



PRACTICAL CHEMISTRY



- * Identification of Ions
- * Organic Functional Groups
- * Quantitative Analysis

Note

A separate text book *Practical Chemistry (Manual)* is printed.

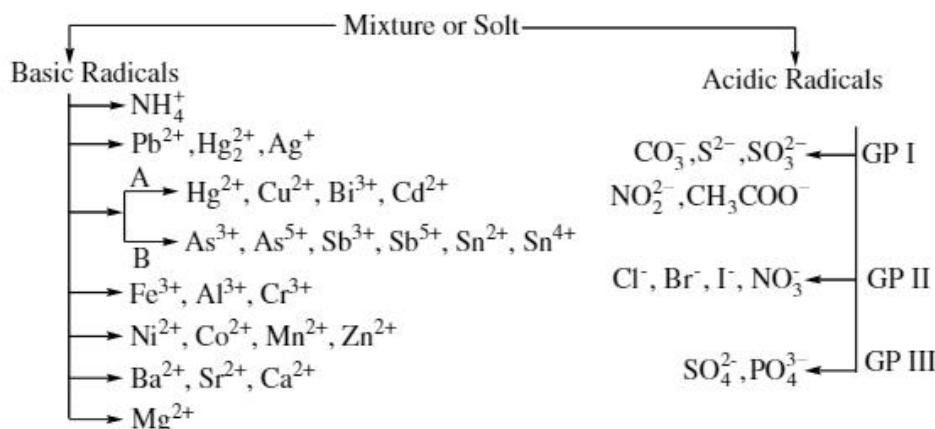
Hence only synopsis is given here.

INORGANIC ANALYSIS

5.1.1

Qualitative Analysis

In qualitative inorganic analysis, the given compound is analysed for the basic and acid radicals (i.e., the cations and the anions), that it contains.. A salt or a mixture contains cations (basic radicals) and anions (acidic radicals) and the detection of these radicals is termed as qualitative analysis.



Some Important Observations during Qualitative Analysis

1. List of different coloured salts

Salts	Colour
Copper salts	Bluish green
Nickel salts	Greenish blue
Chromium salts	Dark green
Cobalt salts	Pinkish or purple
Manganese salts	Light pink
Ferrous salts	Light green
Ferric salts	Pale yellow

2. Action of Heat (Colour of Residue)

S.No.	Colour	Residue
i)	Yellow (hot) and white (cold)	ZnO
ii)	Reddish brown (hot) and yellow (cold)	PbO
iii)	Black (hot) and Red (cold)	HgO, Pb ₃ O ₄
iv)	Black (hot) and Red brown (cold)	Fe ₂ O ₃
v)	Decripitation	Pb(NO ₃) ₂ , NaCl
vi)	White sublimate	Ammonium salts

3. Gases

S.No.	Nature	Gases
i)	Colourless and odourless gases	O ₂ , CO ₂ , N ₂
ii)	Colourless gases with odour	NH ₃ , SO ₂ , HCl, H ₂ S
iii)	Coloured gases	NO ₂ (brown), Br ₂ (reddish brown), I ₂ (violet), Cl ₂ (greenish yellow)

4. Flame Test

Metals	Colour
Li	crimson red
Na	golden yellow
K	violet
Ca	Brick red
Sr	crimson
Ba	apple green

Tests for different gases : Before starting with the study of chemistry involved in the qualitative inorganic analysis, we will study, in brief, the characteristic tests for various gases which evolve during the analysis.

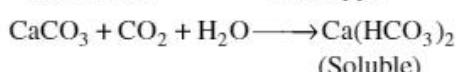
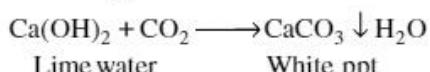
1) Colourless gases : CO₂, CO, O₂, H₂S, SO₂, NH₃, HCl, CH₃COOH vapours

2) Coloured gases : Cl₂, Br₂, I₂, NO₂

Colourless gases :

Tests of CO₂

- (i) It is colourless and odourless gas
- (ii) It gives white ppt. with lime water which dissolves on passing excess of CO₂



Tests for CO

- (i) It is a colourless and odourless gas
- (ii) It burns with a blue flame.



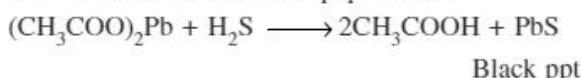
Note : Carbon monoxide is highly poisonous

Tests for O₂

- (i) It is colourless and odourless gas
 - (ii) It rekindles a glowing splinter

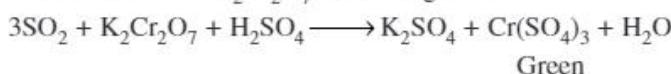
Tests for H₂S

- (i) it is a colourless gas with a smell of rotten eggs
 - (ii) it turns moist lead acetate paper black



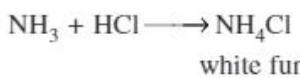
Tests for SO₄²⁻

- (i) It is a colourless gas with a suffocating odour of burning sulphur.
 - (ii) It turns acidified $K_2Cr_2O_7$ solution green.

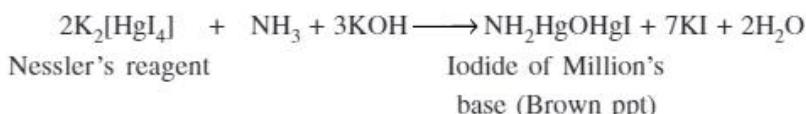


Tests of NH_3

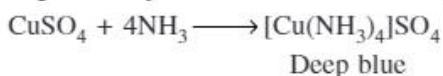
- (i) It is a colourless gas with a characteristic ammonical smell.
 - (ii) It gives white fumes of NH_4Cl with HCl



- (iii) With Nessler's reagents, it gives brown ppt.



- (iv) It gives deep blue colour with CuSO_4 solution.

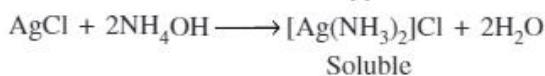
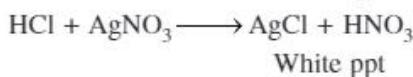


- (v) NH_3 dissolves in water to give NH_4OH , which being basic, turns red litmus blue.



Tests for HCl gas

- (i) It is colourless gas with a pungent irritating smell.
 - (ii) It turns moist blue litmus paper red i.e., it is acidic in nature.
 - (iii) It gives white ppt with AgNO_3 solution. This white ppt. is soluble in NH_4OH .



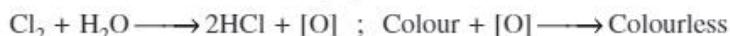
Tests for CH_3COOH vapours. These vapours are colourless with a vinegar like smell.

Coloured gases

Tests for Cl₂

- (i) It is greenish yellow gas with a pungent smell. In small quantity it appears almost colourless.

- (ii) It bleaches a moist litmus paper



Blue litmus paper first turns red and then becomes colourless.

Tests for Br_2

- (i) Brown vapours with a pungent smell
(ii) It turns moist starch paper yellow

Tests for I_2

- (i) Violet vapours with a pungent smell
(ii) It turns moist starch paper blue

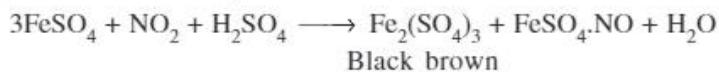
Tests for NO_2

- (i) Brown coloured pungent smelling gas
(ii) It turns moist starch KI paper blue



I_2 + Starch \longrightarrow Blue colour

- (iii) It turns ferrous sulphate solution black



5.1.2

Procedure and preliminary tests

Systematic procedure for qualitative analysis of salts involves the following steps.

- 1) Preliminary tests
- 2) Wet tests for acid radicals and
- 3) Wet tests for basic radicals

Preliminary tests

- (i) **Physical examinations :** It involves the study of colour, smell, density etc
- (a) **Colour :** Blue or bluish green (Cu^{2+} or Ni^{2+}), greenish (Ni^{2+}) light green (Fe^{2+}), deep green (Cr^{3+}), dark brown (Fe^{3+}), pink (Co^{2+}), light pink, flesh colour or earthy colour (Mn^{2+})
- (b) **Smell :** Pinch of mixture is rubbed between the fingers with a drop of water and smelled. Ammoniacal smell (NH_4^+), vinegar like smell (CH_3COO^-), rotten eggs smell (S^{2-}) and burning sulphur smell (some sulphates)
- (c) **Density :** Heavy (salts of Hg^{2+} , Pb^{2+} or Ba^{2+}), light fluffy powder (carbonates)
- (d) **Substance become wet :** Certain deliquescent salts which absorb moisture from the atmosphere and become wet are CaCl_2 , ZnCl_2 , MgCl_2 , MnCl_2 , nitrites, nitrates etc.

Dry heating : A small amount of the mixture is heated in a dry test tube and form carefully noted observations regarding the gases evolved or characteristic changes in the colour of residue, inferences are drawn. (Table 5.1)

- (i) **Flame test :** Is based upon the principle that certain volatile metallic salts, generally chlorides, when heated in a non-luminous (oxidising) Bunsen flame impart characteristic colour to it. The colour is observed with naked eye and through a blue glass (also called cobalt glass)

CHEMISTRY IIA

Table 5.1 General Observations

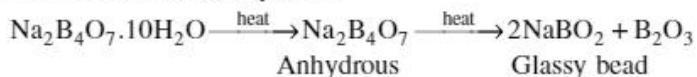
S.No.	Observations	Inference
1.	Substances melts	Salts of alkali metals and salts having water of crystallisation.
2.	Substance decrepitates (Cracking sound)	NaCl, KI, Pb(NO ₃) ₂ and Ba(NO ₃) ₂
3.	The substance sublimes The colour of the sublimate is noted a) White b) Yellow c) Blue black and violet	HgCl ₂ , Hg ₂ Cl ₂ , NH ₄ X (X=Cl, Br, I), AlCl ₃ , As ₂ O ₃ , Sb ₂ O ₃ As ₂ S ₂ and HgI ₂ (turns red when rubbed with glass rod) Iodide
4.	If a residue is left, its colour is noted a) Yellow when hot, white when cold b) Reddish brown when hot, yellow when cold c) Black when hot, red when cold d) Black when hot, red brown when cold	ZnO PbO
5.	Gas evolved (A) Colourless and odourless a) Oxygen b) Carbon dioxide c) Nitrogen d) CO + CO ₂	HgO, Pb ₂ O ₃ Fe ₂ O ₃
	(B) Colourless with odour a) SO ₂ b) HCl c) H ₂ S d) NH ₃	Alkali metal nitrate $2\text{KNO}_2 \xrightarrow{\Delta} 2\text{KNO}_2 + \text{O}_2$ Carbonates (except those of alkali metals) $2\text{KNO}_2 \xrightarrow{\Delta} 2\text{KNO}_2 + \text{O}_2$ NH ₄ NO ₂ $\text{NH}_3\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$ Oxalates $\text{COO}-\text{Ca} \xrightarrow{\Delta} \text{CaO} + \text{CO} \uparrow + \text{CO}_2 \uparrow$
	(C) Coloured gases a) NO ₂ (Brown) b) Br ₂ (Reddish brown) c) I ₂ (Violet Vapours) d) Cl ₂ (Greenish yellow)	Sulphites and thiosulphates $\text{CaSO}_3 \xrightarrow{\Delta} \text{CaO} + \text{SO}_2$ Hydrated chlorides $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + 4\text{H}_2\text{O} + 2\text{HCl} \uparrow$ Sulphides (Hydrated) $\text{Na}_2\text{S} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{S} \uparrow$ Ammonium salts $(\text{NH}_4)_2\text{SO}_4 \xrightarrow{\Delta} \text{NH}_4\text{HSO}_4 + \text{NH}_3 \uparrow$
		Nitrates and nitrites of heavy metals $2\text{Zn}(\text{NO}_3)_2 \longrightarrow 2\text{ZnO} + 4\text{NO}_2 + \text{O}_2$ Bromides $2\text{CdBr}_2 + \text{O}_2 \longrightarrow 2\text{CdO} + 2\text{Br}_2$ Iodides $2\text{ZnI}_2 + \text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{I}_2$ Hydrated chlorides $\text{CuCl}_2 + \text{H}_2\text{O} \longrightarrow \text{CuO} + 2\text{HCl}$

Table 5.2 Flame Test

Experiment	Observation		Inference
	With naked eye	Through blue glass	
Make a paste of a pinch of the salt with few drops of conc. HCl in a watch glass and perform flame test. Note the colour of flame	1. Persistent golden yellow 2. Pale violet 3. Crimson 4. Brick red 5. Grassy green 6. Bluish green 7. Greenish flames	Not visible Pinkish Crimson Light yellow Green ----- -----	Na ⁺ K ⁺ Sr ²⁺ Ca ²⁺ Ba ²⁺ Cu ²⁺ Zn ²⁺ , Mn ²⁺


Borax bead test for colored ions


(i) **Borax bead test :** This test is only for coloured salts. On heating borax on a loop of platinum wire, the colourless glassy bead formed consisting of sodium metaborate and boric anhydride.



(ii) On heating coloured salt on glassy bead, coloured metaborate is formed in the oxidizing flame.



The metaborates give different colours in oxidizing and reducing flames

Table 5.3 Borax Bead Test

Metal	Metaborate	Oxidising flame		Reducing flame	
		Hot	Cold	Hot	Cold
Copper	Cu(BO ₂) ₂	Green	Blue	Colourless	Brown red
Iron	Fe(BO ₂) ₃	Brown	Pale Yellow	Bottle green	Bottle
Chromium	Cr(BO ₂) ₃	Yellow	Green	Green	Green
Nickel	Ni(BO ₂) ₂	Green	Brown	Grey	Green
Cobalt	Co(BO ₂) ₂	Violet	Blue	Blue	Grey
Manganese	Mn(BO ₂) ₂	Blue	Amethyst	Grey	Blue
		Violet			Grey

Microcosmic salt bead test : Microcosmic salt, Na(NH₄)HPO₄·4H₂O is also used to identify certain cations just like borax. When microcosmic salt is heated in a loop platinum wire, a colourless transparent bead of sodium metaphosphate is formed.



Charcoal cavity test-reduction test : A small amount of the mixture is heated with fusion mixture (K₂CO₃+Na₂CO₃) in charcoal cavity in the reducing flame of the Bunsen burner. Inferences are drawn from the carefully observed residue or incrustation of the oxides and metallic beads.


Charcoal cavity test for cations


Table 5.4 Charcoal Cavity Test

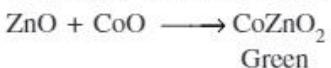
Incrustation or Residue	Metallic bead	Cation indicated
Yellow when hot, white when cold	None	Zn ²⁺
Brown when hot, brown when cold	None	Cd ²⁺
Brown when hot, yellow when cold	Grey bead which marks paper	Pb ²⁺
Characteristic residue	Red bead or scales	Cu ²⁺
White residue which glows on heating	None	Ba ²⁺ , Ca ²⁺ , Mg ²⁺
No characteristic residue	Shining white	Ag ⁺

Cobalt nitrate test : If the residue left in the charcoal cavity is white, it is moistened with cobalt nitrate solution and heated in an oxidizing flame. Not the colour of the residue and drawn inference from the following table.

Table 5.5 Cobalt Nitrate Test

Experiment	Observation (Residue colour)	Inference
Add a drop of cobalt nitrate solution to a white residue in the charcoal cavity and heat it in an oxidizing flame	(i) Blue (infusible) (ii) Blue fusible (iii) Greenish (iv) Pinkish (v) Black residue	Due to Al ³⁺ Due to PO ₄ ³⁻ , BO ₃ ³⁻ Due to Zn ²⁺ Due to Mg ²⁺ Absence of Al ³⁺ , Sn ²⁺ , Zn ²⁺ , Mg ²⁺

The colour of the residue is due to the formation of a double oxide.



Filter paper ash test is a modification of cobalt nitrate charcoal cavity test. A filter paper dipped in a solution of the salt (to be tested) and cobalt nitrate is dried, burned and colour of the ash noted Inference is drawn from the table given above.

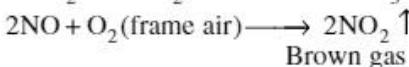
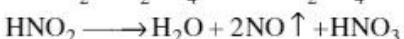
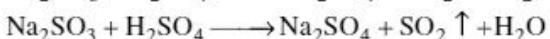
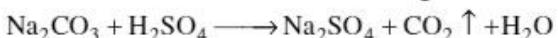
5.1.3

Wet tests for acid radicals **Dil.H₂SO₄ test :** A pinch of mixture is treated with a few drops of dil.H₂SO₄ in a test tube and the gas evolved is tested.

Table 5.6 Dil. H₂SO₄ Test

Gas evolved	Radical	Gas evolved	Radical
CO ₂	CO ₃ ²⁻ , HCO ₃ ⁻	H ₂ S	S ²⁻ , HS ⁻
SO ₂	SO ₃ ²⁻ , HSO ₃ ⁻	NO ₂ + NO	NO ₂ ⁻

Reactions involved in dil. Acid test are given below:

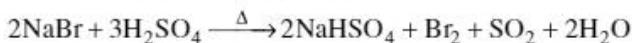


(ii) conc. H_2SO_4 test : A pinch of mixture is treated with conc. H_2SO_4 in a test tube. If a gas is evolved, it is due to the presence of radicals of dil. Acid est. after the expulsion of gas evolved in cold (if any) the test tube is heated. Test the gas evolved.

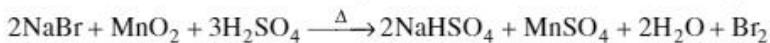
Table 5.7 Conc. H_2SO_4 Test

Gas evolved	Radical	Gas evolved	Radical
HCl (Colourless)	Cl^-	NO_2 (Brown)	NO_3^-
Br_2 (Brown)	Br^-	$CO + CO_2$ (Colourless)	COO^- COO^-
I_2 (Violet)	I^-	CH_3COOH (Vapours)	CH_3COO^-

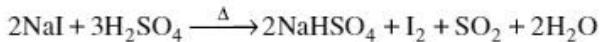
Chemical reactions involved in conc. H_2SO_4 test are given below:



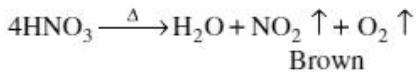
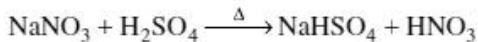
Note : On adding a pinch of MnO_2 , more of brown vapours of Br_2 are evolved.



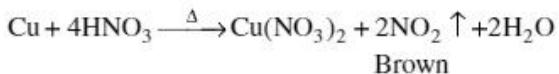
MnO_2 helps in the oxidation of HBr .



Note : On adding a pinch of MnO_2 , more of violet vapours of I_2 are evolved.



Note : On adding a small piece of copper turning, the brown fumes intensifies.



(i) **Potassium permanganate test :** A little of the mixture is treated with dil. H_2SO_4 and any gas evolved is boiled off. A little more dil. H_2SO_4 is added, followed by addition of potassium permanganate dropwise. The following inference, may be drawn regarding the presence of the reducing agent from the observations.

- (a) Decolourisation without the evolution of any gas indicates the presence of ferrous or stannous salt.
- (b) Decolourisation with the evolution of chlorine, bromine or iodine gas indicates the presence of Cl^- , Br^- or I^- respectively.
- (c) Decolourisation with the evolution of CO_2 indicates the presence of oxalate or tartarate.



Sodium carbonate extract for analysis

Preparation of sodium carbonate extract

Sodium carbonate extract is prepared in case of salts which are not soluble in water. To obtain it, a small amount of the salt or mixture is boiled with Na_2CO_3 solution taken in excess. By this process, insoluble salts are converted into corresponding soluble salts. For example.



The solution is filtered. The residue is rejected. The filtrate so obtained is sodium carbonate extract.

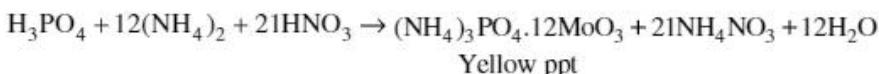
(ii) **Test for sulphate, phosphate and borate :** As these ions are not indicated in dil. H_2SO_4 test are conc. H_2SO_4 test, these ions are tested individually.

(a) **Test for sulphate :** To the water extract (or sodium carbonate extract acidified with dil. HCl) add BaCl_2 solution. A white ppt. insoluble in conc. HCl (or conc. HNO_3) indicates the presence of SO_4^{2-}

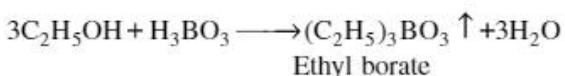


Note : If the reaction mixture contains Pb^{2+} or Ag^+ ions, use $\text{Ba}(\text{NO}_3)_2$ solution in place of BaCl_2 solution. This is because AgCl and PbCl_2 are insoluble in water and as such may give a wrong indication.

(b) **Test for phosphate :** To the water extract (or sodium carbonate extract acidified with HNO_3) add a few drops of conc. HNO_3 and 3-4 mL of ammonium molybdate solution. Formation of yellow crystalline ppt. confirms the presence of phosphate.



(c) **Test for borate :** Salt is mixed with a few mL of ethyl alcohol and a few drops of conc. H_2SO_4 . This mixture is heated in a test tube and the vapours so obtained are ignited. A green edged flame indicates the presence of borate.



Ethyl borate burns with a green edged flames

(iii) Confirmatory tests for acid radicals

(I) **Confirmatory tests for Anions detected in dil. H_2SO_4 test**

(a) **Confirmatory tests for carbonates and bicarbonates**

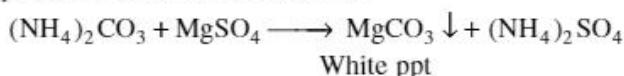
Insoluble carbonates are confirmed only by the dil. Acid test i.e., evolution of CO_2 .

Soluble carbonates like $\text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3$ can be tested with phenolphthalein because aqueous solutions of these carbonates are alkaline in nature due to hydrolysis. However $(\text{NH}_4)_2\text{CO}_3$ will not give this test.



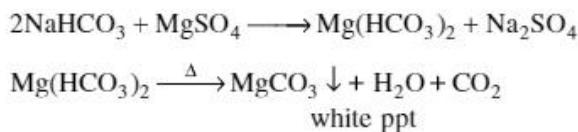
Confirmatory tests for acid radicals

Soluble carbonates can also be tested with $MgSO_4$ solution. A white ppt indicates the presence of soluble carbonate.



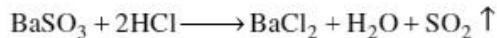
Note: All carbonates except Na_2CO_3 , K_2CO_3 , $(NH_4)_2CO_3$ are insoluble in water.

Only bicarbonates of Na^+ exist in solid state. Bicarbonates of Ca^{2+} and Mg^{2+} exist only in their aqueous solutions. Bicarbonates in their aqueous solutions when boiled with $MgSO_4$ solution, give white ppt. of $MgCO_3$.



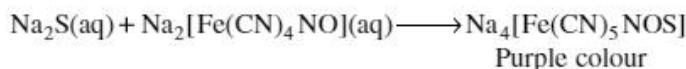
(b) Confirmatory tests for sulphites

Sulphites gives white ppt. of $BaSO_3$ with $BaCl_2$ solution. The white ppt. is soluble in dil. HCl.

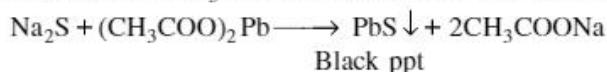


(c) Confirmatory tests for sulphide

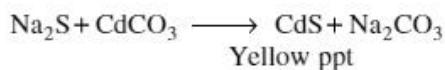
(i) Add a few mL of sodium nitroprusside to water extract or Na_2CO_3 extract. Appearance of transient purple colour confirms the S^{2-}



(ii) Add a few mL of lead acetate solution to the water extract (or Na_2CO_3 extract acidified with dil. CH_3COOH) Black ppt. of PbS confirms S^{2-} .

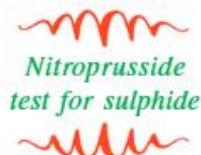
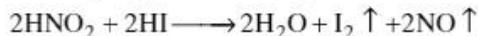


(iii) To Na_2CO_3 extract or water extract add cadmium carbonate. Yellow ppt. of CdS confirms S^{2-}



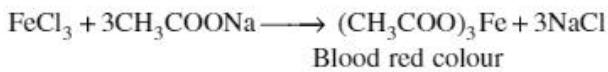
(d) Confirmatory tests for nitrite

When a mixture of a nitrite and KI is treated with dil. H_2SO_4 , the iodide is decomposed to give violet vapours of iodine which turns starch paper blue.



(e) Confirmatory tests for acetate

- (i) FeCl_3 test. All acetates are soluble in water. To water extract add neutral FeCl_3 . A blood red colour confirms CH_3COO^-



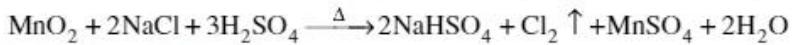
Note : (i) To prepare neutral FeCl_3 solution, add NH_4OH dropwise to FeCl_3 solution provided, till ppt. formed does not dissolve. Filter it and use it as neutral FeCl_3 solution.

(ii) Ions like CO_3^{2-} , SO_3^{2-} , PO_4^{3-} , I^- interfere in this test.

(II) Confirmatory tests for Anions detected in conc. H_2SO_4 test

(a) Confirmatory tests for chloride

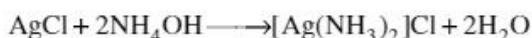
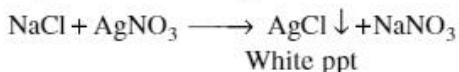
- (i) Heat a pinch of the salt with MnO_2 and conc. H_2SO_4 . Evolution of Cl_2 confirms Cl^- .



(b) Silver nitrate test

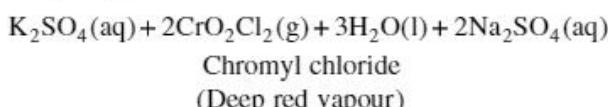
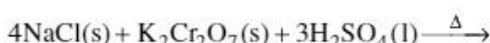
To the water extract (or Na_2CO_3 extract acidified with dil. HNO_3) add AgNO_3 .

White ppt soluble in NH_4OH confirms Cl^-

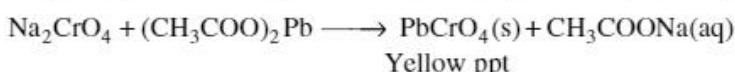


(c) Chromyl chloride test

Heat salt with $\text{K}_2\text{Cr}_2\text{O}_7$ and a few drops of conc. H_2SO_4 in a dry test tube.

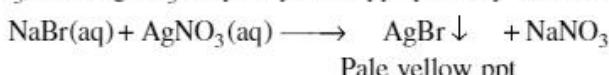


Pass the deep red vapours through NaOH (aq) and lead acetate solution. A yellow ppt of PbCrO_4 confirms Cl^- .



(d) Confirmatory tests for bromides

- (i) **Silver nitrate test:** To the water extract (or Na_2CO_3 extract acidified with dil. HNO_3) add AgNO_3 . A pale yellow ppt partially soluble in NH_4OH confirms Br^- .



*Silver nitrate test
for halides*



(ii) **Chlorine water test** : To the water extract (or Na_2CO_3 extract) and a few drops of CCl_4 (or CHCl_3 or CS_2 or C_6H_6). To this add Cl_2 water (or dil. HNO_3) with constant shaking. An orange colour in CCl_4 layer confirms Br^- .



$\text{Br}_2 + \text{CCl}_4 \longrightarrow$ Orange colour in CCl_4 layer

(e) **with dil. HNO_3**



(f) Confirmatory tests for iodide.

(i) **AgNO_3 test** : to the water extract (or Na_2CO_3 extract acidified with HNO_3) add AgNO_3 . A yellow ppt insoluble in ammonia confirms I^- .



Yellow ppt

(ii) **Cl_2 water test** : To the water extract (or Na_2CO_3 extract) add a few drops of CCl_4 (or CHCl_3 or C_6H_6). To this add Cl_2 water (or dil. HNO_3) with constant stirring. A violet colour in CCl_4 layer confirms I^- .

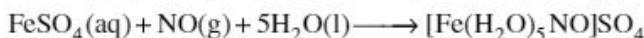


$\text{I}_2 + \text{CCl}_4 \longrightarrow$ Violet colour in CCl_4 layer

with dil. HNO_3 the reaction is similar to that in case of Br^-

(g) **Confirmatory tests for nitrate**

(i) **Ring test** : Mix a few drops of water extract (all nitrates are soluble in water) with a freshly prepared FeSO_4 solution and pour conc. HNO_3 along the sides of the test tube.



Dark brown ring

Note: (i) Ring test is not reliable in the presence of NO_2^- , Br^- and I^-

(ii) Nitrates when boiled with $\text{NaOH}(\text{aq})$ and Zn (or) Al give NH_3 .



(C) Confirmatory Tests for sulphate, phosphate and borate

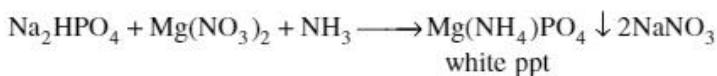
(a) **Confirmatory tests for sulphate**

Lead acetate test : Take water extract (or Na_2CO_3 extract acidified with dil. CH_3COOH) and add to it lead acetate solution. A white ppt. soluble in excess of $\text{CH}_3\text{COONH}_4$ on warming confirms sulphate.



(b) Confirmatory test for phosphate

Take water extract (or Na_2CO_3 extract acidified with CH_3COOH) and add 3-4 mL of magnesia mixture. Wait for 5 minutes. A white ppt. confirms PO_4^{3-} .



(c) Confirmatory test for borate

Turmeric paper test : Dip a piece of turmeric paper in a solution of salt in dil. HCl. Dry the paper. Moisten this paper with NaOH solution. A reddish brown colour changing to bluish black or greenish black confirms BO_3^{3-} .

5.1.4

Wet tests for basic radicals It involves the following three basic tests.

1. To prepare the origin solution
2. To separate the basic radicals into different groups
3. To confirm the basic radicals by their specific tests

1. To prepare the original solution

The following solvents should be used strictly in the order given below

- (a) Cold water
- (b) Hot water
- (c) Dil. HCl
- (d) Conc. HCl

Note

- (i) If the salts is soluble in cold dil. HCl, Pb^{2+} , Hg_2^{2+} and Ag^+ are absent.
- (ii) PbCl_2 is soluble in hot water but insoluble in cold water
- (iii) If the solution is prepared in conc. HCl and on dilution a millessness appears, it is due to the presence of Bi, Sb, Sn in the original mixture Millessness is due to the formation of their oxychlorides.



Milness

- (iv) Do not use dil. or conc. H_2SO_4 to make original solution. It converts Ba, Sr, Ca, Pb, salts (if present) into insoluble sulphates.
- (v) Do not use dil. or conc. HNO_3 to make original solution. It oxidizes sulphides of Ba, Sr, Pb (which are soluble) into insoluble sulphates. Further it oxidizes H_2S (in II or IV groups) into colloidal sulphur, which is difficult to remove.

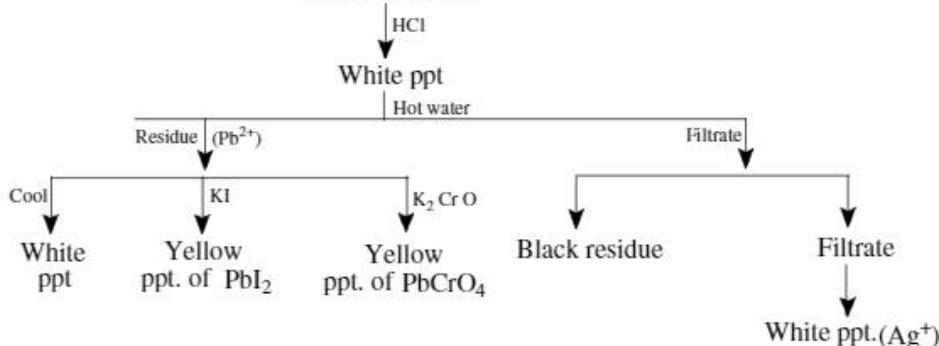
Table 5.8 Separation of basic radicals into groups

Group	Group reagent	Basic radical	Composition and colour of the ppt	
I	Dil. HCl	Ag^+ Pb^{2+} Hg_2^{2+}	AgCl White PbCl_2 White Hg_2Cl_2 White	ppt. insoluble in dil.HCl
II	H_2S in the presence of dil. HCl	Hg^{2+} Pb^{2+} Br^{3+} Cu^{2+} Cd^{2+} As^{3+} Sb^{3+} Sn^{2+} Sn^{4+}	HgS Black PbS Black Bi_2S_3 Black CuS Black CdS Yellow As_2S_3 Yellow Sb_2S_3 Orange SnS Brown SnS_2 Yellow	
III	NH_4OH in the presence of excess of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	FeOH_3 Reddish CrOH_3 Dirty green Al(OH)_3 White gelatinous ppt	ppt. insoluble in NH_4OH
IV	H_2S in the presence of NH_4OH	Co^{2+} Ni^{2+} Zn^{2+} Mn^{2+}	CoS Black NiS Black ZnS Bluish White MnS Buff (flesh) coloured	
V	$(\text{NH}_4)_2\text{CO}_3$ in the presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	BaCO_3 White SrCO_3 White CaCO_3 White	Carbonates insoluble in NH_4OH
VI	Na_2HPO_4 No group reagent No group reagent	Mg^{2+} Na^+ K^+	$\text{Mg}(\text{NH}_4)\text{PO}_4$ White	
Zero	NaOH	NH_4^+	NH_3 gas is evolved	

I Group : Hg^+ , Ag^+ , Pb^{2+}

Original solution

Group I contains
 Hg^+ , Ag^+ , Pb^{2+}



CHEMISTRY IIA

Add dil. HCl to clear solution of the mixture. White precipitate indicates the presence of Hg^+ , Ag^+ or Pb^{2+} .

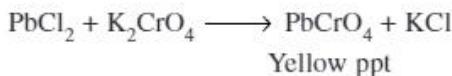


White ppt. so obtained extracted with hot water. The filtrate may contain PbCl_2 (if Pb^{2+} is present). Residue (if any) is extracted with NH_4OH . The filtrate may contain $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$. If Hg^+ ions are present they form a black ppt. of $\text{Hg}(\text{NH}_2)\text{Cl}$ when treated with NH_4OH .

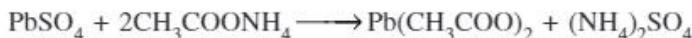
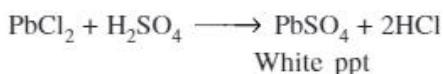
Pb²⁺(lead)

(i) Lead chloride, PbCl_2 , is soluble in hot water and on cooling white crystals are again formed.

(ii) The Pb^{2+} ions give yellow precipitate both with potassium chromate solution and KI solution.

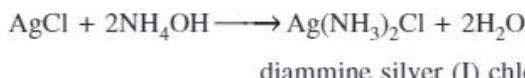
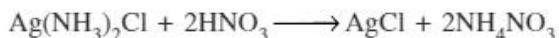


(iii) The Pb^{2+} ions give white precipitate of lead sulphate with dilute H_2SO_4 . The precipitate is soluble in ammonium acetate.

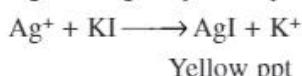


Ag⁺(Silver)

(i) AgCl dissolve in ammonium hydroxide and on adding dilute HNO_3 to the above solution, while precipitate is regained.

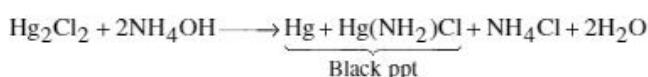


(ii) Ag^+ ions give yellow precipitate with KI solution



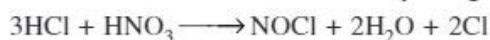
Hg²⁺ (Mercury)

(i) HgCl_2 turns black with NH_4OH .

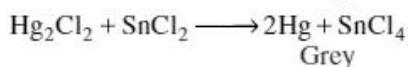
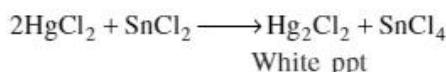



Silver chloride
dissolve in
ammonia

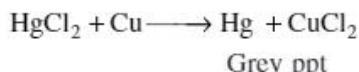

(ii) The black residue dissolves in aqua regia forming mercuric chloride.



(iii) The solution of HgCl_2 forms white precipitate which later on turns to grey, on addition of SnCl_2 .



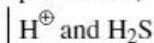
(iv) Copper turning in HgCl_2 solution forms a grey deposit.



II Group : $\text{Hg}^{2+}, \text{Pb}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Bi}^{3+}, \text{As}^{3+}, \text{Sb}^{3+}, \text{Sn}^{2+}, \text{Sn}^{4+}$

To original solution or 1st group filtrate

(If 1st group is absent)



↓ ppt of yellow ammonium sulphide

↓ Residue Group IIA

↓ Filtrate Group IIB

$(\text{Hg}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Bi}^{3+}, \text{Pb}^{2+})$

↓ (i) 50% HNO_3
(ii) Cool and filter

↓ Residue

(Hg^{2+})

Dissolve in aqua-regia, heat to concentrate the solution, evaporate to dryness and add SnCl_2 +aqua-regia

↓ Grey ppt.
 (Hg^{2+})

↓ Filtrate

$(\text{Cu}^{2+}, \text{Cd}^{2+}, \text{Bi}^{3+}, \text{Pb}^{2+})$

↓ Dil H_2SO_4 and alcohol

↓ Residue

(Pb^{2+})

Dissolve in ammonium acetate and add ammonium chromate

↓ Yellow ppt
 (Pb^{2+})

↓ Filtrate

$(\text{Cd}^{2+}, \text{Cu}^{2+}, \text{Bi}^{3+})$

↓ NH_4OH

↓ Residue
 $(\text{White ppt. Bi}^{3+})$

↓ Conc. HCl and sodium Stannite

↓ Black ppt. (Bi^{3+})

$(\text{As}^{3+}, \text{As}^{5+}, \text{Sb}^{3+}) (\text{Sb}^{5+}, \text{Sn}^{2+}, \text{Sn}^{4+})$

↓ Filtrate $(\text{Cu}^{2+}, \text{Cd}^{2+})$

↓ $\text{K}_4\text{Fe}(\text{CN})_6$

↓ Chocolate coloured ppt
 (Cu^{2+})

↓ KCN and H_2O

↓ Yellow ppt
 (Cd^{2+})

CHEMISTRY IIA

(i) The group reagent is hydrogen sulphide in presence of HCl. These radicals are precipitated as their sulphides while the sulphides of other metals remain in solution because of their high solubility product.

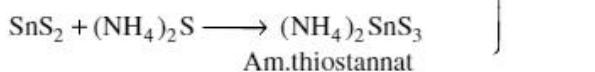
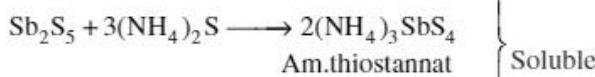
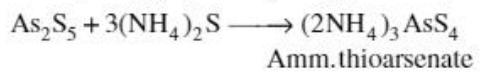
ppt : CdS, Ag ₂ S ₃ , SnS ₂	Yellow
ppt : Sb ₂ S ₃	Orange
ppt : SnS	Brown
ppt : HgS, PbS, Bi ₂ S ₃ , CuS	Black

Function of HCl is to decrease ionization of H₂S (due to common ion effect) so that only the solubility product of sulphides of II group radicals is overpowered and not that of III, IV and V groups. Hence III, IV and V group radicals are not precipitated by H₂S in presence of HCl.

(ii) If more than one kinds of ions are present a mixed colour of precipitate is formed.

(iii) Since the solubility product of PbS and CdS is more than the sulphides of other II group radicals, these are precipitated only on dilutions.

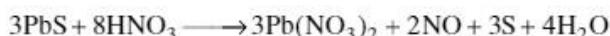
(iv) IIA and IIB group sulphides are separated by yellow ammonium sulphide, (NH₄)₂S_X in which IIA group sulphides are insoluble while that of IIB are soluble forming thiosalts.




Group IIA
contains
Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺, Hg²⁺

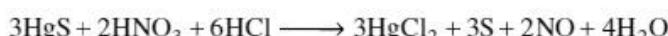

IIA group : Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺, Hg²⁺

Sulphides insoluble in yellow ammonium sulphide may be HgS, or PbS or Bi₂S₃ or CuS or CdS. These are heated with dilute HNO₃. Except HgS, all other sulphides of second group II A are soluble.



Hg²⁺

i) Dissolve the black ppt. of HgS in aqua regia

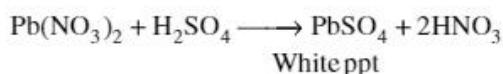


- ii) Copper turnings in Hg^{2+} solution brings a shining deposit on Cu turning

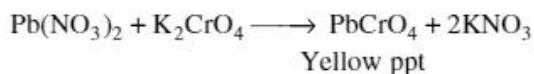


Pb²⁺ (lead)

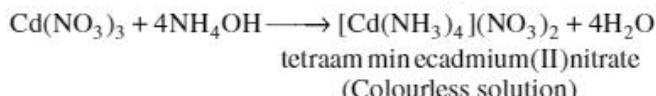
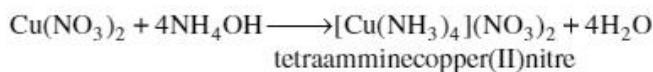
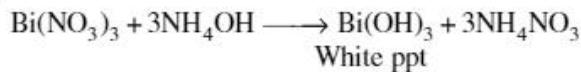
- i) Pb²⁺ ions in solution gives white ppt. with H_2SO_4



- ii) Pb²⁺ ions in solution gives yellow ppt. with KI and K_2CrO_4



In absence of lead, the remaining solution is made alkaline by the addition of excess of NH_4OH . Bismuth forms a white precipitate of $Bi(OH)_3$, copper forms a deep blue coloured solution while cadmium forms a colourless soluble complex

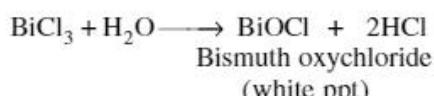


Bi³⁺ (bismuth)

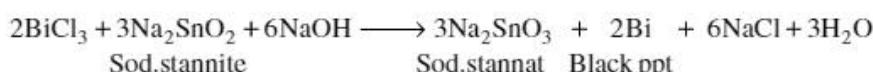
- i) The precipitate dissolves in dilute HCl.



- ii) Addition of excess of water to Bi³⁺ solution gives a white precipitate due to hydrolysis

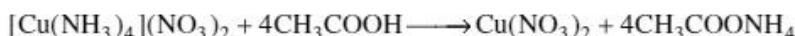


- iii) The solution of Bi³⁺ on treatment with sodium stannite solution gives a black precipitate of metallic bismuth.



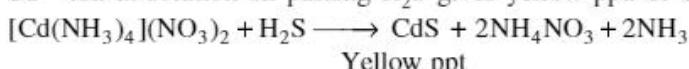
Cu²⁺(copper)

Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added, a chocolate coloured precipitate is formed.



Cd²⁺ (cadmium)

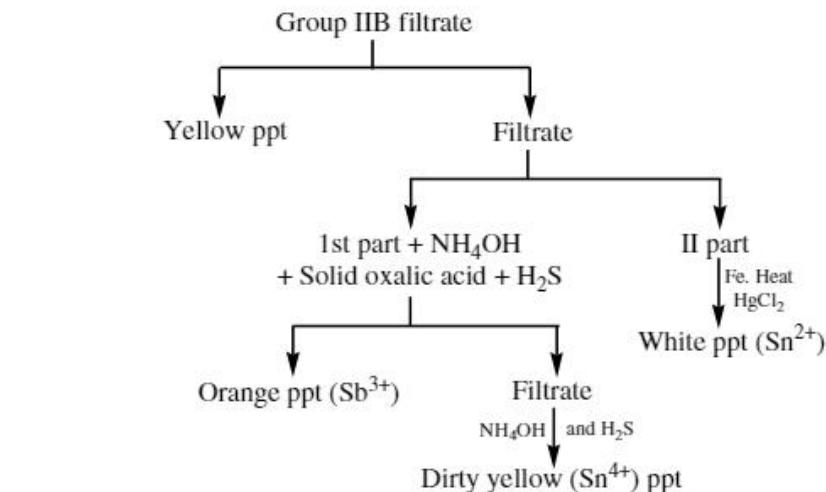
Cd²⁺ ion in solution on passing H_2S gives yellow ppt. of CdS



CHEMISTRY IIA


Group IIB
 contains
 $\text{As}^{3+}, \text{Sb}^{3+}, \text{Sn}^{2+}, \text{Sn}^{4+}$

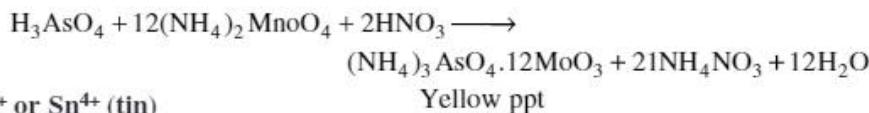
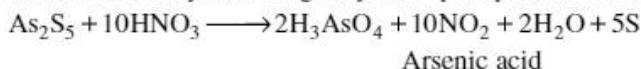

II B group : $\text{As}^{3+}, \text{Sb}^{3+}, \text{Sn}^{2+}, \text{Sn}^{4+}$



The solution containing soluble sulphides of As, Sb and Sn in yellow ammonium sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphides remains soluble while arsenic sulphide remains insoluble.

As^{3+} (arsenic)

The insoluble sulphide is treated with concentration nitric acid and then heated with ammonium molybdate to give yellow precipitate of ammonium arsénomolybdate.

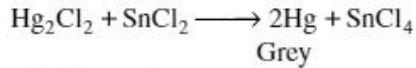
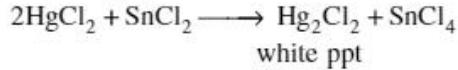


Sn^{2+} or Sn^{4+} (tin)

Solution of sulphide of Sn in concentrated HCl is reduced with iron fillings or granulated zinc to have SnCl_2 in solution state.

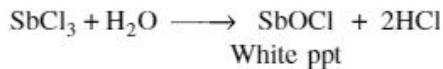


HgCl_2 solution is added to Sn^{2+} solution which gives first a white precipitate that turns to grey.

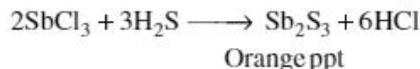


Sb^{3+} (Antimony)

- Solution of Sb^{3+} in conc. HCl on dilution with excess of water forms a white precipitate of antimony oxychloride.

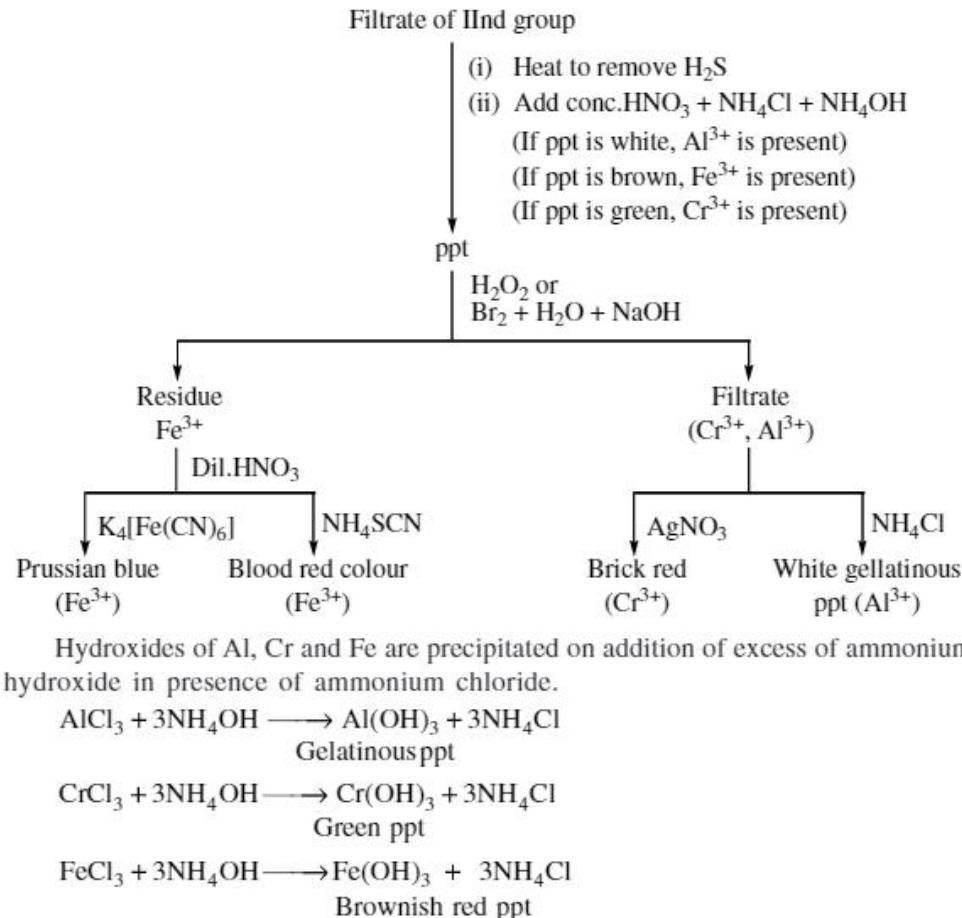


- Solution of Sb^{3+} in conc. HCl on passing H_2S gives orange ppt.

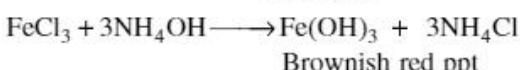
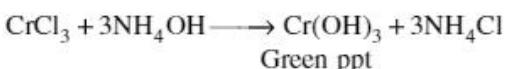
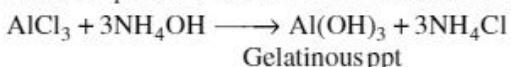



Group III contains
 $\text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}$

III Group : $\text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}$



Hydroxides of Al, Cr and Fe are precipitated on addition of excess of ammonium hydroxide in presence of ammonium chloride.



Note

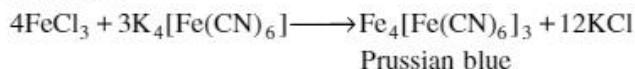
- If Fe^{2+} ions are expected (indicated by light green colour of the mixture) the solution after group II is boiled with a few drops of conc. HNO_3 to oxidize Fe^{2+} to Fe^{3+} . This is because the solubility product of $\text{Fe}(\text{OH})_2$ is high as compared to $\text{Fe}(\text{OH})_3$ and in presence of NH_4Cl (group reagent), the ionization of NH_4OH is suppressed and thus only the solubility product of $\text{Fe}(\text{OH})_3$ is reached. It is important to note that iron in the II group filtrate will be present in the ferrous state no matter if it was originally in the ferric state. It is because on passing H_2S in II group, Fe^{3+} ion is reduced to Fe^{2+} ion.
- Function of NH_4Cl is to suppress the ionization of NH_4OH so that only the III group radicals are precipitated because the solubility product of III group hydroxides is less than that of IV and V group hydroxides.
- Excess of NH_4Cl should be added otherwise manganese will be precipitated in III group as $\text{MnO}_2 \cdot \text{H}_2\text{O}$.
- $(\text{NH}_4)_4\text{SO}_4$ can't be used in place of NH_4Cl because the SO_4^{2-} will precipitate barium (if present) as BaSO_4 .
- NH_4NO_3 can't be used in place of NH_4Cl because NO_3^- ion will oxidize Mn^{2+} to Mn^{3+} and thus $\text{Mn}(\text{OH})_3$ will be precipitated in third group

Fe³⁺ (iron)

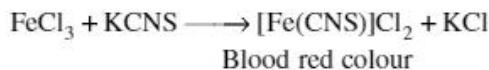
i) The brownish red precipitate is soluble in dilute HCl.



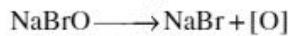
ii) K₄[Fe(CN)₆] solution is added to Fe³⁺ ions in solution to give deep blue solution or precipitate.



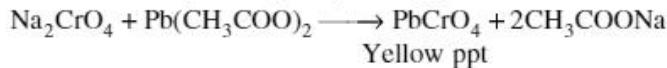
iii) Addition of potassium thiocyanate solution to Fe³⁺ ions gives a blood red colouration.

**Cr²⁺(chromium)**

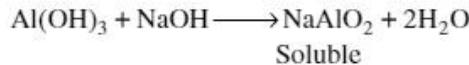
The green precipitate is soluble in NaOH and bromine water.



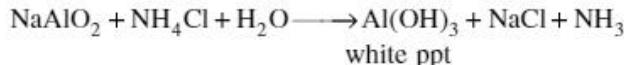
The solution thus obtained as acidified with acetic acid and treated with lead acetate solution. A yellow precipitate appears.

**Al³⁺ (Aluminium)**

The Gelatinous white precipitate dissolves in NaOH.

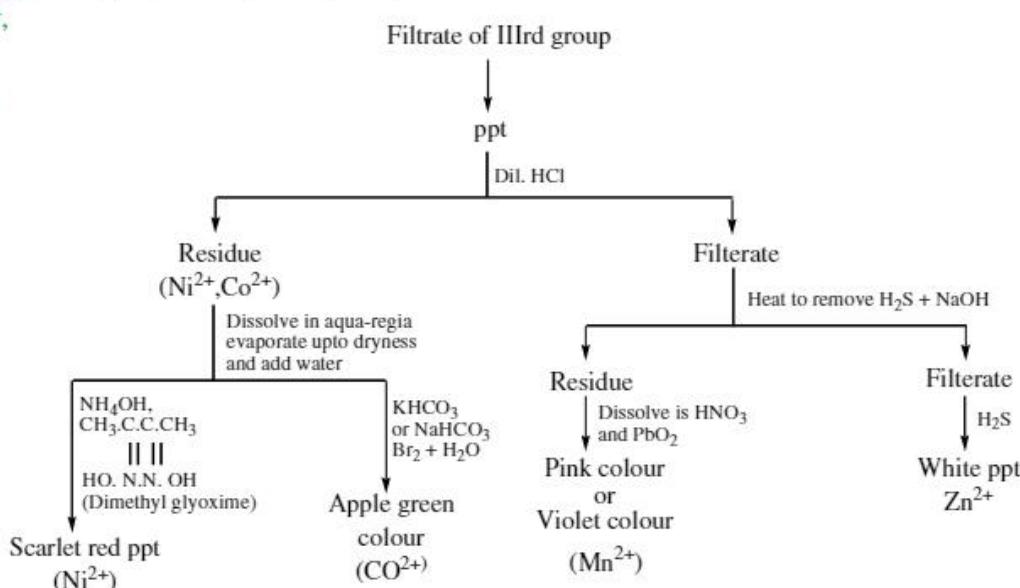


The solution is boiled with ammonium chloride when Al(OH)₃ is again formed



Group IV contains
Zn²⁺, Mn²⁺, Co²⁺, Ni²⁺

IV group : Zn²⁺, Mn²⁺, Co²⁺, Ni²⁺



These are precipitated as sulphides of passing H_2S in III group filtrate in presence of NH_4OH .



CoS , NiS : Black, soluble in aqua regia

ZnS : White, soluble in HCl

MnS : Pink, soluble in HCl

Note : Function of amm.hydroxide is to increase the ionization of H_2S by removing H^+ of H_2S as unionisable water.



Thus excess of sulphide ions will be available and hence the ionic product of IV group sulphides exceeds their solubility product and precipitate will be obtained. In case H_2S is passed through a neutral solution, incomplete precipitation will take place due to the formation of HCl which decreases the ionization of H_2S .

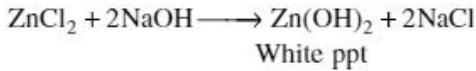


Zn²⁺ (Zinc)

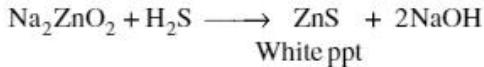
The white precipitate of zinc sulphide is dissolved in HCl and the solution is treated with $NaOH$.



First a white precipitate appears which dissolve in excess of $NaOH$.

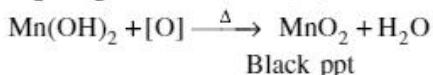
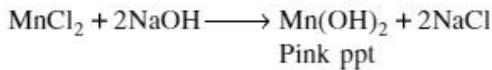
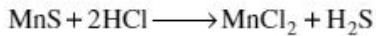


On passing H_2S , white precipitate of zinc sulphide is again formed.



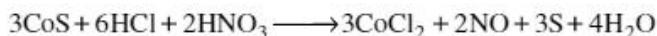
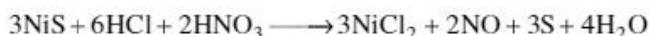
Mn²⁺ (Manganese)

The pink precipitate of MnS is dissolved in HCl and the solution is heated with $NaOH$ and Br_2 water to give pink precipitate again which turns black or brown on heating.



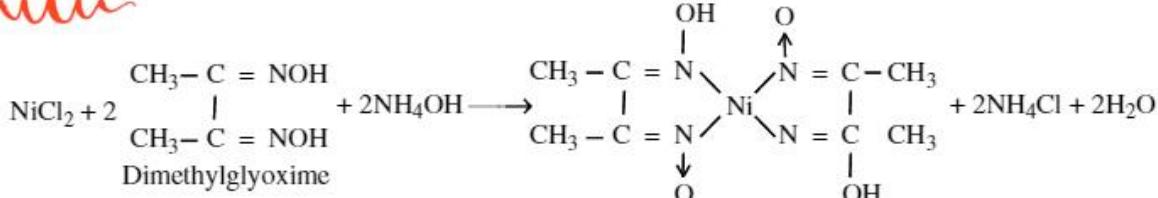
Ni^{2+} (nickel) and Co^{2+} (cobalt)

The black precipitate of NiS is dissolved in aqua regia and the solution is evaporated to dryness and residue is now dissolved in HCl.



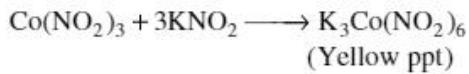
- i) Add NH_4OH (excess) ad dimethylglyoxime in one part of it. A red precipitate confirms the presence of Ni.

Dimethylglyoxime test for nickel

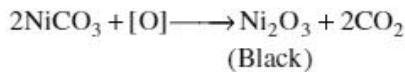
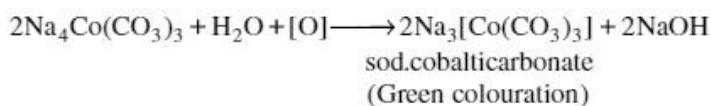
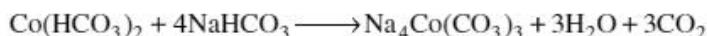


Nickel dimethylglyoxime Red ppt

- ii) Add CH_3COOH (in excess) and KNO_2 to the second part of it. The appearance of yellow precipitate confirms the presence of cobalt.



- iii) Solution containing either nickel or cobalt is treated with NaHCO_3 and bromine water. Appearance of apple green colour confirms the presence of cobalt. If no apple green colour is observed, the solution is heated; if black precipitate is formed, nickel is present.




Group V contains
 $\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$


V Group : $\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$

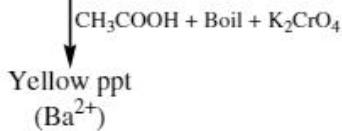
IVth group filtrate

- (i) Heat to remove H_2S
(ii) $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$

White ppt

Residue

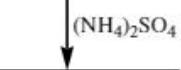
(Ba^{2+})



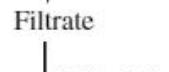
Yellow ppt
 (Ba^{2+})

Filtrate

$(\text{Sr}^{2+}, \text{Ca}^{2+})$

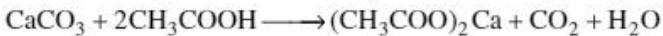
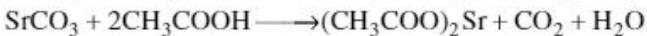
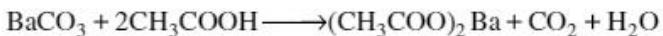


White ppt
 (Sr^{2+})



White ppt
 (Ca^{2+})

These ions are precipitated as carbonates on addition of $(\text{NH}_4)_2$ solution. These carbonates are soluble in acetic acid.



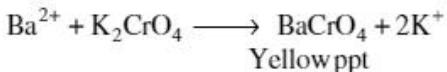
Note

1. Function of amm, chloride is to suppress the ionization of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ and thus check the precipitate of $\text{Mg}(\text{OH})_2$ and MgCO_3 (along with V group carbonates) because the solubility product of $\text{Mg}(\text{OH})_2$ and MgCO_3 is high. NH_4Cl should also be added in excess because high concentration of NH_4^+ ion will decrease the ionization of $(\text{NH}_4)_2\text{CO}_3$ to such an extent that sufficient CO_3^{2-} ions will not be present and hence V group carbonates will not be precipitated.

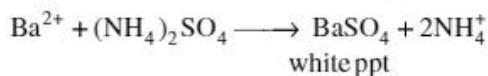
2. Cations of this group are to be tested in the sequence $\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$ (Aid to memory : BSC). This is because the test for Ba^{2+} , i.e., yellow ppt. with K_2CrO_4 is only for Ba^{2+} , while the test for Sr^{2+} i.e., white ppt with $(\text{NH}_4)_2\text{SO}_4$ is given both by Ba^{2+} ions ad the test for Ca^{2+} ions i.e., white ppt, with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is also given by $\text{Ba}^{2+}, \text{Sr}^{2+}$ ions.

Ba^{2+} (barium)

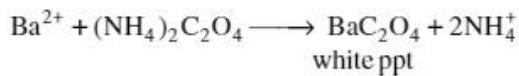
- i) Ba^{2+} ion in solution gives
- a) Yellow precipitate with K_2CrO_4



- b) White precipitate with $(\text{NH}_4)_2\text{SO}_4$



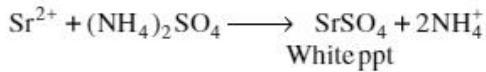
- c) White precipitate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$



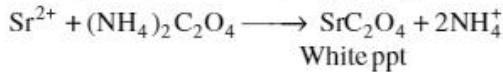
Sr^{2+} (Strontium)

Sr^{2+} ion in solution gives

- a) White precipitate with $(\text{NH}_4)_2\text{SO}_4$

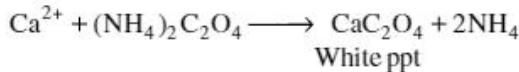


- b) White precipitate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$



Ca^{2+} (calcium)

Ca^{2+} ion gives white precipitate with ammonium oxalate

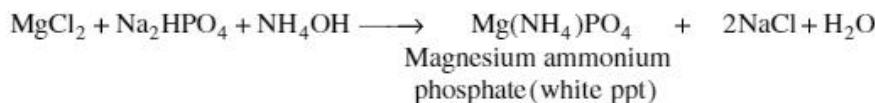


VI group : $\text{Mg}^{2+}, \text{K}^+, \text{Na}^+$

In the filtrate of V group ammonium oxalate is added so as to remove Ba, Ca and Sr completely from the solution. The solution is divided into three parts and tested for Mg^{2+} , K^+ and Na^+ .

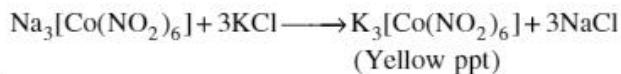
Mg^{2+}

The clear solution is concentrated and made alkaline with NH_4OH and then treated with disodium hydrogen phosphate to give a white precipitate of $\text{Mg}(\text{NH}_4)\text{PO}_4$.



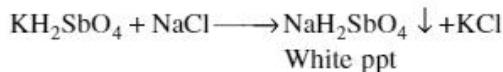
K^+

Potassium salts give a yellow ppt. with sod cobaltinitrite.



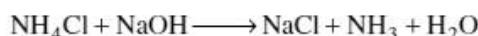
Na^+

Sodium Salts give a heavy white ppt with hot dihydrogen antimonate.



Zero group : NH_4^+ (ammonium)

- i) The salt or mixture when heated with NaOH solution evolves ammonia.



- ii) The gas coming out (NH_3) shows white fumes with HCl .



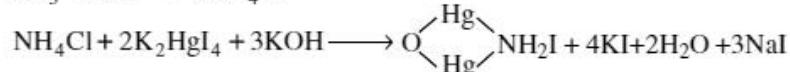
White fumes

- iii) On passing the gas through Nessler's reagent, a brown ppt is formed.

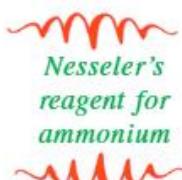


Iodide of Millon's base

(Brown ppt)



(Iodide of Million's
base brown ppt.)



PRACTICAL ORGANIC CHEMISTRY

5.2.1

Functional group 1. Unsaturation : Alkenes and alkynes

analysis a) Bayers test : Cold dil alkaline KMnO_4 decolourisation test
Purple colour ? Colourless + MnO_2 (Brown ppt)

b) Br_2 water decolourisation test
Violet colourless of Br_2 ? Colourless

2. Terminal alkynes

Confirmed by ppt of Acetylidy ion with NaNH_2 or AgNO_3 or $\text{Cu}_2\text{Cl}_2\text{NH}_4\text{OH}$

3. Alkyl halides

a) If they are capable of carbocation formation then they will give ppt with AgNO_3 ,
b) Beilstein's test : A green colour is imparted to the flame if small amount of organic compound is taken on copper wire.

4. Alcohol

a) With Ceric ammonium nitrate ? Give red colour
b) Boil with acetic acid & conc. H_2SO_4 ? fruity odour
c) 2 alkanol & ethanol also give Iodoform test ? Yellow ppt. of CH_3I on reaction with $\text{I}_2 + \text{KOH}$

5. Aldehyde & Ketones

2,4 Dinitrophenyl hydrazine (or) Braddy's reagent give yellow, orange or red color with ald. & Ketones (2,4 DNP)

6. Aldehydes

a) Tollen's test ? Silver mirror.
b) Fehling's test {except benzaldehyde} ? Red colour.
c) Benedict's test ? Red colour.
d) Schiff's dye colour regeneration test ? Pink colour.
e) Gly ppt with HgCl_2 .

7. Ketones

- a) Methyl Ketones give haloform test.
- b) ? hydroxy Ketones give Tollen's & Fehling test's too.

8. Carboxylic acids

- a) Brisk effervescence with aq. NaHCO_3 solution.
- b) HCOOH alone gives silver mirror test with Tollen's reagent.
- c) Blue litmus ? red
- d) Give fruity smell on reaction with alcohols.

9. Phenols

- a) Violet colouration with neural FeCl_3
- b) Liebermann test.
- c) White ppt with Br_2 water.
- d) Brisk effervescence with aq. NaHCO_3 is observed in case of Nitrophenols.

10. Primary amines

- a) Carbylamine reaction ? Isonitriles have very distinctive foul odors
- b) Hoffmann mustard oil reaction ?? Oily liquid with mustard like smell.

11. Aromatic 1° amine ? diazo test.**12. Amide boil with NaOH ? NH_3** **13. Nitrobenzene ? Mullikan Baker test ? Treat it with ZnNH_4Cl then boil with Tollen's reagent ? Silver mirror will appear.****14. Proteins**

- a) Biuret test : Also used for urea ? Alkaline solution of protein treated with a drop of aq CuSO_4 when bluish violet colour is obtained
- b) Ninhydrin test : Protein treated with a puridine solution of ninhydrin give colour ranging from deep blue to violet pink.

DIFFERENTIATION TEST**D1. 1°, 2° & 3° alcohols**

- a) Luca's test : Lucas reagent is conc. $\text{HCl} + \text{ZnCl}_2$
- b) Victor Meyer's test (RBC test)
 - (i) 1° Alcohol gives Blood red colour
 - (ii) 2° Alcohol gives Blue
 - (iii) 3° Alcohol gives Colourless product

D2. 1°, 2° & 3° amines

- a) Hinsberg's reagent
 - (i) 1° Amine yield a clear solution from which upon acidification an insoluble material separated.
 - (ii) 2° Amine yield an insoluble compound which is unaffected by acid.
 - (iii) 3° Amine yield insoluble compound.
- b) Reaction with HNO_2
When a solution of sodium nitrate is acidified, it reacts as a source of nitrosyl cation (^+NO)


Lucas and Victor Meyer tests to distinguish between 1°, 2° and 3° alcohols


Hinsberg test to distinguish between 1°, 2° and 3° amines

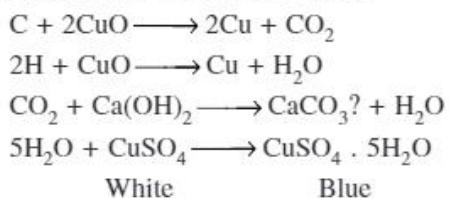
- (i) aliphatic primary amines give primary alcohol with nitrous acid, while aromatic primary amines give diazonium salts.
- (ii) secondary amines give an yellow oily nitrosoamine.
- (iii) tertiary amines give a salt of the type $R_3NH^+NO_2^-$.

5.2.2**Qualitative analysis**

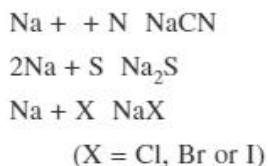
The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

1. Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper (II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

**2. Detection of Other Elements**

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:



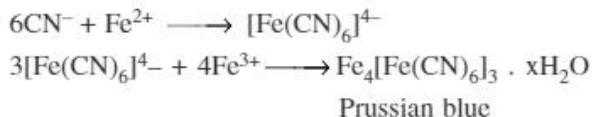
C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

(A) Test of Nitrogen

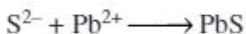
The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II).

On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.



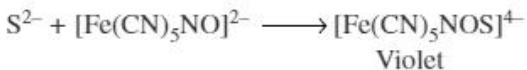
(B) Test for Sulphur

- a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

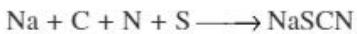


Black

- b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.



In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.



If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.



(C) Test of Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.



X represents a halogen –Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

(D) Test for Phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.



Ammonium molybdate

Ammonium phosphomolybdate


Molybdate test for phosphorus