2+} + 2OH^- \longrightarrow \underset{\text{White ppt}}{Fe(OH)_2\downarrow}$$

$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow \underset{\text{Reddish–brown ppt}}{4Fe(OH)_3\downarrow}$$

$$2Fe(OH)_2 + H_2O_2 \longrightarrow \underset{\text{Reddish–brown ppt}}{2Fe(OH)_3\downarrow}$$

(ii) Potassium Hexacyanoferrate (II) Solution

With potassium hexacyanoferrate(II) solution, Fe^{2+} forms a white precipitate of potassium iron(II) hexacyanoferrate(II) in the absence of air.

$$Fe^{2+} + 2K^{+} + [Fe(CN)_6]^{4-} \longrightarrow \underset{\text{White ppt}}{K_2Fe[Fe(CN)_6]\downarrow}$$

Under ordinary atmospheric conditions, a pale–blue precipitate is obtained.

(iii) Potassium Hexacyanoferrate(III) Solution

With potassium hexacyanoferrate(III) solution, a dark-blue precipitate is obtained. First hexacyanoferrate(III) ions oxidise iron(II) to iron(III) and itself get reduced to hexacyanoferrate(II).

$$Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$$

Fe^{3+} and $[Fe(CN)_6]^{4-}$ ions combine to give a precipitate called Turnbull's blue, which is same as Prussian blue. Earilier Turnbull's blue and Prussian blue were thought to be two different complexes.

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3\downarrow}$$

The identical composition and structure of Turnbulls blue and Prussian blue has recently been proved by Mossbauer spectroscopy.

(iv) Ammonium thiocyanate Solution

With ammonium thiocyanate solution, no colouration is obtained with pure iron(II) salts (distinction from (III) ions)

(v) Dimethylglyoxime Reagent

With dimethylglyoxime reagent soluble red iron(II) dimethyl glyoxime is obtained in ammoniacal solution. Iron(III) salts give no colouration, but nickel, cobalt and large quantities of copper salts interfere and must be absent.

HEATING EFFECT ON DIFFERENT COMPOUNDS

Many inorganic salts decompose on heating, liberating characteristic gases. A few such reaction are as follows:

$$\underset{\text{(Red)}}{2HgO} \xrightarrow{\Delta} \underset{\text{(Silvery deposit)}}{2Hg + O_2}$$

$$\underset{\text{(Red)}}{2Pb_3O_4} \xrightarrow{\Delta} \underset{\text{(Yellow)}}{6PbO + O_2}$$

$$\underset{\text{(Brown)}}{2PbO_2} \xrightarrow{\Delta} 2PbO + O_2$$

$$\underset{\text{(Green)}}{CuCO_3} \xrightarrow{\Delta} CuO + O_2$$

$$\underset{\text{(White)}}{ZnCO_3} \xrightarrow{\Delta} \underset{\substack{\text{Yellow (hot)} \\ \text{White (cold)}}}{ZnO + CO_2}$$

$$\underset{\text{(Blue)}}{CuSO_4.5H_2O} \xrightarrow{\Delta} \underset{\text{(White)}}{CuSO_4 + 5H_2O}$$

$$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

$$\underset{\text{(White)}}{2Zn(NO_3)_2} \longrightarrow 2ZnO + \underset{\text{(Brown)}}{4NO_2} + O_2$$

$$2AgNO_3 \xrightarrow{450°C} 2Ag + 2NO_2 + O_2$$

$$2Ag_2O \longrightarrow 4Ag + O_2$$

$$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

$$\underset{\text{(Orange)}}{(NH_4)_2Cr_2O_7} \longrightarrow N_2 + \underset{\text{(Green)}}{Cr_2O_3} + 4H_2O$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

$$NH_4HCO_3 \longrightarrow NH_3 + CO_2 + H_2O$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

$$MgCO_3 \longrightarrow MgO + CO_2$$

$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$

$$2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$$

$$2CaSO_4.2H_2O \longrightarrow 2CaSO_4.H_2O + 2H_2O$$

(Plaster of Paris)

$$2AlCl_3.6H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$

$$Al_2(SO_4)_3 \xrightarrow{\text{Redhot}} Al_2O_3 + 3SO_3$$

$$2NH_3 \xrightarrow{\text{Redhot}} N_2 + 3H_2$$

$$2AgNO_3 \xrightarrow{350^\circ} 2AgNO_2 + O_2$$

$$2MgSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$$

$$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$$

$$2BeSO_4 \xrightarrow{\Delta} 2BeO + 2SO_2 + O_2$$

$$2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + H_2O + 2NH_3$$

$$2Zn(NH_4)PO_4 \xrightarrow{\Delta} Zn_2P_2O_7 + H_2O + 2NH_3$$

$$(COO)_2Sn \xrightarrow{\Delta} SnO + CO_2 + CO$$

$$CaC_2O_4 \longrightarrow CaCO_3 + CO$$

$$K_4Fe(CN)_6 \xrightarrow{\Delta} 4KCN + Fe + 2C + N_2$$

$$H_3BO_3 \xrightarrow{100^\circ} HBO_2 \xrightarrow{160^\circ} H_2B_4O_7 \xrightarrow{\text{Redhot}} B_2O_3$$

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

$$4K_2Cr_2O_7 \longrightarrow 4\,K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

$$(COO)_2Fe \longrightarrow FeO + CO + CO_2$$

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

$$2FeCl_3 \longrightarrow 2FeCl_2 + Cl_2$$

$$MgCl_2.6H_2O \longrightarrow MgO + 2HCl + 5H_2O$$

$$Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$$

$$NH_4Cl \longrightarrow NH_3 + HCl$$

$$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$$

$$Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$$

$$2CuCl_2 \xrightarrow{\Delta} Cu_2Cl_2 + Cl_2$$

$$ZnCl_2.2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$$

$$2(ZnCl_2.H_2O) \xrightarrow{\Delta} Zn_2OCl_2 + 2HCl + H_2O$$

$$2Co(NO_3)_2 \xrightarrow{\Delta} 2CoO + 4NO_2 + O_2$$

$$ZnSO_4.7H_2O \xrightarrow[-H_2O]{70^\circ} ZnSO_4.\ 6H_2O \xrightarrow[-5H_2O]{100^\circ} ZnSO_4.\ H_2O \xrightarrow{450^\circ} ZnSO_4$$

$$2ZnSO_4 \xrightarrow{800^\circ} 2ZnO + 2SO_2 + O_2$$

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

(Glassy bead)

$$2[FeCl_3.6H_2O] \xrightarrow{\Delta} Fe_2O_3 + 9H_2O + 6HCl$$

$$SnCl_2.\ 2H_2O \xrightarrow{\Delta} Sn(OH)Cl + HCl + H_2O$$

$$(CH_3COO)_2\,Pb \xrightarrow{\Delta} PbCO_3 + CH_3COCH_3$$

$$Na(NH_4)\,HPO_4 \xrightarrow{\Delta} NH_3 + NaPO_3 + H_2O$$