QUALITATIVE ANALYSIS

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

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

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

(**Note**: **Insoluble salts excluded**)

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.

A salt is a product of neutralization of acids and bases and consists of two parts. The part that has come from a base is called a basic radical or cation and the other part which is contributed by the acid is called acid radical or anion. For example, when NaOH a base reacts with an acid HCl, it produces a salt NaCl and water as depicted below:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

NaCl; a salt formed consists of a cation, Na^+(that has come from the base) and an anion, Cl^-(that has come from the acid).

Acid Radical or Anion: Acid radical is an atom or a group of atoms having a negative charge on it. The magnitude of the charge depends on the acid, it has come from. For example, $Cl^-, Br^-, I^-, NO_3^-, S^{2-}, CO_3^{2-}$, etc. have come from the corresponding hydrogen acids $HCl, HBr, HI, HNO_3, H_2S$ and H_2CO_3.

Basic Radical or Cation: A cation is a positively charged atom or group of atoms. The magnitude of positive charge depends upon the base it was in combination with OH^-ions. For example, $Cu^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, NH_4^+$, etc.

The hydroxides of the cations mentioned above have the formula $Cu(OH)_2, Pb(OH)_2, Zn(OH)_2, Al(OH)_3$ and NH_4OH; justifiying the charge in the metal ion (basic radical or cation).

Various experiments called tests are done to identify the cation and anion present in the given unknown salt. The systematic procedure involved in the qualitative analysis of the salt involves the following categories of the tests:

1. **Preliminary tests**
   - **(a)** Physical appearance (Colour and smell).
   - **(b)** Dry heating test.
   - **(c)** Charcoal cavity test.
   - **(d)** Charcoal cavity and cobalt nitrate test.
   - **(e)** Flame test.
   - **(f)** Borax bead test.
2. **Wet tests for acid radicals**
   - **(a)** Dilute Sulphuric acid test

(b) Conc. Sulphuric acid test

3. **Wet tests for basic radical**

1. 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. The observations of the experiments are tabulated below in table 1 along with the inferences that you can draw.

Table 1

Experiment	Observations	Inference
1. **Colour:** Note the colour of the salt.	(i) Blue (ii) Green (iii) Light green (iv) Dark green (v) Yellowish brown (vi) Pink (vii) Light pink or flesh like coloured (viii) Pink violet (ix) White	Cu^{2+} salts Cu^{2+} or Ni^{2+} salts Fe^{2+} salts Cr^{3+} salts Fe^{3+} salts Co^{2+} salts Mn^{2+} salts (i) Shows the absence of Cu^{2+}, Fe^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+}, CO^{2+} etc. (ii) Salts of Pb^{2+}, Cd^{2+}, As^{3+}, Al^{3+}, Zn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+ may be present.
2. **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 of rotten eggs	NH_4^+ CH_3COO^- S^{2-}
3. **Density:** Judge the density of salt placing it in your palm.	(i) Heavy (ii) Light fluffy powder	Salt of Hg^{2+}, or Ba^{2+} Carbonates of Zn^{2+}, Mg^{2+} or Ca^{2+}
4. **Deliquescence:** Take a little of the salt on a piece of a paper and expose to amorphous for the same time.	Salt absorbs moisture and becomes pasty or like liquid.	(i) If Coloured, may be $Cu(NO_3)_2$, $FeCl_3$ etc. (ii) If Colourless, may be $Zn(NO_3)_2$, $AlCl_3$ etc.
5. **Physical state (crystalline or amorphous):** Note whether the constituent salts of the mixture are crystalline or amorphous.	(i) Salt is crystalline. (ii) Salt is amorphous.	-- Carbonates of non-alkali metals, i.e., $CaCO_3$, $MgCO_3$, $PbCO_3$, $CuCO_3$ 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, and potassium nitrite, develop a yellow colour.

(b) Dry Heating Test

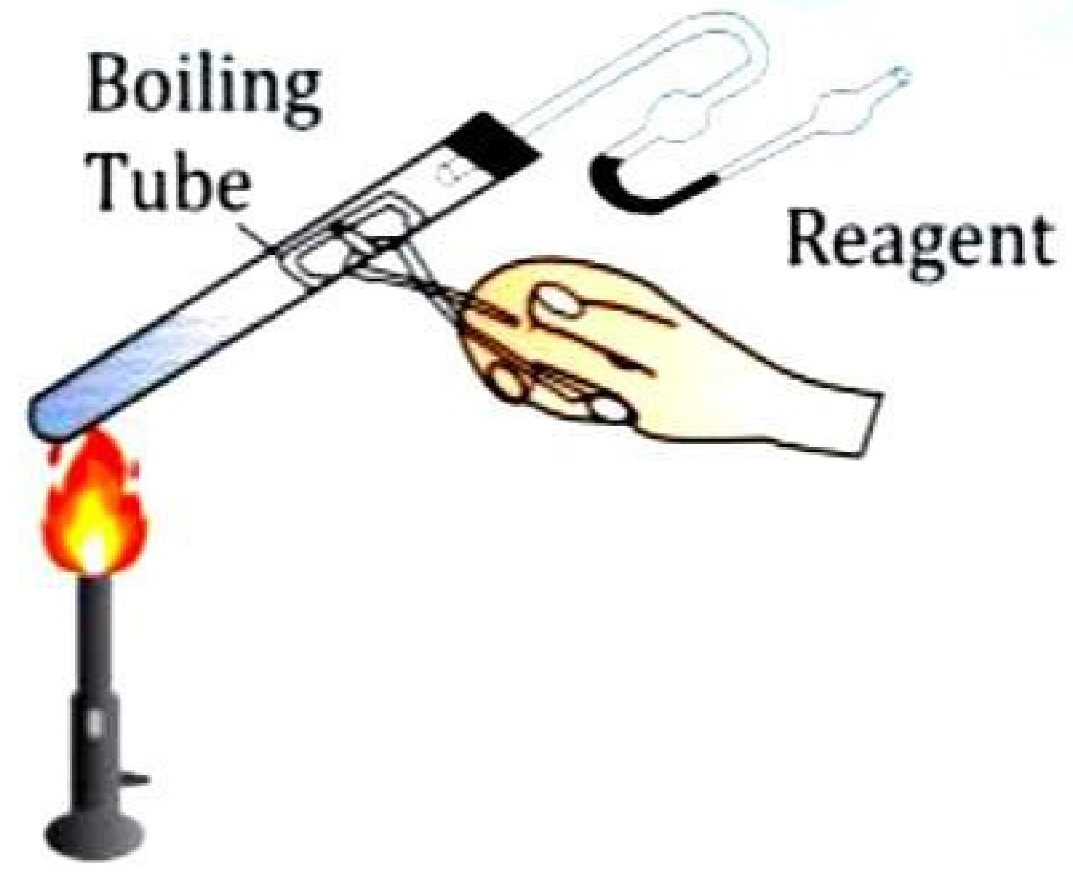
This test is performed by heating a small amount of salt in a dry test tube. Quite valuable information can be gathered by carefully performing and noting the observations here. On heating, some salts undergo decomposition thus evolving the gases or may undergo characteristic changes in the Colour of residue. These observations are tabulated below in table 2 along with the inferences that you can draw.

Table 2

Observations	**Inference**
1. (a) Colourless gas with an odour	
(i) H_2S gas: Smells like rotten eggs and turns lead acetate paper black.	S^{2-}
(ii) SO_2 gas: Smells like burning Sulphur and turns acidified potassium dichromate paper green.	SO_3^{2-}
(iii) HCl gas: Pungent smell, white fumes with ammonia, white ppt with silver nitrate solution.	Cl^-
(iv) Acetic acid vapors: Characteristic a vinegar-like smell.	CH_3COO^-
(v) NH_3 gas: Characteristic smell turns Nessler's solution brown.	NH_4^+
(b) Coloured gases: Pungent smell	
(i) NO_2 gas: Reddish brown, turns ferrous sulphate solution black.	NO_2^- or NO_3^-
(ii) Cl_2 gas: Greenish yellow, turns starch iodide paper blue.	Cl^-
(iii) Br_2 vapors: Reddish brown, turns starch paper orange yellow.	Br^-
(iv) I_2 vapors: Dark violet, turns starch paper blue.	I^-
2. Sublimate formed	
(a) White sublimate	NH_4^- or Hg^+
(b) Black sublimate accompanied by violet vapours	I^-
3. Decrepitation The salt decrepitates (gives cracking sound). For example, $Pb(NO_3)_2$, NaCl, KBr.	A salt having no water of crystallisation or heavy metal salts.
4. Fusion: The salt fuses/melts.	Alkali metal salts or salt containing water of crystallization.

Note:

1. 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.



Dry Heating

2. 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 and do not heat the tube strongly at one point as it may break.

(c) Charcoal Cavity Test

Principle: 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:

(i) $(ZnSO)_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$

$$ZnCO_3 \longrightarrow \underset{\text{Yellow when hot, white when cold}}{ZnO} + CO_2 \uparrow$$

(ii) $Pb(NO_3)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$

$$PbCO_3 \longrightarrow PbO + CO_2 \uparrow$$
$$PbO + C \longrightarrow Pb + CO \uparrow$$

(iii) $CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$

$$CuCO_3 \longrightarrow CuO + CO_2 \uparrow$$
$$CuO + C \longrightarrow Cu + CO \uparrow$$

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.1.) 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.2.) Heat strongly for some time and draw inference according to the Table 3.

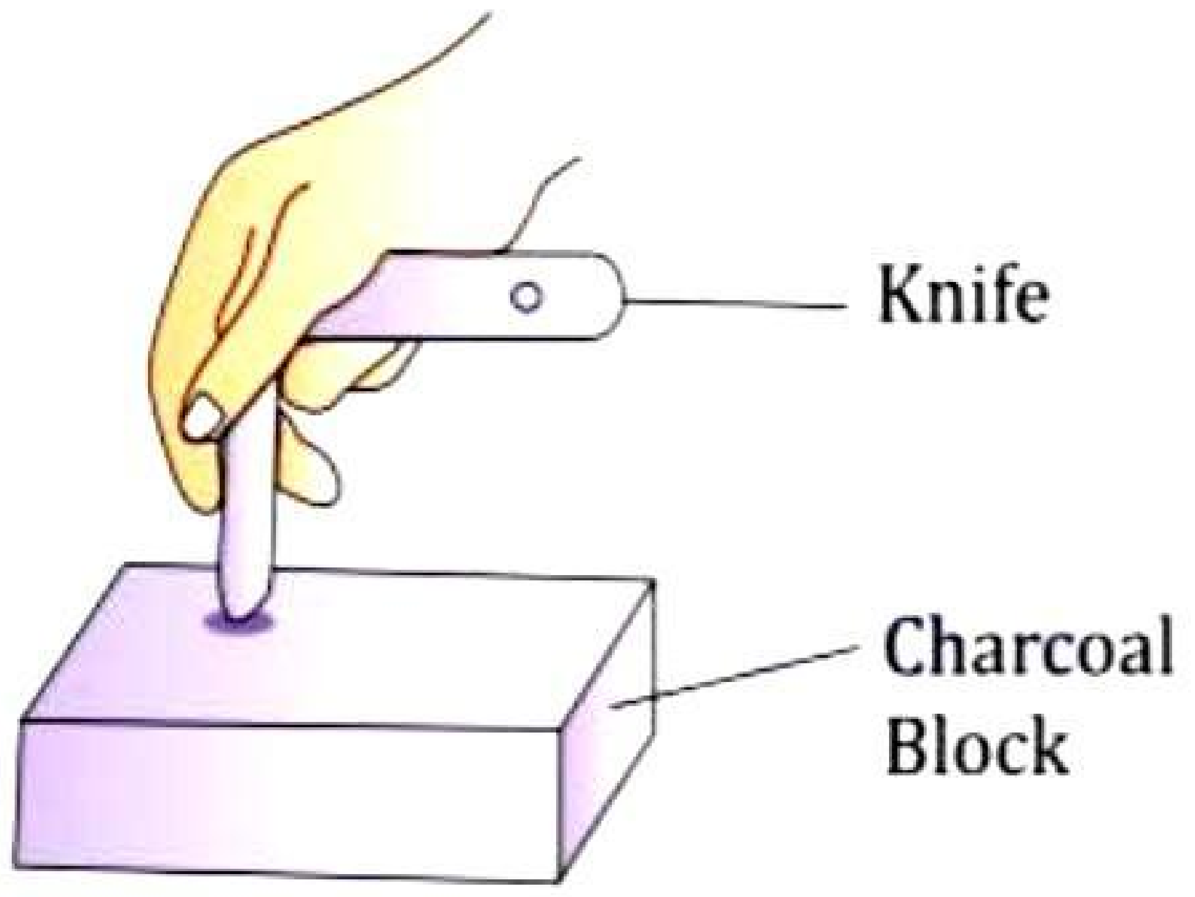


Fig.1. Making bore on a charcoal block

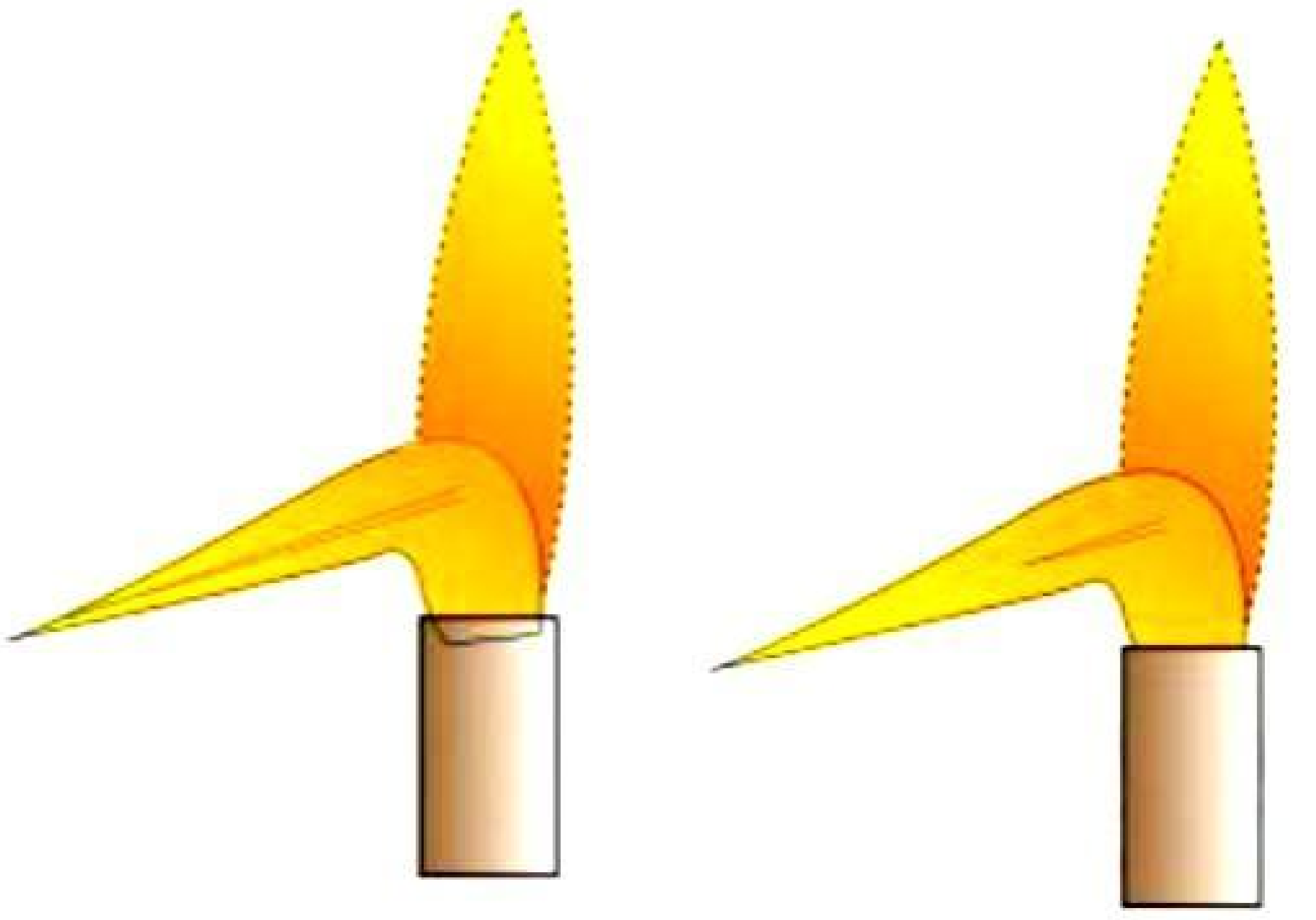


Fig.2. Directing flame with blowpipe

Fig.3. Blowing flame on the cavity

Table.3.

Observations		Inference
Bead	Incrustation/Residue	
1. Grey soft metallic bead	Brown when hot and yellow when cold	Pb^{2+}
2. Red scales	No inscrustation	Cu^{2+}
3. No Bead	White inscrustation 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 (Fig.3.) and blow gently onto the cavity.

(d) Cobalt Nitrate Test

Principle: 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 $Co_3(PO_4)_2$ which are blue.

Some of the reactions involved are given below:

i. **Zinc salt:**

$$2Co(NO_3)_2 \xrightarrow{\Delta} 2CoO + 4NO_2\uparrow + O_2\uparrow$$
$$ZnO + CoO \longrightarrow CoO.ZnO\ (Green)$$

ii. **Magnesium salt:**

$$MgO + CoO \longrightarrow CoO.MgO\ (Pink)$$

Procedure

Add 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 4.

Table 4

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.

(e) Flame Test

Principle: Certain salts on reacting with the cone. 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.

$$BaCo_3 + 2HCl \longrightarrow BaCl_2 + H_2O + CO_2$$

For proceeding to this test, paste the mixture with a conc. HCl is introduced into the flame with the help of platinum wire (Fig.4.).

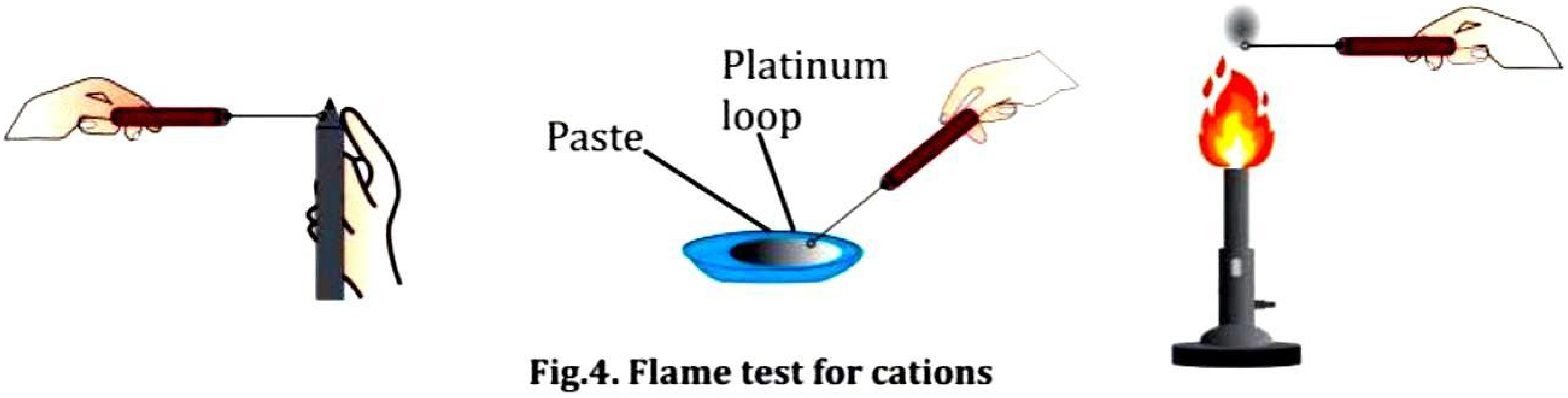


Fig.4. Flame test for cations

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 cone. 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.

Table 5

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

(f) Borax Bead Test

Principle: This test is performed only for coloured salts.

Borax, $Na_2B_4O_7.10H_2O$, 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.

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

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

Boric anhydride is non-volatile. When it is reacted with coloured metallic salt, a characteristic-coloured bead of metal metaborate is formed.

$$CuSO_4 + B_2O_3 \longrightarrow \underset{\text{Copper metaborate(blue)}}{Cu(BO_2)_2} + SO_3 \uparrow$$

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.

$$Fe_2(SO_4)_3 + 3B_2O_3 \longrightarrow \underset{\text{Ferric metaborate(Green)}}{2Fe(BO_2)_3} + 3SO_3 \uparrow$$

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

$$2Fe(BO_2)_3 + C \longrightarrow \underset{\text{Ferrous metaborate(Green)}}{2Fe(BO_2)_2} + B_2O_3 + CO \uparrow$$

Procedure

Borax, $Na_2B_4O_7.10H_2O$ 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.5.).

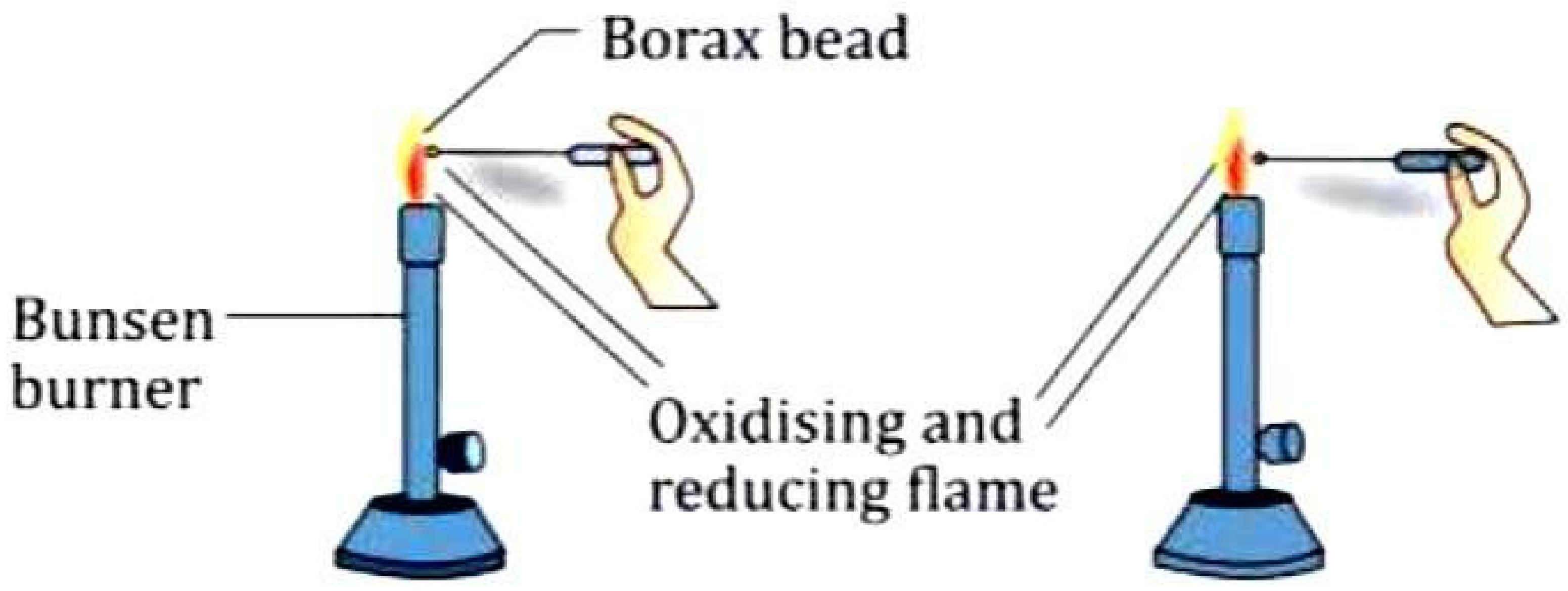


Fig.5.

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

Table 6

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

4. Reddish Brown	Grey-black in hot and cold	Ni^{2+}
5. Deep blue in both hot and cold	Deep blue in both hot and cold	Co^{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.6.).

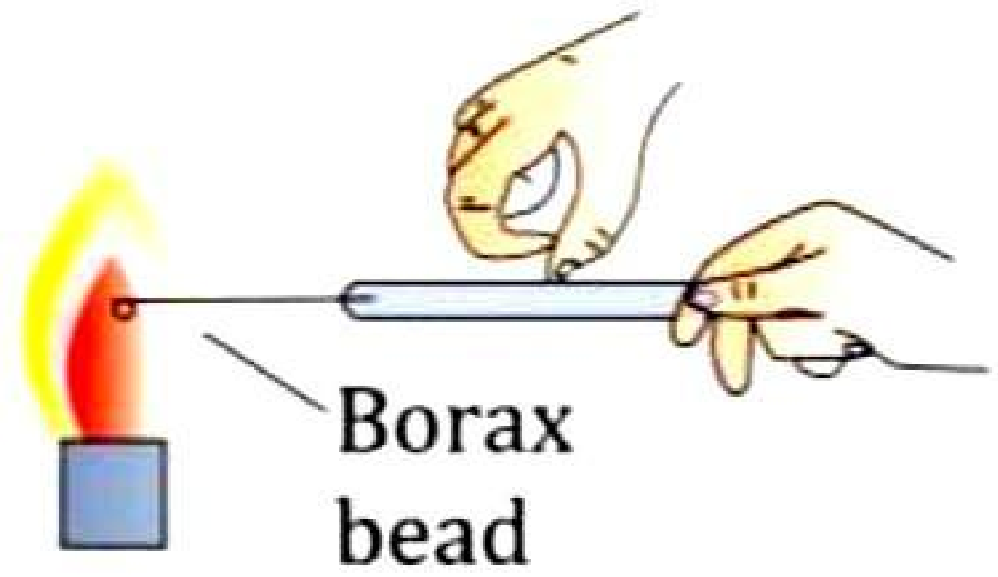


Fig.6
Removing bead from platinum wire

2. Wet tests for acid radicals

On the basis of the reactions the anion undergoes i.e. reaction with dilute sulphuric acid and conc. Suphuric acid.

(a) Dilute Sulphuric 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:

1. $CO_3^{2-}, S^{2-}, NO_2^{-}$ 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.
2. $Cl^-, Br^-, I^-, NO_3^-, C_2O_4^{2-}$ and CH_3COO^- react with conc. H_2SO_4 but not with dil. H_2SO_4 to produce characteristic gases.
3. 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.

Take a small quantity of salt in a test tube(~0.2g) and add about 1-2 ml of dil. H_2SO_4 to it. Observe in cold and then gently warm. Note the colour of the gas (if evolved), its odour (if any) and test the gas if evolved with asuitable reagent as instructed below in table 7:

Table 7

Observations	Inference	
	Gas	Radical
1. Colourless, odourless gas with brisk effervescence, turns lime water milky.	CO_2	CO_3^{2-}(Carbonate)
2. A colourless gas, with a pungent smell, turns acidified potassium dichromate paper or solution green.	SO_2	SO_3^{2-}(Sulphide)

3. Colourless gas with a smell like rotten eggs turns lead acetate paper black.	H_2S	S^{2-}(Sulphite)
4. Reddish brown gas, pungent smell, turns ferrous sulphate solution black.	NO_2	NO_2^-(Nitrite)
5. No gas is evolved.	-	Absence of CO_3^{2-} ,SO_3^{2-}, S^{2-}

Note:

- Do not treat the salt with a large quantity of dilute acid.
- Do not heat the salt with dilute acid.

Chemical reactions of acid radicals/anions with dilute sulphuric acids

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.

$$\underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq.)} \longrightarrow \underset{\text{Calcium Sulphate}}{CaSO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2} \uparrow$$

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

$$\underset{\text{Zinc Sulphide}}{ZnS} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq.)} \longrightarrow \underset{\text{Zinc Sulphate}}{ZnSO_4} + \underset{\text{Hydrogen Sulphide}}{H_2S} \uparrow$$

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

$$\underset{\text{Sodium Sulphite}}{Na_2SO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq.)} \longrightarrow \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Water}}{H_2O} + SO_2 \uparrow$$

4. **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.

$$\underset{\text{Sodium Nitrite}}{2NaNO_2} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq.)} \longrightarrow \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Nitrous acid}}{2HNO_2}$$

$$\underset{\text{Nitrous acid}}{3HNO_2} \longrightarrow \underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Nitric Oxide}}{2NO} + H_2O$$

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

(b) Concentrated Sulfuric Acid Test

Take a small quantity of salt in a test tube (~ 0.2 g) and add about 1-2 mL of conc. H_2SO_4 to it. Observe in cold and then heat the contents of the test tube over the flame. Use test tube holder for holding the test tube while heating. Note the colour and odour of the gas evolved and test the gas evolved with a suitable reagent.

In case the radicals, CO_3^{2-}, S^{2-}, SO_3^{2-} or NO_2^- of dilute acid group are present and you have missed their detection, they will react with conc. H_2SO_4 vigorously. NO_2^- ion will evolve brown fumes with conc. H_2SO_4 also and should not be wrongly reported as NO_3^-. Hence, absence/detection of dil. H_2SO_4 group anions should be concluded before proceeding to conc. H_2SO_4 group anions.

The observation of the test and inferences are given below in table 9:

Table 9

Observations	Test with the evolved gas	Inference
1. Evolution of colourless pungent gas (HCl) that produces white fumes when blown across the mouth of the	Bring a glass rod dipped in ammonium hydroxide near the mouth of the test tube. Formation of dense white fumes.	Cl^-(chloride)

test tube.		
2. Evolution of a reddish-brown vapour of Bromine (Br_2). Addition of MnO_2 intensifies brown colour.	Bring starch-paper near the mouth of the test tube. Orange red stain appears.	Br^-(bromide)
3. Evolution of violet vapour of iodine (I_2). Addition of MnO_2 intensifies violet colour.	Bring starch paper near the mouth of the test tube, it turns deep blue.	I^-(iodide)
4. Evolution of brown fumes which increase on heating the reaction mixture with copper chips or paper pellets.	Pass the brown fumes through a freshly prepared ferrous sulphate solution, it turns black.	NO_3^-(nitrate)
5. Evolution of acetic acid vapour on warming. Recognized by its vinegar like odour.	Vinegar like odour.	CH_3COO^-(acetate)
6. Evolution of colourless gas with effervescence. ($CO+CO_2$)	Pass the gas through lime water. It turns milky.	$C_2O_4^{2-}$ (oxalate)

Chemical reactions of acid radicals/anions with conc. sulphuric acids

1. Chlorides

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

2. Bromides

$$\underset{\text{Sodium Bromide}}{NaBr} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq)} \longrightarrow NaHSO_4 + HBr$$

$$H_2SO_4 + \underset{\text{Hydrogen Bromide}}{2HBr} \longrightarrow SO_2 + Br_2 + 2H_2O$$

3. Iodides

$$\underset{\text{Potassium iodide}}{KI} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq)} \longrightarrow KHSO_4 + HI$$

$$H_2SO_4 + 2HI \longrightarrow SO_2 + 2H_2O(l) + I_2 \uparrow$$

4. Nitrates

$$\underset{\text{Potassium nitrate}}{KNO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq)} \longrightarrow KHSO_4 + HNO_3$$

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

5. Acetates

$$\underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq)} \longrightarrow \underset{\text{Hydrogen Sulphate ion}}{HSO_4^-(aq)} + \underset{\text{Acetic acid(Vinegar smell)}}{CH_3COOH}$$

6. Oxalates

$$C_2O_4^{2-} + \underset{\text{Sulphuric acid}}{H_2SO_4(aq)} \longrightarrow CO(g) + CO_2(g) + H_2O(l) + SO_4^{2-}(aq)$$

The mixture of gases when passed through lime water, it turns milky. This identifies the liberation of CO_2 gas.

$$CO_2(g) + \underset{\text{Lime water}}{Ca(OH)_2(aq)} \longrightarrow \underset{\text{Calcium carbonate(milky)}}{CaCO_3(s)} + H_2O(l)$$

Note:

- Do not boil the salt with cone, sulphuric acid. On boiling, the acid may decompose to give SO_2 gas.
- Nitrates give vapours of nitric acid (Colourless) when heated with cone, 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).

3. Wet tests for basic radical

Once the preliminary and the indicatory tests have been performed; the presence of the anion is to be confirmed by doing confirmatory tests. Confirmatory tests are the conclusive tests which establishes the presence of anion beyond doubt.

Preparation of solution for the test:

For performing wet tests, the solution may be prepared by the one of the following methods:

(a) **Water extract or aqueous solution:** Water extract or aqueous solution is prepared for water soluble salts. It is prepared by simply dissolving the salt in water.

(b) **Sodium carbonate extract:** Water extract or aqueous solution is prepared for water insoluble salt. It is prepared by heating the mixture performing tests.

Theory of preparation of sodium carbonate extract:

When water insoluble salts are heated with a concentrated solution of sodium carbonate, double decomposition get dissolved. The basic radicals present in the mixture combine with CO_3^{2-} ions provided by Na_2CO_3 to form insoluble metal carbonates which get precipitated and are filtered off. For example:

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

Preparation of sodium carbonate extract
Fig. 7

How To Use Sodium Carbonate Extract

Sodium carbonate extract, as prepared above, contains an excess of Na_2CO_3 in solution (besides the sodium salts of the anions of the original salt). Since, it interferes with the wet tests of acid radicals, it has to be destroyed before using the extract for carrying out any tests. To do this, the extract is acidified with some acid. The choice of the acid depends upon the nature of the acid radicals to be detected/identified. The acids sually employed are:

(a) CH_3COOH for $S^{2-}, SO_3^{2-}, PO_4^{3-}$
(b) dil. HNO_3 for Br^-, Cl^-, I^-
(c) dil. HCl for SO_4^{2-}

Confirmation of Carbonate CO_3^{2-}

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

Table 10

Experiment	Observation	Inference
1. Add dil. HCl or dil. H_2SO_4 to the salt solution and pass the gas evolved through lime water. Keep passing the gas for long.	Brisk effervescenes with evolution of CO_2, lime water turns milky. Milkiness is disappeared.	CO_3^{2-} is confirmed.
2. Add $MgSO_4$ solution to the salt solution.	White ppt. is observed.	CO_3^{2-} is confirmed.
3. To a part of salt solution add a few drops of phenolphthalein reagent.	It turns pink.	CO_3^{2-} is confirmed.

Confirmation of Sulphide S^{2-}

Indicated in dilute acid test by the evolution of hydrogen sulphide.
The sulphides of alkali metals are soluble in water while all others are insoluble. Therefore, confirmatory tests of sulphides are carried out either with water extract depending upon their solubility.

Table 11

Experiment	Observation	Inference
1. **Sodium nitroprusside test:** To a portion W.E. of the aqueous solution or the sodium extract, add ammoniacal sodium nitroprusside.	A violet colouration observed.	S^{2-} is confirmed.
2. **Lead acetate test:** To a portion of W.E. (acidified with acetic acid to decompose carbonates and boiled to expel CO_2), add lead acetate solution.	Black ppt. is observed.	S^{2-} is confirmed.
3. **Cadmium carbonate test:** To a portion of W.E. add a suspension of cadmium carbonate in water and shake well.	Yellow ppt. is observed.	S^{2-} is confirmed.
4. **Silver nitrate test:** To a portion of W.E. add $AgNO_3$ solution.	Black ppt. is soluble in HNO_3.	S^{2-} is confirmed.

Confirmation of Nitrite (NO_2^-)

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

Table 12

Experiment	Observation	Inference
1. **Ferrous sulphate test:** To a portion of the aqueous solution of salt, add a few drops of acetic acid and	Solution turns dark-brown or black.	NO_2^- is confirmed.

freshly prepared $FeSO_4$ solution.		
2. **Starch-iodide test:** To a portion of the aqueous solution of salt, add a few drops of dil. H_2SO_4 and a few drops of KI solution followed by freshly prepared starch solution.	Deep-blue colour is produced.	NO_2^- is confirmed.
3. **Potassium permanganate test:** To the W.E. of the salt, add a few drops of acidified $KMnO_4$ solution.	Pink colour of $KMnO_4$ solution is discharged.	NO_2^- is confirmed.
4. **Diphenylamine test:** To a portion of W.E. of the salt, add a fow drons of diphenylamine solution.	A deep-blue colouration is obtained.	NO_2^- is confirmed.

Chemical Reaction

Ions Involved in the Confirmation of Carbonate, Sulphite, Sulphide 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.

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

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

2. **Magnesium sulphate test**

   This test is-performed in case of soluble carbonates only

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

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**

$$\underset{\text{(Orange)}}{K_2Cr_2O_7} + 3Na_2SO_3 + 4H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + 3Na_2SO_4 + 4H_2O$$

Sulphide (S^{2-})

1. **Sodium nitroprusside test**

$$\underset{\text{Sod. nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{(Violet or Purple Colour)}}{Na_4[Fe(CN)_5NOS]}$$

2. **Lead acetate test**

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

3. **Cadmium carbonate test**

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

Nitrite (NO_2^-)

1. **Ferrous sulphate test**

$$\begin{aligned} KNO_2 + CH_3COOH &\longrightarrow CH_3COOK + HNO_2 \\ 3HNO_2 &\longrightarrow HNO_3 + 2NO + H_2O \\ FeSO_4 + NO &\longrightarrow \underset{\text{(Dark brown)}}{FeSO_4\cdot NO} \end{aligned}$$

2. **Potassium iodide test**

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

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).

Table 13

Experiment	Observation	Inference
1. **Silver nitrate test:** To a portion of the aqueous solutions of the salt (W.E.) add dil. **HNO_3** and **$AgNO_3$** solution.	Curdy white ppt. soluble in NH_4OH solution.	Cl^- is confirmed.
2. **Manganese dioxide test:** Heat a pinch of the solid salt with **MnO_2** and conc. **H_2SO_4**.	Cl_2 gas having yellowish-green colour evolved which turns moist starch iodide paper blue or bleaches moist blue litmus paper.	Cl^- is confirmed.
3. **Chromyl chloride test:** Mix a small amount of the solid salt with an equal amount of powdered $K_2Cr_2O_7$ and heat the mixture with conc. H_2SO_4.	Red vapours of chromyl chloride (CrO_2Cl_2) evolved.	Cl^- is confirmed.
(i) Pass these red vapours through NaOH solution.	Solution turns yellow.	Cl^- is confirmed.
(ii) Acidify the yellow solution with acetic acid and then add lead acetate solution.	Yellow ppt. soluble in NaOH.	Cl^- is confirmed.

Confirmation of Bromide (Br^-)

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

Table 14

Experiment	Observation	Inference
1. **Silver nitrate test:** To a	Pale yellow ppt. partially soluble in	Br^- is confirmed.

portion of the aqueous solutions of the salt (W.E.) add dil. **HNO_3** and **$AgNO_3$** solution.	NH_4OH solution.	
2. **Manganese dioxide test:** Heat a pinch of the solid salt with **MnO_2** and conc. **H_2SO_4**.	Yellowish brown vapours of bromine evolved which turn moist starch paper yellow.	Br^- is confirmed.
3. **Chlorine-water and CS_2 or CCl_4 test:** Acidify a portion of the aqueous solution of the salt with dil. **HCl** (in case of S.E. and dil. **HCl** till the effervescence ceases, boil off **CO_2** and cool) and then add **1 − 2 mL** of **CS_2** or **CCl_4** and excess of chlorine water shake vigorously and allow to stand.	Yellow or orange colour in CS_2 or CCl_4 layer.	Br^- is confirmed.

Note: Chlorine water is prepared by adding dropwise conc. 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 conc. H_2SO_4 with the evolution of vapors of iodine).

Table 15

Experiment	Observation	Inference
1. **Silver nitrate test:** To a portion of the aqueous solution of the salt, add dil. HNO_3 and $AgNO_3$ solution or acidify a portion of S.E. with dil. HNO_3 and boil off CO_2, cool and then add a few drops of $AgNO_3$ solution.	Yellow ppt. insoluble in NH_4OH solution.	I^- is confirmed.
2. **Manganese dioxide test:** Heat a pinch of the solid mixture with MnO_2 and conc. H_2SO_4.	Violet vapours of iodine evolved which turn moist starch paper blue.	I^- is confirmed.
3. **Chlorine-water and CS_2/CCl_4 test:** Acidify a portion of the aqueous solution of the salt with dil. HCl (in case of S.E. add dil. HCl till effervescence ceases, boil off CO_2 and cool) and add 1-2 mL of CCl_4 or CS_2 and excess of Cl_2 water. Shake vigorously and allow to stand.	Violet colour in CS_2 or CCl_4 layer.	I^- is confirmed.

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).

Table 16

Experiment	Observation	Inference
1. **Diphenylamine test:** To a portion of the aqueous solution of the salt, add a few drops of diphenylamine solution.	Deep blue colouration.	NO_3^- is confirmed.
2. **Copper turning test:** Heat a pinch of the salt with a few copper turnings and conc. H_2SO_4.	Brown fumes of NO_2 gas is evolved which turn $FeSO_4$ solution black.	NO_3^- is confirmed.
3. **Brown ring test:** To a portion of the aqueous solution of the salt (W.E.) add freshly prepared $FeSO_4$ solution and shake well. Then add conc. H_2SO_4 along the sides of the test tube.	A dark brown ring is formed at the junction of the two layers.	NO_3^- is confirmed.

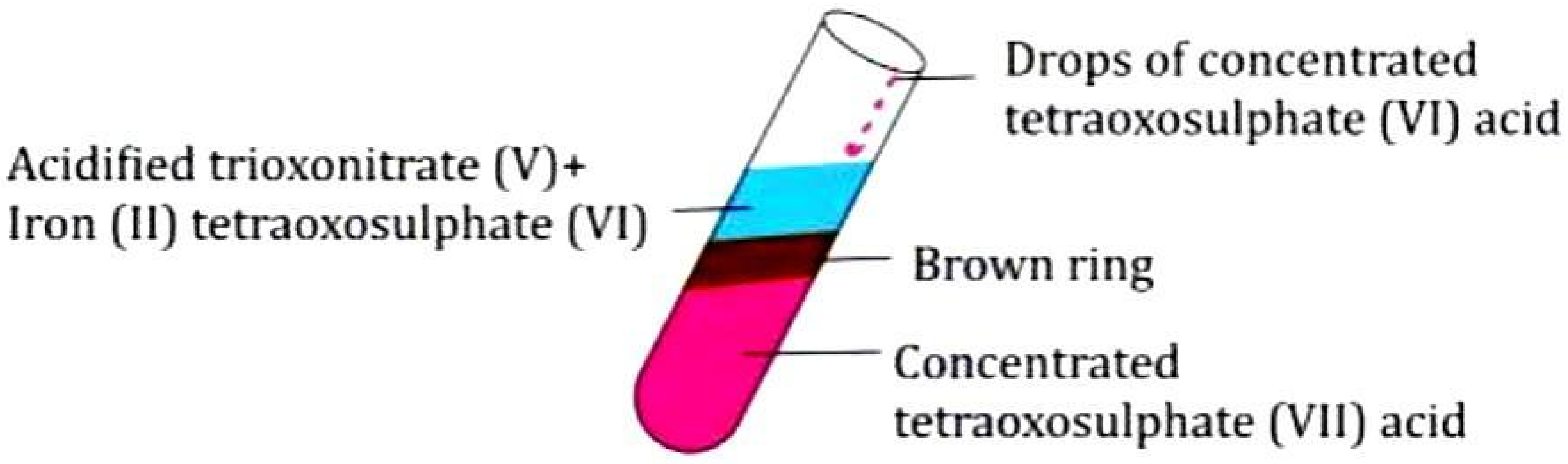


Fig.8 The Brown ring test for nitrate

Confirmation of Acetate $(CH_3COO)^-$

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

Table 17

Experiment	Observation	Inference
1. **Oxalic acid test:** Mix a little of the salt with solid oxalic acid on a watch glass. Prepare a paste of it with a few drops of water. Rub the paste between fingers and smell.	Vinegar like smell is observed.	CH_3COO^- is confirmed.
2. **Ester test:** Take a pinch of the salt in a dry test tube and add to it 1 ml of conc. H_2SO_4 and 4-5 drops of ethyl alcohol	Fruity smell is observed	CH_3COO^- is confirmed.

(rectified spirit). Heat the contents of the test tube and smell.		
3. **Ferric chloride test:** To a portion of the water extract (W.E.) of the salt, add a few drops of neutral $FeCl_3$ solution. Filter, if required, and divide the solution or the filtrate in two parts:	Deep red colouration is produced.	CH_3COO^- is confirmed.
(i) To one part add dil. HCl.	Red colouration is disappeared.	CH_3COO^- is confirmed.
(ii) To the second part add water and boil.	Reddish brown ppt. is observed.	CH_3COO^- is confirmed.

Confirmation of Oxalate ($C_2O_4^{-}$)

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

Table 18

Experiment	Observation	Inference
1. **Calcium chloride test:** Acidify 2-3 ml of sodium carbonate extract with dil. acetic acid. Boil off CO_2 and add calcium chloride ($CaCl_2$) solution.	White ppt. is observed.	Oxalate ($C_2O_4^{-}$) is present.
2. **$KMnO_4$ test:** Dissolve the white ppt. in dil. H_2SO_4 and add 1 ml of $KMnO_4$ solution.	Pink colour is discharged with a steady effervescence.	Oxalate ($C_2O_4^{-}$) is present.

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

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

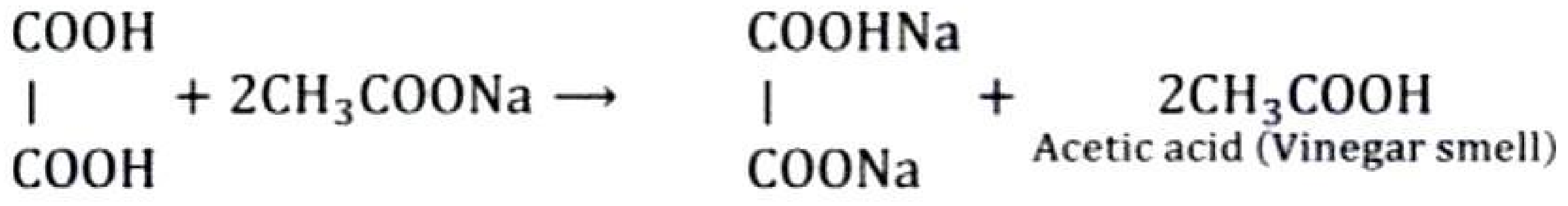
$$4HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + \underset{\text{(Reddish brown)}}{2NO_2} + 2H_2O$$

2. Ring Test

$$\begin{aligned} KNO_3 + H_2SO_4 &\longrightarrow KHSO_4 + HNO_3 \\ 6FeSO_4 + 3H_2SO_4 + 2HNO_3 &\longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO \\ FeSO_4 + NO + 5H_2O &\longrightarrow [Fe(NO)(H_2O)_5]SO_4 \\ &\quad\ \text{(Brown ring)} \end{aligned}$$

Acetate (CH_3COO^-)

1. Oxalic acid test



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

2. Ester test

$$\begin{aligned} 2CH_3COONa + H_2SO_4 &\longrightarrow Na_2SO_4 + 2CH_3COOH \\ CH_3COOH + C_2H_5OH &\longrightarrow CH_3COOC_2H_5 + H_2O \\ &\qquad \text{Ethyl acetate} \\ &\qquad \text{(Fruity smell)} \end{aligned}$$

3. Ferric chloride test

$$\begin{aligned} 3CH_3COONa + FeCl_3 &\longrightarrow (CH_3COO)_3Fe + 3NaCl \\ (CH_3COO)_3Fe + 2H_2O &\longrightarrow (CH_3COO)(OH)_2Fe \downarrow + 2CH_3COOH \\ &\qquad \text{Reddish brown ppt.} \end{aligned}$$

Oxalate ($C_2O_4^-$)

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

$$2KMnO_4 + 3H_2SO_4 + 5C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 \uparrow + 8H_2O$$

Confirmation of Sulphate SO_4^{2-} -

(Not indicated in dilute and concentrated H_2SO_4 acid test)

Table 19

Experiment	Observation	Inference
1. **Barium chloride test:** To a part of the water extract of the salt add a few drops of dil. HCl and then $BaCl_2$ solution. Or a acidify sodium carbonate extract of the mixture with dil. HCl, boil off CO_2 and add $BaCl_2$ solution.	White ppt. insoluble in conc. HCl is obtained.	SO_4^{2-} is confirmed.
2. **Match stick test:** Filter the above white ppt. and mix it with an equal amount of solid sodium carbonate. Make it into a thick paste by adding a drop or two of water. Apply a little of this paste at the end of a carbonized match stick or wooden splinter and heat in the reducing flame of the Bunsen burner till the whole mass fuses, Throw the fused mass into some ammoniacal sodium nitroprusside solution taken in a china dish.	Violet or purple streaks are formed.	SO_4^{2-} is confirmed.
3. **Lead acetate test:** To a portion of the water extract (after acidifying with acetic acid, boiling off CO_2 and cooling) of the mixture, add lead acetate solution.	White ppt. soluble in excess of ammonium acetate solution.	SO_4^{2-} is confirmed.

Confirmation of Phosphate PO_4^{3-}

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

Table 20

Experiment	Observation	Inference
1. **Ammonium molybdate test:** To the given solid salt or	Canary yellow ppt. or colouration is formed.	PO_4^{3-} is confirmed.

water extract of the salt, add conc. HNO_3 and boil. Then, add excess of ammonium molybdate solution and heat.		
2. Magnesia mixture test: To a portion of water extract or sodium carbonate extract (acidified with dil. HCl, boiled off CO_2 and cooled) of the salt, add a pinch of solid NH_4Cl and boil. Cool and then add $MgSO_4$ solution and excess of NH_4OH solution and scratch the sides of the test tube.	White ppt. is formed.	PO_4^{3-} is confirmed.

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

Sulphate (SO_4^{2-})

1. Barium chloride test

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

2. Match-stick test

$$\begin{aligned} Na_2SO_4 + BaCl_2 &\longrightarrow BaSO_4 \downarrow + 2NaCl \\ BaSO_4 + Na_2CO_3 &\longrightarrow Na_2SO_4 + BaCO_3 \\ Na_2SO_4 + 4C &\longrightarrow Na_2S + 4CO \\ Na_2S + Na_2[Fe(CN)_5NO] &\longrightarrow \underset{\text{Purple}}{Na_4[Fe(CN)_5NOS]} \end{aligned}$$

3. Lead acetate test

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

Phosphate (PO_4^{3-})

1. Ammonium molybdate test

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

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

$$\begin{aligned} H_2MoO_4 &\longrightarrow MoO_3 + H_2O \\ (NH_4)_3PO_4 + 12MoO_3 + 6H_2O &\longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O \downarrow \end{aligned}$$

Ammonium phosphate molybdate (yellow ppt).

2. Magnesia mixture test

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

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 21).

Table 21. Classification of Cations

Group	Cation
Group zero	NH_4^+
Group I	Pb^{2+}
Group II	$Cu^{2+}, As^{3+}, Cd^{2+}$
Group III	$Fe^{3+}, Fe^{2+}, Al^{3+}$
Group IV	$Co^{2+}, Ni^{2+}, Zn^{2}, Mn^{2+}$
Group V	$Ba^{2+}, Sr^{2+}, Ca^{2+}$
Group VI	Mg^{2+}

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:

1. Distilled water (cold or hot).
2. Dilute HCl (cold or hot).
3. Conc. 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.).

Notes

- In case some gas is evolved during the preparation of the solution, let the reaction cease. Gas must be completely expelled by heating.
- In case the solution is prepared in dilute HCl, group I is absent. Proceed with group II.
- If the salt is soluble in hot water, and on cooling white precipitates appear, lead chloride is indicated.
- It is necessary to dilute the solution if it is made in concentrated acid before proceeding with the analysis.

The following table 22. will help the students in the choice of a suitable solvent:

Table 22

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.

Table 23. Group Reagents

Group	Group reagent	Cations	Form in which cations are precipitated
Group zero	NaOH	NH_4^+	–
Group I	Dilute HCl	Pb^{2+}	Chlorides
Group II	H_2S in the presence of dilute HCl	Pb^{2+} Cu^{2+}, As^{3+}	Sulphides
Group III	NH_4OH in the presence of NH_4Cl	Fe^{3+}, Al^{3+}	Hydroxides
Group IV	H_2S in the presence of NH_4OH	Ni^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}	Sulphides
Group V	$(NH_4)_2CO_3$ in the presence of NH_4OH	Ca^{2+}, Ba^{2+}, Sr^{2+}	Carbonates
Group VI	Na_2HPO_4	Mg^{2+}	Phosphate

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:

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad \text{... weakly ionised ... (12.1)}$$

$$NH_4Cl \rightarrow NH_4^+(aq) + Cl^-(aq) \quad \text{... strongly ionised ... (12.2)}$$

Due to the addition of NH_4Cl, 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 (12.1) 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 products 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.

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \quad ...(12.3)$$

$$HCl \longrightarrow H^+ + Cl^- \quad ...(12.4)$$

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.

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

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

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+}, Sa^{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.

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

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

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, NaOH are added in various 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:

1. Characteristic ammoniacal smell.
2. The gas gives white fumes when a glass rod is dipped in dil. HCl is brought near the mouth of the test tube.
3. 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:

1. Cool one part of the solution under tap. White crystalline ppt. separates out.
2. Potassium iodide test. To the second part of the solution, add KI solution -yellow ppt.
3. Potassium chromate test. To the third part of the solution add K_2CrO_4 solution-yellow ppt.

Note:

- If the original solution is prepared in cold dilute hydrochloric acid, first group is absent.
- 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

$$Pb(NO_3)_2 + 2HCl \longrightarrow \underset{\text{White ppt.}}{PbCl_2 \downarrow} + 2HNO_3$$

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**

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

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) (Pb^{2+}, Cu^{2+}, As^{2+})

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.

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+}.

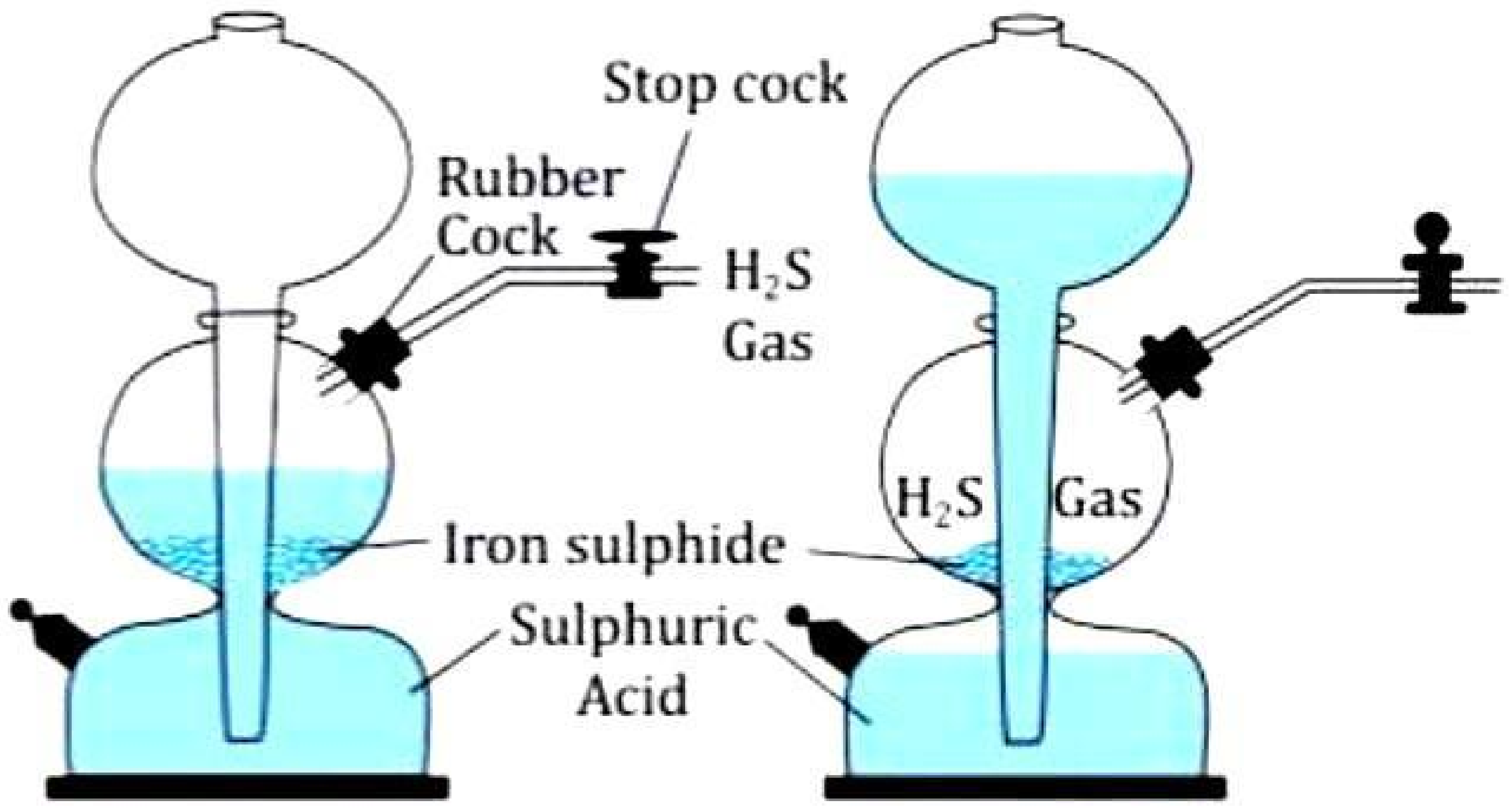


Fig. 9 Kipp's apparatus for H_2S gas

Table 24. Analysis of Group II

Black ppt. (Pb^{2+} or Cu^{2+} *Present*) Heat the black ppt. with minimum quantity (1 – 2 ml) of 50% HNO_3 ppt. dissolves. To one part of the above solution, add dil. H_2SO_4 and alcohol.		Yellow ppt. (As^{+3} Present) Warm a little of the 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+} is present**	Black ppt. dissolves to give a bluish green solution. **Cu^{2+} is present**	Ppt. dissolves. **As^{3+} is present**
To the above solution add 1 ml of alcohol and excess of H_2SO_4 -A white ppt is obtained **Confirmatory tests** **1. Potassium chromate tests:** To one part, add a few drops of K_2CrO_4 solution - Yellow ppt. formed which dissolves in excess	Divide the blue solution into two parts. **Confirmatory tests** **1. Ammonium hydroxide test:** To one Part add NH_4OH Solution dropwise - Light blue ppt. first appears but redissolve in excess	**Confirmatory tests** **1. Dil. HCl test:** To the above solution add dil HCl – yellow ppt. is formed. Dissolve the yellow ppt. by boiling with

of NaOH solution.	of NH_4OH giving deep blue solution.	conc. HNO_3 and divide into two parts.
2. Potassium iodide tests: To the second part, add a few drops of KI solution- yellow ppt. is formed.	**2. Potassium ferrocyanide test:** Acidify a portion of the above blue solution or original solution with dil. Acetic acid and then add a few drops of potassium ferrocyanide solution- Chocolate colour ppt. formed.	**2. Ammonium molybdate test:** To one part add 2-3 ml of ammonium molybdate solution and heat -A yellow ppt. **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.

Chemical reactions involved in the analysis of group II

$$PbCl_2 + H_2S \longrightarrow 2HCl + PbS \downarrow \ \text{(Black)}$$
$$CuCl_2 + H_2S \longrightarrow 2HCl + CuS \downarrow \ \text{(Black)}$$
$$2AsCl_3 + 3H_2S \longrightarrow 6HCl + As_2S_3 \downarrow \ \text{(Yellow)}$$

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**

$$\begin{aligned}[][Cu(NH_3)_4]SO_4 + 4CH_3COOH &\longrightarrow CuSO_4 + 4CH_3COONH_4 \\ 2CuSO_4 + K_4[Fe(CN)_6] &\rightarrow Cu_2[Fe(CN)_6] \downarrow + 2K_2SO_4 \\ &\quad\ \text{(Chocolate} \\ &\quad\ \text{brown Colour)}\end{aligned}$$

2. **Potassium iodide test**

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

Arsenic (As^{3+})

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

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

1. **Ammonium molybdate test**

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3AsO_4 \cdot 12MoO_3 \downarrow + 21NH_4NO_3 + 12H_2O$$

Yellow ppt. of ammonium
arseno molybdate

2. **Magnesia mixture test**

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

Analysis of group III (Iron Group) (Fe^{3+}, Al^{3+})

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 conc, 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 24.

Table 24. Analysis of Group III (Fe^{3+} and Al^{3+})

Fe^{3+} (Reddish brown ppt.)	Al^{3+} (White ppt.)
Dissolve the reddish-brown ppt. in dilute HCl, and divide the solution into two parts.	Dissolve the white precipitate in dilute HCl, and divide the solution into two parts.
Confirmation 1. **Potassium ferrocyanide test:** To one part of the above solution add potassium ferrocyanide solution. Prussian blue Colouration. 2. **Potassium sulphocyanide test:** To the second part, add a little potassium sulphocyanide solution. Blood red Colouration.	**Confirmation** 1. **Lake test:** Dissolve the white ppt. in dilute hydrochloric acid. Add to it two drops of blue litmus solution. To this, add NH_4OH dropwise till blue Colour develops. Blue ppt. floating in the Colourless solution. 2. **Cobalt nitrate test:** Perform charcoal cavity/Cobalt nitrate test with the salt. Blue mass.

Note:

- Test of Fe^{2+} - The addition of conc. 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+}.
- Use sufficient quantity of ammonium chloride, otherwise the hydroxides of higher group may be precipitated along with the radicals of third group.
- 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.

$$FeCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{(Reddish brown ppt.)}}{Fe(OH)_3} \downarrow$$

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

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

$$FeCl_3 + 6KCNS \longrightarrow 3KCl + \underset{\substack{\text{Ferric Sulphocyanide} \\ \text{(Blood Red Colouration)}}}{K_3[Fe(CNS)_6]}$$

Aluminium (Al^{3+})

1. Lake test

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O \quad \text{...dissolution}$$

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

Analysis of group IV (Zinc Group) (Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+})

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 25.

Table 25. Analysis of Group IV Radicals (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+})

Black ppt. (Co^{2+} or Ni^{2+})		Buff (flesh) Coloured ppt. Mn^{2+}	Dull white ppt. Zn^{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.			
Confirmation of Co^{2+} 1. **Potassium nitride test:** To one part of	**Confirmation of Ni^{2+}** 1. **Dimethyl glyoxime test:** To one part of	**Confirmation of Mn^{2+}** 1. **Sodium hydroxide Br_2 test:** To the O.S.	**Confirmation of Zn^{2+}** 1. **Sodium hydroxide Test:**

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.	O.S. add Ammonium hydroxide solution and few drops of dimethyl glyoxime. Bright rose red ppt. is obtained.	add NaOH solution Shake. A white ppt. is formed. Add Br_2water to white ppt. It turns black or brown.	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. **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 $\mathbf{Co^{2+}}$.	2. **Sodium hydroxide Br_2 test:** To another part add sodium hydroxide (in excess) and bromine water Boil. A black ppt. is formed.	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.	2. **Pot. ferrocyanide test:** To another part, add pot. ferrocyanide solution White or bluish white ppt. is formed.
3. **Borax bead test:** Perform borax bead test with the salt. A blue bead 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.	3. **Borax bead test:** Perform borax bead test with the salt. Pinkish bead in oxidizing flame and colourless bead in reducing flame.	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) indicates zinc.

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

Cobalt (Co^{2+})

1. Potassium nitrite test

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

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

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

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

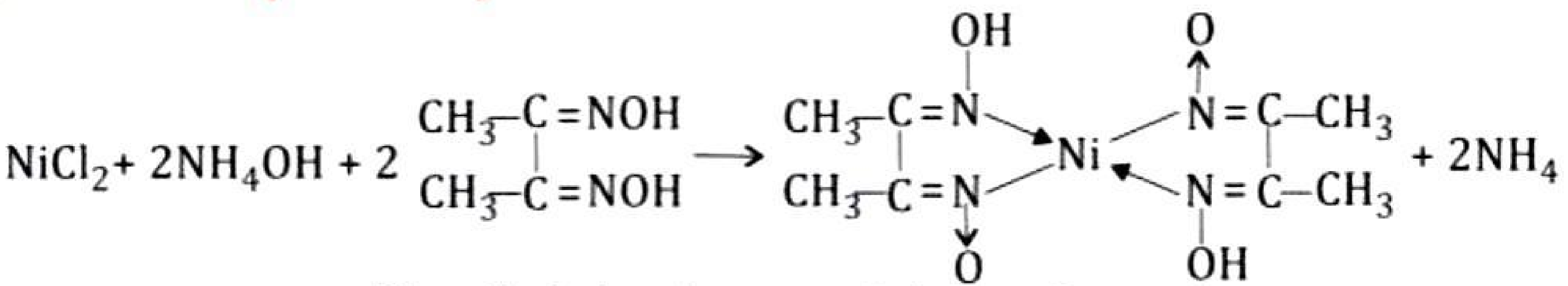
2. Ammonium thiocyanate ether test

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.

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

Nickel (Ni^{2+})

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



Dimethyl glyoxime

Bright red complex (ppt.)

2. Sodium hydroxide-bromine water test

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

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

$$2Ni(OH)_2 + H_2O + [O] \longrightarrow 2Ni(OH)_3\downarrow$$

Nickelic hydroxide (Black ppt.)

Manganese (Mn^{2+})

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

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

1. NaOH and Br_2 water test

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

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

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

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

2. PbO_2 test

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

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

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.

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

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)(Ba^{2+}, Sr^{2+}, Ca^{2+})

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.

Table 26. Analysis of Group V(Ba^{2+}, Sr^{2+}, Ca^{2+})

Ba^{2+}	Sr^{3+}	Ca^{2+}
	Test for Sr^{2+} only if Ba^{2+} is absent.	**Test for Ca^{2+} only if Ba^{2+} and Sr^{2+} are absent.**
Confirmatory Test	**Confirmatory Test**	**Confirmatory Test**
1. **Potassium chromate test:** To one part of the solution, add a few drops of potassium chromate solution. Yellow ppt.	1. **Ammonium sulphate test:** To the second part of the solution, add 1ml of Ammonium sulphate solution and warm. White ppt.	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 a flame test with the original salt. Grassy green flame visible through blue glass.	2. **Flame test:** Perform a flame test with the original salt. Crimson red flame invisible through blue glass.	2. **Flame test:** Perform flame test with the original salt. Brick red flame, light yellowish green through blue glass.

Note:

- 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+}.
- Identify correct colour in flame test. Crimson red or pinkish red in case of Sr^{2+}, whereas brick red or dull red colour in case of Ca^{2+}.

Chemical Reactions Involved in The Analysis of Group V

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.

$$BaCl_2 + (NH_4)_2CO_3 \longrightarrow BaCO_3 \downarrow + 2NH_4Cl$$

$$SrCl_2 + (NH_4)_2CO_3 \longrightarrow SrCO_3 \downarrow + 2NH_4Cl$$

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NH_4Cl$$

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+}.

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

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

2. **Charcoal cavity cobalt nitrate test**

Perform charcoal cavity cobalt nitrate test with the original salt. A pink mass is obtained.