Chemistry Qualitative Analysis

Analytical chemistry deals with qualitative and quantitative analysis of the substances. In 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, therefore qualitative analysis is studied under cation analysis and anion analysis. The systematic procedure for qualitative analysis of an inorganic salt involves the following steps:
(a) Preliminary tests

1. Physical appearance (colour and smell).
2. Dry heating test.
3. Charcoal cavity test.
4. Charcoal cavity and cobalt nitrate test.
5. Flame test.
6. Borax bead test.
7. Dilute acid test.
8. Potassium permanganate test.
9. Concentrated sulphuric acid test.
10. Tests for sulphate, phosphate and borate.

(b) Wet tests for acid radical.
(c) Wet tests (group analysis) for basic radical.

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 sulphide. (See Table 12.1 on next page)
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.

Table 12.1. Physical Examination

Experiment	*Observations*	*Inference*
1. *Colour*	Blue or Bluish green	Cu^{2+} or Ni^{2+}
	Greenish	Ni^{2+}
	Light green	Fe^{2+}
	Dark brown	Fe^{3+}
	Pink	Co^{2+}
	Light pink, flesh colour or earthy colour	Mn^{2+}
	White	Shows the absence of Cu^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}
2. *Smell* Take a pinch of the salt between your fingers and rub with a drop of water	Ammoniacal smell	NH_4^+
	Vinegar like smell	CH_3COO^-
	Smell like that of rotten eggs	S^{2-}
3. *Density*	(*i*) Heavy	Salt of Pb^{2+}, or Ba^{2+}
	(*ii*) Light fluffy powder	Carbonate
4. *Deliquescence*	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.

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 in Table 12.2 along with the inferences that you can draw.

Table 12.2. Dry Heating Test

Table 12.2. Dry Heating Test

Observations	***Inference***
1. Gas evolved	
(*a*) **Colourless and odourless gas**	
CO_2 gas—turns lime water milky	CO_3^{2-} or $C_2O_4^{2-}$ present
(*b*) **Colourless gas with odour**	
(*i*) *H_2S gas*—Smells like rotten eggs, turns lead acetate paper black.	Hydrated S^{2-}
(*ii*) *SO_2 gas*—characteristics suffocating smell, turns acidified potassium dichromate paper (or solution) green.	SO_3^{2-}
(*iii*) *HCl gas*—Pungent smell, white fumes with ammonia, white ppt with silver nitrate solution.	Cl^-
(*iv*) *Acetic acid vapours*—Characteristic vinegar like smell.	CH_3COO^-
(*v*) *NH_3 gas*—Characteristic smell, gives white fumes when a glass rod dipped in dilute HCl is brought near the mouth of the test tube, turns Nessler's solution brown.	NH_4^+
(*c*) **Coloured gases**—Pungent smell	
(*i*) *NO_2 gas*—Reddish brown, turns ferrous sulphate solution black.	NO_2^- or NO_3^-
(*ii*) *Cl_2 gas*—Greenish yellow, turns starch-iodide paper blue.	Cl^-
(*iii*) *Br_2 vapours*—Reddish brown, turns starch paper orange yellow.	Br^-
(*iv*) *I_2 vapours*—Dark violet, turns starch paper blue.	I^-

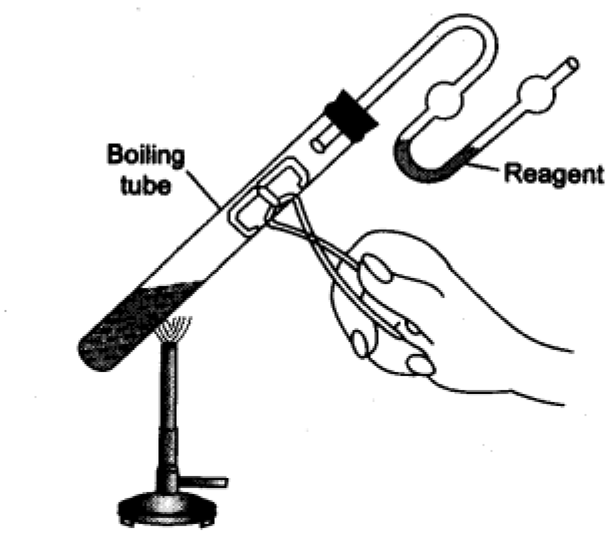
2. **Sublimate formed**	
(*a*) White sublimate	NH_4^+
(*b*) Black sublimate accompanied by violet vapours	I^-
3. **Decrepitation** The salt decrepitates.	A salt having no water of crystallisation. For example, $Pb(NO_3)_2$, NaCl, KBr.
4. **Swelling** The salt swells up into voluminous mass.	PO_4^{3-} indicated
5. **Residue**	
(*i*) Yellow when hot white when cold	Zn^{2+}
(*ii*) Brown when hot and yellow when cold	Pb^{2+}
(*iii*) White salt becomes black on heating	CH_3COO^- indicated
(*iv*) White residue, glows on heating	Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, etc.

Observations	*Inference*
(*v*) Original salt blue becomes white on heating	**Hydrated $CuSO_4$ indicated**
(*vi*) Coloured salt becomes brown or black on heating.	**Co^{2+}, Cu^{2+}, Mn^{2+} indicated.**

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.
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.

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



Charcoal cavity test

This test is based on the fact that metallic carbonates when heated in a charcoal cavity decom¬pose 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:

(a)

$$ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$$

$$ZnCO_3 \longrightarrow ZnO + CO_2 \uparrow$$

ZnO: Yellow when hot, white when cold

(b)

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

$$PbCO_3 \longrightarrow PbO + CO_2 \uparrow$$

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

Pb: Bead

(c)

$$CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$$

$$CuCO_3 \longrightarrow CuO + CO_2 \uparrow$$

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

Cu: Reddish scales

Procedure

While performing charcoal cavity test, make a small cavity on a charcoal block with the help of borer as shown in Fig. 12.2. Mix 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 by means of a mouth blowpipe as shown in Fig. 12.3. Heat strongly for sometime and draw inference according to the Table 12.3.

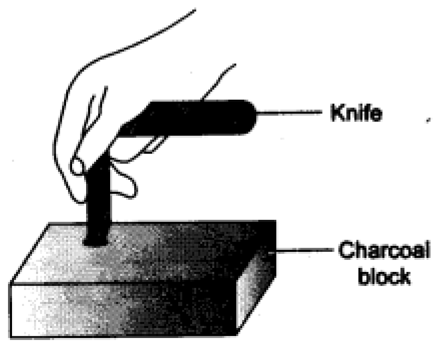


Fig. 12.2. Making bore on a charcoal block.

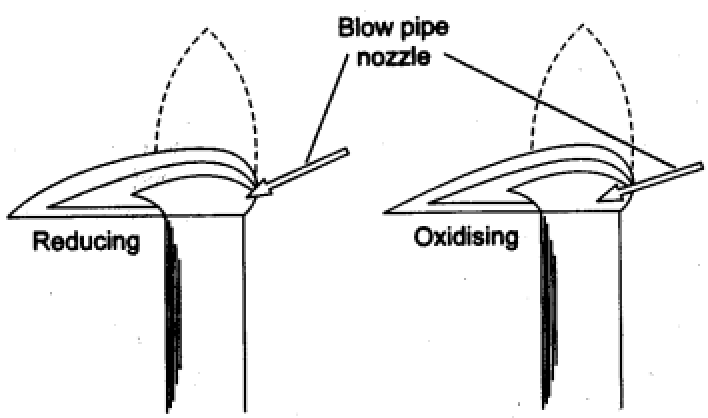


Fig. 12.3. Directing flame with blow pipe.

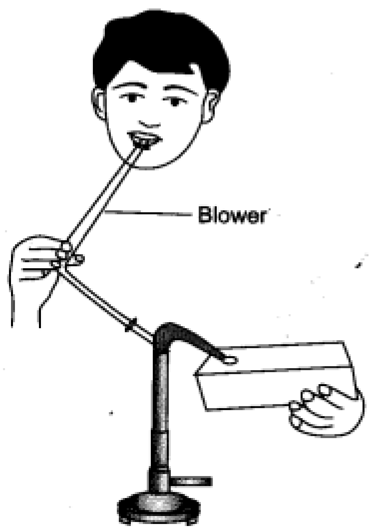


Fig. 12.4. Blowing flame on the cavity.

Table 12.3. Charcoal Cavity Test

Observations			*Inference*
Incrustation or Residue		*Metallic bead*	
Hot	*Cold*		
Yellow	White	None	Zn^{2+}
Brown	Yellow	Grey bead which marks the paper	Pb^{2+}
None	None	Red beads or scales	Cu^{2+}
White residue which glows	None	None	Ba^{2+}, Ca^{2+}, Mg^{2+}
Black	None	None	Nothing definite—generally coloured salt

To obtain a reducing flame with the help of a mouth blow pipe, make the bunsen burner flame luminous by closing the air holes of the burner. Keep the nozzle of the blow pipe just outside the flame (Fig. 12.4) and blow gently on to the cavity.

Cobalt nitrate test

This test is applied to those salts which leave white residue in 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 white residue in the charcoal cavity forming coloured compounds. For example, when a magnesium salt undergoes 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 in colour.
Some of the reactions involved are given below:

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

(i) Zinc salt:

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

(ii) Magnesium salt:

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

(iii) Aluminium salt:

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

Procedure

Put one or two drops of cobalt nitrate solution on the white residue left after charcoal cavity test. Heat for one or two minutes by means of a blow pipe in oxidising flame. Observe the colour of the residue and draw
inferences

Table 12.4. Cobalt Nitrate-Charcoal Cavity Test

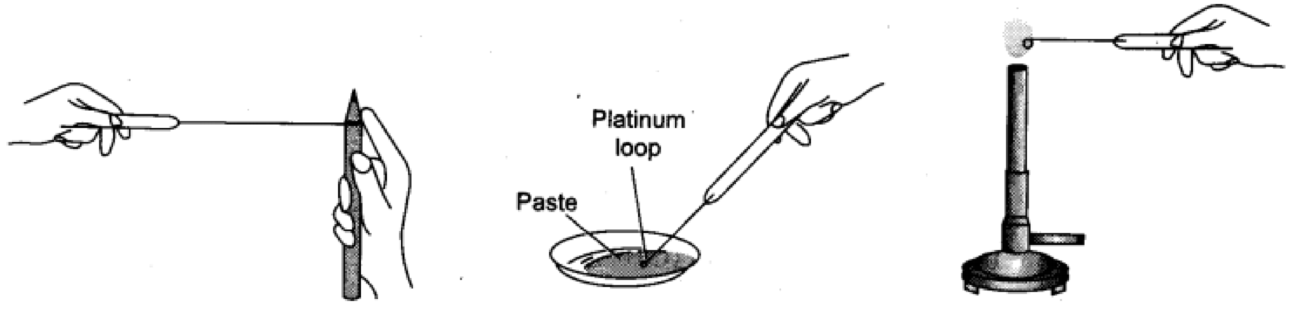
Colour of the residue	*Inference*
Green	Zn^{2+}
Pink	Mg^{2+}
Blue	Al^{3+} or PO_4^{3-}
Black	It is due to the formation of CoO. No definite indication.

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.

Flame test

Certain salts on reacting with cone. HCl from their chlorides, that are volatile in non-luminous flame. Their vapours impart characteristic colour to the flame. This colour cfan give reliable information of the presence of certain basic radicals.
For proceeding to this test, the paste of the mixture with cone. HCl is introduced into the flame with the help of platinum wire (Fig. 12.5).



(a) Making a loop of platinum wire.

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

(c) Introducing the wire in the flame.

Fig. 12.5. Flame test.

Procedure

Clean the platinum wire by dipping it in some cone. HCl taken on a watch glass and then heating 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 cone. HCl on a deem watch glass. Place small amount of this paste on platinum wire loop and introduce it into the flame. Note the colour imparted to the flame.

Table 12.5. Flame Test

Colour of the flame	*Inference*
1. Brick-red (not persistent)	Ca^{2+}
2. Crimson-red (persistent)	Sr^{2+}
3. Persistent grassy-green (appears after prolonged heating)	Ba^{2+}
4. Golden yellow	Na^{+}
5. Pink-violet	K^{+}
6. Bright-bluish green	Cu^{2+}
7. Green flashes	Zn^{2+} or Mn^{2+}
8. Dull bluish-white	Pb^{2+}

Borax bead test

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.

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

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

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, $Na_2B_4O_7.10H_2O$ 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. 12.6).

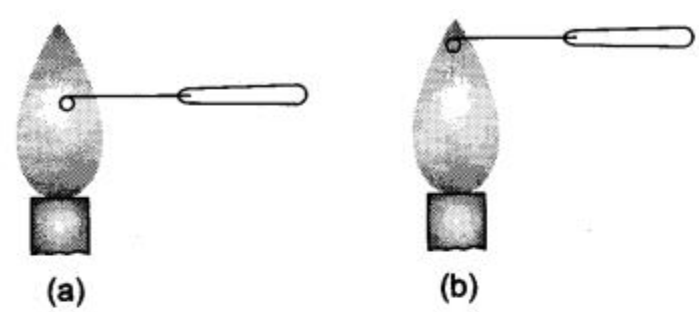


Fig. 12.6. Borax bead test (*a*) Heating in reducing flame, (*b*) Heating in oxidising flame.

Table 12.6. Borax Bead Test

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. Amethyst (pinkish violet) in both hot and cold.	Colourless, hot and cold.	Mn^{2+}
4. Brown when hot, pale brown when cold.	Grey or black when hot and opaque when 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 platinum wire, heat the head to redness. Tap the rod with finger stroke, till the bead jumps off (Fig. 12.7).

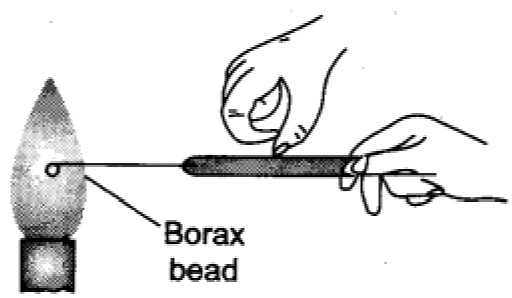


Fig. 12.7. Removing bead from platinum wire.

The identification of the acid radicals is first done on the basis of preliminary tests. 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 upon 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 individual 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 sulphuric add. Identify the gas and draw

Table 12.7. Dilute Sulphuric Acid Test

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

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 Involved in Dil. H_2SO_4 Test

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 add 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*. 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

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

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 oxygen of the air.

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

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

$$3KNO_2 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HNO_3 + H_2O + 2NO$$

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

Potassium permanganate test

To a pinch of salt in test tube add about 2 ml of dilute sulphuric acid. Boil off any gas evolved, add little more of dilute acid and then potassium permanganate solution dropwise. Note the changes as given in Table 12.8. This test helps in detection of Cl^-, Br^-, I^-, $C_2O_4^{2-}$ and Fe^{2+} radicals.

Table 12.8. 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*	
	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+}.

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 Fe2+ 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.

Chemical Reactions Involved

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

1. *Ferrous salts*: $2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$

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 sulphuric acid test

This test is performed by treating small quantity of salt with cone, sulphuric acid (2-3 ml) in a test tube. Identify the gas evolved in cold and then on heating. Draw inferences from Table 12.9

Table 12.9. Conc. Sulphuric Acid Test

Observations	Inference	
	Gas	**Radical**
1. Colourless gas with pungent smell, white fumes with aqueous ammonia (NH_4OH), white ppt. with $AgNO_3$ solution.	HCl	Cl^-
2. Reddish brown vapours with pungent smell, turns starch paper yellow. It does not turn $FeSO_4$ solution black.	Br_2	Br^-
3. Deep violet vapours with pungent smell, turns 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 $FeSO_4$ solution black.	NO_2	NO_3^-
5. Colourless vapours, vinegar smell, turns blue litmus red.	CH_3COOH vapours,	CH_3COO^-
6. A colourless gas wich turns lime water milky and also a gas which burns with pale-bluish flame	$CO_2 + CO$	$C_2O_4^{2-}$
7. No gas/vapours evolved.	—	Cl^-, Br^-, I^-, NO_3^-, CH_3COO^- absent

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 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).

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

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

Chemical Reactions Involved in conc. H_2SO_4 Test

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* $$KI + H_2SO_4 \longrightarrow KHSO_4 + HI$$ $$H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + 2H_2O$$

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

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 BaCl2 solution. A white ppt. insoluble in cone. HCl indicates presence of sulphate.
2. **Phosphate (PO_4^{3-})**
   Add cone. HNOs 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 or cone. 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.

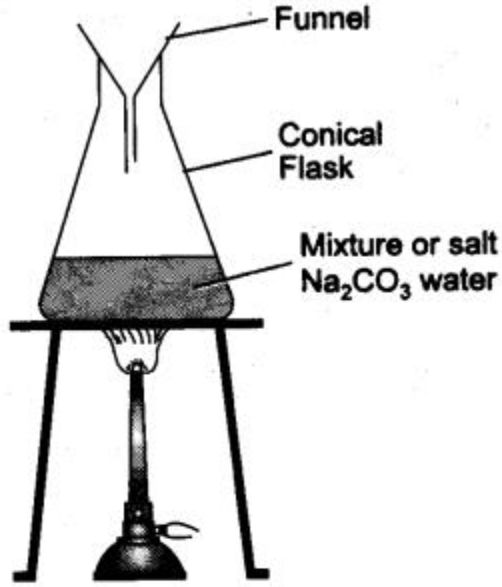


Fig. 12.8. Preparation of sodium carbonate extract.

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. 12.8). 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.

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 sometime. The suspension obtained is filtered.The filtrate is sodium carbonate extract. p.g 12 8. Preparation of sodium carbonate extract.

Theory of Preparation of Sodium Carbon-ate Extract.

When the salts are boiled with strong solution of sodium carbonate, double decompo-sition 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 predpitated

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

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 addified with some suitable acid and is boiled to expel carbon dioxide. The selection of add used for destroying excess Na_2CO_3depends 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*
If the salt dissolves, soluble carbonate is indicated.	If the salt remains insoluble, the presence of insoluble carbonate is indicated.
1. **Dil HCl test**	
To one portion of the solution, add dil. HCl.	To the salt add dil. HCl.
Brisk effervescence and evolution of carbon dioxide which turns lime water milky confirms the presence of soluble carbonate.	**Brisk effervescence** and **evolution of carbon dioxide** which turns lime water milky confirms the presence of **insoluble carbonate.**
2. **Magnesium sulphate test**	
To another portion of the solution, add magnesium sulphate solution.	
Formation of **white precipitate** in the cold confirms the presence of **soluble carbonate.**	

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.

Confirmation of Sulphide, S^{2-}

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

Experiment	*Observations*
1. **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.	A white ppt. is formed.
To a portion of the above ppt. add dil. HCl.	The ppt. dissolves with the evolution of sulphur dioxide.
2. **$KMnO_4$ test** To a second part of the ppt. from (1) add a few drops of acidified potassium permanganate solution.	The pink colour is discharged.
3. **$K_2Cr_2O_7$ 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*
1. **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.
2. **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.
3. **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 vapours of nitrogen peroxide)

Experiment	*Observations*
1. **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.
2. **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.
3. **Diphenylamine test** To a portion of aqueous solution, add a few drops of diphenylamine.	A **deep blue colouration** is obtained.

Chemical Reactions Involved in the Confirmation of Carbonate, 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

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

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*

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

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

Sulphide (S^{2-})

1. *Sod. nitroprusside test*

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

2. *Lead acetate test*

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

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*

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

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

$$FeSO_4 + NO \longrightarrow \underset{\text{(Dark brown)}}{FeSO_4 . NO}$$

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 cone. H_2SO_4 with the evolution of HCl gas).

Experiment	***Observations***
1. 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.
2. 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.
3. 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 vapours 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 cone. H_2SO_4 with the evolution of bromine vapours).

Experiment	Observations
1. 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.
2. Manganese dioxide test Heat a small quantity of the salt with solid MnO_2 and conc. H_2SO_4.	Evolution of **yellowish brown vapours** of bromine which turn starch paper yellow.
3. 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 disulphide 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 solutio/i 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 vapours of iodine).

Experiment	Observations
1. 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.
2. Manganese dioxide test Heat a small quantity of the salt with a little MnO_2 and conc. H_2SO_4.	Evolution of **violet vapours of iodine** which turn starch paper blue.
3. Chlorine water test Acidify a part of the aqueous solution (or sodium carbonate extract) with dil. HCl, add 1-2 ml of carbon disulphide and then chlorine water. Shake vigorously and allow to stand.	Carbon disulphide layer acquires a violet colouration.

Confirmation of Nitrate, NO_3^-
(No action with dilute acids but decomposed by cone. H_2SO_4 with the evolution of brown vapours of nitrogen peroxide).

Experiment	Observations
1. **Diphenylamine test** Add a few drops of diphenylamine to a part of aqueous solution of the salt.	A **deep blue colouration** is obtained.
2. **Copper chips test** Heat a small quantity of the original salt with concentrated sulphuric acid and a few copper chips.	**Dark brown fumes** of nitrogen dioxide are evolved.
3. **Ring Test** Add a small quantity of freshly prepared solution of ferrous sulphate to a part of the aqueous solution and then pour concentrated sulphuric acid slowly along the sides of the test tube as shown in Fig. 12.9.	A **dark brown ring** is formed at the junction of the layers of the acid and the solution.

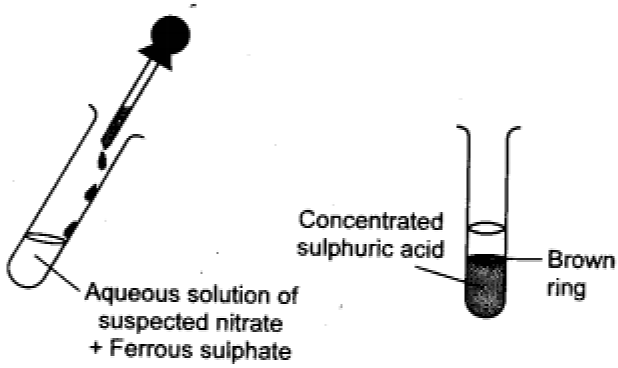


Fig. 12.9. The brown ring test for nitrates.

Confirmation of Acetate, CH_3COO^-

(No action with dilute acids but decomposed by cone. H_2SO_4 with the evolution of CH_3COOH vapours

Experiment	*Observations*
1. 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.
2. Ester test Take a small quantity of the salt in a test-tube. Add conc. H_2SO_4 (2 ml) 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.
3. Ferric chloride test Take water extract of the salt. Add *neutral* ferric chloride solution. Filter. Divide the filtrate into two portions.	Reddish coloured filtrate.
(*i*) To one part, add dil. HCl.	Reddish colour disappears.
(*ii*) To second part, add water and boil.	Reddish brown ppt.

Confirmation of Oxalate, $C_2O_4^-$
(No action with dilute acids but decomposed by cone. H_2SO_4 with the evolution of CO_2 and CO gas)

Experiment	*Observations*
1. 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.	A **white ppt.** is formed.
Add dil HNO_3 to the white ppt and warm.	The ppt. dissolves.
2. Potassium permanganate test Take a pinch of the salt in test tube and add dil sulphuric 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 are 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*

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2CH_3COONa \longrightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + 2CH_3COOH$$

Acetic acid (Vinegar smell)

2. *Ester test*

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

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

Ethyl acetate
(Fruity smell)

3. *Ferric chloride test*

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

$$(CH_3COO)_3Fe + 2H_2O \longrightarrow (CH_3COO)(OH)_2\,Fe\downarrow + 2CH_3COOH$$

Reddish brown ppt.

Oxalate ($C_2O_4^{2-}$)

1. *Calcium chloride test*

$$(NH_4)_2C_2O_4 + CaCl_2 \longrightarrow CaC_2O_4\downarrow + 2NH_4Cl$$

White ppt.

2. *Potassium permanganate test*

$$2KMnO_4 + 3H_2SO_4 + 5\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2\uparrow + 8H_2O$$

Confirmation of Sulphate, SO_4^{2-}

(Not indicated in dilute and concentrated H_2SO_4 acid 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. **Match stick 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*
1. **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.
2 **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*

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

2. *Match-stick test*

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

$$BaSO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + BaCO_3$$

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

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

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*

$$K_3PO_4 + \underset{\text{Amm. molybdate}}{3(NH_4)_2MoO_4} \longrightarrow 2(NH_4)_3PO_4 + \underset{\text{Pot. molybdate}}{3K_2MoO_4}$$

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

$$H_2MoO_4 \longrightarrow MoO_3 + H_2O$$

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

2. *Magnesia mixture test*

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

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 12.10).

Table 12.10. Classification of Cations

Group	Cations
Group zero	NH_4^+
Group I	Pb^{2+}
Group IIA	Pb^{2+}, Cu^{2+}
Group IIB	As^{3+}
Group III	Fe^{3+}
Group IV	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{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. 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 sometime, take the fresh quantity of the salt again and treat it in a similar manner with next solvent. The clear solution thus obtained is labelled as Original Solution (O.S.).

Important Notes:

1. In case some gas is evolved during the preparation of solution, let the reaction cease. Gas must be completely expelled by heating.
2. In case solution is prepared in dilute HCl, group I is absent. Proceed with group II.
3. If the salt is soluble in hot water, and on cooling white precipitates appear, lead chloride is indicated.
4. 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, 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 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 (ous) will precipitate, since all other chlorides are soluble. Thus, these cations form a group of ions which may be precipitated from solution by addition of group reagent HCl. Similarly, H_2S is a group reagent for group II. The following Table 12.11 clearly shows the group reagents for different groups and the form in which cations of the particular group are precipitated out.

Table 12.11. Group Reagents

Group	***Group reagent***	***Cations***	***Form in which cations are precipitated***
Group zero	No	—	—
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	No	Mg^{2+}	—

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. On the basis of 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 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 ion common with the ions furnished by weak electrolyte, is added to its solution. This effect is called common ion effect. For example, 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:

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

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

Common ion

Due to the addition of NH_4Cl, which is strongly ionised in the solution, concentration of NH4+ ions increases in the solution. Therefore, according to Le-Chatelier's principle equilibrium in equation (12.1) shifts in the backward direction in favour of unionised NH_4OH. In this way, addi¬tion 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.
Application of concept of 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 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 which suppresses degree of ionisation of H_2S by common ion effect.

$$H_2S \rightleftharpoons \boxed{2H^+} + S^{2-} \quad ...(12.3)$$
$$HCl \longrightarrow \boxed{H^+} + Cl \quad ...(12.4)$$

Common ion

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 solubility products of their sulphides are quite high. In order that ionic products exceed solubility products, concentration of S2- ions should be high in this case. 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 ionised form.

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

Hence, 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 NH4OH 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 in order to decrease the concentration of OH^- ions.

$$NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$$
$$NH_4Cl \longrightarrow \boxed{NH_4^+} + Cl^-$$

Common ion

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 $Mg2^+$ will also be precipitated along with radicals of group III.

Radicals of group V ($Ba2^+$, $Sa2^+$, $Ca2^+$) are precipitated as their carbonates by the addition of $(NH_4)_2$ CO_3 in the presence of NH_4Cl and NH_4OH. NH_4Cl suppresses the degree of ionisation of $(NH_4)_2$ CO_3 by common ion effect and hence decreases the concentration of $CO_3$2- ions.

$$(NH_4)_2CO_3 \rightleftharpoons \boxed{2NH_4^+} + CO_3^{2-}$$
$$NH_4Cl \longrightarrow \boxed{NH_4^+} + Cl^-$$

Common ion

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, H_4^+ ion is detected in the beginning using solid salt.

Procedure

The solid salt is heated with concentrated solution of sodium hydroxide. In case, ammonia gas is evolved, NH_4^+ is present. 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 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 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

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

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+}. Group reagent for this group is dil. hydrochloric acid.

Procedure

1. To the original solution add dil. hydrochloric acid. If a white precipitate is formed, first group (Pb^{2+}) is present.
2. Filter and wash the ppt. with cold water and examine as in Table 12.12.

Table 12.12. Analysis of Group I (Pb^{2+})

Boil the white precipitate with 5–10 ml of water. Precipitate dissolves. Divide the solution obtained into three parts. *Confirmation* 1. Cool one part of the solution under tap. *White crystalline ppt.* separate 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:

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

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

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

Confirmatory tests:

1. On cooling, precipitates settle down as $PbCl_2$ is less soluble in cold water.
2. *Potassium iodide test*

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

3. *Potassium chromate test*

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

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_2Sgas 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 the Kipp's apparatus by turning

the stop cock as shown in Fig. 12.10, 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.

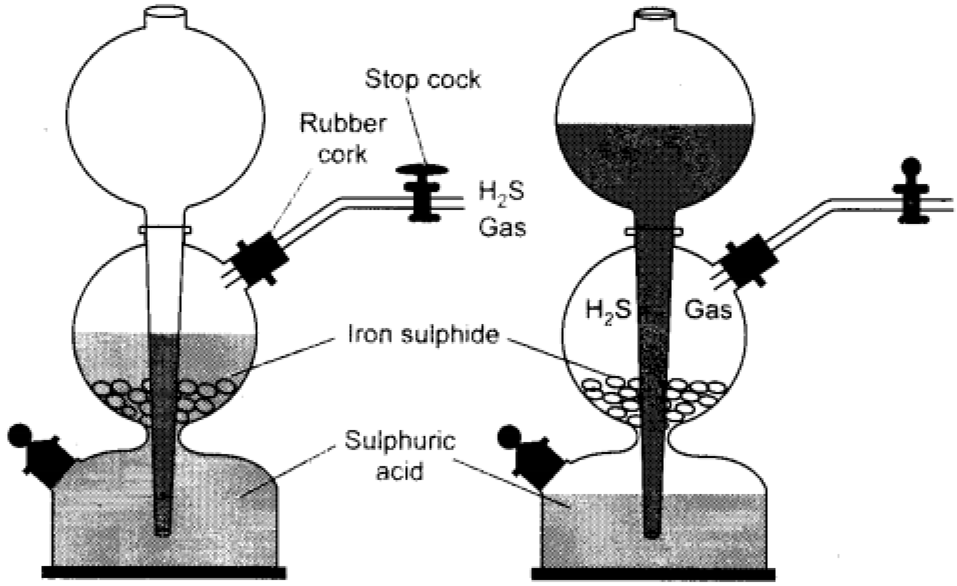


Fig. 12.10. Kipp's apparatus for H_2S gas.

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

Table 12.13. Analysis of Group II

Black ppt. **(Pb^{2+} or Cu^{2+})** ***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+}***
White ppt. (Pb^{2+}) **Confirmation** Dissolve the ppt. in hot ammonium acetate solution. Divide the solution into two parts : 1. **Potassium iodide test** To one part add pot. iodide solution. **Yellow ppt.** is formed. The ppt. dissolves in boiling water and on cooling recrystallises. 2. **Potassium chromate test** To another part add pot. chromate solution. **Yellow ppt.** is formed which dissolves in NaOH solution.	*No white ppt.* *To rest of the solution add NH_4OH in excess* Blue coloured solution (Cu^{2+}) **Confirmation** 1. **Potassium ferrocyanide test** To one part of the blue solution add acetic acid and pot. ferrocyanide solution. **A chocolate brown ppt.** is formed. 2. **Potassium iodide test** To another part add acetic acid and pot. iodide solution. A **white ppt.** is formed in brown coloured solution.	**Confirmation** Dissolve the yellow ppt. in conc. HNO_3 and divide it into two parts. 1. **Ammonium molybdate test.** To a part of the solution, add ammonium molybdate solution and heat—**A yellow ppt.** 2. **Magnesia mixture test.** Make the second part of the solution alkaline with NH_4OH solution and add magnesia mixture (contains solutions of $MgSO_4$, NH_4Cl and NH_4OH mixed in equal volumes)—**A white ppt.**

Chemical Reactions Involved in the Analysis of Group II

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

Lead (Pb^{2+})

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

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

1. *Potassium iodide test*:

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

2. *Potassium chromate test*:

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

Copper (Cu^{2+})

Black ppt. of CuS dissolves in 50% nitric acid and a blue solution is obtained on addition of 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*:

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

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

2. *Potassium iodide test*:

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

Arsenic (As^{3+})

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

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

1. *Ammonium molybdate test*:

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Yellow ppt. of ammonium arseno molybdate}}{(NH_4)_3AsO_4.\ 12MoO_3\downarrow} + 21NH_4NO_3 + 12H_2O$$

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)

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 sometime. 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+}. Analyse the ppt. and draw inferences as in Table 12.14.

Table 12.14. 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.	
Confirmation	**Confirmation**
1. **Potassium ferrocyanide test.** To one part of the above solution add potassium ferrocyanide solution. **Prussian blue colouration.**	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. **Potassium sulphocyanide test.** To the second part, add a little potassium sulphocyanide solution. **Blood red colouration.**	2. **Cobalt nitrate test.** Perform charcoal cavity/Cobalt nitrate test with the salt. **Blue mass.**

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 cone, 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.

$$FeCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Fe(OH)_3 \downarrow$$

(Reddish brown ppt.)

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Al(OH)_3 \downarrow$$

(White ppt.)

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*:

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow 12KCl + Fe_4[Fe(CN)_6]_3$$

Ferric ferrocyanide (Prussian blue)

2. *Potassium sulphocyanide test*:

$$FeCl_3 + 3KCNS \longrightarrow 3KCl + Fe(CNS)_3$$

Ferric sulphocyanide (Blood red colouration)

Aluminium (Al^{3+})

1. *Lake test*:

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

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Al(OH)_3 \downarrow$$

Blue colour adsorbs on this ppt.

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 ammonical 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 ammonical 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 analyse the ppt. according to the Table 12.15.

Table 12.15. 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 nitrite 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. Amm. thiocyanate ether test** To another part add ether (1 ml). Add a crystal of amm. 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 amm. hydroxide soln. 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 soln. 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** soln. 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 soln. **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) indictes zinc

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

Cobalt (Co^{2+})

1. Potassium nitrite test

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

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

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

$$Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$$

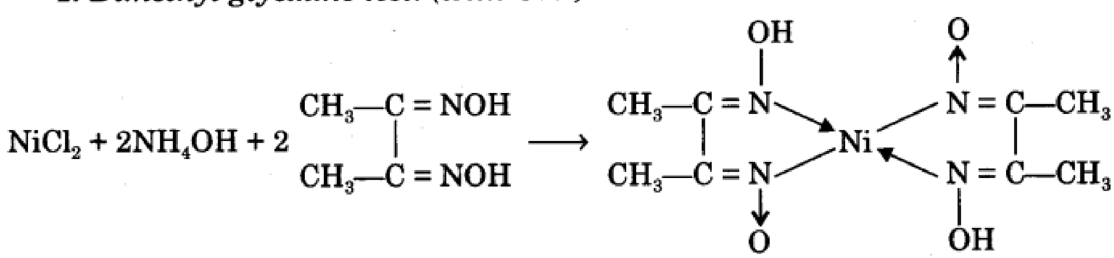
Pot. cobalti nitrite
(yellow ppt.)

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 cobhlti 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.)

$+ 2NH_4Cl + 2H_2O$

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 dissolves 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

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

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

2. Potassium ferrocyanide test

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

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 ofNH_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 12.16.

Table 12.16. Analysis of Group V (Ba^{2+}, Sr^{2+}, Ca^{2+})

Ba^{2+}	Sr^{2+}	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.**
1. **Potassium chromate test** To one part of the solution, add a few drops of potassium chromate solution. **Yellow ppt.**	1. **Amm. sulphate test** To the second part of the solution, add 1 ml of amm. sulphate solution and warm. **White ppt.**	1. **Amm. oxalate test** To the third portion of the solution, add 1–2 ml of amm. oxalate solution. Add a little amm. hydroxide to it and scratch the sides. **White ppt.**
2. **Flame test** Perform flame test with the original salt. **Grassy green flame.**	2. **Flame test** Perform flame test with the original salt. **Crimson red flame.**	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 carbonates of 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 acetate.

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

$$(CH_3COO)_2\,Ca + (NH_4)_2C_2O_4 \longrightarrow 2CH_3COONH_4 + \underset{\text{(white ppt.)}}{CaC_2O_4 \downarrow}$$

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 (Magnesium group)

Table 12.17. Analysis of Group VI (Mg^{2+})

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.*

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

1. Ammonium phosphate test

$$MgCl_2 + NH_4OH + (NH_4)_2HPO_4 \longrightarrow Mg(NH_4)PO_4 \downarrow + 2NH_4Cl + H_2O$$