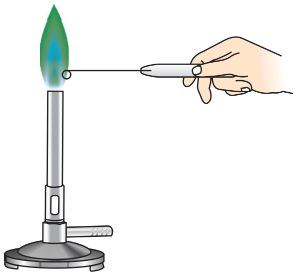
UNIT-7

SYSTEMATIC QUALITATIVE ANALYSIS



ANALYSIS always does not mean breaking of substance into its ultimate constituents. Finding out the nature of substance and identity of its constituents is also analysis and is known as qualitative analysis. Qualitative analysis of inorganic salts means the identification of cations and anions present in the salt or a mixture of salts. Inorganic salts may be obtained by complete or partial neutralisation of acid with base or vice-versa. In the formation of a salt, the part contributed by the acid is called anion and the part contributed by the base is called cation. For example, in the salts $CuSO_4$ and NaCl, Cu^{2+} and Na^+ ions are cations and SO_4^{2-} and Cl^- ions are anions. Qualitative analysis is carried out on various scales. Amount of substance employed in these is different. In macro analysis, 0.1 to 0.5 g of substance and about 20 mL of solution is used. For semimicro analysis, 0.05 g substance and 1 mL solution is needed while for micro analysis amount required is very small. Qualitative analysis is carried out through the reactions which are easily perceptible to our senses such as sight and smell. Such reactions involve:

(a) Formation of a precipitate

(b) Change in colour

(c) Evolution of gas etc.

Systematic analysis of an inorganic salt involves the following steps:

(i) Preliminary examination of solid salt and its solution.

(ii) Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.

(iii) Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

Preliminary examination of a salt often furnishes important information, which simplifies further course of analysis. Although these tests are not conclusive but sometimes they give quite important clues for the presence of certain anions or cations. These tests can be performed within 10–15 minutes. These involve noting the general appearance and physical properties, such as colour, smell, solubility etc. of the salt. These are named as dry tests.

Heating of dry salt, blow pipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests. Some of these tests are given later in this unit.

Solubility of a salt in water and the pH of aqueous solutions give important information about the nature of ions present in the salt. If a solution of the salt is acidic or basic in nature, this means that it is being hydrolysed in water. If the solution is basic in nature then salt may be some carbonate or sulphide etc. If the solution shows acidic nature then it may be an acid salt or salt of weak base and strong acid. In this case it is best to neutralise the solution with sodium carbonate before testing it for anions.

Gases evolved in the preliminary tests with dil. H_2SO_4/dil. HCl and conc. H_2SO_4 also give good indication about the presence of acid radicals (see Tables 7.1 and 7.3). Preliminary tests should always be performed before starting the confirmatory tests for the ions.

EXPERIMENT 7.1

Aim

To detect one cation and one anion in the given salt from the following ions:

Cations - Pb^{2+}, Cu^{2+}, As^{3+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+

Anions - CO_3^{2-}, S^{2-}, SO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^-, Cl^-, Br^-, I^-, PO_4^{3-}, $C_2O_4^{2-}$, CH_3COO^-.

(Insoluble salts to be excluded)

Theory

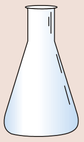
Two basic principles of great use in the analysis are:

(i) the Solubility product and

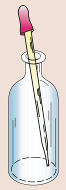
(ii) the Common ion effect

When ionic product of a salt exceeds its solubility product, precipitation takes place. Ionic product of salt is controlled by making use of common ion effect which you have studied in the textbook of chemistry.

Material Required



• Boiling tube	:	As per need
• Test tubes	:	As per requirement
• Measuring cylinder	:	One
• Test tube stand	:	One
• Test tube holder	:	One
• Delivery tube	:	One
• Corks	:	As per need
• Filter paper	:	As per need



- Reagents : As per need

7.1 SYSTEMATIC ANALYSIS OF ANIONS

Step - I : Preliminary Test with Dilute Sulphuric Acid

In this test the action of dilute sulphuric acid (procedure is given below) on the salt is noted at room temperature and on warming.

Carbonate (CO_3^{2-}), sulphide (S^{2-}), sulphite (SO_3^{2-}), nitrite (NO_2^-) and acetate (CH_3COO^-) react with dilute sulphuric acid to evolve different gases. Study of the characteristics of the gases evolved gives information about the anions. Summary of characteristic properties of gases is given in Table 7.1 below.

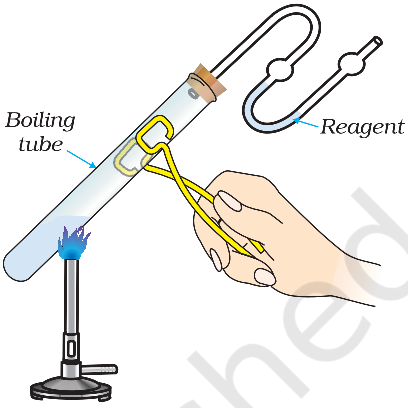


***Fig. 7.1** : Testing a Gas*

Procedure

(a) Take 0.1 g of the salt in a test tube and add 1–2 mL of dilute sulphuric acid. Observe the change, if any, at room temperature. If no gas is evolved, warm the content of the test tube. If gas is evolved test it by using the apparatus shown in Fig.7.1 and identify the gas evolved (See Table 7.1).

Table 7.1 : Preliminary test with dilute sulphuric acid

Observations	Inference	
	Gas evolved	**Possible Anion**
A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky.	CO_2	Carbonate (CO_3^{2-})
Colourless gas with the smell of rotten eggs is evolved which turns lead acetate paper black.	H_2S	Sulphide (S^{2-})
Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green.	SO_2	Sulphite (SO_3^{2-})
Brown fumes which turn acidified potassium iodide solution containing starch solution blue.	NO_2	Nitrite (NO_2^-)
Colourless vapours with smell of vinegar. Vapours turn blue litmus red.	CH_3COOH vapours	Acetate, (CH_3COO^-)

Confirmatory tests for CO_3^{2-} S^{2-}, SO_3^{2-}, NO_2^- and CH_3COO^-

Confirmatory (wet) tests for anions are performed by using **water extract** when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water. Confirmation of CO_3^{2-} is done by using aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water. Preparation of sodium carbonate extract is given below.

Preparation of sodium carbonate extract

Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter and collect the filtrate in a test tube and label it as sodium carbonate extract.

Confirmatory tests for acid radicals, which react with dilute sulphuric acid are given below in Table 7.2.

Table 7.2 : Confirmatory tests for CO_3^{2-}, S^{2-}, SO_3^{2-}, NO_3^- , CH_3COO^-

Anion	Confirmatory test
Carbonate (CO_3^{2-})	Take 0.1 g of salt in a test tube, add dilute sulphuric acid. CO_2 gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.
Sulphide (S^{2-})	Take 1 mL of water extract and make it alkaline by adding ammonium hydroxide or sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears.
*Sulphite (SO_3^{2-})	(a) Take 1 mL of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved. (b) Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. H_2SO_4. Colour of potassium permanganate solution gets discharged.
Nitrite (NO_2^-)	(a) Take 1 mL of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, acidify with acetic acid. Blue colour appears. (b) Acidify 1 mL of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1-naphthylamine reagent. Appearance of red colour indicates the presence of nitrite ion.

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* *Like CO_2 sulphur dioxide also turns lime water milky. But CO_2 is odourless gas and SO_2 has a characteristic smell.*

Acetate (CH_3COO^-)	(a) Take 0.1 g of salt in a china dish. Add 1 mL of ethanol and 0.2 mL conc. H_2SO_4 and heat. Fruity odour confirms the presence of acetate ion. (b) Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well filter if necessary. Add 1 to 2 mL neutral** ferric chloride solution to the filtrate. Deep red colour appears which disappears on boiling and a brown-red precipitate is formed.

** *Prepareation of neutral Ferric Chloride : Add dilute NaOH solution to ferric chloride solution drop by drop with shaking until a small but permanent precipitate of ferric hydroxide is obtained. Filter the precipitate and use the filtrate for analysis.*

Chemistry of Confirmatory Tests

1. Test for Carbonate ion [CO_3^{2-}]

If there is effervescence with the evolution of a colourless and odourless gas on adding dil. H_2SO_4 to the solid salt, this indicates the presence of carbonate ion. The gas turns lime water milky due to the formation of $CaCO_3$ (Fig. 7.1)

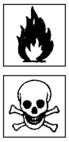
$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

If CO_2 gas is passed in excess through lime water, the milkiness produced disappears due to the formation of calcium hydrogen carbonate which is soluble in water.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca\,(HCO_3)_2$$

Hydrogen sulphide



2. Test for Sulphide ion [S^{2-}]

(a) With warm dilute H_2SO_4 a sulphide gives hydrogen sulphide gas which smells like rotten eggs. A piece of filter paper dipped in lead acetate solution turns black on exposure to the gas due to the formation of lead sulphide which is black in colour.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\substack{\text{Lead sulphide}\\ \text{Black precipitate}}}{PbS} + 2CH_3COOH$$

(b) If the salt is soluble in water, take the solution of salt in water make it alkaline with ammonium hydroxide and add sodium nitroprusside solution. If it is insoluble in water take sodium carbonate extract and add a few drops of sodium nitroprusside solution. Purple or violet colouration due to the formation of complex compound $Na_4[Fe(CN)_5NOS]$ confirms the presence of sulphide ion in the salt.

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

3. Test for Sulphite ion $[SO_3^{2-}]$

(a) On treating sulphite with warm dil. H_2SO_4, SO_2 gas is evolved which is suffocating with the smell of burning sulphur.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$

Barium compounds

The gas turns potassium dichromate paper acidified with dil. H_2SO_4, green.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{Chromium sulphate (green)}}{Cr_2(SO_4)_3} + H_2O$$

Potassium permanganate

(b) An aqueous solution or sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.

$$Na_2SO_3 + BaCl_2 \longrightarrow 2NaCl + BaSO_3$$

This precipitate gives following tests.

(i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl. Evolved SO_2 gas can be tested.

$$BaSO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + SO_2$$

(ii) Precipitate of sulphite decolourises acidified potassium permanganate solution.

$$BaSO_3 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + SO_2$$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$SO_2 + H_2O + [O] \longrightarrow H_2SO_4$$

4. Test for Nitrite ion $[NO_2^-]$

(a) On treating a solid nitrite with dil. H_2SO_4 and warming, reddish brown fumes of NO_2 gas are evolved. Addition of potassium iodide solution to the salt solution followed by freshly prepared starch solution and acidification with acetic acid produces blue colour. Alternatively, a filter paper moistened with potassium iodide and starch solution and a few drops of acetic acid turns blue on exposure to the gas due to the interaction of liberated iodine with starch.

(i) $$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$

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

$$2NO + O_2 \longrightarrow \underset{\text{Brown gas}}{2NO_2}$$

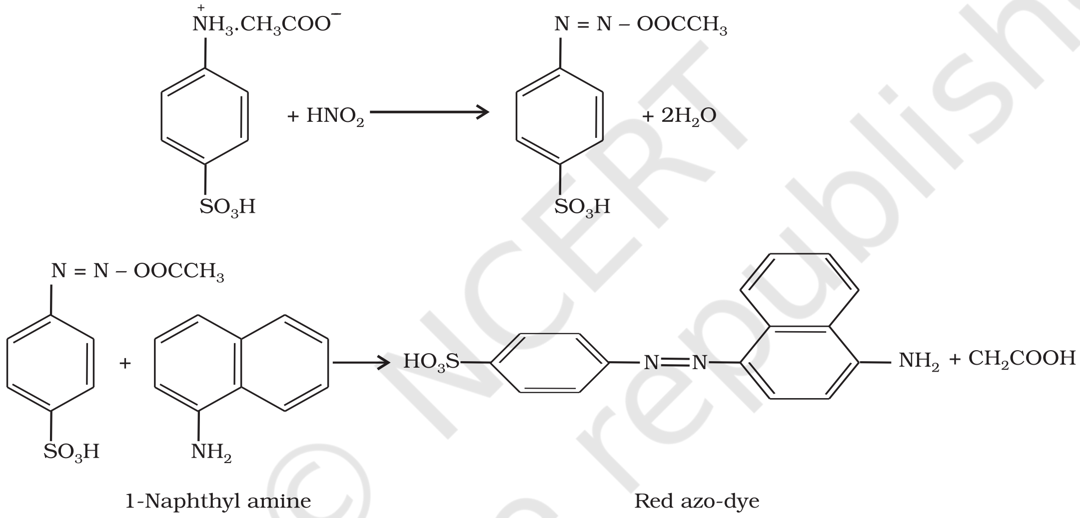
(ii) $NO_2^- + CH_3COOH \longrightarrow HNO_2 + CH_3COO^-$

$$2HNO_2 + 2KI + 2CH_3COOH \longrightarrow 2CH_3COOK + 2H_2O + 2NO + I_2$$

$$I_2 + \text{Starch} \longrightarrow \text{Blue complex}$$

(b) Sulphanilic acid — 1-naphthylamine reagent test (Griss-Ilosvay test)
On adding sulphanilic acid and 1-naphthylamine reagent to the water extract or acidified with acetic acid, sulphanilic acid is diazotised in the reaction by nitrous acid formed. Diazotised acid couples with 1-naphthylamine to form a red azo-dye.

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



The test solution should be very dilute. In concentrated solutions reaction does not proceed beyond diazotisation.

5. Test for Acetate ion [CH_3COO^-]

(a) If the salt smells like vinegar on treatment with dil. H_2SO_4, this indicates the presence of acetate ions. Take 0.1 g of salt in a china dish and add 1 mL of ethanol. Then add about 0.2 mL of conc. H_2SO_4 and heat. Fruity odour of ethyl acetate indicates the presence of CH_3COO^- ion.

$$2\,CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,CH_3COOH$$

$$CH_3COOH + C_2H_5OH \xrightarrow{H^+} \underset{\substack{\text{Ethylacetate}\\ \text{(Fruity odour)}}}{CH_3COOC_2H_5} + H_2O$$

(b) Acetate gives deep red colour on reaction with neutral ferric chloride solution due to the formation of complex ion which decomposes on heating to give Iron (III) dihydroxyacetate as brown red precipitate.

$$6\,CH_3COO^- + 3Fe^{3+} + 2H_2O \longrightarrow [Fe_3(OH)_2\,(CH_3COO)_6]^+ + 2H^+$$

$$[Fe_3(OH)_2\,(CH_3COO)_6]^+ + 4H_2O \longrightarrow \underset{\substack{\text{Iron(III)dihydroxyacetate} \\ \text{(Brown-red precipitate)}}}{3[Fe\,(OH)_2\,(CH_3COO)]} + 3CH_3COOH + H^+$$

Step-II : Preliminary Test with Concentrated Suphuric Acid

If no positive result is obtained from dil. $H_2\,SO_4$ test, take 0.1 g of salt in a test tube and 3-4 drops of conc. H_2SO_4. Observe the change in the reaction mixture in cold and then warm it. Identify the gas evolved on heating (see Table 7.3).

Table 7.3 : Preliminary examination with concentrated sulphuric acid

Observations	Inference	
	Gas/vapours evolved	**Possible anions**
A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	HCl	Chloride, (Cl^-)
Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid MnO_2 to the reaction mixture. Solution also acquires red colour.	Br_2 vapours	Bromide, (Br^-)
Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding MnO_2 to the reaction mixture.	I_2 vapours	Iodide, (I^-)
Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.	NO_2	Nitrate, (NO_3^-)
Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.	CO and CO_2	Oxalate, ($C_2O_4^{2-}$)

Confirmatory tests for the anions which react with concentrated sulphuric acid

Table 7.4 : Confirmatory tests for Cl^-, Br^-, I^-, NO_3^- and $C_2O_4^{2-}$

Anion	Confirmatory test
Chloride (Cl^-)	(a) Take 0.1 g of salt in a test tube, add a pinch of manganese dioxide and 3-4 drops of conc. sulphuric acid. Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action. (b) Take 1 mL of sodium carbonate extract in a test tube, acidfy it with dil. HNO_3 or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution. (c) Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, add conc. H_2SO_4, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 mL of amyl alcohol followed by 1 mL of 10% hydrogen peroxide. After gentle shaking the organic layer turns blue.
Bromide (Br^-)	(a) Take 0.1 g of salt and a pinch of MnO_2 in a test tube. Add 3-4 drops conc.sulphuric acid and heat. Intense brown fumes are evolved. (b) Neutralise 1 mL of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 mL carbon tetrachloride (CCl_4)/chloroform ($CHCl_3$)/ carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ion. (c) Acidify 1 mL of sodium carbonate extract with dil. HNO_3 (or take 1 mL water extract) and add silver nitrate solution. A pale yellow precipitate soluble with difficulty in ammonium hydroxide solution is obtained.
Iodide (I^-)	(a) Take 1 mL of salt solution neutralised with HCl and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water drop wise and shake the test tube. A violet colour appears in the organic layer. (b) Take 1 mL of sodium carbonate extract acidify it with dil. HNO_3 (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in NH_4OH solution is obtained.

*Nitrate (NO_3^-)	Take 1 mL of salt solution in water in a test tube. Add 2 mL conc. of H_2SO_4 and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.
Oxalate $(C_2O_4^{2-})$	(a) Take 1 mL of water extract or sodium carbonate extract acidified with acetic acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed. (b) Take the precipitate from test (a) and dissolve it in dilute H_2SO_4. Add very dilute solution of $KMnO_4$ and warm. Colour of $KMnO_4$ solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.

Chemistry of Confirmatory Tests

1. Test for Chloride ion $[Cl^-]$

(a) If on treatment with warm conc. H_2SO_4 the salt gives a colourless gas with pungent smell or and if the gas which gives dense white fumes with ammonia solution, then the salt may contain Cl^- ions and the following reaction occurs.

Manganese dioxide

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

NaHSO₄: Sodium hydrogen sulphate; HCl: Hydrogen chloride, Colourless gas

Silver nitrate

$$HCl + NH_3 \longrightarrow NH_4Cl$$

Ammonium chloride
White fumes

(b) If a salt gives effervescence on heating with conc. H_2SO_4 and MnO_2 and a light greenish yellow pungent gas is evolved, this indicates the presence of Cl^- ions.

$$MnO_2 + 2NaCl + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

Hazard Warning

- *The solution obtained after dissolving AgCl/AgBr/AgI precipitate in ammonium hydroxide should be acidified with 2M HNO_3 and should be discarded quickly to avoid serious explosion.*

(c) Salt solution acidified with dilute HNO_3 on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of Cl^- ions in the salt.

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + Ag\,Cl$$

Silver chloride
(White precipitate)

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2\,]Cl + 2H_2O$$

Diammine silver (I)
chloride

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* *This test can also be performed by adding first ferrous sulphate solution and then conc. H_2SO_4.*

(d) Mix a little amount of salt and an equal amount of solid potassium dichromate ($K_2Cr_2O_7$) in a test tube and add conc. H_2SO_4 to it. Heat the test tube and pass the evolved gas through sodium hydroxide solution. If a yellow solution is obtained, divide the solution into two parts. Acidify the first part with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate confirms the presence of chloride ions in the salt. This test is called **chromyl chloride test**.*

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow 2KHSO_4 + \underset{\text{(Chromyl chloride)}}{2CrO_2Cl_2} + 4NaHSO_4 + 3H_2O$$

Chromyl chloride

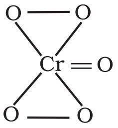
$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

$$(CH_3COO)_2Pb + \underset{\substack{\text{Sodium}\\\text{chromate}}}{Na_2CrO_4} \longrightarrow \underset{\substack{\text{Lead chromate}\\\text{(Yellow precipitate)}}}{PbCrO_4} + 2CH_3COONa$$

Lead chromate

Acidify the second part with dilute sulphuric acid and add small amounts of amyl alcohol and then 1 mL of 10% hydrogen peroxide solution. On gentle shaking organic layer turns blue. CrO_4^{2-} ion formed in the reaction of chromyl chloride with sodium hydroxide reacts with hydrogen peroxide to form chromium pentoxide (CrO_5) (See structure) which dissolves in amyl alcohol to give blue colour.

$$CrO_4^{2-} + 2H^+ + 2H_2O_2 \longrightarrow \underset{\substack{\text{Chromium}\\\text{pentoxide}}}{CrO_5} + 3H_2O$$



Structure of chromium pentoxide

2. Test for Bromide ion (Br^-)

If on heating the salt with conc. H_2SO_4 reddish brown fumes of bromine are evolved in excess, this indicates the presence of Br^- ions. The fumes get intensified on addition of MnO_2. Bromine vapours turn starch paper yellow.

$$2NaBr + 2H_2SO_4 \longrightarrow Br_2 + SO_2 + Na_2SO_4 + 2H_2O$$

$$2NaBr + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Br_2$$

Bromine very toxic by inhalation corrosive

(a) Add 1 mL of carbon tetrachloride (CCl_4)/chloroform ($CHCl_3$)** and excess of freshly prepared chlorine water dropwise to the salt solution in water or sodium carbonate extract neutralised with dilute HCl. Shake the test tube vigorously. The appearance of an orange brown colouration in the organic layer due to the dissolution of bromine in it, confirms the presence of bromide ions.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$

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* *Chromyl chloride test should be performed with minimum amount of substance to avoid pollution by Cr^{3+} ions.*

** *In place of carbon tetrachloride or chloroform, carbon disulphide or dichloromethane (CH_2Cl_2) can also be used.*

(b) Acidify the sodium carbonate extract of the salt with dil. HNO_3. Add silver nitrate ($AgNO_3$) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

$$NaBr + AgNO_3 \longrightarrow NaNO_3 + \underset{\substack{\text{Silver bromide}\\ \text{Pale yellow precipitate}}}{AgBr}$$

3. Test for Iodide ion (I^-)

(a) If on heating the salt with conc. H_2SO_4 , deep violet vapours with a pungent smell are evolved. These turns starch paper blue and a violet sublimate is formed on the sides of the test tube, it indicates the presence of I^- ions. Some HI, sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.

Iodine, harmful by inhalation and contact with skin ✖

Chlorine, toxic by inhalation ☠

Chloroform, harmful and toxic by inhalation ✖ ☠

$$2NaI + 2H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + 2H_2O + I_2$$

$$I_2 + \underset{\text{solution}}{\text{Starch}} \longrightarrow \text{Blue colour}$$

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

$$2HI + H_2SO_4 \longrightarrow 2H_2O + I_2 + SO_2$$

$$6NaI + 4H_2SO_4 \longrightarrow 3I_2 + 4H_2O + S + 3Na_2SO_4$$

$$8NaI + 5\,H_2SO_4 \longrightarrow 4I_2 + H_2S + 4Na_2SO_4 + 4H_2O$$

On adding MnO_2 to the reaction mixture, the violet vapours become dense.

$$2NaI + MnO_2 + 2H_2SO_4 \longrightarrow I_2 + MnSO_4 + Na_2SO_4 + 2H_2O$$

(b) Add 1 mL of $CHCl_3$ or CCl_4 and chlorine water in excess to the salt solution in water or sodium carbonate extract neutralised with dil.HCl and shake the test tube vigorously. Presence of violet colouration in the organic layer confirms the presence of iodide ions.

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$$

Iodine dissolves in the organic solvent and the solution becomes violet.

(c) Acidify sodium carbonate extract of the salt with dil.HNO_3 and add $AgNO_3$ solution. Appearance of a yellow precipitate insoluble in excess of NH_4OH confirms the presence of iodide ions.

$$NaI + AgNO_3 \longrightarrow \underset{\substack{\text{silver iodide}\\ \text{(Yellow precipitate)}}}{AgI} + NaNO_3$$

4. Test for Nitrate ion [NO_3^-]

(a) If on heating the salt with conc. H_2SO_4 light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc. H_2SO_4. Evolution of excess of brown fumes indicates the presence of nitrate ions. The solution turns blue due to the formation of copper sulphate.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

$$2NaNO_3 + 4H_2SO_4 + 3Cu \longrightarrow \underset{\substack{\text{Copper sulphate}\\ \text{(Blue)}}}{3\,CuSO_4} + Na_2SO_4 + 4H_2O + 2NO$$

$$2NO + O_2 \longrightarrow \underset{\text{(Brown fumes)}}{2NO_2}$$

Copper sulphate

Nitric acid

Oxalates

(b) Take 1 mL of an aqueous solution of the salt and add 2 mL conc. H_2SO_4 slowly. Mix the solutions thoroughly and cool the test tube under the tap. Now, add freshly prepared ferrous sulphate solution along the sides of the test tube dropwise so that it forms a layer on the top of the liquid already present in the test tube. A dark brown ring is formed at the junction of the two solutions due to the formation of nitroso ferrous sulphate (Fig. 7.2). Alternatively first ferrous sulphate is added and then concentrated sulphuric acid is added.

Fig. 7.2 : *Formation of brown ring*

$$NaNO_3 + H_2SO_4 \longrightarrow Na\,HSO_4 + HNO_3$$

$$6\,FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2\,(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO \longrightarrow \underset{\substack{\text{Nitroso ferrous sulphate}\\ \text{(Brown)}}}{[Fe(NO)]SO_4}$$

5. Test for Oxalate ion [$C_2O_4^{2-}$]

If carbon dioxide gas along with carbon monoxide gas is evolved in the preliminary examination with concentrated sulphuric acid, this gives indication about the presence of oxalate ion.

$$(COONa)_2 + \text{Conc. } H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow + CO\uparrow$$

Oxalate is confirmed by the following tests:

(a) Acidify sodium carbonate extract with acetic acid and add calcium chloride solution. A white precipitate of calcium oxalate, insoluble in ammonium oxalate and oxalic acid solution indicates the presence of oxalate ion.

$$CaCl_2 + Na_2C_2O_4 \longrightarrow \underset{\substack{\text{Calcium oxalate} \\ \text{(White precipitate)}}}{CaC_2O_4} + 2NaCl$$

(b) $KMnO_4$ test

Filter the precipitate from test (a). Add dil. H_2SO_4 to it followed by dilute $KMnO_4$ solution and warm. Pink colour of $KMnO_4$ is discharged:

$$CaC_2O_4 + H_2SO_4 \longrightarrow \underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Oxalic acid}}{H_2C_2O_4}$$

$$2\,KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Pass the gas evolved through lime water. A white precipitate is formed which dissolves on passing the gas for some more time.

Step-III : Test for Sulphate and Phosphate

If no positive test is obtained in Steps-I and II, then tests for the presence of sulphate and phosphate ions are performed. These tests are summarised in Table 7.5.

Table 7.5 : Confirmatory tests for Sulphate and Phosphate

Ion	Confirmatory Test
Sulphate (SO_4^{2-})	(a) Take 1 mL water extract of the salt in water or sodium carbonate and after acidifying with dilute hydrochloric acid add $BaCl_2$ solution. White precipitate insoluble in conc. HCl or conc. HNO_3 is obtained. (b) Acidify the aqueous solution or sodium carbonate extract with acetic acid and add lead acetate solution. Appearance of white precipitate confirms the presence of SO_4^{2-} ion.
Phosphate (PO_4^{3-})	(a) Acidify sodium carbonate extract or the solution of the salt in water with conc. HNO_3 and add ammonium molybdate solution and heat to boiling. A canary yellow precipitate is formed.

Chemistry of Confirmatory Tests

1. Test of Sulphate ions [SO_4^{2-}]

(a) Aqueous solution or sodium carbonate extract of the salt acidified with acetic acid on addition of barium chloride gives a white precipitate of barium sulphate insoluble in conc. HCl or conc. HNO_3.

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\substack{\text{Barium sulphate} \\ \text{(White precipitate)}}}{BaSO_4} + 2NaCl$$

(b) Sulphate ions give white precipitate of lead sulphate when aqueous solution or sodium carbonate extract neutralised with acetic acid is treated with lead acetate solution.

$$Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\text{Lead sulphate} \\ \text{(White precipitate)}}}{PbSO_4} + 2CH_3COONa$$

2. Test for Phosphate ion [PO_4^{3-}]

(a) Add conc. HNO_3 and ammonium molybdate solution to the test solution containing phosphate ions and boil. A yellow colouration in solution or a canary yellow precipitate of ammonium-phosphomolybdate, $(NH_4)_3[P\ (Mo_3O_{10})_4]$ is formed. Each oxygen of phosphate has been replaced by Mo_3O_{10} group.

$$Na_2HPO_4 + 12\ (NH_4)_2\ MoO_4 + 23\ HNO_3 \longrightarrow \underset{\substack{\text{Canary yellow} \\ \text{precipitate}}}{(NH_4)_3[P\ (Mo_3O_{10})_4]} + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$$

SYSTEMATIC ANALYSIS OF CATIONS

The tests for cations may be carried out according to the following scheme.

Step - I : Preliminary Examination of the Salt for Identification of Cation

1. Colour Test

Observe the colour of the salt carefully, which may provide useful information about the cations. Table 7.6 gives the characteristic colours of the salts of some cations.

Table 7.6 : Characteristic colours of some metal ions

Colour	Cations Indicated
Light green, Yellow, Brown	Fe^{2+}, Fe^{3+}
Blue	Cu^{2+}
Bright green	Ni^{2+}
Blue, Red, Violet, Pink	Co^{2+}
Light pink	Mn^{2+}

2. Dry Heating Test

(i) Take about 0.1 g of the dry salt in a clean and dry test tube.

(ii) Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold. Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence (see Table 7.7).

Table 7.7 : Inferences from the colour of the salt in cold and on heating

Colour when cold	Colour when hot	Inference
Blue	White	Cu^{2+}
Green	Dirty white or yellow	Fe^{2+}
White	Yellow	Zn^{2+}
Pink	Blue	Co^{2+}

3. Flame Test

The chlorides of several metals impart characteristic colour to the flame because they are volatile in non-luminous flame. This test is performed with the help of a platinum wire as follows :

(i) Make a tiny loop at one end of a platinum wire.

(ii) To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame (Fig. 7.3).

(iii) Repeat step (ii) until the wire imparts no colour to the flame.

(iv) Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.

(v) Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame (Fig. 7.3).

(vi) Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion with the help of Table 7.8.

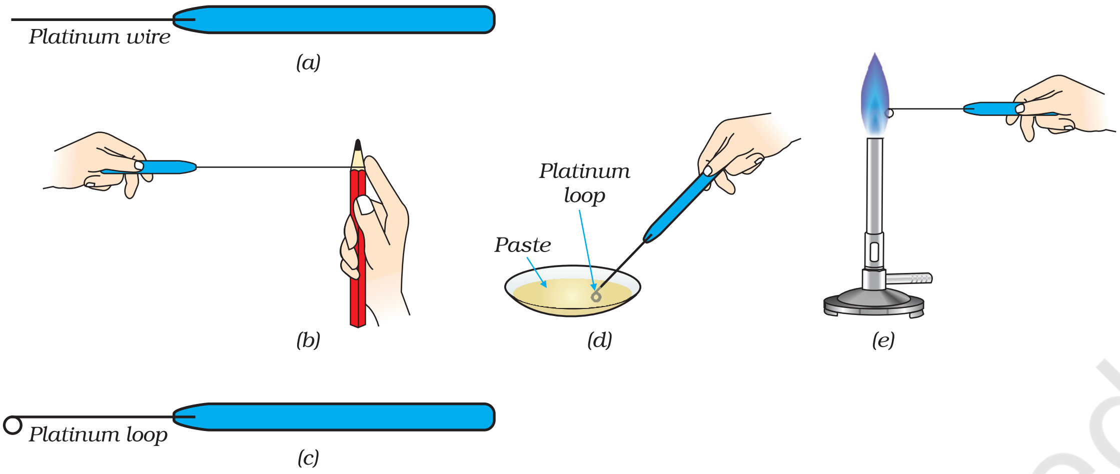


Fig.7.3 : *Performing flame test*

Table 7.8 : Inference from the flame test

Colour of the flame observed by naked eye	Colour of the flame observed through blue glass	Inference
Green flame with blue centre	Same colour as observed without glass	Cu^{2+}
Crimson red	Purple	Sr^{2+}
Apple green	Bluish green	Ba^{2+}
Brick red	Green	Ca^{2+}

4. Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

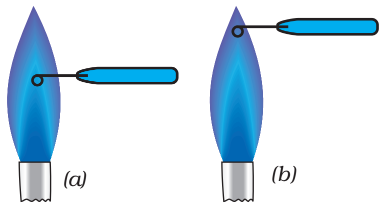


Fig. 7.4 *: Borax bead test (a) Heating in reducing flame (b) Heating in oxidising flame*

(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.

(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.

(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.

(iv) Observe the colour imparted to the bead in the non - luminous flame as well as in the luminous flame while it is hot and when it is cold (Fig. 7.4).

(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger. (Fig. 7.5).

On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.

$$\underset{\text{Borax}}{Na_2B_4O_7 \cdot 10H_2O} \longrightarrow Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

On treatment with metal salt, boric anhydride forms metaborate of the metal which gives different colours in oxidising and reducing flame. For example, in the case of copper sulphate, following reactions occur.

$$CuSO_4 + B_2O_3 \xrightarrow{\text{Non-luminous flame}} \underset{\substack{\text{Cupric metaborate}\\ \text{Blue-green}}}{Cu(BO_2)_2} + SO_3$$

Two reactions may take place in the reducing flame:

(i) The blue $Cu(BO_2)_2$ is reduced to colourless cuprous metaborate as follows:

$$2Cu(BO_2)_2 + 2NaBO_2 + C \xrightarrow{\text{Luminous flame}} 2CuBO_2 + Na_2B_4O_7 + CO$$

or (ii) Cupric metaborate may be reduced to metallic copper and the bead appears red and opaque.

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C \xrightarrow{\text{Luminous flame}} 2Cu + 2Na_2B_4O_7 + 2CO$$

The preliminary identification of metal ion can be made from Table 7.9.

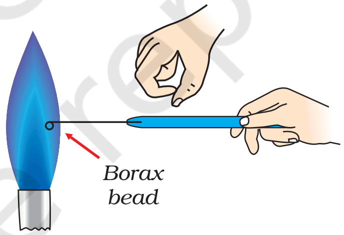


***Fig. 7.5** : Removing borax bead*

Table 7.9 : Inference from the borax bead test

Heating in oxidising (non-luminous) flame		Heating in reducing (luminous) flame		Inference
Colour of the salt bead		Colour of the salt bead		
In cold	**In hot**	**In cold**	**In hot**	
Blue	Green	Red opaque	Colourless	Cu^{2+}
Reddish brown	Violet	Grey	Grey	Ni^{2+}
Light violet	Light violet	Colourless	Colourless	Mn^{2+}
Yellow	Yellowish brown	Green	Green	Fe^{3+}

5. Charcoal Cavity Test

Metallic carbonate when heated in a charcoal cavity decomposes to give corresponding oxide. The oxide appears as a coloured residue in the cavity. Sometimes oxide may be reduced to metal by the carbon of the charcoal cavity. The test may be performed as follows:

(i) Make a small cavity in a charcoal block with the help of a charcoal borer. Do not apply pressure otherwise it will crack [Fig.7.6 (a)].

(ii) Fill the cavity with about 0.2 g of the salt and about 0.5 g of anhydrous sodium carbonate.

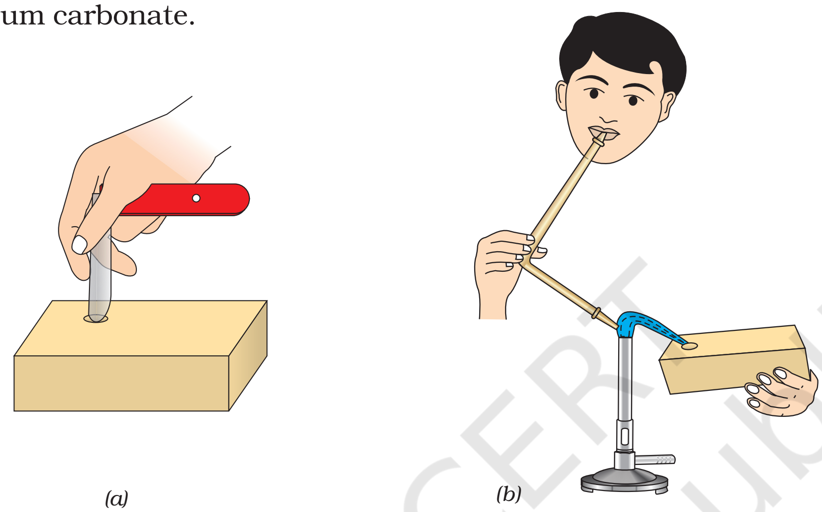
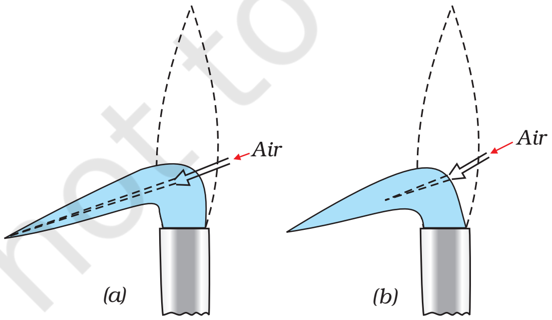


Fig. 7.6 : *(a) Making charcoal cavity (b) Heating salt in the cavity*

(iii) Moisten the salt in the cavity with one or two drops of water, otherwise salt/mixture will blow away.

(iv) Use a blowpipe to heat the salt in a luminous (reducing) flame and observe the colour of oxide/ metallic bead formed in the cavity both when hot and cold [Fig. (7.6 b)]. Obtain oxidising and reducing flame as shown in Fig. 7.7 a and b.

(v) Always bore a fresh cavity for testing the new salt.



Note :
- *To obtain oxidising flame hold the nozzle of the blowpipe about one third within the flame.*
- *To obtain reducing flame place nozzle of the blowpipe just outside the flame.*

Fig. 7.7 : *Obtaining oxidising and reducing flame (a) Oxidising flame (b) Reducing flame*

When test is performed with $CuSO_4$, the following change occurs.

$$CuSO_4 + Na_2CO_3 \xrightarrow{\text{Heat}} CuCO_3 + Na_2\,SO_4$$

$$CuCO_3 \xrightarrow{\text{Heat}} CuO + CO_2$$

$$CuO + C \xrightarrow{\text{Heat}} \underset{\text{Red colour}}{Cu} + CO$$

In case of $ZnSO_4$:

$$ZnSO_4 + Na_2CO_3 \xrightarrow{\text{Heat}} ZnCO_3 + Na_2\,SO_4$$

$$ZnCO_3 \xrightarrow{\text{Heat}} ZnO + CO_2$$

Yellow when hot,
White when cold

The metal ion can be inferred from Table 7.10.

Table 7.10 : Inference from the charcoal cavity test

Observations	Inference
Yellow residue when hot and grey metal when cold	Pb^{2+}
White residue with the odour of garlic	As^{3+}
Brown residue	Cd^{2+}
Yellow residue when hot and white when cold	Zn^{2+}

6. Cobalt Nitrate Test

If the residue in the charcoal cavity is white, cobalt nitrate test is performed.

(i) Treat the residue with two or three drops of cobalt nitrate solution.

(ii) Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue.

On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity.

Thus, with ZnO, Al_2O_3 and MgO, the following reactions occur.

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

$$CoO + ZnO \longrightarrow \underset{\text{Green}}{CoO.ZnO}$$

$$CoO + MgO \longrightarrow \underset{\text{Pink}}{CoO.\,MgO}$$

$$CoO + Al_2O_3 \longrightarrow \underset{\text{Blue}}{CoO.\,Al_2O_3}$$

Step-II : Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below.

The first essential step is to prepare a clear and transparent solution of the salt. This is called **original solution**. It is prepared as follows:

Preparation of Original Solution (O.S.)

To prepare the original solution, following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent.

The following solvents are tried:

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolved, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil.HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO_3 in the ratio 3:1 is tried. This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

Group Analysis

(I) Analysis of Group-zero cation (NH_4^+ ion)

(a) Take 0.1 g of salt in a test tube and add 1-2 mL of NaOH solution to it and heat. If there is a smell of ammonia, this indicates the presence of ammonium ions. Bring a glass rod dipped in hydrochloric acid near the mouth of the test tube. White fumes are observed.

(b) Pass the gas through Nessler's reagent. Brown precipitate is obtained.

Chemistry of Confirmatory Tests for NH_4^+ ion

(a) Ammonia gas evolved by the action of sodium hydroxide on ammonium salts reacts with hydrochloric acid to give ammonium chloride, which is visible as dense white fume.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$NH_3 + HCl \rightarrow NH_4Cl$$

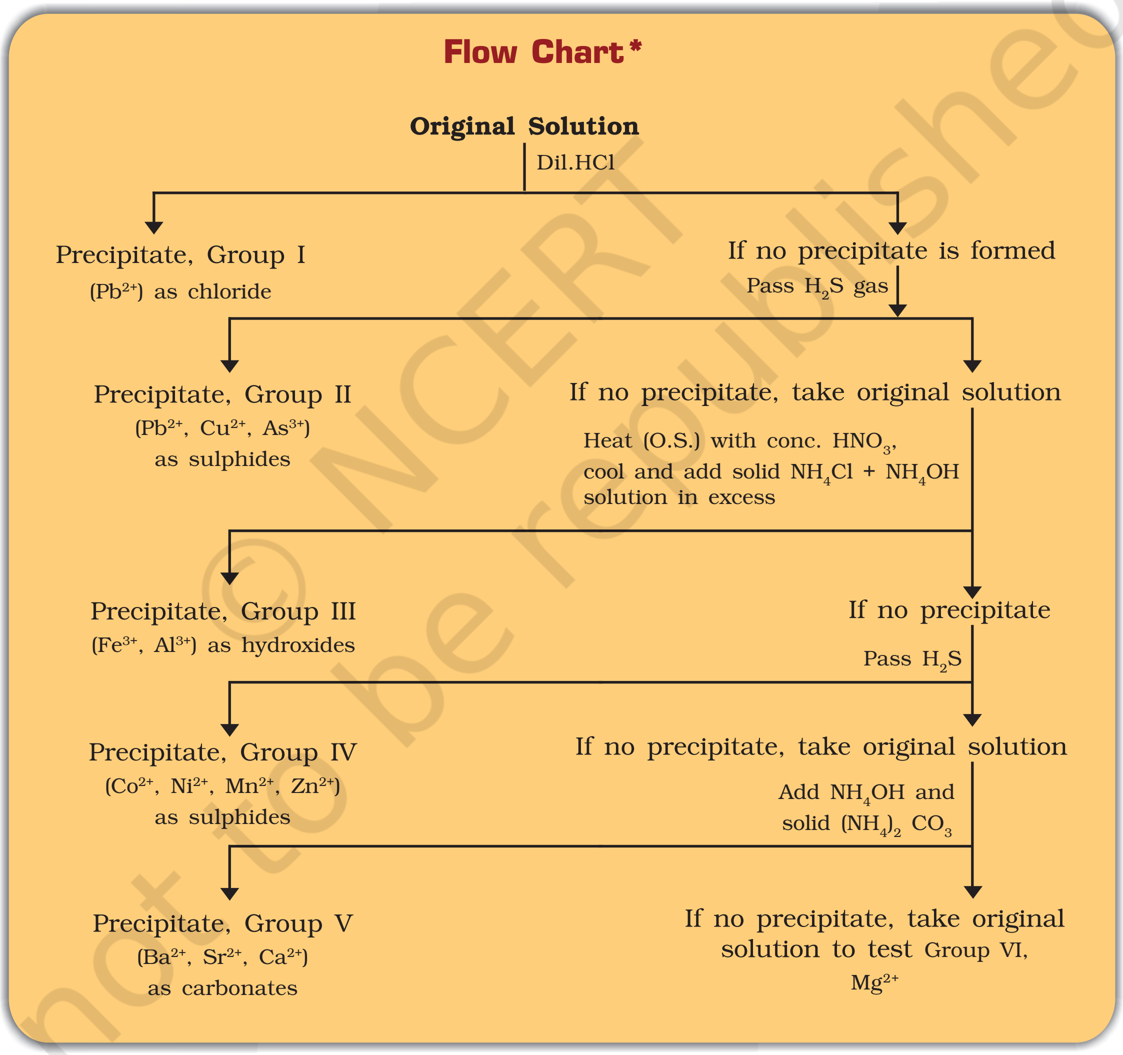
On passing the gas through Nessler's reagent, a brown colouration or a precipitate of basic mercury(II) amido-iodine is formed.

Mercury Salts

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow \underset{\substack{\text{Basic mercury (II)}\\ \text{amido-iodine}\\ \text{(Brown precipitate)}}}{HgO.Hg(NH_2)I} + 7KI + 2H_2O$$

For the analysis of cations belonging to groups I-VI, the cations are precipitated from the original solution by using the group reagents (see Table 7.11) according to the scheme shown in the flow chart given below:

The separation of all the six groups is represented as below:



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* *This flow chart is for the detection of one cation only.*
For detection of more than one cation modification will be required.

Table 7.11 : Group reagents for precipitating ions

Group	Cations*	Group Reagent
Group zero	NH_4^+	None
Group-I	Pb^{2+}	Dilute HCl
Group-II	Pb^{2+}, Cu^{2+}, As^{3+}	H_2S gas in presence of dil. HCl
Group-III	Al^{3+}, Fe^{3+}	NH_4OH in presence of NH_4Cl
Group-IV	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}	H_2S in presence of NH_4OH
Group-V	Ba^{2+}, Sr^{2+}, Ca^{2+}	$(NH_4)_2CO_3$ in presence of NH_4OH
Group-VI	Mg^{2+}	None

(II) Analysis of Group-I cations

Take a small amount of original solution (if prepared in hot conc. HCl) in a test tube and add cold water to it and cool the test tube under tap water. If a white precipitate appears, this indicates the presence of Pb^{2+} ions in group –I. On the other hand, if the original solution is prepared in water and on addition of dil. HCl, a white precipitate appears, this may also be Pb^{2+}. Confirmatory tests are described below in Table 7.12.

Table 7.12 : Confirmatory tests for Group-I cation (Pb^{2+})

Experiment	Observation
Dissolve the precipitate in hot water and divide the hot solution into three parts.	
1. Add potassium iodide solution to the first part.	A yellow precipitate is obtained.
2. To the second part add potassium chromate solution.	A yellow precipitate is obtained which is soluble in NaOH and insoluble in ammonium acetate solution.
3. To the third part of the hot solution add few drops of alcohol and dilute sulphuric acid.	A white precipitate is obtained which is soluble in ammonium acetate solution.

Chemistry of the Confirmatory Tests of Pb^{2+} ions

Lead is precipitated as lead chloride in the first group. The precipitate is soluble in hot water.

1. On adding potassium iodide (KI) solution, a yellow precipitate of lead iodide is obtained which confirms the presence of Pb^{2+} ions.

$$\underset{\text{(Hot solution)}}{PbCl_2} + 2KI \longrightarrow \underset{\text{Yellow precipitate}}{PbI_2} + 2KCl$$

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* *Here only those cations are given which are in the syllabus.*

This yellow precipitate (PbI_2) is soluble in boiling water and reappears on cooling as shining crystals.

2. On addition of potassium chromate (K_2CrO_4) solution a yellow precipitate of lead chromate is obtained. This confirms the presence of Pb^{2+} ions.

$$\underset{\text{(Hot solution)}}{PbCl_2} + K_2CrO_4 \longrightarrow \underset{\substack{\text{Lead chromate}\\\text{(Yellow precipitate)}}}{PbCrO_4} + 2KCl$$

The yellow precipitate ($PbCrO_4$) is soluble in hot NaOH solution.

$$PbCrO_4 + 4NaOH \rightleftharpoons \underset{\substack{\text{Sodium tetra}\\\text{hydroxoplumbate (II)}}}{Na_2[Pb(OH)_4]} + Na_2CrO_4$$

3. A white precipitate of lead sulphate ($PbSO_4$) is formed on addition of alcohol followed by dil. H_2SO_4.

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\substack{\text{Lead sulphate}\\\text{(White precipitate)}}}{PbSO_4} + 2\,HCl$$

Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetoplumbate(II) ions. This reaction may be promoted by addition of few drops of acetic acid.

Hydrogen sulphide

$$PbSO_4 + 4\,CH_3COONH_4 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{tetraacetoplumbate(II)}}}{(NH_4)_2\,[Pb(CH_3COO)_4]} + (NH_4)_2SO_4$$

(III) Analysis of Group–II cations

If group-I is absent, add excess of water to the same test tube. Warm the solution and pass H_2S gas for 1-2 minutes (Fig. 7.6). Shake the test tube. If a precipitate appears, this indicates the presence of group-II cations. Pass more H_2S gas through the solution to ensure complete precipitation and separate the precipitate. If the colour of the precipitate is black, it indicates the presence of Cu^{2+} or Pb^{2+} ions. If it is yellow in colour, then presence of As^{3+} ions is indicated.

Take the precipitate of group-II in a test tube and add excess of yellow ammonium sulphide solution to it. Shake the test tube. If the precipitate is insoluble, **group II-A (copper group)** is present. If the precipitate is soluble, this indicates the presence of **group-II B (arsenic group)**.

Confirmatory tests for the groups II A and II B are given in Table 7.13.

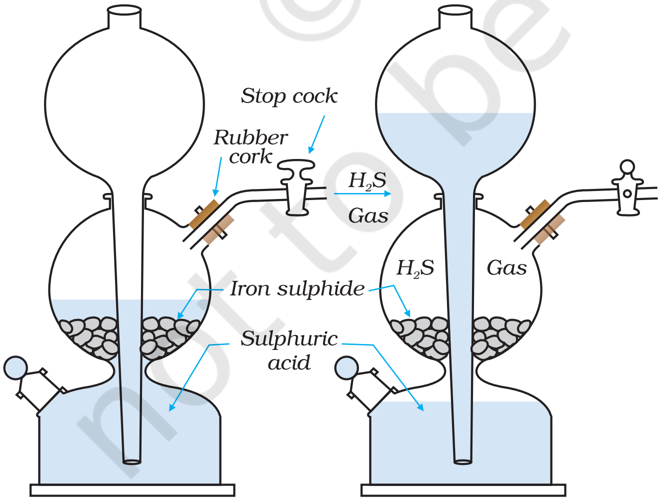


Fig. 7.8 : *Kipp's apparatus for preparation of H_2S gas*

Table 7.13 : Confirmatory tests for Group-II A and II B cations

<table>
<tr><td colspan="2">Black precipitate of Group II A ions (Pb^{2+}, Cu^{2+}) insoluble in yellow ammonium sulphide is formed.</td><td>If a yellow precipitate soluble in yellow ammonium sulphide is formed then As^{3+} ion is present.</td></tr>
<tr><td colspan="2">Boil the precipitate of Group II A with dilute nitric acid and add a few drops of alcohol and dil. H_2SO_4.</td><td rowspan="2">Acidify this solution with dilute HCl. A yellow precipitate is formed. Heat the precipitate with concentrated nitric acid and add ammonium molybdate solution. A canary yellow precipitate is formed.</td></tr>
<tr><td>White precipitate confirms the presence of Pb^{2+} ions. Dissolve the precipitate in ammonium acetate solution. Acidify with acetic acid and divide the solution into two parts.
(i) To the first part add potassium chromate solution, a yellow precipitate is formed.
(ii) To the second part, add potassium iodide solution, a yellow precipitate is formed.</td><td>If no precipitate is formed, add excess of ammonium hydroxide solution. A blue solution is obtained, acidify it with acetic acid and add potassium ferrocyanide solution. A chocolate brown precipitate is formed.</td></tr>
</table>

Group-II A (Copper Group)

Alcohol 🔥 ☠

Chemistry of confirmatory tests of Group-II A cations

1. Test for Lead ion (Pb^{2+})

Lead sulphide precipitate dissolves in dilute HNO_3. On adding dil. H_2SO_4 and a few drops of alcohol to this solution a white precipitate of lead sulphate appears. This indicates the presence of lead ions.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$$

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HNO_3$$

The white precipitate dissolves in ammonium acetate solution on boiling. When this solution is acidified with acetic acid and potassium chromate solution is added, a yellow precipitate of $PbCrO_4$ is formed. On adding potassium iodide solution, a yellow precipitate of lead iodide is formed.

$$PbSO_4 + 4CH_3COONH_4 \longrightarrow (NH_4)_2[Pb(CH_3COO)_4] + (NH_4)_2SO_4$$

$$\underset{\text{Ammonium tetraacetoplumbate(II)}}{(NH_4)_2[Pb(CH_3COO)_4]} + K_2CrO_4 \longrightarrow \underset{\text{Yellow precipitate}}{PbCrO_4} + 2CH_3COOK + 2(NH_4)_2SO_4$$

2. Test for Copper ion (Cu^{2+})

(a) Copper sulphide dissolves in nitric acid due to the formation of copper nitrate.

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

On heating the reaction mixture for long time, sulphur is oxidised to sulphate and copper sulphate is formed and the solution turns blue. A small amount of NH_4OH precipitates basic copper sulphate which is soluble in excess of ammonium hydroxide due to the formation of tetraamminecopper (II) complex.

$$S + 2HNO_3 \longrightarrow H_2SO_4 + 2NO$$

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

$$Cu(OH)_2.CuSO_4 + 8NH_3 \longrightarrow \underset{\substack{\text{Tetraamminecopper (II)}\\ \text{sulphate (Deep blue)}}}{2\,[Cu(NH_3)_4]SO_4} + 2OH^- + SO_4^{2-}$$

(b) The blue solution on acidification with acetic acid and then adding potassium ferrocyanide $[K_4Fe(CN)_6]$ solution gives a chocolate colouration due to the formation of copper ferrocyanide i.e. $Cu_2[Fe(CN)_6]$.

$$[Cu(NH_3)_4]\,SO_4 + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$2CuSO_4 + \underset{\substack{\text{Potassium}\\ \text{hexacyanoferrate (II)}}}{K_4[Fe(CN)_6]} \longrightarrow \underset{\substack{\text{Copper}\\ \text{hexacyanoferrate (II)}\\ \text{(Chocolate brown precipitate)}}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

Group-II B (Arsenic Group)

If group- II precipitate dissolves in yellow ammonium sulphide and the colour of the solution is yellow, this indicates the presence of As^{3+} ions. Ammonium thioarsenide formed on dissolution of As_2S_3 decomposes with dil. HCl, and a yellow precipitate of arsenic (V) sulphide is formed which dissolves in concentrated nitric acid on heating due to the formation of arsenic acid. On adding ammonium molybdate solution to the reaction mixture and heating, a canary yellow precipitate is formed. This confirms the presence of As^{3+} ions.

$$As_2S_3 + \underset{\substack{\text{Yellow ammonium}\\ \text{sulphide}}}{3\,(NH_4)_2S_2} \longrightarrow 2\,(NH_4)_3As\,S_4 + S$$

$$2(NH_4)_3AsS_4 + 6HCl \longrightarrow As_2S_5 + 3H_2S + 6NH_4Cl$$

$$3As_2S_5 + 10HNO_3 + 4H_2O \longrightarrow \underset{\text{Arsenic acid}}{6H_3AsO_4} + 10NO + 15S$$

$$\underset{\text{Arsenic acid}}{H_3AsO_4} + \underset{\substack{\text{Ammonium}\\\text{molybdate}}}{12(NH_4)_2\,MoO_4} + 21HNO_3 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{arsinomolybdate}\\\text{(yellow precipitate)}}}{(NH_4)_3[As\,(Mo_3\,O_{10})_4]} + 21NH_4NO_3 + 12H_2O$$

(IV) Analysis of Group–III cations

If group-II is absent, take original solution and add 2-3 drops of conc. HNO_3 to oxidise Fe^{2+} ions to Fe^{3+} ions. Heat the solution for a few minutes. After cooling add a small amount of solid ammonium chloride (NH_4Cl) and an excess of ammonium hydroxide (NH_4OH) solution till it smells of ammonia. Shake the test tube. If a brown or white precipitate is formed, this indicates the presence of group-III cations. Confirmatory tests of group-III cations are summarised in Table 7.14.

Observe the colour and the nature of the precipitate. A gelatinous white precipitate indicates the presence of aluminium ion ($A1^{3+}$). If the precipitate is brown in colour, this indicates the presence of ferric ions (Fe^{3+}).

Table 7.14 : Confirmatory test for Group-III cations

Brown precipitate $\mathbf{Fe^{3+}}$	**White precipitate** $\mathbf{Al^{3+}}$
Dissolve the precipitate in dilute HCl and divide the solution into two parts. (a) To the first part add potassium ferrocyanide solution [Potasium hexacyanoferrate (II)]. A blue precipitate/colouration appears. (b) To the second part add potassium thiocyanate solution. A blood red colouration appears.	Dissolve the white precipitate in dilute HCl and divide into two parts. (a) To the first part add sodium hydroxide solution and warm. A white gelatinous precipitate soluble in excess of sodium hydroxide solution. (b) To the second part first add blue litmus solution and then ammonium hydroxide solution drop by drop along the sides of the test tube. A blue floating mass in the colourless solution is obtained.

Chemistry of confirmatory tests of Group-III cations

When original solution is heated with concentrated nitric acid, ferrous ions are oxidised to ferric ions.

$$2FeCl_2 + 2HCl + [O] \longrightarrow 2FeCl_3 + H_2O$$

Third group cations are precipitated as their hydroxides, which dissolve in dilute hydrochloric acid due to the formation of corresponding chlorides.

1. Test for Aluminium ions ($A1^{3+}$)

(a) When the solution containing aluminium chloride is treated with sodium hydroxide, a white gelatinous precipitate of aluminium hydroxide is formed which is soluble in excess of sodium hydroxide solution due to the formation of sodium aluminate.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$

$$\underset{\substack{\text{White gelatinous}\\ \text{precipitate}}}{Al(OH)_3} + NaOH \longrightarrow \underset{\substack{\text{Sodium}\\ \text{aluminate}}}{NaAlO_2} + 2H_2O$$

(b) In the second test when blue litmus is added to the solution, a red colouration is obtained due to the acidic nature of the solution. On addition of NH_4OH solution drop by drop the solution becomes alkaline and aluminium hydroxide is precipitated. Aluminium hydroxide adsorbs blue colour from the solution and forms insoluble adsorption complex named 'lake'. Thus a blue mass floating in the colourless solution is obtained. The test is therefore called **lake test**.

2. Test for ferric ions (Fe^{3+})

Reddish brown precipitate of ferric hydroxide dissolves in hydrochloric acid and ferric chloride is formed.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

(a) When the solution containing ferric chloride is treated with potassium ferrocyanide solution a blue precipitate/colouration is obtained. The colour of the precipitate is Prussian blue. It is ferric ferro-cyanide. The reaction takes place as follows:

$$4FeCl_3 + \underset{\substack{\text{Potassium}\\ \text{ferrocyanide}}}{3K_4[Fe(CN)_6]} \longrightarrow \underset{\substack{\text{Prussian blue}\\ \text{precipitate}}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

If potassium hexacyanoferrate (II) (i.e. potassium ferrocyanide) is added in excess then a product of composition $KFe[Fe(CN)_6]$ is formed. This tends to form a colloidal solution ('soluble Prussian blue') and cannot be filtered.

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Soluble prussian blue)}}{KFe[Fe(CN)_6]} + 3KCl$$

(b) To the second part of the solution, add potassium thiocyanate (potassium sulphocyanide) solution. The appearance of a blood red colouration confirms the presence of Fe^{3+} ions.

$$Fe^{3+} + SCN^{-} \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)]^{2+}}$$

(V) Analysis of Group-IV cations

If Group-III is absent, pass H_2S gas in the solution of group-III for a few minutes. If a precipitate appears (white, black or flesh coloured), this indicates the presence of group-IV cations. Table 7.15 gives a summary of confirmatory tests of group-IV cations.

Table 7.15 : Confirmatory test for Group-IV cations

White precipitate (Zn^{2+})	**Flesh coloured precipitate (Mn^{2+})**	**Black precipitate (Ni^{2+}, Co^{2+})**
Dissolve the precipitate in dilute HCl by boiling. Divide the solution into two parts. (a) To the first part add sodium hydroxide solution. A white precipitate soluble in excess of sodium hydroxide solution confirms the presence of Zn^{2+} ions. (b) Neutralise the second part with ammonium hydroxide solution and add potassium ferrocyanide solution. A bluish white precipitate appears.	Dissolve the precipitate in dilute HCl by boiling, then add sodium hydroxide solution in excess. A white precipitate is formed which turns brown on keeping.	Dissolve the precipitate in aqua regia. Heat the solution to dryness and cool. Dissolve the residue in water and divide the solution into two parts. (a) To the first part of the solution add ammonium hydroxide solution till it becomes alkaline. Add a few drops of dimethyl glyoxime and shake the test tube. Formation of a bright red precipitate confirms the presence of Ni^{2+} ions. (b) Neutralise the second part with ammonium hydroxide solution. Acidify it with dilute acetic acid and add solid potassium nitrite. A yellow precipitate confirms the presence of Co^{2+} ions.

Chemistry of confirmatory tests of Group–IV cations

Fourth group cations are precipitated as their sulphides. Observe the colour of the precipitate. A white colour of the precipitate indicates the presence of zinc ions, a flesh colour indicates the presence of manganese ions and a black colour indicates the presence of Ni^{2+} or Co^{2+} ions.

1. Test for Zinc ion (Zn^{2+})

Zinc sulphide dissolves in hydrochloric acid to form zinc chloride.

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$$

(a) On addition of sodium hydroxide solution it gives a white precipitate of zinc hydroxide, which is soluble in excess of NaOH solution on heating. This confirms the presence of Zn^{2+} ions.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + 2H_2O$$

(b) When potassium ferrocyanide $K_4Fe(CN)_6$ solution is added to the solution after neutralisation by NH_4OH solution, a white or a bluish white precipitate of zinc ferrocyanide appears.

$$2\,ZnCl_2 + K_4\,[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Zinc}\\ \text{ferrocyanide}}}{Zn_2\,[Fe(CN)_6]} + 4\,KCl$$

2. Test for Manganese ion (Mn^{2+})

Manganese sulphide precipitate dissolves in dil. HCl on boiling. On addition of NaOH solution in excess, a white precipitate of manganese hydroxide is formed which turns brown due to atmospheric oxidation into hydrated manganese dioxide.

$$MnS + 2HCl \longrightarrow Mn\,Cl_2 + H_2S$$

$$MnCl_2 + 2NaOH \longrightarrow \underset{\text{(White precipitate)}}{Mn(OH)_2} + 2NaCl$$

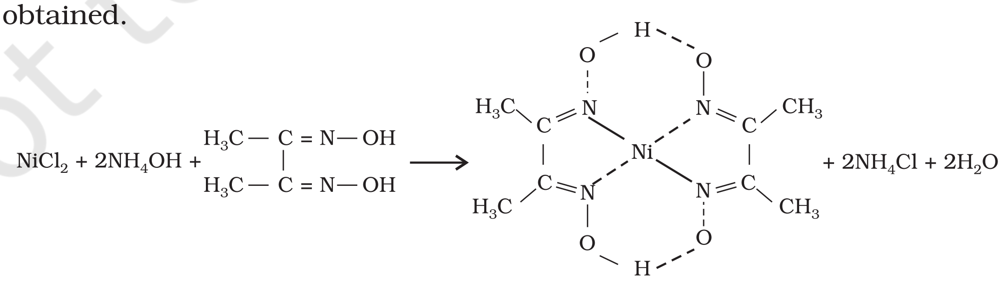
$$Mn\,(OH)_2 + [O] \rightarrow \underset{\substack{\text{Hydrated manganese dioxide}\\ \text{(Brown colour)}}}{MnO(OH)_2}$$

3. Test for Nickel ion (Ni^{2+})

The black precipitate of nickel sulphide dissolves in aqua regia and the reaction takes place as follows:

$$3NiS + 2HNO_3 + 6HCl \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$$

After treatment with aqua regia nickel-chloride is obtained which is soluble in water. When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding NH_4OH solution, a brilliant red precipitate is obtained.



Complex of red colour
(Stable form of complex)

4. Test for Cobalt ion (Co^{2+})

Cobalt sulphide dissolves in aqua regia in the same manner as nickel sulphide. When the aqueous solution of the residue obtained after treatment with aqua regia is treated with a strong solution of potassium nitrite after neutralisation with ammonium hydroxide and the solution is acidified with dil. acetic acid, a yellow precipitate of the complex of cobalt named potassium hexanitritocobaltate (III) is formed.

$$CoS + HNO_3 + 3HCl \longrightarrow CoCl_2 + NOCl + S + 2H_2O$$

$$CoCl_2 + 7KNO_2 + 2CH_3COOH \longrightarrow K_3[Co(NO_2)_6] + 2KCl + 2CH_3COOK + NO + H_2O$$

Potassium
hexanitritocobaltate(III)
(Yellow precipitate)

(VI) Analysis of Group–V cations

If group-IV is absent then take original solution and add a small amount of solid NH_4Cl and an excess of NH_4OH solution followed by solid ammonium carbonate $(NH_4)_2CO_3$. If a white precipitate appears, this indicates the presence of group–V cations.

Dissolve the white precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba^{2+}, Sr^{2+} and Ca^{2+} ions. **Preserve a small amount of the precipitate for flame test**. Summary of confirmatory tests is given in Table 7.16.

Table 7.16 : Confirmatory test for Group–V cations

Dissolve the precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba^{2+}, Sr^{2+} and Ca^{2+} ions		
Ba^{2+} ions	**Sr^{2+} ions**	**Ca^{2+} ions**
(a) To the first part add potassium chromate solution. A yellow precipitate appears. (b) Perform the flame test with the preserved precipitate. A grassy green flame is obtained.	(a) If barium is absent, take second part of the solution and add ammonium sulphate solution. Heat and scratch the sides of the test tube with a glass rod and cool. A white precipitate is formed. (b) Perform the flame test with the preserved precipitate. A crimson-red flame confirms the presence of Sr^{2+} ions.	(a) If both barium and strontium are absent, take the third part of the solution. Add ammonium oxalate solution and shake well. A white precipitate of calcium oxalate is obtained. (b) Perform the flame test with the preserved precipitate. A brick red flame, which looks greenish-yellow through blue glass, confirms the presence of Ca^{2+} ions.

Chemistry of Confirmatory Tests of Group–V cations

The Group–V cations are precipitated as their carbonates which dissolve in acetic acid due to the formation of corresponding acetates.

1. Test for Barium ion (Ba^{2+})

(a) Potassium chromate (K_2CrO_4) solution gives a yellow precipitate of barium chromate when the solution of fifth group precipitate in acetic acid is treated with it.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2\,Ba + H_2O + CO_2$$

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\substack{\text{Barium chromate}\\ \text{(yellow precipitate)}}}{BaCrO_4} + 2CH_3COOK$$

(b) **Flame test –** Take a platinum wire and dip it in conc. HCl. Heat it strongly until the wire does not impart any colour to the non-luminous flame. Now dip the wire in the paste of the (Group–V) precipitate in conc. HCl. Heat it in the flame. A grassy green colour of the flame confirms the presence of Ba^{2+} ions.

2. Test for Strontium ion (Sr^{2+})

(a) Solution of V group precipitate in acetic acid gives a white precipitate of strontium sulphate with ammonium sulphate, $(NH_4)_2SO_4$, solution on heating and scratching the sides of the test tube with a glass rod.

$$SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2\,Sr + H_2O + CO_2$$

$$(CH_3COO)_2\,Sr + (NH_4)_2SO_4 \longrightarrow \underset{\substack{\text{Strontium}\\ \text{sulphate}\\ \text{(White precipitate)}}}{SrSO_4} + 2CH_3COONH_4$$

(b) **Flame test –** Perform the flame test as given in the case of Ba^{2+}. A crimson red flame confirms the presence of Sr^{2+} ions.

3. Test for Calcium ion (Ca^{2+})

(a) Solution of the fifth group precipitate in acetic acid gives a white precipitate with ammonium oxalate solution.

$$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2\,Ca + H_2O + CO_2$$

$$(CH_3COO)_2Ca + \underset{\substack{\text{Ammonium}\\ \text{oxalate}}}{(NH_4)_2C_2O_4} \longrightarrow \underset{\substack{\text{Calcium oxalate}\\ \text{(White precipitate)}}}{(COO)_2Ca} + 2CH_3COONH_4$$

(b) **Flame test –** Perform the flame test as mentioned above. Calcium imparts brick red colour to the flame which looks greenish-yellow through blue glass.

(VII) Analysis of Group–VI cations

If group–V is absent then perform the test for Mg^{2+} ions as given below.

Chemistry of Confirmatory Tests of Group–VI cations

Test for Magnesium ion (Mg^{2+})

(a) If group–V is absent the solution may contain magnesium carbonate, which is soluble in water in the presence of ammonium salts because the equilibrium is shifted towards the right hand side.

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

The concentration of carbonate ions required to produce a precipitate is not attained. When disodium hydrogenphosphate solution is added and the inner walls of the test tube are scratched with a glass rod, a white crystalline precipitate of magnesium ammonium phosphate is formed which indicates the presence of Mg^{2+} ions.

$$Mg^{2+} + Na_2HPO_4 \longrightarrow \underset{\text{Magnesium ammonium phosphate (White precipitate)}}{Mg(NH_4)PO_4} + NH_4OH + 2Na^+ + H_2O$$

Note down the observations and the inferences of the qualitative analysis in tabular form as given in the specimen record given in pages 114-115.

Note : *Some times precipitate of magnesium ammonium phosphate appears after some time. So warm the solution and scrach the sides of test tube after adding sodium hydrogen phosphate solution.*

Precautions

(a) Always use an apron, an eye protector and hand gloves while working in the chemistry laboratory.

(b) Before using any reagent or a chemical, read the label on the bottle carefully. Never use unlabelled reagent.

(c) Do not mix chemicals and reagents unnecessarily. Never taste any chemical.

(d) Be careful in smelling chemicals or vapours. Always fan the vapours gently towards your nose (Fig. 7.9).

(e) Never add sodium metal to water or throw it in the sink or dustbin.

(f) Always pour acid into water for dilution. Never add water to acid.

(g) Be careful while heating the test tube. The test tube should never point towards yourself or towards your neighbours while heating or adding a reagent.

Fig. 7.9 : *How to smell a gas*

(h) Be careful while dealing with the explosive compounds, inflammable substances, poisonous gases, electric appliances, glass wares, flame and the hot substances.
(i) Keep your working surroundings clean. Never throw papers and glass in the sink. Always use dustbin for this purpose.
(j) Always wash your hands after the completion of the laboratory work.
(k) Always use the reagents in minimum quantity. Use of reagents in excess, not only leads to wastage of chemicals but also causes damage to the environment.

Discussion Questions

(i) What is the difference between a qualitative and a quantitative analysis?

(ii) Can we use glass rod instead of platinum wire for performing the flame test? Explain your answer.

(iii) Why is platinum metal preferred to other metals for the flame test?

(iv) Name the anions detected with the help of dilute H_2SO_4?

(v) Why is dilute H_2SO_4 preferred over dilute HCl while testing anions?

(vi) Name the anions detected by conc. H_2SO_4.

(vii) How is sodium carbonate extract prepared ?

(viii) What is lime water and what happens on passing carbon dioxide gas through it?

(ix) Carbon dioxide gas and sulphur dioxide gas both turn lime water milky. How will you distinguish between the two?

(x) How will you test the presence of carbonate ion?

(xi) What is the composition of dark brown ring which is formed at the junction of two layers in the ring test for nitrates?

(xii) Name the radical confirmed by sodium nitroprusside test.

(xiii) What is chromyl chloride test ? How do you justify that CrO_2Cl_2 is acidic in nature?

(xiv) Why do bromides and iodides not give tests similar to chromyl chloride test?

(xv) Describe the layer test for bromide and iodide ions.

(xvi) Why is silver nitrate solution stored in dark coloured bottles?

(xvii) How do you test the presence of sulphide ion?

(xviii) Why does iodine give a blue colour with starch solution?

(xix) What is Nessler's reagent?

(xx) Why is original solution for cations not prepared in conc. HNO_3 or H_2SO_4?

(xxi) Why cannot conc. HCl be used as a group reagent in place of dil. HCl for the precipitation of Ist group cations?

(xxii) How can one prevent the precipitation of Group–IV radicals, with the second group radicals?

(xxiii) Why is it essential to boil off H_2S gas before precipitation of radicals of group–III?

(xxiv) Why is heating with conc. nitric acid done before precipitation of group–III?

(xxv) Can we use ammonium sulphate instead of ammonium chloride in group–III?

(xxvi) Why is NH_4OH added before $(NH_4)_2CO_3$ solution while precipitating group–V cations?

(xxvii) Why do we sometimes get a white precipitate in group–VI even if the salt does not contain Mg^{2+} radical?

(xxviii) What is aqua regia?

(xxix) Name a cation, which is not obtained from a metal.

(xxx) How can you test the presence of ammonium ion?

(xxxi) Why are the group–V radicals tested in the order Ba^{2+}, Sr^{2+} and Ca^{2+}?

(xxxii) Why does conc. HNO_3 kept in a bottle turn yellow in colour?

(xxxiii) Why should the solution be concentrated before proceeding to group–V?

(xxxiv) Why is the reagent bottle containing sodium hydroxide solution never stoppered?

(xxxv) What do you understand by the term common ion effect?

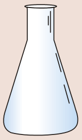
(xxxvi) Why is zinc sulphide not precipitated in group–II?

SPECIMEN RECORD OF SALT ANALYSIS

Aim

To analyse the given salt for one anion and one cation present in it.

Material required



- Boiling tubes, test tubes, test tube holder, test tube stand, delivery tube, corks, filter papers, reagents

Sl. No.	Experiment	Observation	Inference
1.	Noted the colour of the given salt.	White	Cu^{2+}, Fe^{2+}, Ni^{2+},Co^{2+}, Mn^{2+} are absent.
2.	Noted the smell of the salt.	No specific smell.	S^{2-}, SO_3^{2-} CH_3COO^- may be absent.
3.	Heated 0.5 g of the salt in a dry test tube and noted the colour of the gas evolved and change in the colour of the residue on heating and cooling.	(i) No gas was evolved. (ii) No particular change in colour of the residue is observed when heated and when cooled.	(i) CO_3^{2-} may be present, NO_3^-, NO_2^-, Br^- may be absent. (ii) Zn^{2+} may be absent.
4.	Prepared a paste of the salt with conc. HCl and performed the flame test.	No distinct colour of the flame seen.	Ca^{2+}, Sr^{2+}, Ba^{2+} Cu^{2+} may be absent.
5.	Borax bead test was not performed as the salt was white in colour.	—	—
6.	Treated 0.1 g of salt with 1 mL dil.H_2SO_4 and warmed.	No effervescence and evolution of vapours.	CO_3^{2-}, SO_3^{2-}, S^{2-}, NO_2^-, CH_3COO^- absent.
7.	Heated 0.1 g of salt with 1 mL conc. H_2SO_4.	No gas evolved.	Cl^-, Br^-, I^-, NO_3^- , $C_2O_4^-$ are absent.
8.	Acidified 1mL of aqueous salt solution with conc. HNO_3. Warmed the contents and then added 4-5 drops of ammonium molybdate solution.	No yellow precipitate	PO_4^{3-} absent.

9.	Acidified water extract of the salt with dil. HCl and then added 2mL of $BaCl_2$ solution.	A white ppt. is obtained which is insoluble in conc. HNO_3 and conc. HCl.	SO_4^{2-} present.
10.	Heated 0.1 g of salt with 2 mL NaOH solution.	Ammonia gas is not evolved.	NH_4^+ absent.
11.	Attempted to prepare original solution of the salt by dissolving 1g of it in 20 mL water.	Clear solution formed	Water soluble salt is present.
12.	To a small part of the above salt solution added 2 mL of dil. HCl.	No white precipitate formed.	Group–I absent.
13.	Passed H_2S gas through one portion of the solution of step 12.	No precipitate formed.	Group–II absent.
14.	Since salt is white, heating with conc. HNO_3 is not required. Added about 0.2 g of solid ammonium chloride and then added excess of ammonium hydroxide to the solution of step 12.	No precipitate formed.	Group–III absent.
15.	Passed H_2S gas through the above solution.	No precipitate formed.	Group–IV absent.
16.	Added excess of ammonium hydroxide solution to the original solution and then added 0.5 g of ammonium carbonate.	No precipitate formed.	Group–V absent.
17.	To the original solution of salt added ammonium hydroxide solution, followed by disodium hydrogen phosphate solution. Heated and scratched the sides of the test tube.	White precipitate.	Mg^{2+} confirmed.

Result

The given salt contains:

Anion : SO_4^{2-}

Cation : Mg^{2+}

EXPERIMENT 7.2

Aim

Detection of nitrogen, sulphur and halogens in an organic compound.

Theory

In contrast to inorganic compounds the atoms in an organic compound are linked to each other by covalent bonds, hence organic compounds don't furnish ions in solutions. Therefore, in order to test the presence of above elements in an organic compound, it is fused with sodium metal to form ionisable sodium salts. Though we may also fuse the organic compounds with potassium; we prefer sodium because it is easily available and its reaction is easily controllable as compared to potassium. Following reactions occur on fusion of the organic compound with sodium metal.

$$Na + C + N \rightarrow NaCN$$

$$2Na + S \rightarrow Na_2S$$

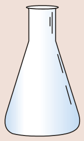
$$Na + X \rightarrow NaX \qquad \text{Where X is (Cl, Br or I)}$$

If nitrogen and sulphur both are present in the compound then sodium thiocyanate (also known as sodium sulphocyanide) is formed.

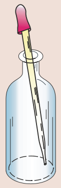
$$Na + C + N + S \rightarrow NaSCN$$

Formation of sodium thiocyanate is possible only when sodium metal is present in small amounts. The solution obtained on fusing organic compound with sodium metal and making water extract of fused mass is known as sodium extract or Lassaigne's extract.

Material Required



- China dish : One
- Funnel : One
- Tripod stand with wire gauze : One
- Pair of tongs : One
- Test tubes : As per need
- Ignition tubes : As per need



- Organic compound : 100 mg
- Distilled water : 30 mL
- Sodium metal stored under Kerosine oil : As per need

***Note:* Chloroform and carbon tetrachloride should never be subjected to Lassaigne's solution test as violent explosions may result.**

Procedure

[a] Preparation of Sodium Extract of [Lassaigne's extract]

(i) Dry a small piece of sodium between the folds of a filter paper. Cut a small piece of the metal with the help of a sharp knife. Clean it and insert it into the ignition tube. Melt the metal by gently heating the ignition tube in the flame to expose the clean surface. A shining globule of metal is formed. Cool the ignition tube slightly then add a pinch of organic compound into the ignition tube, so as to cover the sodium metal completely with the organic compound as shown in the fig. 7.10 (a)

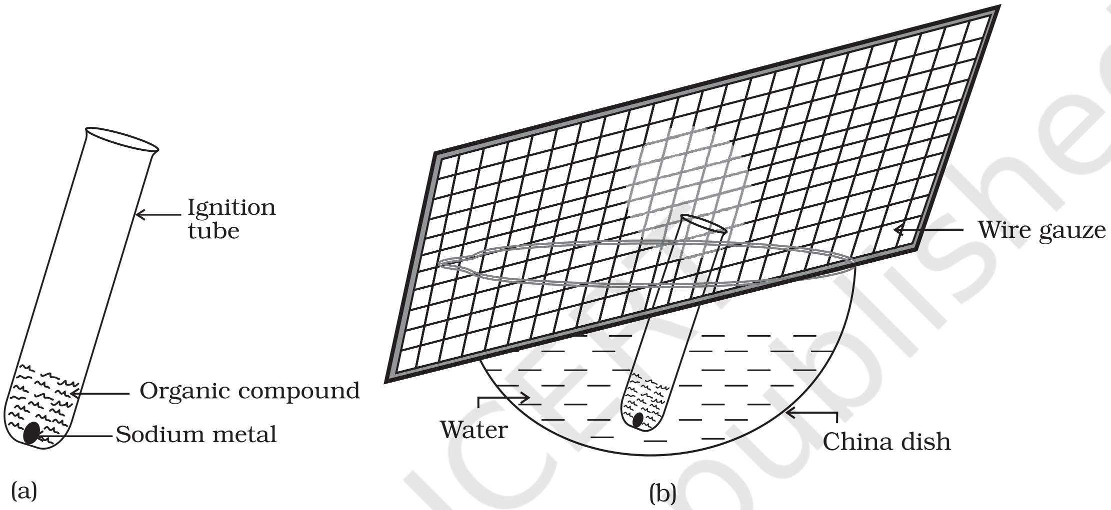


Fig. 7.10: *(a) Covering the sodium metal with organic commpound.*
(b) Dropping the ignition tube in water after ignition

(ii) Heat the ignition tube gently in the flame. If a vigorous initial reaction occurs, remove it from the flame and keep it out of the flame until the reaction subsides. Then continue heating. Repeat the process till organic compound reacts completely. After completion of the reaction heat the ignition tube strongly till it becomes red hot.

(iii) Drop the red hot ignition tube quickly into the china dish containing 15mL of distilled water and cover the china dish immediately with a wire guaze. Break the tube. Repeat this process twice or thrice to obtain Lassaigne's extract of sufficient concentration.

(iv) Boil the contents of the china dish for about 10 minutes and then filter the solution. The filtrate so obtained is named as Lassaigne's extract or sodium extract. It is alkaline due to sodium hydroxide formed by the reaction of unreacted sodium metal during fusion with water.

[b] Detection of Nitrogen

(i) Take approximately 1mL of sodium extract in a test tube and add 3-4 drops of freshly prepared saturated solution of ferrous sulphate to it or add a few crystals of ferrous sulphate.

(ii) Boil the mixture obtained in step (i) and finally cool. A green precipitate of ferrous hydroxide is formed. If it is not formed add a few drops of sodium hydroxide solution, boil the solution again and cool.

(iii) Acidify the solution obtained in step (ii) with a few drops of dilute sulphuric acid and warm. Add ferric chloride solution. A Prussian blue precipitate or green/blue colouration indicates the presence of nitrogen.

$$6NaCN + Fe(OH)_2 \xrightarrow{\Delta} \underset{\text{Sodium (I) hexacyanidoferrate (II)}}{Na_4[Fe(CN)_6]} + 2NaOH$$

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \xrightarrow{\Delta} \underset{\text{Prussian blue or Iron (III) hexacyanidoferrate (II)}}{Fe_4[Fe(CN)_6]_3}$$

If hexacyanidoferrate(II) ion is in excess in solution then on adding ferric chloride solution blue coloured soluble sodium(I) iron (III) hexacyanidoferrate(II) is formed.

$$Na^+ Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow \underset{\text{Sodium (I) Iron (III) hexacyanidoferrate (II)}}{NaFe[Fe(CN)_6]}$$

If a small amount of CN^- ions is formed during fusion then a green solution is obtained at first, which deposits prussian blue on standing.

The ferric ions are formed by the oxidation of ferrous sulphate by the oxygen of the air in the presence of dilute sulphuric acid. Therefore, some times there is no need of adding ferric chloride solution. Some times blood red colour is obtained when sulphur and nitrogen both are present, the test for which is given later in this section.

(c) Detection of sulphur when nitrogen is not present

1. Sodium nitroprusside test

Take approximately 1 mL of sodium extract in a test tube and add a few drops of sodium nitroprusside solutions and shake. Appearance of purple colour confirms the presence of sulphur.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \xrightarrow{\Delta} \underset{\text{Sodium thionitroprusside (Purple colour)}}{Na_4[Fe(CN)_5NOS]}$$

2. Lead acetate test

Take approximately 1mL of sodium extract in a test tube. Acidify it with acetic acid and add a few drops of lead acetate solution. Appearance of a black precipitate confirms the presence of sulphur.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{Black precipitate}}{PbS} + 2CH_33COONa$$

(d) Test for nitrogen and sulphur when present together

When nitrogen and sulphur both are present in an organic compound, sodium thiocyanate may be formed on fusion with sodium metal.

1. Acidify 1 mL of sodium extract with dilute hydrochloric acid.
2. Add a few drops of ferric chloride solution to the solution obtained in step (I) and shake well. Appearance of blood red colouration confirms the presence of both nitrogen and sulphur in the organic compound.

$$FeCI_3 + 3NaSCN \longrightarrow \underset{\text{Blood red colour}}{Fe(SCN)_3} + 3NaCI$$

(e) Detection of halogens

(I) Test for the Presence of Halogens with $AgNO_3$ Solution.

1. If nitrogen and sulphur both are present in the organic compound, acidify 1 mL of sodium extract with a few drops of conc. HNO_3.
2. Boil the above solution for 1-2 minutes to remove HCN or H_2S formed due to the presence of nitrogen and sulphur respectively.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

3. (a) Cool the above solution and add $AgNO_3$ solution. If a white precipitate soluble in ammonium hydroxide is formed, presence of chlorine is confirmed.

$$Ag^+ + CI^- \longrightarrow \underset{\text{(White ppt)}}{AgCI}$$

$$AgCI + \underset{\substack{\text{(from}\\ NH_4OH\\ \text{solution)}}}{2NH_3} \longrightarrow \underset{\text{(Soluble)}}{[Ag(NH_3)_2]CI}$$

Hazard Warning

- *The solution obtained after dissolving precipitates of AgCl/AgBr/AgI in ammonium hydroxide should be acidified with 2M nitric acid and should be discarded quickly to avoid serious explosion.*

(b) If a yellow precipitate partially soluble in ammonium hydroxide solution is formed the presence of bromine is confirmed in the organic compound.

$$Ag^+ + Br^- \rightarrow \underset{\text{Yellow ppt}}{AgBr}$$

(c) If a dark yellow precipitate insoluble in ammonium hydroxide is formed, the presence of iodine in the organic compound is confirmed.

$$Ag^+ + I^- \rightarrow \underset{\text{Dark yellow precipitate}}{AgI}$$

(II) Layer test for bromine and iodine

1. If nitrogen and sulphur both are present in the compound, acidify 1 mL sodium extract with concentrated nitric acid and boil it for 1-2 minutes.

2. Now add a little of CCl_4/CS_2 followed by excess of chlorine water. Shake the solution vigorously. The presence of halogens causes the following reactions to take place.

$$2\mathrm{Br}^- + \mathrm{CI}_2 \longrightarrow 2\mathrm{CI}^- + \mathrm{Br}_2$$

$$2\mathrm{I}^- + \mathrm{CI}_2 \longrightarrow 2\mathrm{CI}^- + \mathrm{I}_2$$

Appearance of orange colour in carbon tetrachloride layer indicates the presence of bromine and the appearance of purple/violet colour indicates the presence of iodine.

Precautions

(a) Sodium metal is highly reactive so handle it with care. Never touch sodium metal with fingers.
(b) Dry the sodium metal between the folds of filter paper before use.
(c) Use only distilled water to prepare Lassaigne's extract.
(d) While performing test for halogens, test tube rinsed with distilled water should be used.
(e) Ensure dryness of ignition tube before using it for fusion. Moisture present in the ignition tube may cause a vigorous reaction with sodium metal.
(f) Always take a small piece of sodium metal for fusion, as the unreacted sodium (excess of sodium) may react with water violently during the process of breaking the ignition tube in water.
(g) Solutions obtained after dissolving precipitates of AgCl/AgBr/AgI should be acidified with 2M nitric acid and the solution should be discarded immediately to avoid explosion.
(h) Aqueous solution of sodium nitropruside is not stable hence always use freshly prepared solution.

Discussion Questions

(i) Why is sodium extract alkaline in nature. Explain?

(ii) Why is the sodium extract prepared for the detection of elements in an organic compound?

(iii) Why should the sodium extract be boiled with concentrated nitric acid before using for the test of halogens?

(iv) Why chlorine water is added in the layer test for bromine and iodine? Can any other reagent be used in its place?

(v) Apply the concept of electrode potential to justify the occurrence of the following reactions:

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

$$2I^- + Cl_2 \longrightarrow 2Cl^- + I_2$$

(vi) Can chlorine be librated from sodium chloride solution by adding bromine water?

(vii) Out of AgCl and $[Ag(NH_3)_2]Cl$, the value of solubility product of which substance is high? Explain

(viii) Can a sodium salt be used in place of sodium metal in the fusion reaction? If so, name the compound.