Systematic Qualitative Analysis

a -Determination of one cation and one anion in a given salt

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

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

Qualitative Analysis

Analytical chemistry deals with qualitative and quantitative analysis of the substances. In inorganic qualitative analysis, the given compound is analyzed for the radicals, i.e., cation and the anion, that it contains. Physical procedures like noting the Colour, smell or taste of the substance have very limited scope because of the corrosive, poisonous nature of the chemical compounds. Therefore, what one has to resort to is the chemical analysis of the substance that has to be carried out along with the physical examination of the compound under consideration.

The common procedure for testing any unknown sample is to make its solution and then test this solution for the ions present in it. There are separate procedures for detecting cations and anions.The systematic procedure for qualitative analysis of an inorganic salt involves the following steps.

1. Preliminary tests
   - (i) Physical appearance (Colour and smell)
   - (ii) Dry heating test
   - (iii) Charcoal cavity test
   - (iv) Charcoal cavity and cobalt nitrate test
   - (v) Flame test
   - (vi) Borax bead test
   - (vii) Dilute acid test
   - (viii) Potassium permanganate test
   - (ix) Concentrated sulfuric acid test
   - (x) Tests for sulphate and phosphate
2. Wet tests for acid radicals
3. Wet tests for basic radical

Preliminary Tests

(a) Physical Examination of The Salt

The physical examination of the unknown salt involves the study of Colour, smell and density. The test is not much reliable but is certainly helpful in identifying some Coloured cations. Characteristic smell helps to identify some ions such as ammonium, acetate and Sulfide.

Experiment	Observations	Inference
Colour: Note the salt colour	(i) Blue (ii) Green (iii) Light green (iv) Dark green (v) Yellowish brown (vi) Green (vii) Pink (viii) Light pink or flesh Colour (ix) White	Cu^{2+} Cu^{2+} Fe^{2+} Cr^{3+} Fe^{3+} Ni^{2+} Co^{2+} Mn^{2+} (i) Shows the absence of $Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, CO^{2+}$ etc. (ii) Shows the presence of $Pb^{2+}, As^{3+}, Al^{3+}$,

		$Cd^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, K^{+}$, Na^{+} and NH_4^{+} etc.
Smell: Take a pinch of the salt between your fingers and rub with a drop of water	(i) Ammoniacal smell (ii) Vinegar like smell (iii) Smell like that of rotten eggs	NH_4^{+} CH_3COO^{-} S^{2-}
Density: Guess the salt density by placing it on your palm.	(i) Heavy (ii) Light fluffy powder	Salt of Pb^{2+} or Ba^{2+} Carbonate of Zn^{2+}, Ca^{2+} or Mg^{2+}
Deliquescence: Take small quantity of salt on a paper and expose to atmosphere for sometimes.	Salt absorbs moisture and becomes paste like	(i) If Coloured, may be $Cu(NO_3)_2$, $FeCl_3$. (ii) If Colourless, may be $Zn(NO_3)_2$, chlorides of Zn^{2+}, Mg^{2+} etc.
Physical state: (Amorphous or Crystalline) Write whether the constituent salts of the mixture are amorphous or crystalline.	(i) Salt is amorphous. (ii) Salt is crystalline.	Carbonates of non-alkali metals i.e, $CuCO_3$, $CaCO_3$, $PbCO_3$, $MgCO_3$ etc. -----

Note:

1. **If you have touched any salt, wash your hands at once. It may be corrosive to skin.**
2. **Never taste any salt, it may be poisonous. Salts of arsenic and mercury are highly poisonous.**
3. **Salts like sodium sulphide, sodium nitrite, potassium nitrite, develop a yellow colour.**

(b) Dry Heating Test

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

Dry Heating Test	
Observations	**Inference**
1. Gas evolved	
(a) Colourless and odourless gas CO_2 gas turns lime water milky	CO_3^{2-} or C_2O_4
(b) Colourless gas with an odour	
(i) H_2S gas-Smells like rotten eggs and turns lead acetate paper black.	Hydrated S^{2-}
(ii) SO_2 gas-Smells like burning Sulphur and turns acidified potassium dichromate paper green.	SO^{2-}

(iii) HCl gas-Pungent smell, white fumes with ammonia, white ppt with silver nitrate solution. (iv) Acetic acid vapors-Characteristic a vinegar-like smell. (v) NH_3 gas-Characteristic smell turns Nessler's solution brown.	Cl^- CH_3COO^- NH_4^+
(c) Coloured gases—Pungent smell (i) NO_2 gas-reddish brown turns ferrous sulphate solution black. (ii) Cl_2 gas-Greenish yellow turns starch iodide paper blue. (iii) Br_2 vapors-reddish brown turns starch paper orange yellow. (iv) I_2 vapors-Dark violet turns starch paper blue.	 NO_2^- or NO_3^- Cl^- Br^- I^-
2. Sublimate formed (a) White sublimate (b) Black sublimate accompanied by violet vapours	 NH_4^+ I^-
3. Decrepitation The salt decrepitates.	A salt having no water of crystallisation, For example, $Pb(NO_3)_2$, NaCl, KBr.
4. Swelling The salt swells up into a voluminous mass.	 PO_4^{3-} indicated
5. Residue Yellow when hot white when cold Brown when hot and yellow when cold White salt becomes black on heating White residue glows on heating Original salt blue becomes white on heating Coloured salt becomes brown or black on heating.	 Zn^{2+} Pb^{2+} CH_3COO^- indicated $Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}$, etc. Hydrated $CuSO_4$ indicated $CO^{2+}, CU^{2+}, MN^{2+}$

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

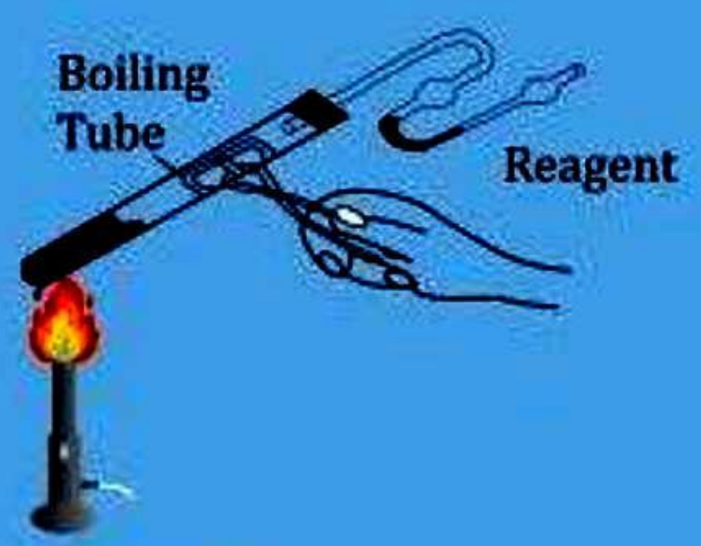


Fig. 1. Testing a gas

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

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

(c) Charcoal Cavity Test

This test is based on the fact that metallic carbonates when heated in a charcoal cavity decompose to give corresponding oxides. The oxides appear as Coloured incrustation or residue in the cavity. In certain cases, the oxides formed partially undergo reduction to the metallic state producing metallic beads or scales.

Examples:

$$ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$$
$$ZnCO_3 \rightarrow ZnO + CO_2 \uparrow$$

Yellow when hot, white when cold

$$Pb(NO_3)_2 + Na_2CO_3 \rightarrow PbCO_3 + 2NaNO_3$$
$$PbCO_3 \rightarrow PbO + CO_2 \uparrow$$
$$PbO + C \rightarrow \underset{\text{Bead}}{Pb} + CO \uparrow$$

$$CuSO_4 + Na_2CO_3 \rightarrow CuCO_3 + Na_2SO_4$$
$$CuCO_3 \rightarrow CuO + CO_2 \uparrow$$
$$CuO + C \rightarrow \underset{\substack{\text{Reddish} \\ \text{scales}}}{Cu} + CO \uparrow$$

PROCEDURE

While performing the charcoal cavity test, make a small cavity on a charcoal block with the help of a borer as shown in (Fig. 2) Mix a small amount of salt with double its quantity of sodium carbonate. Place it in the cavity made on the block of charcoal. Moisten with a drop of water and direct the reducing flame of the Bunsen Burner on the cavity using a mouth blowpipe as shown in (Fig. 3) Heat strongly for some time and draw inference according to the Table.

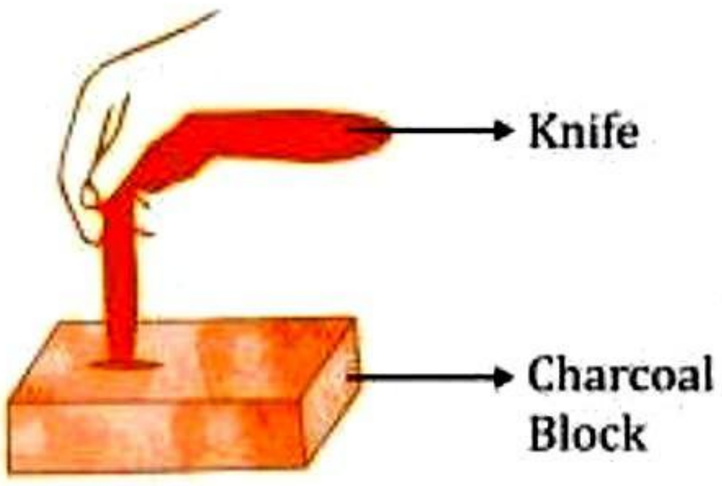


Fig. 2 Making bore on a charcoal block

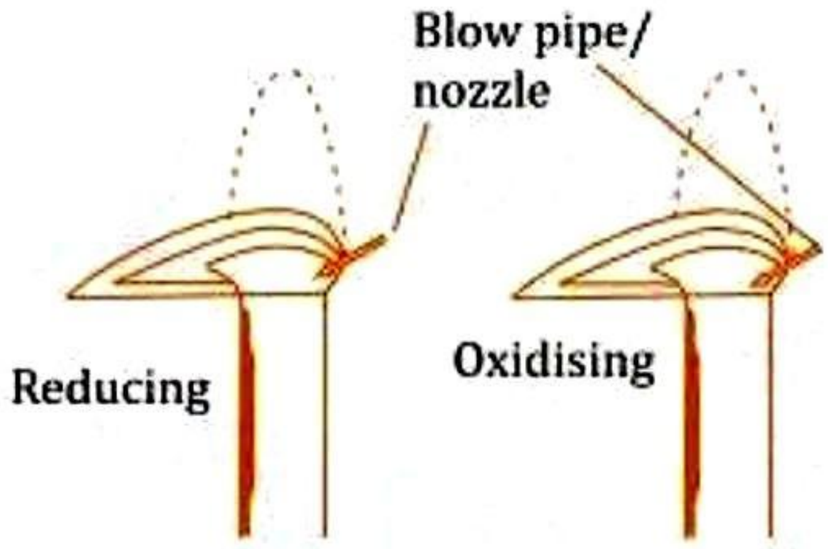


Fig. 3 Directing flame with blowpipe

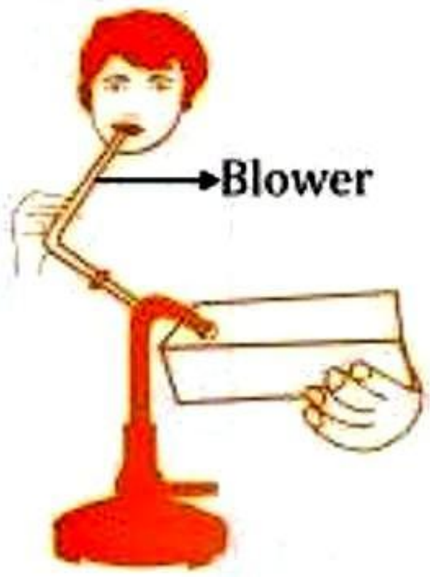


Fig. 4 Blowing flame on the cavity

Observations		Inference
Bead	**Incrustation/Residue**	
1. Grey soft metallic bead	Brown when hot and yellow when cold	Pb^{2+}
2. Red scales	No incrustation	Cu^{2+}
3. No bead	White incrustation and garlic smell	As^{3+}
4. No bead	Residue which is yellow when hot and white when cold	Zn^{2+}
5. No bead	White residue that glows on heating	Al^{3+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, PO_4^{3-}
6. No bead	Black residue	Co^{2+}, Ni^{2+}, Fe^{2+}

To obtain a reducing flame with the help of a mouth blowpipe, make the Bunsen Burner flame luminous by closing the air holes of the Burner. Keep the nozzle of the blowpipe just outside the flame and blow gently onto the cavity.

(d) Cobalt Nitrate Test

This test is applied to those salts which leave white residue in the charcoal cavity test.

The test is based on the fact that cobalt nitrate decomposes on heating to give cobalt oxide, CoO. This combines with the metallic oxides, present as a white residue in the charcoal cavity forming Coloured compounds. For example, when a magnesium salt undergoes a charcoal cavity test, a white residue of MgO is left behind. This on treatment with cobalt nitrate and subsequent heating forms a double salt of the formula MgO-CoO which is pink in Colour. In addition to metallic oxides, phosphates and borates also react with cobalt oxide to form $Co_3(PO_4)_2$ and $Co_3(BO_3)_2$ which are blue.

Some of the reactions involved are given below.

Zinc salt:

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

$$ZnO + CoO \longrightarrow ZnO \cdot CoO \text{ (Green)}$$

Magnesium salt:

$$MgO + CoO \longrightarrow MgO.CoO \text{ (Pink)}$$

PROCEDURE

Put one or two drops of cobalt nitrate solution on the white residue left after the charcoal cavity test. Heat for one or two minutes using a blowpipe in an oxidising flame. Observe the Colour of the residue and draw inferences from Table

Cobalt Nitrate-Charcoal Cavity Test

Colour of the Residue	Inference
Green	Zn^{2+}
Pink	Mg^{2+}
Blue	PO_4^{3-}

Note:

1. **Perform this test only if the residue in the charcoal cavity test is white.**
2. **Do not put more than 2 drops of cobalt nitrate on the white residue. Excess cobalt nitrate may decompose to give cobalt oxide which is black in Colour.**
3. **Use dilute solution of cobalt nitrate.**

(e) Flame Test

Certain salts on reacting with the conc. HCl from their chlorides, which are volatile in non-luminous flame. Their vapours impart characteristic Colour to the flame. This Colour can give reliable information about the presence of certain basic radicals.

For proceeding to this test, paste the mixture with a conc. HCl is introduced into the flame with the help of platinum wire (Fig. 5).

(a) Making a loop of platinum wire

(b) Diping the platinum wire in the paste of salt and HCl.

(c) Introducing the wire in the flame

Fig. 5 Flame Test

PROCEDURE

Clean the platinum wire by dipping it in some cones. HCl is taken on a watch glass and then heated strongly in the flame. This process is repeated till the wire imparts no Colour to the flame. Now prepare a paste of the mixture with a conc. HCl on a clean watch glass. Place a small amount of this paste on a platinum wire loop and introduce it into the flame. Note the Colour imparted to the flame with the naked eye and through blue glass.

Flame colour with naked eye	Flame colour through blue glass	Inference
1. Dark-green	Bluish-green	Cu^{2+}
2. Pink-violet	Pink	K^{+}
3. Brick-red	Light-green	Ca^{2+}
4. Grassy-green	Bluish-green	Ba^{2+}
5. Crimson (deep-red)	Purple	Sr^{2+}

(f) Borax Bead Test

This test is performed only for Coloured salts.

Borax, $Na_2B_4O_7 \cdot 10H_2O$, on heating gets fused and loses water of crystallisation. It swells up into a fluffy white porous mass which then melts into a Colourless liquid which later forms, a clear transparent glassy bead consisting of boric anhydride and sodium metaborate.

$$Na_2B_4O_7 \cdot 10H_2O \longrightarrow Na_2B_4O_7 + 10H_2O\uparrow$$

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

Boric anhydride is non-volatile. When it is reacted with Coloured metallic salt, a characteristic

Coloured bead of metal metaborate is formed.

$$Cr_2(SO_4)_3 + 3B_2O_3 \longrightarrow \underset{\text{Deep Green}}{2Cr(BO_2)_3} + 3SO_3$$

In the cases where different Coloured beads are obtained in the oxidising and reducing flames, metaborates in various oxidation states of metals are formed. For example, in oxidising flame, copper forms blue copper metaborate.

$$Na_2B_4O_7 + CuSO_4 \longrightarrow 2NaBO_2 + \underset{\text{Blue}}{Cu(BO_2)_2} + SO_3$$

In reducing flame cupric metaborate is reduced to metallic copper, which is red and opaque.

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C \longrightarrow \underset{\text{Red opaque}}{2Cu} + 2Na_2B_4O_7 + 2CO$$

PROCEDURE

Borax, $Na_2B_4O_7 \cdot 10H_2O$ is heated in the loop of platinum wire, it swells and forms transparent Colourless glassy bead. When this hot bead is touched with small amount of Coloured salt and is heated again, it acquires a characteristic Colour. The Colour of bead gives indication of the type of the cation present. The Colour of the bead is noted separately in oxidising and in reducing flame (Fig. 6).

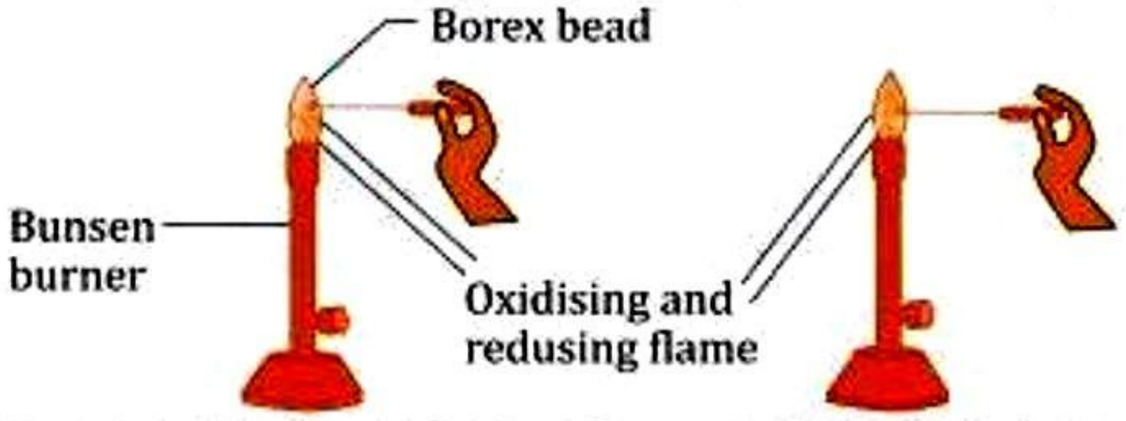


Fig. 6 Borax Bead Test Heating in reducing flame and Heating in an oxidising flame.

Colour of the bead		Inference
In Oxidising flame	In Reducing flame	
1. Green when hot, light blue when cold.	Colourless when hot, red (opaque) when cold.	Cu^{2+}
2. Yellowish brown when hot, pale yellow when cold	Green both when hot and cold.	Fe^{2+} or Fe^{3+}
3. Pinkish violet in both hot and cold	Colourless in hot and cold.	Mn^{2+}
4. Deep blue in both when hot and cold	Deep blue in both hot and cold	Co^{2+}
5. Reddish brown	Grey black in both hot and cold	Ni^{2+}

To remove the head from the platinum wire, heat the head to redness. Tap the rod with a finger stroke, till the bead jumps off (Fig. 7).

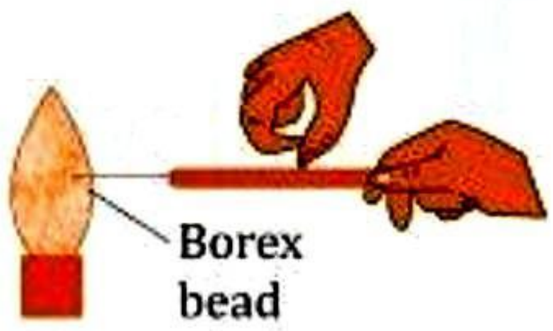


Fig. 7 Removing bead from platinum wire.

(g) Dilute Acid Test

The identification of the acid radicals is first done based on preliminary tests. The dry heating test is one of the preliminary tests performed earlier which may give some important information about the acid radical present. The other preliminary tests are based on the fact that.

(i) $CO_3^{2-}, S^{2-}, NO_2^-$ and SO_3^{2-} react with dil. H_2SO_4 to give out CO_2, H_2S, NO_2 and SO_2 gases respectively which can be identified by certain tests.

(ii) $Cl^-, Br, I^-, NO_3^-, C_2O_4^{2}$ and CH_3COO^- react with conc. H_2SO_4 but not with dil. H_2SO_4 to produce characteristic gases.

(iii) SO_4^{2-} and PO_4^{3-} react neither with dil. H_2SO_4 nor with conc. H_2SO_4. These are, therefore, identified by individual tests.

Thus, the acid radicals may be identified by performing the following tests in the order given below.

(i) Dil. H_2SO_4 test. Treat a pinch of the salt with dil. H_2SO_4 and identify the gas evolved.

(ii) Conc. H_2SO_4 test. If no action takes place with dil. H_2SO_4, warm a pinch of the salt with conc. H_2SO_4 and identify the gas evolved.

(iii) Independent Group. (SO_4^{2-} and PO_4^{3-}). If the salt does not react with dil. H_2SO_4 as well as with conc. H_2SO_4, test for SO_4^{2-} and PO_4^{3-} by performing their tests.

Let us now discuss these tests in detail one by one.

Take a small quantity of the salt in a test tube and add 1-2 ml of dilute sulfuric add. Identify the gas and draw.

Dilute Sulfuric Acid Test		
Observations	**Inference**	
	Gas	**Radical**
1. Colourless, odourless gas with brisk effervescence, turns lime water milky.	CO_2	CO_3^{2-}
2. A colourless gas, with a pungent smell, turns acidified potassium dichromate paper or solution green.	SO_2	SO_3^{2-}
3. Colourless gas with a smell like that of rotten eggs turns lead acetate paper black.	H_2S	S^{2-}
4. Reddish brown gas, pungent smell, turns ferrous sulphate solution black.	NO_2	NO_2^-
5. No gas is evolved.	---	Absence of $CO_3^{2-}, SO_3^{2-}, S^{2-}$ and NO_2^-

Note:

1. **Do not treat the salt with a large quantity of dilute acid.**
2. **Do not heat the salt with dilute acid.**

Chemical Reactions

Dilute H_2SO_4 (or dilute HCl) decomposes carbonates, sulphides and nitrites in cold to give gases. These gases on identification indicate the nature of the added radical present in the salt.

1. **Carbonates:** On treating the solid carbonate, CO_2 is given off in the cold with brisk effervescence.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

2. **Sulphides:** When treated with dil. H_2SO_4 give H_2S gas.

$$ZnS + H_2SO_4 \longrightarrow ZnSO_4 + H_2S \uparrow$$

3. **Sulphites**: On treating solid sulphite with dil. H_2SO_4, SO_2 gas is evolved

$$ZnS + H_2SO_4 \longrightarrow ZnSO_4 + H_2S \uparrow$$

Nitrites. On treating the solid nitrite with dil. H_2SO_4 nitric oxide (NO) gas is evolved which readily gives dense brown fumes of NO_2 with the oxygen of the air.

$$KNO_2 + H_2SO_4 \longrightarrow [KHSO_4 + HNO_2] \times 3$$

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

$$3KNO_2 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HNO_3 + H_2O + 2NO$$
$$2NO + O_2 \longrightarrow 2NO_2$$
Colourless — Brown fumes

(h) Potassium Permanganate Test

To a pinch of salt in the test, tube adds about 2 ml of dilute sulfuric acid. Boil off any gas evolved, add a little more dilute acid and then potassium permanganate solution dropwise. Note the changes as given in Table. This test helps in the detection of Cl^-, Br^-, I^-, $C_2O_4^{2-}$ and Fe^{2+} radicals.

Note:

1. As sulphides are oxidised by $KMnO_4$ so they have to be completely decomposed by heating with dilute sulphuric acid before this test is performed.
2. Potassium permanganate oxidises Fe^{2+} salts in cold. Oil H_2SO_4 acid is added to the salt and heated till sulphides, sulphites and nitrites are completely decomposed. Then $KMnO_4$ is added dropwise to cold solution.

Potassium Permanganate Test	
Observations	**Inference**
1. Potassium permanganate DeColourised without the evolution of any gas.	Presence of Fe^{2+} salts.
2. Potassium permanganate DeColourised.	
a. In cold	
i. With the evolution of chlorine.	Cl^-
ii. With the evolution of bromine.	Br^-
iii. With the evolution of iodine.	I^-
b. On warming	
c. With evolution of CO_2	$C_2O_4^{2-}$
3. $KMnO_4$ not DeColourised.	Absence of Cl^-, Br^-, I^-, $C_2O_4^{2-}$ and Fe^{2+}

Chemical Reactions

1. Ferrous salts
$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

2. Chlorides
$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$2HCl + [O] \longrightarrow H_2O + Cl_2 \uparrow$$

3. Bromides
$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$
$$2HBr + [O] \longrightarrow H_2O + Br_2 \uparrow$$

4. Iodides
$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$
$$2HI + [O] \longrightarrow H_2O + I_2 \uparrow$$

5. Oxalates
$$\begin{matrix}COONa\\|\\COONa\end{matrix} + H_2SO_4 \longrightarrow \begin{matrix}COOH\\|\\COOH\end{matrix} + Na_2SO_4$$
$$\begin{matrix}COOH\\|\\COOH\end{matrix} + [O] \longrightarrow 2CO_2 \uparrow + H_2O$$

Concentrated Sulfuric Acid Test

This test is performed by treating small quantity of salt with cone, sulfuric acid (2-3 ml) in a test tube. Identify the gas evolved in cold and then on heating. Draw inferences from table

Conc. Sulfuric Acid Test		
Observations	**Inference**	
	Gas	**Radical**
1. Colourless gas with a pungent smell, white fumes with aqueous ammonia, white ppt. with solution.	HCl	Cl^-
2. Reddish brown vapours with a pungent smell turn starch paper yellow. It does not turn the solution black.	Br_2	Br^-
3. Deep violet vapours with pungent smell, turn starch paper blue. A sublimate is formed on the sides of the tube.	I_2 vapours	I^-
4. Reddish brown gas with pungent smell turns solution black.	NO_2	NO_3^-
5. Colourless vapours, vinegar smell, turns blue litmus red.	CH_3COOH vapors	CH_3COO^-
6. A Colourless gas with turns lime water milky and also a gas which burns with pale-bluish flame	$CO_2 + CO$	$C_2O_4^{2-}$
7. No gas/vapors evolved.		Cl^-, Br^-, I^-, NO_3^-, CH_3COO^- absent

Chemical Reactions

1. Chlorides

$$NaCl + H_2SO_4 \longrightarrow \underset{\text{Sod. Bisulphate}}{NaHSO_4} + HCl$$

2. Bromides

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$
$$H_2SO_4 + 2HBr \longrightarrow SO_2 + Br_2 + 2H_2O$$

3. Iodides

$$KI + H_2SO_4 \longrightarrow KHSO_4 + HI$$
$$H_2SO_4 + 2HBr \longrightarrow SO_2 + Br_2 + 2I_2$$

4. Nitrates

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$
$$4HNO_3 + \underset{\text{(Paper pellet)}}{C} \longrightarrow 4NO_2 \uparrow + CO_2 + 2H_2O$$

5. Acetates

$$CH_3COONa + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Acetic acid}}{CH_3COOH}$$

6. Oxalates

$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 \uparrow + CO \uparrow + H_2O$$

Note:

1. Do not boil the salt with cone, sulphuric acid. On boiling, the acid may decompose to give SO_2 gas.
2. Nitrates give vapors of nitric acid (Colourless) when heated with conc. sulphuric acid. When a paper pellet or copper chips is added, dense brown fumes evolve. Paper pellet acts as a reducing agent and reduces nitric acid to NO_2 (Reddish brown gas).

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
$$4HNO_3 + \underset{\text{From paper pellet}}{C} \rightarrow 2H_2O + 4NO_2 \uparrow + CO_2 \uparrow$$

Tests For Independent Radicals (So_4^{2-} And Po_4^{3-})

As already discussed, these radicals are not detected by dilute or concentrated H_2SO_4.They are tested individually.

1. **SULPHATE (So_4^{2-})**
   Boil a small amount of salt with dilute HCl in a test tube. Filter the contents, and to the filtrate add few drops of $BaCl_2$ solution. A white ppt. insoluble in conc. HCl indicates presence of sulphate.
2. **PHOSPHATE (Po_4^{3-})**
   Add cone. HNO_3 to the salt in a test tube. Boil the contents and add excess of ammonium molybdate solution. A yellow precipitate indicates presence of phosphate.

CONFIRMATION OF ACID RADICALS BY WET TESTS

The acid radical indicated by dil. H_2SO_4 tests is further confirmed by wet tests.

Preparation of solution for wet tests of acid radicals.

The confirmatory tests for acid radicals are performed with salt solutions. The solution used for the purpose is any one of the following.

1. **Aqueous solution or 'water extract'** Shake a little of the salt with water. If the salt dissolves, this aqueous solution obtained is used for the wet tests of acid radical and is called water extract or W.E.. If the salt is not completely soluble in water, the salt is shaken with water and is filtered. The filtrate is treated as water extract.
2. **Sodium carbonate extract:** This is prepared only if the salt is insoluble in water. Preparation of Sodium Carbonate Extract. Mix about 1 g of the salt with about 2 g of pure sodium carbonate and boil it for 10-15 minutes with 20-25 ml of distilled water in a small conical flask having a funnel in its mouth (Fig. 8). The funnel acts as a condenser. This arrangement prevents the loss of water due to evaporation. Filter the solution, cool it and label it as sodium carbonate extract or S.E.

Fig. 8. Preparation of sodium carbonate extract.

Alternatively, sodium carbonate extract can be prepared in a test tube. A pinch of salt is mixed with double the amount of sodium carbonate and is boiled with distilled water for some time. The suspension obtained is filtered. The filtrate is sodium carbonate extract. (Fig. 8.). Preparation of sodium carbonate extract.

Theory Of Preparation Of Sodium Carbonate Extract

When the salts are boiled with strong solution of sodium carbonate, double decomposition takes place resulting in the formation of the carbonates of heavy metallic radicals and sodium salts of the acid radicals. The sodium salts of corresponding add radicals being soluble in water pass into the solution and carbonates of heavy metals are predicated.

$$ZnS(s) + Na_2CO_3(aq) \longrightarrow ZnCO_3(s) \downarrow + Na_2S(aq)$$

How To Use Sodium Carbonate Extract

Sodium carbonate extract always contains unreacted sodium carbonate in solution which has to be destroyed before using the extract for various tests. To do this, the extract is acidified with some suitable acid and is boiled to expel carbon dioxide. The selection of add used for destroying excess Na_2CO_3 depends upon the radical to be identified.

Now we describe in detail the confirmatory tests for various add radicals discussed so far.

Confirmation of Carbonate, CO_3^{2-}

(Indicated in dilute acid test by occurrence of brisk effervescence and evolution of carbon dioxide).

Confirmation of soluble carbonate	Confirmation of insoluble carbonate
1. If the salt dissolves, soluble carbonate is indicated. 2. Dil. HCl test 3. To one portion of the solution, add dil. HCl. 4. Brisk effervescence and evolution of carbon dioxide which turns lime water milky confirms the presence of soluble carbonate. 5. Magnesium sulphate test 6. To another portion of the solution, add magnesium sulphate solution. 7. Formation of white precipitate in the cold confirms the presence of soluble carbonate.	1. If the salt remains insoluble, the presence of insoluble carbonate is indicated. 2. To the salt add dil. HCl. 3. Brisk effervescence and evolution of carbon dioxide which turns lime water milky confirms the presence of insoluble carbonate.

Confirmation Of Sulphite, SO_3^{2-}

(Indicated in dilute acid test by the evolution of hydrogen sulphide).

Experiment	Observations
Barium chloride test Take a portion of aqueous solution (or sodium carbonate extract and dil. acetic acid and boil off CO_2). Add barium chloride solution to it. Filter. To a portion of the above ppt. add dil. HCl.	A white ppt. is formed.
$KMnO_4$ test To a second part of the ppt. from first add a few drops of acidified potassium permanganate solution.	The ppt. dissolves with the evolution of sulphur dioxide. The pink Colour is discharged.
$K_2Cr_2O_7$ test To a portion of aqueous solution or sodium carbonate extract add potassium dichromate solution acidified with dil. H_2SO_4.	A green Colour is obtained.

Confirmation Of Sulphide, S^{2-}

(Indicated in dilute acid test by the evolution of hydrogen sulphide).

Experiment	Observations
Sodium nitroprusside test Take a portion of aqueous solution (or sodium carbonate extract) in a test tube and add a few drops of sodium nitroprusside solution.	Purple or violet Colouration is obtained.
Lead acetate test To a portion of aqueous solution (or sodium carbonate extract acidified with dil. acetic acid) add lead acetate solution.	A black ppt. is obtained.

Cadmium carbonate test To a portion of aqueous solution (or sodium carbonate extract) add a suspension of cadmium carbonate in water.	A yellow ppt. is formed.

Confirmation Of Nitrite, NO_2^-

(Indicated in dilute acid test by the evolution of brown vapors of nitrogen peroxide)

Note:

1. **Do not use sodium carbonate extract for performing the tests of carbonates because it contains sodium carbonate.**
2. **Perform magnesium sulphate test only in case of soluble carbonates.**

Experiment	Observations
Ferrous sulphate test To a portion of aqueous solution, add some dil. acetic acid and ferrous sulphate solution.	A dark brown or black Colouration is obtained.
Starch-iodide test To a portion of aqueous solution add a few drops of dil. H_2SO_4, and a few drops of potassium iodide solution followed by freshly prepared starch solution.	A blue solution is obtained.
Diphenylamine test To a portion of aqueous solution, add a few drops of diphenylamine.	A deep blue Colouration is obtained.

Chemical Reaction

Ions Involved in the Confirmation of Carbonate, Sulphide, Sulphite and Nitrite

Carbonate (CO_3^{2-})

1. Reaction with dil. HCl

Carbonates on reaction with dil. HCl give CO_2 gas which turns lime water milky. In case of soluble carbonates this test is performed with water extract and in case of insoluble carbonates this test is performed with the solid salt.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Milkiness}}{CaCO_3} + H_2O$$

Lime water

2. Magnesium sulphate test

This test is-performed in case of soluble carbonates only

$$Na_2CO_3 + MgSO_4 \longrightarrow \underset{\text{(White ppt.)}}{MgCO_3\downarrow} + Na_2SO_4$$

Sulphite (SO_3^{2-})

1. Barium chloride test

$$Na_2SO_3 + BaCl_2 \longrightarrow 2NaCl + \underset{\text{(White ppt.)}}{BaSO_3\downarrow}$$

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

2. Potassium permanganate test

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

$$Na_2SO_3 + [O] \longrightarrow Na_2SO_4$$

3. Potassium dichromate test

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + 4H_2O + 3[O]$$
(orange)

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4$$

Sulphide (S^{2-})

1. Sod. nitroprusside test

$$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$$
Sod. nitroprusside — (Violet or Purple Colour)

2. Lead acetate test

$$Na_2S + (CH_3COO)_2Pb \rightarrow \underset{\text{Blackppt.}}{PbS\downarrow} + 2CH_3COONa$$

3. Cadmium carbonate test

$$Na_2S + CdCO_3 \rightarrow \underset{\text{Yellow ppt.}}{CdS\downarrow} + Na_2CO_3$$

Nitrite (NO^{2-})

1. Ferrous sulphate test

$$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$$

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

$$FeSO_4 + NO \rightarrow \underset{\text{(Dark brown)}}{FeSO_4 \cdot NO}$$

2. Potassium iodide test

$$2KI + 2H_2SO_4 + 2HNO_2 \rightarrow 2KHSO_4 + I_2 + 2NO + 2H_2O$$

I_2 turns starch paper blue.

Confirmation Of Chloride, Cl^-

(No action with dilute H_2SO_4 but decomposed by conc. H_2SO_4 with the evolution of HCl gas).

Experiment	Observations
Silver nitrate test Acidify a portion of aqueous solution (or sodium carbonate extract) with dil. HNO_3. Boil for some time, cool and add $AgNO_3$ solution.	A white ppt. is formed which is soluble in ammonium hydroxide.
Manganese dioxide test Heat a pinch of the salt with a small quantity of MnO_2 and conc. H_2SO_4.	Evolution of greenish yellow gas having a pungent irritating smell. It turns moist starch-iodide paper blue.
Chromyl chloride test Mix a small quantity of the salt with a small amount of powdered potassium dichromate. Take the mixture in a test tube and add conc. H_2SO_4. Heat the tube and pass the red vapors evolved into the gas detector containing NaOH solution. To the yellow solution thus obtained, add dil. CH_3COOH and lead acetate solution.	A yellow ppt. is formed.

Confirmation Of Bromide, Br^-

(No action with dilute H_2SO_4 but decomposed by conc. H_2SO_4 with the evolution of bromine vapors).

Experiment	Observations
Silver nitrate test Acidify a portion of aqueous solution (or sodium carbonate extract) with dil. HNO_3. Boil, cool and add $AgNO_3$ solution.	A light-yellow ppt. is obtained which is partially soluble in NH_4OH.
Manganese dioxide test Heat a small quantity of the salt with solid MnO_2 and conc. H_2SO_4.	Evolution of yellowish-brown vapors of bromine which turn

	starch paper yellow.
Chlorine water test Acidify a portion of aqueous solution (or sodium carbonate extract) with dil. HCl and add 1-2 ml of carbon disulphide and then chlorine water. Shake vigorously and allow to stand.	Carbon di-sulphide layer acquires orange Colouration.

Note: Chlorine water is prepared by adding dropwise cone. HCl to a small volume of $KMnO_4$ solution till the pink colour is just discharged, the resulting solution is chlorine water.

Confirmation Of Iodide, I^-

(No action with dilute H_2SO_4 but decomposed by cone. H_2SO_4 with the evolution of vapors of iodine).

Experiment	Observations
Silver nitrate test Acidify a portion of aqueous solution (or sodium carbonate extract) with dil. HNO_3. Boil, cool and add $AgNO_3$ solution.	A yellow ppt. is formed which is insoluble in NH_4OH.
Manganese dioxide test Heat a small quantity of the salt with a little MnO_2 and conc. H_2SO_4.	Evolution of violet vapors of iodine which turn starch paper blue.
Chlorine water test Acidify a part of the aqueous solution (or sodium carbonate extract) with dil. HCl, add 1-2 ml of carbon di-sulphide and then chlorine water. Shake vigorously and allow to stand.	Carbon di-sulphide layer acquires a violet Colouration.

Confirmation Of Nitrate, NO_3^-

(No action with dilute acids but decomposed by conc. H_2SO_4 with the evolution of brown vapors of nitrogen peroxide).

Experiment	Observations
Diphenylamine test Add a few drops of diphenylamine to a part of aqueous solution of the salt.	A deep blue Colouration is obtained.
Copper chips test Heat a small quantity of the original salt with concentrated sulfuric acid and a few copper chips.	Dark brown fumes of nitrogen dioxide are evolved.
Ring Test Add a small quantity of freshly prepared solution of ferrous sulphate to a part of the aqueous solution and then pour concentrated sulfuric acid slowly along the sides of the test tube as shown in (Fig.9).	A dark brown ring is formed at the junction of the layers of the acid and the solution.

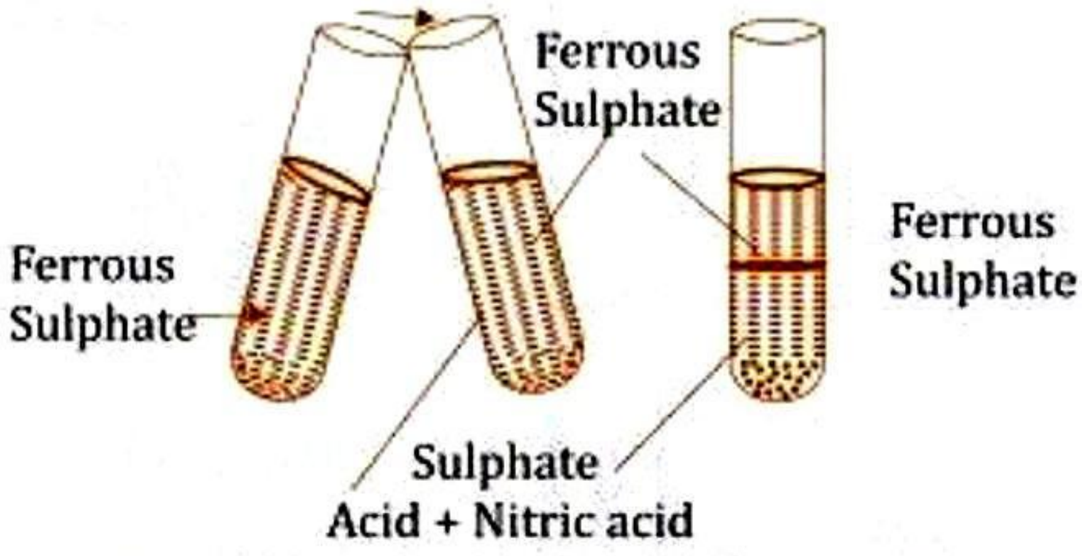


Fig. 9 The brown ring test for nitrates

Confirmation Of Acetate, CH_3COO^-

(No action with dilute acids but decomposed by conc. H_2SO_4 with the evolution of CH_3COOH vapors)

Experiment	Observations
Oxalic acid test Take a small quantity of the salt on a watch glass. Mix it with solid oxalic acid. Prepare paste of it with a few drops of water. Rub the paste and smell.	Smell like that of vinegar.
Ester test Take a small quantity of the salt in a test-tube. Add conc. H_2SO_4(2ml) and heat. Now add ethyl alcohol (1 ml). Shake. Pour the contents of the tube in a beaker full of water. Stir.	Pleasant fruity smell of ester.
Ferric chloride test Take water extract of the salt. Add neutral ferric chloride solution. Filter. Divide the filtrate into two portions. i. To one part, add dil. HCl. ii. To second part, add water and boil.	Reddish Coloured filtrate. Reddish Colour disappears. Reddish brown ppt.

Confirmation Of Oxalate, $C_2O_4^{2-}$

(No action with dilute acids but decomposed by conc. H_2SO_4 with the evolution of CO_2 and CO gas)

Experiment	Observations
Calcium chloride test Take water extract (or soda extract if salt is insoluble in water). Add small amount dil acetic acid and boil off CO_2. Add calcium chloride solution. Add dil HNO_3 to the white ppt and warm.	A white ppt. is formed. The ppt. dissolves.
Potassium permanganate test Take a pinch of the salt in test tube and add dil. sulfuric acid. Warm to $60-70°C$ and add $2-3$ drops of $KMnO_4$ solution.	The pink Colour of $KMnO_4$ solution is deColourized with the evolution of CO_2 gas.

Chemical Reactions Involved in the Confirmation of Chloride, Bromide, Iodide, Nitrate Acetate and Oxalate.

Chloride (Cl^-)

1. Silver nitrate test

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + NaNO_3$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Soluble complex}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

2. MnO_2 test

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$$

3. Chromyl chloride test

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow 2Na_2SO_4 + K_2SO_4 + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2} + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Sod. chromate}}{Na_2CrO_4} + 2H_2O + 2NaCl$$

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

Bromide (Br^-)

1. **Silver nitrate test**

$$KBr + AgNO_3 \longrightarrow KNO_3 + \underset{\text{(Pale yellow ppt.)}}{AgBr\downarrow}$$

Pale yellow ppt. of silver bromide is sparingly soluble in ammonium hydroxide.

2. **MnO_2 test**

$$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2$$

3. **Chlorine water test**

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

Bromine being soluble in CCl_4 imparts an orange Colour to the CCl_4 layer.

Iodide (I^-)

1. **Silver nitrate test**

$$KI + AgNO_3 \longrightarrow KNO_3 + \underset{\text{(yellow ppt.)}}{AgI}$$

2. **MnO_2 test**

$$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

3. **Chlorine water test**

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

Iodine being soluble in CCl_4 imparts a violet Colour to the CCl_4 layer.

Nitrate (NO_3^-)

1. **Copper test**

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$$

$$4HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + \underset{\text{(Reddish brown)}}{2NO_2} + 2H_2O$$

2. **Ring Test**

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

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

$$FeSO_4 + NO + 5H_2O \longrightarrow \underset{\text{(Brown ring)}}{[Fe(NO)(H_2O)_5]SO_4}$$

Acetate (CH_3COO^-)

1. **Oxalic acid test**

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2CH_3COONa \longrightarrow \begin{matrix}COONa\\|\\COONa\end{matrix} + \underset{\text{Acetic acid (Vinegar smell)}}{2CH_3COOH}$$

2. **Ester test**

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

$$CH_3COOH + C_2H_5OH \longrightarrow \underset{\substack{\text{Ethyl acetate}\\\text{(Fruity smell)}}}{CH_3COOC_2H_5} + H_2O$$

3. **Ferric chloride test**

$$3CH_3COONa + FeCl_3 \longrightarrow (CH_3COO)_3Fe + 3NaCl$$

$$(CH_3COO)_3Fe + 2H_2O \longrightarrow \underset{\text{Reddish brown ppt}}{(CH_3COO)(OH)_2Fe\downarrow} + 2CH_3COOH$$

Oxalate ($C_2O_4^{2-}$)

1. **Calcium chloride test**

$$(NH_4)_2C_2O_4 + CaCl_2 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4\downarrow} + 2NH_4Cl$$

2. Potassium permanganate test

$$2KMnO_4 + 3H_2SO_4 + 5\overset{COOH}{\underset{COOH}{|}} \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 \uparrow + 8H_2O$$

Confirmation Of Sulphate, SO_4^{2-}

(Not indicated in dilute and concentrated H_2SO_4 acid tests).

Experiment	Observations
1. Barium chloride test To a part of the aqueous solution of the salt add barium chloride solution.	A white ppt. is formed which is insoluble in dil HCl.
2. Matchstick test Mix a small amount of the salt with sodium carbonate and a little powdered charcoal so as to get a paste. Take some of this paste on one end of a wooden splinter and heat in the reducing flame till the mass fuses. Dip the fused mass into sodium nitroprusside solution taken in a China dish.	Violet streaks are produced.
3. Lead acetate test To a part of aqueous solution of the salt add lead acetate solution.	A white ppt. is formed which is soluble in excess of hot ammonium acetate solution.

Confirmation Of Phosphate, PO_4^{3-}

(Not indicated in dilute and concentrated H_2SO_4 acid test).

Experiment	Observations
Ammonium molybdate test To the aqueous solution or sodium carbonate extract (or the original salt) add concentrated nitric acid and boil. Add ammonium molybdate solution in excess and again boil.	A deep yellow ppt. or Colouration is obtained.
Magnesia mixture test Take a portion of aqueous solution (or a part of sodium carbonate extract, add hydrochloric acid to acidify it and boil off CO_2). Add magnesia mixture (to prepare it, add solid NH_4Cl to magnesium chloride solution. Boil, cool and add NH_4OH till a strong smell of ammonia is obtained) and allow to stand.	A white ppt. is obtained.

Chemical reactions involved in the confirmation of SO_4^{2-} and PO_4^{3-}

Sulphate (SO_4^{2-})

1. Barium chloride test

$$Na_2SO_4 + BaCl_2 \rightarrow \underset{\text{white}}{BaSO_4} \downarrow + 2NaCl$$

2. Match-stick test

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + 2NaCl$$

$$BaSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + BaCO_3$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$

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

3. Lead acetate test

$$Na_2SO_4 + Pb(CH_3COO)_2 \rightarrow PbSO_4 \downarrow + 2CH_3COONa$$

Phosphate (PO_4^{3-})

1. Ammonium molybdate test

$$K_3PO_4 + \underset{\text{Ammonium molybdate}}{3(NH_4)_2MoO_4} \rightarrow 2(NH_4)_3PO_4 + \underset{\text{Pot. molybdate}}{SK_2MoO_4}$$

$$K_2MoO_4 + 2HNO_3 \rightarrow \underset{\text{Molybdic acid}}{H_2MoO_4} + 2KNO_3$$

$$H_2MoO_4 \rightarrow MoO_3 + H_2O$$

$$(NH_4)_3PO_4 + 12MoO_3 + 6H_2O \rightarrow \underset{\text{Ammonium phosphate molybdate (yellow ppt).}}{(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O \downarrow}$$

2. Magnesia mixture test

$$\underset{\text{Disodium hydrogen phosphate}}{Na_2HPO_4} + MgCl_2 + NH_4OH \rightarrow \underset{\text{Mag. Ammonium phosphate (white ppt.)}}{Mg(NH_4)PO_4 \downarrow} + 2NaCl + H_2O.$$

Wet Tests For Basic (Cations)

Preliminary tests such as dry heating test, charcoal cavity test, flame test and borax bead test may give us some indication about the cation present in the salt. However, the cation is finally detected and confirmed through a systematic analysis involving wet tests. For the sake of qualitative analysis, the cations are Classified into the following groups (Table).

Classification of Cations

Group	Cation	Group reagent	Colour of the ppt.
Group - 0	NH_4^+ (ammonium)	-	-
Group - I	Pb^{2+} (lead)	dil. HCl	$PbCl_2$ (White)
Group - II	Pb^{2+} (lead) Cu^{2+} (copper) Cd^{2+} (cadmium) As^{3+} (arsenic)	H_2S in presence of dis HCl	PhS (Brownish-black) CuS (Black) CdS (Yellow) As_2S_3 (Yellow)
Group - III	Fe^{2+}, Fe^{3+} (iron) Al^{3+} (aluminium)	Solid NH_4Cl + excess NH_6OH	$Fe(OH)_3$ (Brown) $Al(OH)_2$ (Dirty-white)
Group - IV	Zn^{2+} (zinc) Ni^{2+} (nickel) Mn^{2+} (manganese) Co^{2+} (cobalt)	H_2S in presence of $NH_4Cl + NH_4OH$	ZnS (Dirty-white) NiS (Black) MnS (Light-pink) CoS (Black)
Group - V	Ba^{2+} (barium) Sr^{2+} (strontium) Ca^{2+} (calcium)	$(NH_4)_2CO_3$ in presence of NH_4Cl and NH_4OH	$BaCO_7$ (White) $SrCO_4$ (White) $CaCO_3$ (White)
Group - VI	Mg^{2+} (magnesium)	None	-

Before carrying out the wet tests for the analysis of cation, the salt has to be dissolved in some suitable solvent to prepare its solution.

Preparation Of Solution For Wet Tests Of Basic Radicals

The very first essential step is to prepare a Clear and transparent solution of the salt under investigation. For this purpose, the under-noted solvents are tried one after another 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.

(i) Distilled water (cold or hot).
(ii) Dilute HCl (cold or hot).
(iii) Cone. HCl (cold or hot).

Procedure For The Preparation Of Solution

Take a small quantity of the given salt in a test tube. Add some suitable solvent into it and shake. If it does not dissolve even after heating for some time, take the fresh quantity of the salt again and treat it similarly with the next solvent. The Clear solution thus obtained is labelled as the Original Solution (O.S.).

Important Notes

(i) In case some gas is evolved during the preparation of the solution, let the reaction cease. Gas must be completely expelled by heating.

(ii) In case the solution is prepared in dilute HCl, group I is absent. Proceed with group II.

(iii) If the salt is soluble in hot water, and on cooling white precipitates appear, lead chloride is indicated.

(iv) It is necessary to dilute the solution if it is made in concentrated acid before proceeding with the analysis.

The following table will help the students in the choice of a suitable solvent.

Solvent	Salts which dissolve
1. Cold water	a) All NH_4^+, Na^+ and K^+ salts. b) All nitrites, nitrates and acetates. c) Most of the sulphates except those of Pb, Ba, Ca, and Sr. d) All chlorides except that of lead.
2. Hot water	Lead chloride, lead nitrate.
3. Dil. HCl	All carbonates which do not dissolve in water i.e., Carbonates of Ca, Ba, Sr, Mg, Zn, Al, Cu, Ni, Mn, Fe etc., but not of Pb.

The separation of cations into various groups by making use of suitable reagents (known as group reagents) is based on the differences in the chemical properties of cations. For example, if hydrochloric acid is added to a solution containing all cations, only the chlorides of lead, silver and mercury will precipitate, since all other chlorides are soluble. Thus, these cations form a group of ions which may be precipitated from the solution by the addition of group reagent HCl. Similarly, H_2S is a group reagent for group II. The following Table Clearly shows the group reagents for different groups and the form in which cations of the particular group are precipitated out.

Theory Of Precipitation Of Different Groups

The Classification of cations into different groups in the inorganic qualitative analysis is based upon the knowledge of solubility products of salts of these basic radicals. For example, chlorides of Hg_2^{2+}, Pb^{2+} and Ag^+ have very low solubility products. Based on this knowledge these radicals are grouped together in group-I and are precipitated as their chlorides by adding dilute HCl to their solutions. For adjusting the conditions for precipitation, another concept called common ion effect plays very important role. Before we consider the precipitation of radicals of other groups, let us discuss in brief the concept of common ion effect.

Common Ion Effect

Weak acids and weak bases are ionised only to a small extent in their aqueous solutions. In their solutions, unionised molecules are in dynamic equilibrium with ions. The degree of ionisation of a weak electrolyte (weak acid or weak base) is further suppressed if some strong electrolyte which can furnish some in common with the ions furnished by a weak electrolyte, is added to its solution. This effect is called the common ion effect. For example, the degree of ionisation of NH_4OH (a weak base) is suppressed by the addition of NH_4Cl (a strong electrolyte). The ionisation of NH_4OH and NH_4Cl in solution is represented as follows.

$$NH_4OH(aq) \rightleftharpoons \underset{\text{Common ion}}{NH_4^+(aq)} + OH^-(aq) \quad \text{.....weakly ionised ... (1)}$$

$$NH_4Cl \rightarrow \underset{\text{Common ion}}{NH_4^+(aq)} + Cl^+(aq) \quad \text{..... strongly ionised ... (2)}$$

Due to the addition of NH_4OH, which is strongly ionised in the solution, the concentration of NH_4 ions increase in the solution. Therefore, according to Le-Chatelier's principal equilibrium in equation (1)shifts in the backward direction in favour of unionised NH_4OH. In this way, the addition of NH_4Cl suppresses the degree of ionisation of NH_4OH. Thus, the concentration of OH^- ions in the solution is considerably reduced and the weak base NH_4OH becomes a still weaker base.

The suppression of the degree of ionisation of a weak electrolyte (weak acid or weak base) by the addition of some strong electrolyte having a common ion, is called the common ion effect.

The application of the concept of the common ion effect in the qualitative analysis is illustrated as follows.

The cations of group II (Pb^{2+}, Cu^{2+}, AS^{3+}) are precipitated as their sulphides. Solubility product of sulphides of group II radicals are very low. Therefore, even with a low concentration of S^{2-} ions, the ionic products (Qs_p) exceed the value of their solubility products (KS_p) and the radicals of group II get precipitated. The low concentration of S^{2-} ions is obtained by passing H_2S gas through the solution of the salts in the presence of dil. HCl suppresses the degree of ionisation of H_2S by the common ion effect.

$$H_2S \rightleftharpoons \underset{\text{Common ion}}{2H^+} + S^{2-} \quad ...(3)$$

$$HCl \longrightarrow \underset{\text{Common ion}}{H^+} + Cl \quad ...(4)$$

It is necessary to suppress the concentration of S^{2-} ions, otherwise, radicals of group IV will also get precipitated along with group II radicals.

Radicals of group IV (Ni^{2+}, CO^{2+}, Mn^{2+}, Zn^{2+}) are also precipitated as their sulphides. But the solubility products of their sulphides are quite high. So that ionic products exceed solubility products, the concentration of S^{2-} ions should be high in this case. A high concentration of sulphide ions is achieved by passing H_2S gas through the solutions of the salts in the presence of NH_4OH. Hydroxyl ions from NH_4OH combine with H^+ ions from H_2S. Due to the removal of H^+ ions the equilibrium of H_2S shifts in favour of the ionised form.

$$\begin{aligned} H_2S &\rightleftharpoons 2H^+ + S^{2-} \\ NH_4OH &\rightleftharpoons NH_4^+ + OH^- \\ H^+ + OH^- &\rightleftharpoons H_2O \end{aligned}$$

Hence, the concentration of S^{2-} ions increases. With this increased concentration of S^{2-} ions ionic products exceed solubility products and radicals of group IV get precipitated.

Radicals of group III (Fe^{3+}, Al^{3+}) are precipitated as their hydroxides by NH_4OH in the presence of NH_4Cl. The purpose of NH_4Cl is to suppress the degree of ionisation of NH_4OH by common ion effect to decrease the concentration of OH^- ions.

$$NH_4OH \rightleftharpoons \underset{\text{Common ion}}{NH_4^+} + OH^-$$

$$NH_4Cl \longrightarrow \underset{\text{Common ion}}{Cl_4{}^+} + Cl^-$$

The solubility products of hydroxides of group III radicals are quite low. Therefore, even with this suppressed concentration of OH^- ions their ionic products exceed solubility products and hence they get precipitated. If the concentration of OH^- ions is not suppressed, the radicals of groups IV, V and Mg^{2+} will also be precipitated along with radicals of group III.

Radicals of group V (Ba^{2+}, Sr^{2+}, Ca^{2+}) are precipitated as their carbonates by the addition of $(NH_4)_2CO_3$ in the presence of NH_4Cl and NH_4OH.

NH_4Cl suppresses the degree of ionisation of $(NH_4)_2CO_3$ by common ion effect and hence decreases the concentration of CO_3^{2-} ions.

$$(NH_4)_2CO_3 \rightleftharpoons \underset{\text{Common ion}}{2NH_4^+} + CO_3^{2-}$$

$$NH_4Cl \longrightarrow \underset{\text{Common ion}}{NH_4^+} + Cl^-$$

But solubility products of carbonates of group V radicals are quite low and hence even with the suppressed concentration of CO_3^{2-} ions their ionic products exceed solubility products, and they get precipitated whereas Mg^{2+} and other radicals of group VI having relatively high solubility products are not precipitated.

Analysis Of Group Zero (NH_4^+)

This group includes NH_4^+ cation. During the analysis of cations, NH_4Cl and NH_4OH are added in many steps. Therefore, the NH_4^+ ion is detected in the beginning using solid salt.

PROCEDURE

The solid salt is heated with a concentrated solution of sodium hydroxide. In case, ammonia gas is evolved, NH_4^+ is present. The evolution of NH_3 gas is confirmed by the following tests.

(i) Characteristic ammoniacal smell.

(ii) The gas gives white fumes when a glass rod is dipped in dil. HCl is brought near the mouth of the test tube.

(iii) When the gas is passed through Nessler's reagent, it would give brown ppt. in the case of NH_3 .

Chemical Reactions Involved In Group-Zero Analysis

$$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + H_2O + NH_3\uparrow$$

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

Nessler's Reagent Test

$$\underset{\text{Nessler's Reagent}}{2K_2[HgI_4]} + NH_3 + 3KOH \longrightarrow \underset{\text{Brown ppt.}}{H_2N.HgO \cdot HgI\downarrow} + 7KI + 2H_2O$$

Analysis Of Group I (Silver Group)

This group includes Pb^{2+}, $Ag^+$and Hg_2^{2+}. But in the present context, we shall study only Pb^{2+}. The group reagent for this group is dil. hydrochloric acid.

PROCEDURE

To the original solution add dil. hydrochloric acid. If a white precipitate is formed, first group (Pb^{2+}) is present.

Filter and wash the ppt. with cold water and follow the instructions as given below.

Analysis Of Group I (Pb^{2+})

Boil the white precipitate with 5 – 10ml of water. Precipitate dissolves. Divide the solution tained into three parts. Confirmation.

(i) Cool one part of the solution under tap. White crystalline ppt. separates out.

(ii) Potassium iodide test. To the second part of the solution, add KI solution -yellow ppt.

(iii) Potassium chromate test. To the third part of the solution add K_2CrO_4 solution-yellow ppt.

Note:

1. **If the original solution is prepared in cold dilute hydrochloric acid, first group is absent.**
2. **If the original solution is prepared in cone, hydrochloric acid, simply add water. White ppt. shows the presence of first group.**

Chemical Reactions Involved In Group I Analysis

The addition of HCl to the solution will precipitate Pb^{2+} as chloride

$$Pb^{2+} + 2HCl \longrightarrow \underset{\text{White ppt.}}{PbCl_2\downarrow} + 2HNO_3$$

When the white ppt. is boiled with water, the precipitates dissolve because the $PbCl_2$ is soluble in hot water.

Confirmatory Tests

On cooling, precipitates settle down as $PbCl_2$ is less soluble in cold water.

1. **Potassium iodide test**

$$\underset{\text{(Hot solution)}}{PbCl_2} + 2KI \rightarrow \underset{\text{Yellow ppt.}}{PbI_2 \downarrow} + 2KCl$$

2. **Potassium chromate test**

$$\underset{\text{(Hot solution)}}{PbCl_2} + K_2CrO_4 \rightarrow \underset{\text{Yellow ppt}}{PbCrO_4 \downarrow} + 2KCl.$$

Analysis Of Group II (Copper Group)

This group includes Pb^{2+} and Cu^{2+} in IIA group and As^{3+} in IIB Group. These are precipitated as their sulphides. If group I is absent, the tests for radicals of group II are carried out. Group reagent for this group is H_2S gas in the presence of dil. HCl.

PROCEDURE

Take about 2 ml of the original solution in a test tube. Make it acidic with dil. HCl and warm the contents. Through this solution pass H_2S gas from Kipp's apparatus by turning the stop cock as shown in Fig.10, Formation of the black or yellow precipitates indicates the presence of group II radical. If this is observed, pass more of H_2S gas to ensure complete precipitation of the radical sulphide. Centrifuge and separate the precipitates.

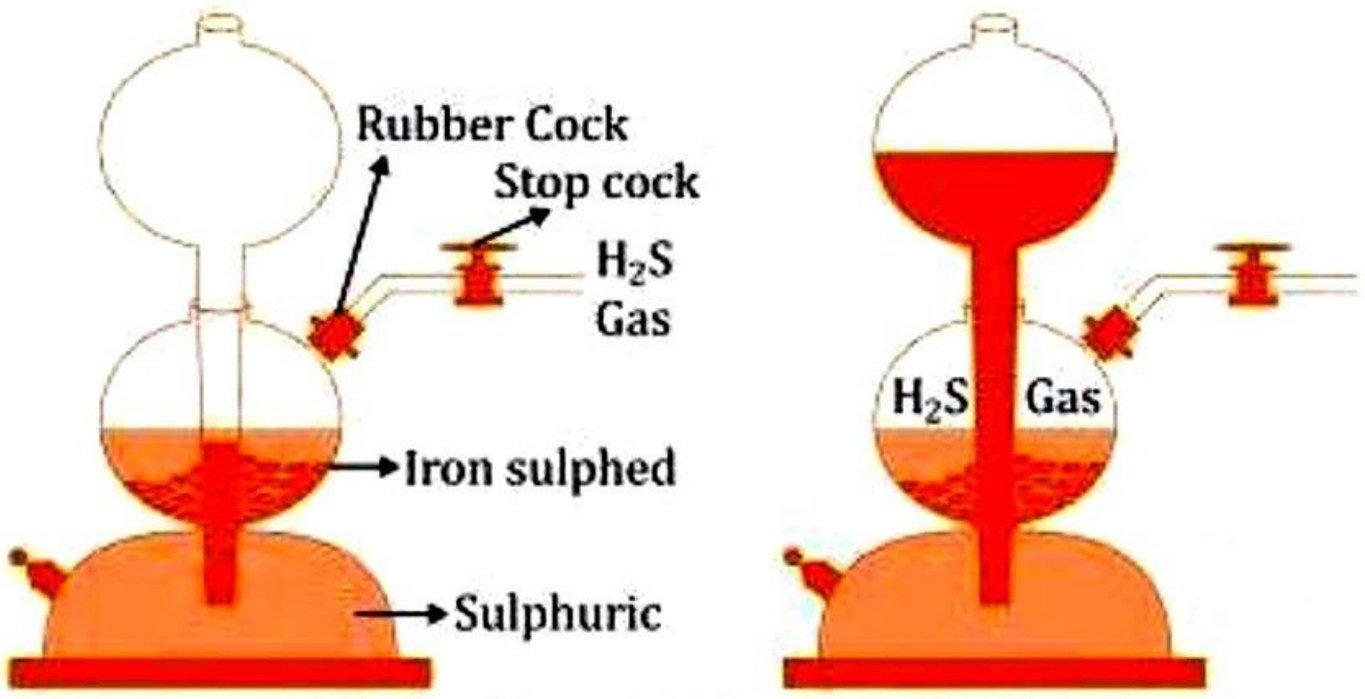


Fig. 10 Kipp's apparatus for H_2S gas

Identification of IIA and IIB GroupS. Note the Colour of the precipitate. If the precipitate is black, it indicates Pb^{2+} or Cu^{2+}. If the Colour of the precipitate is yellow this indicates As^{3+}

Analysis of Group II (Pb^{2+}, Cu^{2+}, As^{3+})		
Black ppt. (Pb^{2+} or Cu^{2+} present). Boil the black ppt, with 5mL of 50% HNO_3 in a test tube		**Yellow ppt. (As^{3+} present). Warm a some yellow ppt. with 3 – 4 mL of yellow ammonium sulphide solution for 2 – 3 minutes**
Black ppt. dissolves to give a colourless solution **Pb^{2+} present**	Black ppt. dissolves to give a bluish green solution **Cu^{2+} present**	ppt. dissolves **As^{3+} present**
To the above solution, add 1 mL of alcohol and excess of H_2SO_4 – A white ppt. is obtained. **Pb^{2+} present** Confirmatory tests **1.** Potassium chromate test. To	Divide the blue solution into two parts. Confirmatory tests **1.** Ammonium hydroxide test.	Confirmatory tests **1.** Dil. HCl test. To the above

one part, add a few drops of K_2CrO_4 solution-Yellow ppt. formed which dissolves in excess of NaOH solution. **Pb^{2+} confirmed.** 2. Potassium iodide test. To the second part, add a few drops of KI solution-Yellow ppt. formed. **Pb^{2+} confirmed.**	To one part, add NH_4OH solution dropwise-Light blue ppt. first appear but redissolve in excess of NH_4OH giving deep blue solution. **Cu^{2+} confirmed.** 2. Potassium ferrocyanide test. Acidify a portion of the above blue solution or O.S. with dil. acetic acid and then add a few drops of potassium ferrocyanide solution-Chocolate coloured ppt. formed. **Cu^{2+} confirmed.**	solution add dil. HCl – Yellow ppt.formed. **As^{3+} confirmed.** Dissolve the yellow ppt. by boiling with conc. HNO_3 and divide into two parts. 2. Ammonium molybdate test. To one part add 2 – 3mL of ammonium molybdate solution and heat. A yellow ppt. **As^{3+} confirmed.** 3. Magnesia mixture test. To the second part add NH_4OH till it becomes alkaline. To this add magnesia mixture (a mixture containing equal volumes of $MgSO_4$, NH_4Cl and NH_4OH solutions)-A white ppt. **As^{3+} confirmed.**

Chemical Reactions Involved In The Analysis Of Group II

$$PbCl_2 + H_2S \rightarrow 2HCl + PbS\downarrow \text{ (Black)}$$
$$CuCl_2 + H_2S \rightarrow 2HCl + CuS\downarrow \text{ (Black)}$$
$$2AsCl_2 + 3H_2S \rightarrow 6HCl + As_2S_3\downarrow \text{ (Yellow)}$$

Lead (Pb^{2+})

Black ppt. of PbS dissolves in 50% nitric acid. On adding sulfuric acid, lead sulphate precipitates.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + 2NO + 3S$$
$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow 2HNO_3 + \underset{\text{(white)}}{PbSO_4}\downarrow$$

1. Potassium iodide test

$$Pb(NO_3)_2 + 2KI \longrightarrow 2KNO_3 + \underset{\text{(yellow)}}{PbI_2}\downarrow$$

2. Potassium chromate test

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow 2KNO_3 + \underset{\text{(yellow)}}{PbCrO_4}\downarrow$$

Copper (Cu^{2+})

Black ppt. of CuS dissolves in 50% nitric acid and a blue solution is obtained on a excess of NH_4OH.

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO + 3S$$
$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\text{(Blue solution)}}{[Cu(NH_3)_4][NO_3]_2} + 4H_2O$$

1. Potassium ferrocyanide test

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

$$2CuSO_4 + K_4[Fe(CN)_6] \rightarrow \underset{\text{(Chocolate brown Colour)}}{Cu_2[Fe(CN)_6]\downarrow} + 2K_2SO_4$$

2. Potassium iodide test

$$2CuSO_4 + 4KI \rightarrow \underset{\text{White ppt.}}{Cu_2I_2\downarrow} + \underset{\text{Brown Colouration}}{I_2} + 2K_2SO_4$$

Arsenic (As^{3+})

The yellow residue of As_2S_3 is dissolved in conc. HNO_3 forming arsenic acid.

$$As_2S_3 + 10HNO_3 \rightarrow \underset{\text{Soluble}}{2H_3AsO_4} + 10NO_2 + 3S + 2H_2O$$

1. Ammonium molybdate test

$$\underset{\text{Arsenous sulphide}}{As_2S_3(s)} + \underset{\text{Nitric acid}}{10HNO_3} \rightarrow \underset{\text{Arsenic acid}}{2H_3AsO_4} + \underset{\text{Nitrogen dioxide}}{10NO_2} + \underset{\text{Sulphur}}{3S} + \underset{\text{Water}}{2H_2O(l)}$$

$$\underset{\text{Arsenic ion}}{H_3AsO_4} + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \rightarrow \underset{\text{Ammonium arseno molybdate (yellow ppt.)}}{(NH_4)_3AsO_4.12MoO_3} + \underset{\text{Ammonium nitrate}}{21NH_4NO_3} + \underset{\text{Water}}{12H_2O(l)}$$

Or

$$\underset{\text{Arsenate ion}}{AsO_4^{3-}} + \underset{\text{Molybdate ion}}{12MoO_4^{2-}} + \underset{\text{acid}}{24H^+} \rightarrow \underset{\text{Arseno molybdate ion}}{As(Mo_{12}O_{40})^{3-}} + 12H_2O(l)$$

2. Magnesia mixture test

$$H_3AsO_4 + MgSO_4 + 3NH_4OH \rightarrow \underset{\text{White ppt.}}{Mg(NH_4)_2AsO_4} + (NH_4)_2SO_4 + 3H_2O$$

Analysis Of Group III (Iron Group)

The cations present in this group are Fe^{2+}, Fe^{3+}, Cr^{3+} and Al^{3+}. Only Fe^{2+}/Fe^{3+} and Al^{3+} are included in the syllabus of this Class. These cations are precipitated as hydroxides by adding ammonium hydroxide in presence of ammonium chloride. Thus, group reagent for this group is NH_4OH in the presence of NH_4Cl.

PROCEDURE

In case, first and second groups are absent proceed for group III with the original solution. Take about 5 ml of the original solution and add 4-5 drops of cone, nitric acid. Boil the solution for some time. Add to it about 2 g of solid NH_4Cl and boil again. Cool the solution under tap water. Add excess of ammonium hydroxide to it and shake. A ppt. shows the presence of some cation of group III. Filter the ppt. and wash with water. Note the Colour of the ppt. If the ppt. is reddish brown in Colour, it indicates the presence of Fe^{3+} and if the Colour is white, it indicates the presence of Al^{3+}. Analyses the ppt. and draw inferences as in Table.

Analysis of Group III (Fe^{3+} and Al^{3+})	
Fe^{3+} (Reddish brown ppt.)	**Al^{3+} (Gelatinous White ppt.)**
Confirmatory Test	**Confirmatory Test**
Dissolve the reddish-brown ppt. in dilute HCl, and divide the solution into two parts. 1. **Potassium ferrocyanide test:** To one part of the above solution add potassium ferrocyanide solution – A deep blue colouration or ppt. 2. **Potassium sulphocyanide test:** To the second part, add a little potassium	1. **Sodium Hydroxide test:** To one part of the above solution add NaOH solution. – White ppt. soluble in excess of NaOH solution. 2. **Lake test:** To the second part of the above solution, add few drops of blue litmus solution –

sulphocyanide solution. Blood red Colouration.	Solution turns pink. Now add NH4OH solution dropwise till alkaline and shake. Allow it to stand —A blue lake (a blue ppt. floating in a coloueless solution) is formed.

Note:

1. Test of Fe^{2+}. The addition of cone, nitric acid in the analysis of group III serves to oxidise Fe^{2+}ions to Fe^{3+} ions. Add conc. nitric acid only if the cation is Fe^{2+} otherwise the addition of nitric acid may be avoided. To test this, add a few drops of potassium ferricyanide solution to the original salt solution. A deep blue colouration shows Fe^{2+}.
2. Use sufficient quantity of ammonium chloride, otherwise the hydroxides of higher group may be precipitated along with the radicals of third group.
3. Add NH_4OH until the solution gives the smell of ammonia.

Chemical Reactions Involved in the Analysis of Group III

The group III cations are precipitated as hydroxides on the addition of excess of ammonium hydroxide.

$$FeCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{(Reddish brown ppt.)}}{Fe(OH)\downarrow}$$

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{(White ppt.)}}{Al(OH)_3\downarrow}$$

Iron (Fe^{3+})

The reddish-brown ppt. of $Fe(OH)_3$ is dissolved in HCl.

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

1. Potassium ferrocyanide test

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

2. Potassium sulphocyanide test

$$FeCl_3 + 3KCNS \longrightarrow 3KCl + \underset{\substack{\text{Ferric sulphocyanide}\\ \text{(Blood red Colouration)}}}{Fe(CNS)_3}$$

Aluminium (Al^{3+})

1. Lake test

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\substack{\text{Blue Colour}\\ \text{adsorbs on this ppt.}}}{Al(OH)_3\downarrow}$$

Analysis Of Group IV (Zinc Group)

The radicals present in this group are CO^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}. These are precipitated as sulphides by passing H_2S gas through the ammoniacal solution of the salt.

The group reagent for this group is H_2S gas in the presence of NH_4Cl and NH_4OH.

PROCEDURE

If there is no ppt. in the third group, then use the same ammoniacal solution for the fourth group. Pass H_2S gas through the solution. If some ppt. is formed, presence of some radical of group IV is indicated. Filter the ppt. and wash it with water. Note the Colour of the ppt. and analyses the ppt. according to the Table.

Analysis of Group IV Radicals (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+})			
Black ppt. (Co^{2+} or Ni^{2+}) Observe the Colour of the original salt. If the salt is purple or deep violet in Colour perform confirmatory tests for Co^{2+} and if it is greenish perform confirmatory tests for Ni^{2+} with the original solution.		**Buff (flesh) Coloured ppt. Mn^{2+}**	**Dull white ppt. Zn^{2+}**
Confirmation of Co^{2+} **1. Potassium nitride test** To one part of the O.S. add ammonium hydroxide to neutralise the solution. Add acetic acid and a crystal of potassium nitrite. Warm. A yellow ppt. is formed. **2. Ammonium thiocyanate ether test** To another part add ether (1 ml). Add a crystal of Ammonium thiocyanate, shake. Allow to settle. Blue Colour in ethereal layer confirms Co^{2+}. **3. Borax bead test** Perform borax bead test with the salt. A blue bead is formed.	Confirmation of Ni^{2+} **1. Dimethyl glyoxime test** To one part of O.S. add Ammonium hydroxide solution and few drops of dimethyl glyoxime. Bright rose red ppt. is obtained. **2. Sodium hydroxide Br_2 test** To another part add sodium hydroxide (in excess) and bromine water Boil. A black ppt. is formed. **3. Borax bead test** Perform borax bead test with the salt. Brown bead in oxidizing and grey bead in reducing flame is obtained.	Confirmation of Mn^{2+} **1. Sodium hydroxide Br_2 test** To the O.S. add NaOH solution Shake. A white ppt. is formed. Add Br_2 water to white ppt. It turns black or brown. **2. Lead peroxide test** To black ppt. obtained in above test add conc. HNO_3 and lead peroxide. Boil, cool and allow to settle. Pink-Coloured solution is formed. **3. Borax bead test** Perform borax bead test with the salt. Pinkish bead in oxidizing flame and Colourless bead in reducing flame.	Confirmation of Zn^{2+} **1. Sodium hydroxide. test** To one part of O. S. add sodium hydroxide solution dropwise. A white ppt. is formed. Add more of NaOH. The white ppt. dissolves. **2. Pot. ferrocyanide test** To another part, add pot. ferrocyanide solution White or bluish white ppt. is formed. **3. Charcoal Cavity/Cobalt Nitrite 'Test** Perform Charcoal Cavity/Cobalt Nitrate test with the salt. Greenish residue is obtained.

Chemical Reactions Involved In The Analysis Of Group IV

Passing of H_2S gas through the group III solution will precipitate the radicals CO^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} as their sulphides. Formation of black ppt. (CoS or NiS) indicates cobalt or nickel. Formation of buff-Coloured ppt. (MnS) indicates manganese and dirty white ppt. (ZnS) indicts zinc.

$$Co(OH)_2 + H_2S \longrightarrow 2H_2O + CoS\downarrow \quad \text{(Black)}$$
$$Ni(OH)_2 + H_2S \longrightarrow 2H_2O + NiS\downarrow \quad \text{(Black)}$$
$$Zn(OH)_2 + H_2S \longrightarrow 2H_2O + ZnS\downarrow \quad \text{(White)}$$
$$Mn(OH)_2 + H_2S \longrightarrow 2H_2O + MnS\downarrow \quad \text{(Buff-Coloured)}$$

Cobalt (Co^{2+})

1. Potassium nitrite test

$$\underset{\text{(O.S)}}{CoCl_2} + 2KNO_2 \longrightarrow 2KCl + \underset{\text{Cobaltous nitrite}}{Co(NO_2)_2}$$

$$KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2$$

$$Co(NO_2)_2 + 2HNO_2 \rightarrow \underset{\text{cobaltic nitrite}}{Co(NO_2)_3} + H_2O + NO$$

$$Co(NO_2)_3 + 3KNO_2 \rightarrow \underset{\substack{\text{Pot. cobalti nitrite}\\ \text{(yellow ppt.)}}}{K_3[Co(NO_2)_6]}$$

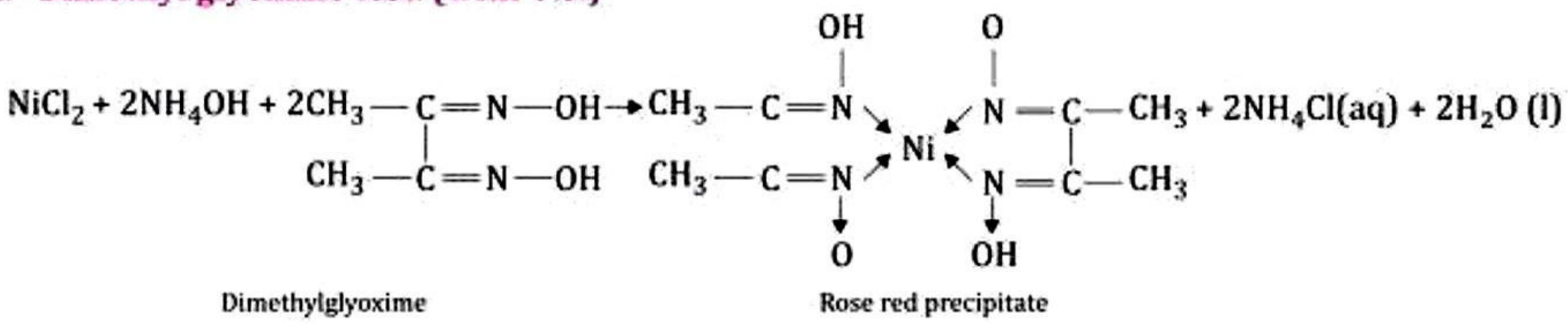
2. Ammonium thiocyanate ether test

On addition of ether and a crystal of ammonium thiocyanate (shaking and allowing to stand), a blue Colour due to the formation of ammonium cobalt thiocyanate, is obtained in the ethereal layer.

$$CoCl_2 + 4NH_4CNS \rightarrow (NH_4)_2[Co(CNS)_4] + 2NH_4Cl$$

Nickel (Ni^{2+})

1. Dimethyl glyoxime test. (with O.S.)



2. Sodium hydroxide-bromine water test

$$NiCl_2 + 2NaOH \rightarrow 2NaCl + \underset{\text{(green ppt.)}}{Ni(OH)_2}\downarrow$$

$$Br_2 + H_2O \rightarrow 2HBr + [O]$$

$$2Ni(OH)_2 + H_2O + [O] \rightarrow \underset{\substack{\text{Nickelic hydroxide}\\ \text{(Black ppt.)}}}{2Ni(OH)_3}\downarrow$$

Manganese (Mn^{2+})

Manganese sulphides dissolve in dil. HCl forming manganese chloride, and H_2S is boiled off.

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S\uparrow$$

1. NaOH and Br_2 water test

$$MnCl_2 + 2NaOH \rightarrow \underset{\text{White ppt.}}{Mn(OH)_2}\downarrow + 2NaCl$$

The white ppt. of manganese hydroxide turns brown on adding Br_2 water due to its oxidation to brown manganic hydroxide $MnO(OH)_2$

$$Br_2 + H_2O \rightarrow 2HBr + [O]$$

$$Mn(OH)_2 + [O] \rightarrow \underset{\text{Brown ppt.}}{MnO(OH)_2}\downarrow$$

2. PbO_2 test

$$MnS + 2HNO_3 \rightarrow Mn(NO_3)_2 + H_2S$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \rightarrow \underset{\text{Pink solution}}{2HMnO_4} + 5Pb(NO_3)_2 + 2H_2O$$

Zinc (Zn^{2+})

The precipitate of ZnS obtained in Group IV is white.

The white ppt. of ZnS dissolves in dil. HCl, and H_2S is boiled off.

$$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S\uparrow$$

1. **NaOH test**

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2}\downarrow + 2NaCl$$

$$\underset{\text{White ppt.}}{Zn(OH)_2} + 2NaOH \longrightarrow \underset{\text{Solute}}{Na_2ZnO_2} + 2H_2O$$

2. **Potassium ferrocyanide test**

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{White Bluish-white ppt.}}{Zn_2[Fe(CN)_6]}\downarrow + 4KCl$$

Analysis Of Group V (Calcium Group)

Group V consists of three radicals. Ba^{2+}, Sr^{2+} and Ca^{2+}. These cations are precipitated as their carbonates.

Group reagent for this group is $(NH_4)_2CO_3$ in the presence of NH_4Cl and NH_4OH.

PROCEDURE

If the fourth group is absent, then proceed for radicals of group V.

To the O.S. add 2-3 gins of solid NH_4Cl, boil, cool and add NH_4OH till the solution smells of ammonia. Then add $(NH_4)_2CO_3$ solution. Appearance of white ppt. indicates the presence of group V cation. Filter and wash the ppt. with water. Dissolve the ppt. in hot dil. acetic acid. Divide the solution into three parts and proceed as in table.

Analysis of Group V(Ba^{2+}, Sr^{2+}, Ca^{2+})		
Ba^{2+}	**Sr^{2+}**	**Ca^{2+}**
1. Potassium chromate test To one part of the solution, add a few drops of potassium chromate solution. Yellow ppt. **2. Flame test** Perform a flame test with the original salt. Grassy green flame.	Test for Sr^{2+} only if Ba^{2+} is absent. **1. Ammonium sulphate test** To the second part of the solution, add 1ml of Ammonium sulphate solution and warm. White ppt. **2. Flame test** Perform a flame test with the original salt. Crimson red flame.	Test for Ca^{2+} only if Ba^{2+} and Sr^{2+} are absent. **1. Ammonium oxalate test** To the third portion of the solution, add 1-2 ml of Ammonium oxalate solution. Add a little Ammonium hydroxide to it and scratch the sides. White ppt. **2. Flame test** Perform flame test with the original salt. Brick red flame.

Note:

1. Proceed to test for group V cations in the order, Ba^{2+}, Sr^{2+} and Ca^{2+}. If Ba^{2+} is confirmed, do not test for Sr^{2+} or Ca^{2+} Similarly if Sr^{2+} is confirmed, do not test for Ca^{2+}.
2. Original solution can be preferably used for testing Sr^{2+} and Ca^{2+}.

Chemical Reactions Involved In The Analysis Of Group V Radicals

When $(NH_4)_2CO_3$ is added to a salt solution containing NH_4Cl and NH_4OH, the Ba^{2+}, Sr^{2+} and Ca^{2+} are precipitated.

$$Ba^{2+}(aq) + (NH_4)_2CO_3 \longrightarrow BaCO_3\downarrow + 2NH_4^+$$

$$Sr^{2+}(aq) + (NH_4)_2CO_3 \longrightarrow SrCO_3\downarrow + 2NH_4^+$$

$$Ca^{2+}(aq) + (NH_4)_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NH_4^+$$

This insoluble carbonate dissolves in acetic acid due to formation of soluble Barium.

Barium (Ba^{2+})

White ppt. of $BaCO_3$ dissolves in hot dilute acetic acid.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 \downarrow + H_2O$$

1. **Potassium chromate test**

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow 2CH_3COOK + \underset{\text{(yellow ppt.)}}{BaCrO_4 \downarrow}$$

2. **Flame test**

   Barium imparts grassy green Colour to the flame.

Strontium (Sr^{2+})

White ppt. of $SrCO_3$ dissolves in hot dilute acetic acid.

$$SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Sr + CO_2 \uparrow + H_2O$$

1. **Ammonium sulphate test**

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow 2CH_3COONH_4 + \underset{\text{(white ppt.)}}{SrSO_4 \downarrow}$$

2. **Flame test**

   Strontium produces crimson red flame.

Calcium (Ca^{2+})

White ppt. of $CaCO_3$ dissolves in hot dil. acetic acid.

$$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 \uparrow + H_2O$$

1. **Ammonium oxalate test**

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \longrightarrow 2CH_3COONH_4 + \underset{\text{(white ppt.)}}{CaC_2O_4 \downarrow}$$

2. **Flame test**

   Calcium imparts brick red Colour to the flame.

   When $(NH_4)_2CO_3$ is added to a salt solution containing NH_4Cl and NH_4OH, the carbonates of Ba^{2+}, Sr^{2+} and Ca^{2+} are precipitated.

Analysis Of Group VI (Mg^{2+})

1. **Ammonium phosphate test**

   To a part of the original solution add some solid NH_4Cl and NH_4OH in slight excess. Then add ammonium phosphate solution and rub the sides of the test-tube with a glass rod.

   A white ppt. confirms Mg^{2+}.

2. **Charcoal cavity cobalt nitrate test**

   Perform charcoal cavity cobalt nitrate test with the original salt.

   A pink mass is obtained.

3. **Ammonium Phosphate Test**

   Chemical Reactions Involved in Confirmation of Mg^{2+}

$$MgCl_2 + NH_4OH + (NH_4)_2HPO_4 \longrightarrow Mg(NH_4)PO_4 \downarrow + 2NH_4Cl + H_2$$

VIVA VOCE

Q-1. What do you mean by qualitative and quantitative analysis?

Ans. Qualitative analysis deals with the identification of mere presence of acidic or basic radicals in inorganic salts or presence of extra elements such as N, O, P, S or halogens in an organic compound or testing the presence of functional group in an organic compound.

Quantitative analysis on the other hand helps to estimate the amount/concentration/percentage of these elements present.

Q-2. Give an example to differentiate between qualitative and quantitative analysis.

Ans. When a given salt e.g., lead salt is analyses say with KI; appearance of yellow ppt. will indicate the qualitative presence of lead ions but in case if an alloy containing lead is dissolved in nitric acid and the amount of lead present is estimated by weighing the exact amount of lead iodide precipitated to calculate the percentage of lead in the alloy; it will be called as quantitative analysis.

Q-3. What is a radical?

Ans. An atom or a group of atoms having a distinct positive or negative charge on it is called a radical; for example, $NH_4^+, Cu^{2+}, Br^-, SO_4^{2-}$ etc.

Q-4. What is the Colour of iron salts?

Ans. Ferrous salts are generally green and ferric salts are brown.

Q-5. What is the Colour of nickel salts?

Ans. Bluish green or green.

Q-6. Give one example of red salt.

Ans. Cobalt nitrate is red in Colour.

Q-7. Generally, what is the Colour of manganese salts?

Ans. Light pink or flesh Coloured.

Q-8. What are deliquescent salts?

Ans. Salts which absorb moisture from the atmosphere and dissolve in it are called deliquescent salts e.g., $MgCl_2, FeCl_3, ZnCl_2$.

Q-9. What are efflorescent salts?

Ans. Salts which give out water of crystallisation are termed as efflorescent salts e.g., $FeSO_4.7H_2O$ or $Na_2CO_3 \cdot 10H_2O$ loses water of crystallisation to become $FeSO_4 x H_2O (3 < x < 7)$ and $Na_2CO_3.H_2O$ (On losing 9 molecules of water of crystallisation).

Q-10. What is sublimation?

Ans. Sublimation is a process by which a salt directly changes its state from solid to gaseous without melting on heating. On cooling, the vapors condense to give back the solid.

Q-11. What do you mean by the term decrepitation?

Ans. Some salts that do not contain any water of crystallisation contain some mother liquor entrapped in their crystals during crystallisation.

On heating, these trapped molecules (liquid) of mother liquor escape producing crackling sound called decrepitation. Some examples of such salts are; $Ba(NO_3)_2, NaCl, Pb(NO_3)_2$

Q-12. Why are silver nitrate and hydrogen peroxide solutions kept in Coloured bottles?

Ans. Because they can get decomposed when exposed to light.

Q-13. Why do blue crystals of copper sulphate become Colourless on heating?

Ans. Because the blue Coloured hydrated copper sulphate ($CuSO_4.5H_2O$) loses its water of crystallisation on heating and become Colourless anhydrous copper sulphate.

Detection Of Elements In Organic Compounds

Detection of elements present in an organic compound constitutes an important step in its analysis. All the organic compounds contain carbon. Hydrogen is also present in most of the organic compounds (the few exceptions are the compounds such as CCl_4, CS_2, etc.). In addition to carbon and hydrogen other elements which are generally present in organic compounds are oxygen, nitrogen, sulphur and halogens.
Since nearly all the organic compounds contain carbon as well as hydrogen it is usually not necessary to carry out tests to detect them and their presence can be assumed without testing for them. Here, we shall study the tests for the detection of nitrogen, sulphur and halogens only.

Detection of Nitrogen, Sulphur, Chlorine, Bromine and Iodine by Lassaigne ' s Test

This is the most dependable test for the detection of nitrogen, Sulphur and halogens. This test is also known as sodium fusion test. In order to perform this test, first of all sodium extract or Lassaigne's extract is prepared as described below:

Preparation Of Lassaigne's Extract

Take a small piece of dry sodium in a fusion tube. Heat the tube slightly so that it melts to a shining globule. Add a pinch of the organic compound. Heat it slowly to start with so that the compound reacts with sodium metal. Now heat it strongly. Plunge the red-hot tube into a China dish containing distilled water. Crush the contents with a glass rod and heat to boiling. Remove the insoluble matter by filtration. The filtrate is called Lassaigne's extract.
Nitrogen, Sulphur and halogens present in an organic compound are detected by making use of Lassaigne's extract.

Detection Of Nitrogen

To a small portion of Lassaigne 's extract (usually alkaline), add 2 ml of freshly prepared ferrous sulphate solution and heat. Now add to it 2-3 drops of ferric chloride solution and acidify with cone, hydrochloric acid. A Prussian blue Colouration indicates the presence of nitrogen in the compound.

Chemistry Of The Test

If nitrogen is present in the compound, the sodium extract would contain sodium cyanide formed during fusion. On adding the required reagents, sodium cyanide reacts to form Ferric-Ferro cyanide which has Prussian blue Colour.

OBSERVATIONS

Solution in Burette = HCl, Solution in pipette = Na_2CO_3, Indicator = Methyl orange, Colour change = Yellow to light pink
The volume of the pipette = 10 ml

$$\underset{\substack{\text{(From organic}\\\text{compound)}}}{Na + C + N} \xrightarrow{\text{Fuse}} NaCN$$

$$FeSO_4 + 2NaOH \longrightarrow \underset{\text{Green ppt.}}{Fe(OH)_2 \downarrow} + Na_2SO_4$$

$$\underset{\substack{\text{(From sodium}\\\text{extract)}}}{Fe(OH)_2 + NaCN} \longrightarrow Fe(CN)_2 + 2NaOH$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{Sod. ferrocyanide}}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\ \text{(prussian blue Colour)}}}{Fe_4[Fe(CN_6]_3} + 12NaCl$$

The purpose of acidifying the reaction mixture in the end is to dissolve any green ppt. of $Fe(OH)_2$ since it may lead to wrong inferences.

Nitrogen And Sulphur Present Together

If the organic compound contains both nitrogen and Sulphur, sodium sulphocyanide (NaCNS) is formed during preparation of Lassaigne's extract. Sodium sulphocyanide reacts with ferric chloride and gives blood red Colouration due to formation of ferric sulphocyanide.

$$Na + C + \underset{\substack{\text{From}\\ \text{organic}\\ \text{compound}}}{N} + S \longrightarrow NaCNS$$

$$3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{Blood red}\\ \text{Colouration}}}{Fe(CNS)_3} + 3NaCl$$

Thus, appearance of a blood red Colouration on performing Lassaigne's test for nitrogen indicates the presence of both nitrogen and Sulphur in the organic compound.

Detection Of Sulphur

Sodium Nitroprusside Test

To a small portion of Lassaigne's extract add a few drops of sodium nitroprusside solution. A purple Colouration indicates the presence of Sulphur in the compound.

Chemistry Of The Test

During preparation of Lassaigne's extract Sulphur from the organic compound combines with sodium to form sodium supplied. Sulphides give purple Colouration on reaction with sodium nitroprusside.

$$2Na + \underset{\substack{\text{(From}\\ \text{organic}\\ \text{Compound)}}}{S} \xrightarrow{\text{Fuse}} Na_2S$$

$$\underset{\substack{\text{(From}\\ \text{Sodium}\\ \text{extract)}}}{Na_2S} + \underset{\text{Sod. nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Purple Colouration}}{Na_4[Fe(CN)_5NOS]}$$

Lead Acetate Test

Acidify a small portion of Lassaigne's extract with acetic acid and add a few drops of lead acetate solution. The formation of black ppt. indicates the presence of Sulphur in the compound.

Chemistry Of The Test

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\text{Black}\\ \text{ppt.}}}{PbS\downarrow} + 2CH_3COONa$$

Detection Of Chlorine, Bromine, And Iodine

Silver Nitrate Test

To a small portion about 2 ml of Lassaigne's extract add 1ml of cone, nitric acid and boil for some time. Cool the contents and add to it silver nitrate solution.

(i) **White precipitate, soluble in ammonium hydroxide**, indicates the presence of chlorine in the organic compound.

(ii) **Pale yellow precipitate, sparingly soluble in ammonium hydroxide**, indicates the presence of bromine in the compound.

(iii) **Yellow precipitate, insoluble in ammonium hydroxide**, indicates the presence of iodine in the organic compound.

Chemistry Of The Test

(a) For Chlorine

$$Na + \underset{\text{(From org. compound)}}{Cl} \xrightarrow{\text{Heat}} NaCl$$

$$NaCl + AgNO_3 \longrightarrow \underset{\substack{\text{Silver chloride}\\\text{(White ppt.)}}}{AgCl\downarrow} + NaNO_3$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(Soluble)}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

(b) For Bromine

$$Na + \underset{\text{(From org. compound)}}{Br} \xrightarrow{\text{Heat}} NaBr$$

$$NaBr + AgNO_3 \longrightarrow \underset{\substack{\text{Silver bromide}\\\text{(Pale yellow ppt.)}}}{AgBr\downarrow} + NaNO_3$$

(c) For Iodine

$$Na + \underset{\text{(From org. compound)}}{I} \xrightarrow{\text{Heat}} NaI$$

$$NaI + AgNO_3 \longrightarrow \underset{\substack{\text{Silver iodide}\\\text{(Yellow ppt.)}}}{AgI\downarrow} + NaNO_3$$

The function of adding cone. HNO_3 and boiling is to decompose any sodium cyanide or sodium supplied present in the extract. Otherwise, these compounds will interfere with the tests of halides since NaCN gives a white ppt. with silver nitrate while Na_2S gives a black ppt.

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

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

Carbon Disulphide Test

Acidify a small portion of Lassaigne's extract with dil. HCl and add a few drops of carbon disulphide (or CCl_4 or $CHCl_3$). Now add freshly prepared chlorine water and shake vigorously.

(i) Appearance of **orange Colour** in the carbon disulphide layer indicates the presence of **bromine**.

(ii) Appearance of **violet Colour** in the carbon disulphide layer indicates the presence of **iodine**.

Chemistry Of The Test

Chlorine can displace bromine and iodine from their respective halides in solution. Bromine or iodine thus liberated can turn the carbon disulphide layer orange or violet.

$$Cl_2 + \underset{\text{(From sodium)}}{2NaBr} \rightarrow Br_2 + 2NaCl$$

$$Cl_2 + 2NaI \longrightarrow I_2 + 2NaCl$$
$$\text{(From sodium extract)}$$

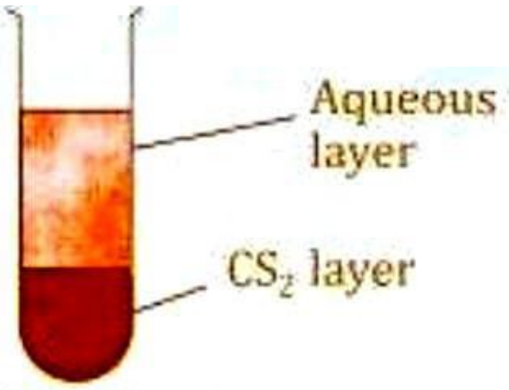


Fig. 1 Carbon disulphide test

TEST FOR NITROGEN		
Experiment	**Observation**	**Inference**
Ferrous sulphate test: To 2-3 mL of the Lassaigne's is extract in a test tube, add 2 mL of freshly prepared concentrated solution of ferrous sulphate. In case no green ppt, is formed, add 2 drops of sodium hydroxide solution and boil for a minute. Acidify the hot solution with dilute sulphuric acid and shake.	(i) A deep blue or greenish-blue colouration or ppt. is obtained. (ii) A blood red colouration is obtained.	Nitrogen confirmed. Both nitrogen and sulphur confirmed.

TEST FOR SULPHUR		
(i) Sodium nitroprusside test: To 2-3 mL of Lassaigne's extract add a few drops of freshly prepared sodium nitroprusside solution.	(i) A violet or purple colouration is produced. (ii) Violet or purple colouration is not produced.	(i) Sulphur confirmed. (ii) Sulphur absent.
(ii) Lead acetate test: Acidify 2-3 mL of Lassaigne's extract with dilute acetic acid and then add lead acetate solution to it.	(i) A black ppt. is formed. (ii) Black ppt. is not formed.	(i) Sulphur confirmed (ii) Sulphur absent.

TEST FOR HALOGENS		
(i) Beilstein's test: Perform Beilstein's test with a pinch of the given organic compound.	(i) Blue or greenish-blue flame is produced. (ii) Blue or greenish-blue flame is not seen.	(i) Halogens may be present. (ii) Halogens absent.
(ii) Silver nitrate test: Acidify 2-3 mL of Lassaigne's extract with conc. HNO_3 (slight excess) and boil to expel HCN and H_2S (if present due to nitrogen and sulphur). Cool the solution and add to it silver nitrate solution.	(i) A curdy white ppt. soluble in excess of NH_4OH. (ii) A pale yellow ppt. sparingly soluble in NH_4OH. (iii) A yellow ppt. insoluble in NH_4OH. (iv) Curdy white or yellow ppt. is not obtained.	(i) Chlorine confirmed. (ii) Bromine confirmed. (iii) Iodine confirmed. (iv) Halogens absent.
(iii) Carbon disulphide and chlorine water test: Acidify	(i) A yellow or orange colour in CS_2 layer.	(i) Bromine confirmed.

about 2 mL of Lassaigne's extract with dil. HCl and add to it about 1 mL of CS_2 or $CHCl_3$ or CCl_4. Then add a few drops of freshly prepared chlorine water. Shake well and allow to stand.	(ii) A violet colour in CS_2 layer. (iii) CS_2 layer remains colourless.	(ii) Iodine confirmed. (iii) Bromine and iodine absent.

VIVA VOCE

Q-1. What is Lassaigne's extract?

Ans. Lassaigne's extract is prepared by fusing the organic compound with sodium metal and the fused product is then extracted with water. The extract so obtained is called L.E. or sodium extract.

Q-2. Why is sodium kept under kerosene?

Ans. Sodium metal reacts with oxygen and moisture present in air, hence kept under kerosene which prevents it's coming in contact with air.

Q-3. Can we use potassium in place of sodium in L.E.?

Ans. No, potassium is too reactive metal, hence dangerous to use.

Q-4. What are extra elements present in an organic compound? Why are they said so?

Ans. Organic compounds generally contain C and H. Other elements than these present in an organic compound are called extra elements. They are S, P, N, O and halogens.

Q-5. What is the purpose of fusion of organic compound with sodium metal for the preparation of L.E.?

Ans. When the organic compound is heated with sodium, the element such as nitrogen, Sulphur and halogens if present in the compound is converted into sodium salts which are soluble in water. The aqueous solution is then used to identify these elements.

Q-6. How is sodium extract prepared?

Ans. Sodium extract is prepared by fusing the organic compound with sodium metal. This fused product is further extracted with water. The extract finally formed is known as sodium extract.

- Nitrogen - urea
- Sulphur - thiourea
- Chlorine - chloroform

Q-7. If we use potassium in the place of sodium in sodium extract, what will happen?

Ans. Since, potassium is more reactive metal, so we cannot use it because it is very dangerous to use.

Q-8. In the Lassaigne's test for nitrogen, why bluish green Colour appears?

Ans. When few drops of $FeCl_3$ solution is added to warm the solution of sodium extract and $FeSO_4$ solution, ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ is formed which gives bluish green Colour.

Q-9. In the test of sulphur, why violet Colour appears?

Ans. Because there is a formation of $Na_4[Fe(CN)_5NOS]$ which gives violet Colour at glance.

Q-10. Why CS_2 layer is Coloured in the test of detecting halogen?

Ans. Because Br_2 and I_2 have covalent bonding and hence, are more soluble in organic solvent CS_2 than

in water. Thus CS_2 layer is Coloured.

Q-11. Why is L.E. usually alkaline?

Ans. Because during fusion, some sodium is generally left unreacted. This extra sodium when reacts with water forms NaOH solution which is basic in nature.

Q-12. Why is only distilled water used for preparing L.E.?

Ans. Tap water contains chloride ions, hence only distilled water is recommended.

Q-13. Why is freshly prepared ferrous sulphate solution used to test for nitrogen?

Ans. Because $FeSO_4$ solution on keeping gets oxidised to basic ferric sulphate by atmospheric oxygen.

$$\underset{\text{Ferrous sulphate}}{4FeSO_4} + O_2 + 2H_2O \longrightarrow \underset{\text{Basic ferric sulphate}}{4Fe(OH)SO_4}$$

Consequently Fe^{2+} ions needed for the test are not available, hence freshly prepared $FeSO_4$ is used.

Q-14. What is the formula of sodium nitroprusside?

Ans. $Na_2[Fe(CN)_5NO]$.

Q-15. Why do we get violet Colour in the test for sulphur?

Ans. Due to the formation of $Na_4[Fe(CN)_5NOS]$ complex.

Q-16. In the detection of bromine and iodine, why the CS_2 layer is Coloured and not the aqueous layer?

Ans. Because Br_2 and I_2 have covalent bonding in it and hence are more soluble in organic solvent CS_2 then in water.

Q-17. How will you test bromine or iodine in the given organic compound?

Ans. Acidify the L.E. with dil HCl. Add to it 1ml of CCl_4 and then a few drops of freshly prepared Cl_2 water and shake. Orange Colour in CCl_4 layer indicates Br_2 while a violet Colour in CCl_4 layer indicates iodine.