# QUALITATIVE ANALYSIS (Anion)

# PART-1

## Introduction :

Qualitative analysis involves the detection of cation(s) and anion(s) of a salt or a mixture of salts. The systematic procedure for qualitative analysis of an inorganic salt involves the following steps : (a) Preliminary tests

- Physical appearance (colour and smell).
  - Dry heating test.
  - Flame test.
  - Borax bead test.
  - Charcoal cavity test.
- Charcoal cavity and cobalt nitrate test.
- (b) Wet tests for acid radicals.

(c) Wet tests (group analysis) for basic radicals.

### Section (A) : Heating in dry test tube

#### 1. Physical appearance (smell).

Table : 1 Physical Examination

Take a pinch of the salt between your fingers and rub with a drop of water		
Smell	Inference	
Ammoniacal smell	NH4 <sup>+</sup>	
Vinegar like smell	CH₃COO⁻	
Smell like that of rotten eggs	S <sup>2–</sup>	

#### 2. Dry Heating Test :

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

	Observation	Inference		
1.	Gas evolved			
	(a) Colourless and odourless gas			
	CO <sub>2</sub> gas – turns lime water milky	CO <sub>3</sub> <sup>2–</sup>		
	(b) Colourless gas with odour			
	(i) H <sub>2</sub> S gas – Smells like rotten eggs, turns lead acetate paper black.	Hydrated S <sup>2–</sup> or S <sup>2–</sup>		
	(ii) SO <sub>2</sub> gas – Characteristic suffocating smell of burning sulphur turns acidified potassium dichromate solution or paper green.	SO3 <sup>2-</sup>		
	(iii) HCI gas – Pungent smell, white fumes with ammonia, white precipitate with silver nitrate solution.	C⊢		
	(iv) Acetic acid vapours-Characteristic vinegar like smell.	CH₃COO⁻		
	(v) NH <sub>3</sub> gas– Characteristic smell, turns Nessler's solution brown.	NH4 <sup>+</sup>		
	(c) Coloured gases – Pungent smell			
	(i) NO <sub>2</sub> gas – Reddish brown, turns ferrous sulphate solution brownish black.	NO <sub>2</sub> - or NO <sub>3</sub> -		
	(ii) Cl <sub>2</sub> gas – Greenish yellow, turns starch iodide paper blue.	C⊢		
	(iii) Br <sub>2</sub> vapours – Reddish brown, turns starch paper orange red.	Br−		
	(iv) I <sub>2</sub> vapours – Dark violet, turns starch paper blue.	I-		
2.	Sublimate formed			

	(a) White sublimate	NH <sub>4</sub> +
	(b) Black sublimate accompanied by violet vapours.	I-
3.	Fusion	
	The mixture fuses.	Alkali metal salts or salt containing water of crystallisation.
4.	Swelling	
	The mixture swells up into voluminous mass.	PO <sub>4</sub> <sup>3–</sup> , BO <sub>3</sub> <sup>3–</sup> indicated
5.	Residue	
	(i) Yellow when hot, white when cold.	Zn <sup>2+</sup>
	(ii) Brown when hot and yellow when cold.	Pb <sup>2+</sup>
	(iii) Original salt blue becomes white on heating.	Hydrated CuSO <sub>4</sub> indicated
	(iv) Coloured salt becomes brown or black on indicated.	Co <sup>2+</sup> , Fe <sup>2+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup> heating.

#### Note :

Ο Use a perfectly dry test-tube for performing thes test. While drying a test-tube, keeps 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.

Ο 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. Gas detector tube



## Section (B) : Flame and borax bead test

#### 3. Flame test :

The chlorides of the metals are more volatile as compared to other salts and these are prepared in situ by mixing the compounds with a little concentrated hydrochloric acid. On heating in a non-luminous Bunsen flame they are volatilized and impart a characteristic colour to the flame as these absorb energy from the flame and transmit the same as light as characteristic colour.

Table : 3				
Colour of Flame	Inference			
Crimson Red / Carmine Red	Lithium			
Golden yellow	Sodium			
Violet/Lilac	Potassium			
Brick red	Calcium			
Crimson	Strontium			
Apple Green/Yellowish Green	Barium			
Green with a Blue centre/Greenish Blue	Copper			





(A) Dipping the platinum wire in the paste of salt and HCI. Figure : Flame test

(B) Introducing the wire in the flame

#### 4. **Borax Bead test :**

On Heating borax forms a colourless glassy bead of  $NaBO_2$  and  $B_2O_3$ .

 $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ 

On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame. For example, in oxidising flame copper salts give blue bead.

 $CuSO_4 \longrightarrow CuO + SO_3$  $CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$  (blue bead) ;

However, in reducing flame the colours may be different due to different reactions.

 $2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$  $2Cu(BO_2)_2 + 2C \longrightarrow 2Cu$  (brown red/red and opaque bead) +  $2B_2O_3 + 2CO$ .

Following metals impart a characteristic colour to the Bunsen flame :

Na, Κ, Li, Sr, Rb, Cs, Be, Ca, Cu

l able : 4						
Metal	Colour in c	oxidising flame	Colour in reducing flame			
Wetai	When Hot	When Hot When Cold		When Cold		
Copper	Green	Blue	Colourless	Brown red		
Iron	Brown yellow	Pale yellow/Yellow	Bottle green	Bottle green		
Chromium	Yellow	Green	Green	Green		
Cobalt	Blue	Blue	Blue	Blue		
Manganese	Violet/Amethyst	Red/Amethyst	Grey/Colourless	Grey/Colourless		
Nickel	Violet	Brown/Reddish brown	Grey	Grey		

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(AP) Non luminous flame is called oxidising flame.





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œ All acid radicals which are in JEE syllabus are colourless and diamagnetic. Hence the colour of the salts is only due to the basic radicals.

#### 5. **Charcoal Cavity Test:**

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

Example :

 $ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$ (a)  $ZnCO_3 \longrightarrow ZnO$  (Yellow when hot, white when cold) +  $CO_2^{\uparrow}$  $CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$ (b)

 $CuCO_3 \longrightarrow CuO + CO_2^{\uparrow}$  $CuO + C \longrightarrow Cu$  (Reddish scales) +  $CO^{\uparrow}$ 

Table : 5			
Observati	Inference		
Incrustation or Residue Metallic bead			
Yellow when hot, white when cold	None	Zn <sup>2+</sup>	
Brown when hot, yellow when cold	Grey bead which marks the paper	Pb <sup>2+</sup>	
No characteristic residue	Red beads or scales	Cu <sup>2+</sup>	
White residue which glows on heating	None	Ba <sup>2+</sup> ,Ca <sup>2+</sup> , Mg <sup>2+</sup>	
Black	None	Nothing definite–generally coloured salt	

#### 6. **Cobalt Nitrate Test :**

In case the residue is white in colour after charcoal cavity test, add a drop of cobalt nitrate in the charcoal cavity. A drop of water is then added and the mass is heated in an oxidising flame using blow pipe. It is cooled and one or two drops of cobalt nitrate solution is added and then again heated in the oxidising flame. Different metal salts give different coloured mass as given in the table. To illustrate :

 $ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$ ;

 $ZnCO_3 \longrightarrow ZnO + CO_2$ 

 $2Co (NO_3)_2 \longrightarrow 2CoO + 4 NO_2 + O_2$ ;  $ZnO + CoO \longrightarrow ZnO. CoO (or CoZnO_2)$ (Rinmann's green)

Table : 6				
S.No. Metal Colour of the mass				
1.	Zinc	Green		
2.	Aluminium	Blue		
3.	Magnesium	Pink		
4.	Tin	Bluish – green		

#### Table : 7

#### SOLUBILITY CHART

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S.No.	Anion	Solubility / Exception
1.	CO32-	Except carbonates of alkali metals and of ammonium, all other normal carbonates are insoluble.
2.	SO32-	Only the sulphites of the alkali metals and of ammonium are water soluble. The sulphite of other metals are either sparingly soluble or insoluble.
3.	S <sup>2-</sup>	The acid, normal and polysulphide of alkali metals are soluble in water. The normal sulphides of most other metals are insoluble; those of the alkaline earths are sparingly soluble, but are gradually changed by contact with water into soluble hydrogen sulphides.
4.	NO₂⁻, NO₃⁻	Almost all nitrites and nitrates are soluble in water. AgNO <sub>2</sub> is sparingly soluble. Nitrates of mercury and bismuth give basic salts on treatment with water. These are soluble in dilute nitric acid.
5.	CH₃COO-	Acetates are water soluble except Ag(I) and Hg(II) acetates which are sparingly soluble.
6.	Cŀ	Most chlorides are soluble in water. PbCl <sub>2</sub> (sparingly soluble in cold but readily soluble in boiling water), Hg <sub>2</sub> Cl <sub>2</sub> , AgCl, CuCl, BiOCl, SbOCl and Hg <sub>2</sub> OCl <sub>2</sub> are insoluble in water.
7.	Br-	Silver, mercury(I) and copper(I), bromides are insoluble. Lead bromide is sparingly soluble in cold but more soluble in boiling water. All other bromides are soluble in water.
8.	ŀ	Silver, mercury(I), mercury(II), copper(I), lead and bismuth(III) iodides are the least soluble salts. All other iodides are water soluble.
9.	SO4 <sup>2-</sup>	The sulphates of barium, silver lead are insoluble in water, those of calcium and mercury(II) are slightly soluble. Some basic sulphates of mercury, bismuth and chromium are also insoluble, but these dissolves in dilute hydrochloric or nitric acid.
10.	PO4 <sup>3-</sup>	The phosphate of the alkali metals, with the exception of lithium and ammonium, are soluble in water; the primary phosphate of the alkaline earth metals are soluble. All the phosphates of the other metals and also the secondary and tertiary phosphate of the alkaline earth metals are sparingly soluble or insoluble in water.

### Analysis of ANIONS (Acidic Radicals) :

Analysis of anions (acidic radicals) can be broadly divided in to two groups.

- (A) **GROUP 'A' RADICALS :** It involves those anions which are characterised by volatile products by reaction with HCl/ H<sub>2</sub>SO<sub>4</sub> It is further subdivided in to two groups as given below.
  - (a) Dilute Sulphuric acid/Dilute Hydrochloric acid : The anions of this group liberate gases or acid vapours with dilute sulphuric acid/hydrochloric acid.

Observation	Inference		
Observation		Radical	
Effervescence with the evolution of a colourless and odourless gas which turns lime water milky.	CO <sub>2</sub>	CO32-	
Evolution of colourless gas having smell of rotten egg which turns lead acetate paper black.	H₂S	S <sup>2–</sup>	
Colourless gas having suffocating odour (like burning sulphur) which turns acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> paper green.	SO <sub>2</sub>	SO32-	
Evolution of reddish brown pungent smelling gas which turns			
(i) FeSO <sub>4</sub> solution brownish-black and	NO <sub>2</sub>	NO <sub>2</sub> -	

Table : 8

(ii) wet starch –iodide paper blue. Colourless gas having smell of vinegar.	HAC(g)	CH₃COO-
No peculiar gas is evolved.	-	All above are absent

(b) Concentrated Sulphuric acid group : The anions of this group liberate acid vapours or gases with conc. H<sub>2</sub>SO<sub>4</sub>.

Table : 9			
Observation	Inference		
Observation	Gas	Radical	
Colourless gas with pungent smell which gives dense white fumes with a glass rod dipped in NH <sub>4</sub> OH.	HCI	C⊢	
Reddish brown gas with pungent smell, intensity of reddish brown fumes increases on addition of a pinch of solid MnO <sub>2</sub> . Also it turns starch paper orange red.	Br <sub>2</sub>	Br−	
Evolution of violet vapours which turns starch paper blue.	I <sub>2</sub>	I-	
Evolution of reddish brown fumes which intensifies on addition of copper turnings or bits of filter paper.	NO <sub>2</sub>	NO₃⁻	
Starch iodide paper develops a blue–black spot due to the formation of a $I_2$ –starch complex. (NO <sub>2</sub> liberated acts as oxidising agent).			

(B) GROUP 'B' RADICALS : Anions of this group do not give acid vapours or gases with dilute as well as concentrated H<sub>2</sub>SO<sub>4</sub> but are characterised by their specific reactions in solutions. This group is further sub divided into two groups based on the type of the reactions.

- (a) Oxidation and reduction in solutions :  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$  etc.
- (b) Precipitation reactions : These are given by  $SO_{4^{2-}}$ ,  $PO_{4^{3-}}$  etc.

Table : 10			
Observation	Inference		
W.E. or S.E. + BaCl <sub>2</sub> (aq) White precipitate insoluble in dil. HCl and HNO <sub>3</sub>	SO4 <sup>2-</sup>		
W.E or S.E + conc. HNO <sub>3</sub> (1–2 mL) + ammonium molybdate and boil	DO.3-		
$\rightarrow$ Canary yellow precipitate			

W.E. = Water extract. (Salt is dissolved in distilled water)

S.E. = Sodium carbonate extract

#### Preparation of sodium carbonate extract :

Take 1-2 g of salt/salts mixture and three times the amount of pure solid sodium carbonate in a borosil conical flask. Add 20 mL of distilled water and boil the contents for 10 minutes. Cool the solution and then filter. The Filtrate is termed as "Sodium carbonate extract".

Sodium carbonate reacts with the inorganic salt to form water soluble sodium salt of the acid radical.

 $BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 \downarrow$  (white) + 2NaCl (aq)

 $Cd_3 (PO_4)_2 + 3Na_2CO_3 \longrightarrow 3CdCO_3 \downarrow + 2Na_3PO_4 (aq)$ 

Sodium carbonate extract is used when

(a) salt is only partially soluble in water or insoluble

(b) cations interfere with the tests for acid radicals or the coloured salt solutions may be too intense in colour that the test results are not too clear.

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As sodium carbonate extract contains excess of sodium carbonate, it should be neutralised with a suitable acid before proceeding for analysis of an anion.

**Note :** S.E. is not used for testing  $CO_3^2$ -or  $HCO_3^-$  ions.



Figure : Preparation of sodium carbonate extract

## Individual tests :

#### Section (C) : dil. HCl / dil. $H_2SO_4$ group

#### (A) GROUP 'A' RADICALS :

# (a) DILUTE SULPHURIC ACID/DILUTE HYDROCHLORIC ACID GROUP :

- 1. CARBONATE ION (CO3<sup>2-</sup>) :
- Dilute H<sub>2</sub>SO<sub>4</sub> test : A colourless odourless gas is evolved with brisk effervescence.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2^{\uparrow}$$

• Lime water/Baryta water (Ba(OH)<sub>2</sub>) test : The liberated gas can be identified by its property of rendering lime water (or baryta water) turbid.

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

On prolonged passage of CO2 the milkiness disappears.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$
 (soluble)  $\xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2$ 

Magnesium sulphate test (for soluble carbonates) :

 $CO_{3^{2-}}(aq) + MgSO_{4}(aq) \longrightarrow MgCO_{3} \downarrow (white) + SO_{4^{2-}}(aq)$ 

 $CO_3^{2-} + Ag^+ \longrightarrow Ag_2CO_3 \downarrow$ 

White precipitate is soluble in  $HNO_3$  and ammonia. The precipitate becomes yellow or brown upon addition of excess reagent owing to the formation of silver oxide ; the same happens if the mixture is boiled.

 $Ag_2CO_3 \longrightarrow Ag_2O \downarrow + CO_2 \uparrow$ 

- Phenolphthalein is turned pink by soluble carbonates and colourless by soluble hydrogen carbonates.
- Mercury(II) chloride does not form precipitate with hydrogen carbonate ions, while in a solution of normal carbonates a reddish-brown precipitate of basic mercury(II) carbonate (3HgO. HgCO<sub>3</sub>=Hg<sub>4</sub>O<sub>3</sub>CO<sub>3</sub>) is formed.

$$CO_3^{2-}$$
 + 4 Hg<sup>2+</sup> + 3 H<sub>2</sub>O  $\longrightarrow$  Hg<sub>4</sub>O<sub>3</sub>.CO<sub>3</sub>  $\downarrow$  + 6H<sup>+</sup>

**Note:** Lime water milky test is also shown by SO<sub>2</sub> but CO<sub>2</sub> does not turn the filter paper soaked in acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> green.

- Soluble bicarbonates give white precipitate with MgSO<sub>4</sub> (aq) / MgCl<sub>2</sub>(aq) only on heating. Mg<sup>2+</sup> + 2HCO<sub>3</sub><sup>-</sup>  $\longrightarrow$  Mg(HCO<sub>3</sub>)<sub>2</sub>  $\xrightarrow{\Lambda}$  MgCO<sub>3</sub>  $\downarrow$  + H<sub>2</sub>O + CO<sub>2</sub>

Carbonates : Except carbonates of Na, K, Rb, Cs ; the Li<sub>2</sub>CO<sub>3</sub> and all alkaline earth metals decompose as given below :

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 $Li_2CO_3 \longrightarrow Li_2O + CO_2$ ; MgCO<sub>3</sub>  $\longrightarrow$  MgO + CO<sub>2</sub>; Ag<sub>2</sub>CO<sub>3</sub>  $\longrightarrow$  2Ag + CO<sub>2</sub>  $CaCO_3 \xrightarrow{\Lambda} CaO + CO_2$ 

2. SULPHITE ION (SO $_3^{2-}$ ) :

**Dilute H<sub>2</sub>SO**<sub>4</sub> test : Decomposition of salt is more rapidly on warming, with the evolution of sulphur dioxide.

 $CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + SO_2 \uparrow$ 

SO<sub>2</sub> has suffocating odour of burning sulphur.

- Acidified potassium dichromate test : The filter paper dipped in acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> turns green.
  - $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+}$  (green) +  $3SO_4^{2-} + H_2O_2$ .
- Barium chloride/Strontium chloride solution : White precipitate of barium (or strontium) sulphite is obtained.

 $SO_3^{2-}$  +  $Ba^{2+}/Sr^{2+} \longrightarrow BaSO_3/SrSO_3 \downarrow$  (white).

White precipitate dissolves in dilute HCI, when sulphur dioxide is evolved. CO-

$$BaSO_3 \downarrow + 2H^+ \longrightarrow Ba^{2+} + SO_2 \uparrow + H_2O.$$

White precipitate (BaSO<sub>3</sub>) on standing is slowly oxidised to sulphate which is insoluble in dilute mineral acids. This change is rapidly effected by warming with bromine water, a little concentrated nitric acid or with hydrogen peroxide.

 $2 \operatorname{BaSO}_3 \downarrow + \operatorname{O}_2 \longrightarrow 2 \operatorname{BaSO}_4 \downarrow$ 

 $BaSO_3 \downarrow + Br_2 + H_2O \longrightarrow 2 BaSO_4 \downarrow + 2 HBr$ 

Hence, reddish brown colour of bromine water is decolourised.

 $3BaSO_3 \downarrow + 2 HNO_3 \longrightarrow 3 BaSO_4 \downarrow + 2NO \uparrow + H_2O$ R

$$aSO_3 \downarrow + H_2O_2 \longrightarrow BaSO_4 \downarrow + H_2O$$

æ These reactions are not given by carbonates (distinction from carbonates).

Zinc and sulphuric acid test : Hydrogen sulphide gas is evolved. SO

$$D_3^{2-} + 3Zn^{2+} + 8H^+ \longrightarrow H_2S \uparrow + 3Zn^{2+} + 3H_2O$$

Lime water test : A white turbidity is formed. The precipitate dissolves on prolonged passage of the gas, due to the formation of hydrogen sulphite ions.

 $Ca(OH)_2 + SO_2 \longrightarrow CaSO_3(milky) + H_2O$ 

 $CaSO_3 \downarrow + SO_2 + H_2O \longrightarrow Ca(HSO_3)_2$  (soluble)

æ A turbidity is also produced by carbonates; sulphur dioxide must therefore be first removed when testing for the latter. This may be affected by adding potassium dichromate solution to the test-tube before acidifying. The dichromate oxidizes and destroys the sulphur dioxide without affecting the carbon dioxide.

Lead acetate or lead nitrate solution : White precipitate of PbSO<sub>3</sub> is obtained.

 $SO_3^{2-} + Pb^{2+} \longrightarrow PbSO_3 \downarrow (white)$ 

White precipitate gets soluble in dil. HNO<sub>3</sub> on boiling. The precipitate is oxidized by atmospheric oxygen and PbSO<sub>4</sub> is formed.

 $2PbSO_3 \downarrow + O_2 \longrightarrow 2PbSO_4 \downarrow$ 

3. SULPHIDE ION (S<sup>2-</sup>) :

**Dilute H\_2SO\_4 test :** Pungent smelling gas like that of rotten egg is obtained.

- $S^{2-} + 2H^+ \longrightarrow H_2S^{\uparrow}$
- Lead acetate test : Filter paper moistened with lead acetate solution turns black.
- $(CH_3COO)_2Pb + H_2S \longrightarrow PbS \downarrow (black) + 2CH_3COOH.$
- Sodium nitroprusside test : Purple coloration is obtained.

 $S^{2-} + [Fe(CN)_5(NO)]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$  (purple).

It is a ligand change reaction not a redox where NO<sup>+</sup> changes to (NOS)<sup>-1</sup>.

No reaction occurs with solution of H<sub>2</sub>S or free gas. If however, filter paper moistened with a solution of the reagent is made alkaline with NaOH or NH<sub>3</sub> solution, a purple colouration is produced with free H<sub>2</sub>S also.

#### **Note:** $H_2S$ does not provide sufficient concentration of $S^{2-}$ ions so that it does not give sodium nitroprusside test. Solubility is low 0.1 M and $K_1$ is just $10^{-7}$ .

- Cadmium carbonate suspension/ Cadmium acetate solution : Yellow precipitate is formed. Na<sub>2</sub>S + CdCO<sub>3</sub>- $\rightarrow$  CdS  $\downarrow$  + Na<sub>2</sub>CO<sub>3</sub>
- æ Filter paper moistened with cadmium acetate when brought in contact with evolving gas it turns yellow.  $S^{2-} + 2H^+ \longrightarrow H_2S$  ;  $H_2S + Cd^{2+} \longrightarrow CdS \downarrow (yellow) + 2H^+.$

• Silver nitrate solution : Black precipitate is formed which is insoluble in cold, but soluble in hot, dilute nitric acid.

 $Ag^+ + S^{2-} \longrightarrow Ag_2S \downarrow (black)$ 

• **Methylene blue test :** NN–Dimethyl–p–phenylenediamine is converted by iron(III) chloride and hydrogen sulphide in strongly acid solution into the water–soluble dyestuff, methylene blue. This is a sensitive test for soluble sulphides and hydrogen sulphide.

## 4. NITRITE ION ( $NO_2^-$ ) :

Dilute H<sub>2</sub>SO<sub>4</sub> test : Solid nitrite in cold produces a transient pale blue liquid (due to the presence of free nitrous acid, HNO<sub>2</sub> or its anhydride, N<sub>2</sub>O<sub>3</sub>) first and then evolution of pungent smelling reddish brown vapours of NO<sub>2</sub> takes place.

 $\begin{array}{ll} \mathsf{NO}_2^- + \mathsf{H}^+ \longrightarrow \mathsf{HNO}_2 \ ; & (2\mathsf{HNO}_2 \longrightarrow \mathsf{H}_2\mathsf{O} + \mathsf{N}_2\mathsf{O}_3); \\ \mathsf{3}\mathsf{HNO}_2 \longrightarrow \mathsf{HNO}_3 + 2\mathsf{NO} + \mathsf{H}_2\mathsf{O}; & 2\mathsf{NO} + \mathsf{O}_2 \longrightarrow \mathbf{2}\mathsf{NO}_2^{\uparrow} \end{array}$ 

• **Starch iodide test :** The addition of a nitrite solution to a solution of potassium iodide, followed by acidification with acetic acid or with dilute sulphuric acid, results in the liberation of iodine, which may be identified by the blue colour produced with starch paste. A similar result is obtained by dipping potassium iodide–starch paper moistened with a little dilute acid into the solution.

 $2NO_2^- + 3I^- + 4CH_3COOH \longrightarrow I_3^- + 2NO \uparrow + 4CH_3COO^- + 2H_2O$ Starch +  $I_3^- \longrightarrow$  Blue (starch iodine adsorption complex)

Ferrous sulphate test (Brown ring test) : When the nitrite solution is added carefully to a concentrated solution of iron(II) sulphate acidified with dilute acetic acid or dilute sulphuric acid, a brown ring appears due to the formation of [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO₄ at the junction of the two liquids. If the addition has not been made slowly and caustiously, a brown colouration results.

 $\begin{array}{l} \mathsf{NO}_2^- + \mathsf{CH}_3\mathsf{COOH} \longrightarrow \mathsf{HNO}_2 + \mathsf{CH}_3\mathsf{COO}^- \\ \mathsf{3HNO}_2 \longrightarrow \mathsf{H}_2\mathsf{O} + \mathsf{HNO}_3 + \mathsf{2NO} \uparrow \end{array}$ 

#### $Fe^{2+} + SO_{4^{2-}} + NO \uparrow \longrightarrow [Fe(H_2O)_5 NO]SO_4 (brown ring complex)$

 Thiourea test : When a dilute acetic acid solution of a nitrite is treated with a little solid thiourea, nitrogen is evolved and thiocyanic acid is produced. The latter may be identified by the red colour produced with dilute HCI and FeCl<sub>3</sub> solution.

NaNO<sub>2</sub> + CH<sub>3</sub>COOH  $\longrightarrow$  HNO<sub>2</sub> + CH<sub>3</sub>COONa HNO<sub>2</sub> + H<sub>2</sub>NCSNH<sub>2</sub>(s) (thiourea)  $\longrightarrow$  N<sub>2</sub> + HSCN + 2H<sub>2</sub>O

FeCl<sub>3</sub> + 3HSCN → Fe(SCN)<sub>3</sub> (blood red colouration) + 3HCl

• Acidified potassium permanganate solution : Pink colour of KMnO₄ is decolourised by a solution of a nitrite, but no gas is evolved.

 $5 \text{ NO}_2^- + 2 \text{ MnO}_4^- + 6 \text{ H}^+ \longrightarrow 5 \text{ NO}_3^- + 2 \text{ Mn}^{2+} + 3 \text{ H}_2\text{O}$ 

Silver nitrate solution : White crystalline precipitate of silver nitrite from concentrated solutions.  $NO_2^- + Ag^+ \longrightarrow AgNO_2 \downarrow$  (white)

#### 5. ACETATE ION (CH<sub>3</sub>COO<sup>-</sup>)

- With dilute H<sub>2</sub>SO<sub>4</sub> a vinegar like smell is obtained.
  - $(CH_3COO)_2Ca + H_2SO_4 \longrightarrow 2CH_3COOH + CaSO_4$
- Neutral ferric chloride test : A deep red/ blood red colouration (no precipitate) indicates the presence of acetate.

 $6CH_{3}COO^{-} + 3Fe^{3+} + 2H_{2}O \longrightarrow [Fe_{3}(OH)_{2}(CH_{3}COO)_{6}]^{+} + 2H^{+}$ 

When solution is diluted with water and boiled, brownish red precipitate of basic iron (III) acetate is obtained.

 $[Fe_{3}(OH)_{2}(CH_{3}COO)_{6}]^{+} + 4H_{2}O \xrightarrow{Boil} 3Fe(OH)_{2}CH_{3}COO \downarrow + 3CH_{3}COOH + H^{+}$ 

• Silver nitrate solution test : A white crystalline precipitate is produced in concentrated solution in the cold.

 $CH_3COO^- + Ag^+ \longrightarrow CH_3COOAg \downarrow (white)$ 

Precipitate is more soluble in boiling water and readily soluble in dilute ammonia solution.

Sectio	on (D) : Conc. H₂SO₄ group
(b) CO	NC. H <sub>2</sub> SO <sub>4</sub> GROUP :
	1. CHLORIDE ION (CI <sup>-</sup> ):
•	Concentrated H <sub>2</sub> SO <sub>4</sub> test : Colourless pungent smelling gas (HCI) is evolved which gives fumes of
	NH <sub>4</sub> Cl when a glass rod dipped in aq. ammonia is brought in contact with evolving gas.
	$CF + H_2SO_4 \longrightarrow HCI + HSO_4^-$
•	$NH_4OH + HCI \longrightarrow NH_4CI \uparrow (white fumes) + H_2O.$
(P	$2NaCl + MnO_2 + 2H_2SO_4 (conc.) \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$
•	Silver nitrate test :
	CI <sup>–</sup> + Ag <sup>+</sup> $\longrightarrow$ AgCI ↓ (white)
	With sodium arsenite it is converted into yellow precipitate (distinction from AgBr and AgI) but
	insoluble in dilute nitric acid.
	3AgCl↓ + AsO <sub>3</sub> <sup>3-</sup> → Ag <sub>3</sub> AsO <sub>3</sub> ↓ (yellow) + 3Cl <sup>-</sup> .
(P	White precipitate is soluble in aqueous ammonia and precipitate reappears with HNO <sub>3</sub> .
	$AgCI + 2NH_4OH [Ag(NH_3)_2]CI (Soluble) + 2H_2O$
	$[Ag(NH_3)_2]CI + 2H^+ \longrightarrow AgCI \downarrow + 2NH_4^+.$
•	Chromyl chloride test :
	$4Cl^{-}(s) + Cr_2O_7^{2-}(s) + 6H^{+}(conc.) \longrightarrow 2CrO_2Cl_2$ (deep red vapours) + $3H_2O$
	When deep red vapours are passed into sodium hydroxide solution, a yellow solution of sodium
	chromate is formed, which when treated with lead acetate gives <b>yellow precipitate of lead chromate</b> .
	$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$
	$CrO_4^{2-} + Pb^{+2} \longrightarrow PbCrO_4 \downarrow (yellow)$
Note :	
1.	Heavy metal chlorides such as Hg <sub>2</sub> Cl <sub>2</sub> , HgCl <sub>2</sub> , SnCl <sub>2</sub> , AgCl, PbCl <sub>2</sub> and SbCl <sub>3</sub> , CuCl do not respond to
	this test due to their high covalent character as a result of which sufficient free CI <sup>-</sup> are not available.
2	This test is given generally by lonic chlorides.
Ζ.	
2	$CIU_2U_2 + 2\Pi_2U \longrightarrow \Pi_2U_1U_4 + 2\Pi_U$
5.	and $I_{\rm c}$ (violet vapours) respectively. Both Br <sub>2</sub> and I <sub>2</sub> produce colourless solution with NaOH solution
4	$NO_2^ NO_3^-$ and $CIO_2^-$ radicals also interfere with this test and so should be absent
	2. BROMIDE ION (Br <sup>-</sup> ) :
•	<b>Concentrated H<sub>2</sub>SO<sub>4</sub> test :</b> First a reddish-brown solution is formed, then reddish-brown bromine
	vapour accompanies the hydrogen bromide (fuming in moist air) is evolved.
	$2\text{NaBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HBr}$
	$2HBr + H_2SO_4 \longrightarrow Br_2 \uparrow + 2H_2O + SO_2$
(F	$2KBr + MnO_2 + 2H_2SO_4 \longrightarrow Br_2   + K_2SO_4 + MnSO_4 + 2H_2O_4$
•	Silver nitrate test : Pale yellow precipitate is formed
	$NaBr + AgNO_3 \longrightarrow AgBr \downarrow + NaNO_3$
Ē	Yellow precipitate is partially soluble in dilute aqueous ammonia but readily dissolves in concentrated
	ammonia solution.
	$AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2] Br + H_2O$
•	Lead acetate test · Bromides on treatment with lead acetate solution gives a white crystalline
•	precipitate of lead bromide, which is soluble in boiling water giving colourless solution.
	$2Br^- + Pb^{+2} \longrightarrow PbBr_2 \downarrow$ (white)
•	Chlorine water test (organic layer test) : When to a sodium carbonate extract of metal bromide
	containing CCl <sub>4</sub> , CHCl <sub>3</sub> or CS <sub>2</sub> , chlorine water is added and the content is shaken and then allow to
	settle down reddish brown colour is obtained in organic layer.
	$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2 \uparrow$ .
	$Br_2 + CHCl_3 / CCl_4 \longrightarrow Br_2$ dissolve to give reddish brown colour in organic layer.
	With excess of chlorine water, the bromine is converted into yellow bromine monochloride and a pale
	yellow solution results.
	$Br_2 \uparrow + Cl_2 \uparrow \longrightarrow 2BrCl$
•	Starch paper test : When starch paper is brought in contact with evolving bromine gas orange red
	spots are produced.
	$Br_2$ + starch $\longrightarrow$ starch bromine adsorption complex (orange red)

Potassium dichromate and concentrated H<sub>2</sub>SO<sub>4</sub>: When a mixture of solid bromide, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> is heated and evolved vapours are passed through water, a orange red solution is obtained.

 $6KBr + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Br_2\uparrow + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O_2$ 

3. IODIDE ION  $(\Gamma)$ :

Concentrated H<sub>2</sub>SO<sub>4</sub> test : Pungent smelling violet vapours are evolved.

 $2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$ 

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

Evolution of dark violet fumes intensifies on adding a pinch of MnO<sub>2</sub>. æ

 $3I^{-} + MnO_2 + 2H_2SO_4 \longrightarrow I_3^{-} \uparrow + Mn^{2+} + 2SO_4^{2-} + 2H_2S$ 

Starch paper test : lodides are readily oxidised in acid solution to free iodine; the free iodine may than be identified by deep blue colouration produced with starch solution.

 $3I^{-} + 2NO_2^{-} + 4H^{+} \longrightarrow I_3^{-} + 2NO^{+} + 2H_2O_{-}$ 

- Silver nitrate test : Bright yellow precipitate is formed.
  - $I^- + Ag^+ \longrightarrow AgI \downarrow$  (bright yellow)
- (A) Bright yellow precipitate is **insoluble** in dilute aqueous ammonia but is partially soluble in concentrated ammonia solution.
- Chlorine water test (organic layer test) : When chlorine water is added to a solution of iodide, free iodine is liberated which colours the solution brown and on shaking with CS2, CHCl3 or CCl4, it dissolves in organic layer forming a violet solution, which settles below the aqueous layer.

- $2Nal + Cl_2 \longrightarrow 2NaCl + l_2$  $l_2 + CHCl_3 \longrightarrow l_2$  dissolves to give violet colour in organic layer.
- Lead acetate solution : A yellow precipitate is formed which is soluble in hot water forming a colourless solution and yielding golden yellow plates ('spangles') on cooling.
  - $2l^- + Pb^{+2} \longrightarrow Pbl_2 \downarrow (vellow)$
- Potassium dichromate and concentrated sulphuric acid: Violet vapours are liberated, and no chromate is present in distillate. 61-

+ 
$$Cr_2O_7^2$$
 +  $2H_2SO_4 \longrightarrow 3I_2 + Cr^{3+} + 7SO_4^{2-} + 7H_2O_4^{2-}$ 

æ Action of heat : Most of halides are stable but few decompose as

 $2\text{FeCl}_3 \longrightarrow 2\text{FeCl}_2 + \text{Cl}_2$ ;  $MgCl_{2.6}H_{2}O \longrightarrow MgO + 2HCI + 5H_{2}O$  $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg;$  $NH_4CI \longrightarrow NH_3 + HCI$ 

 $2Cul_2 \longrightarrow Cul + l_2$  (without heating)

Solvent	NH <sub>3</sub>	HNO <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	NaCN/KCN
Precipitate				
AgCl	Completely soluble	Insoluble	Soluble	Soluble
AgBr	Partially soluble	Insoluble	Soluble	Soluble
Agl	Insoluble	Insoluble	Soluble	Soluble

**Note :** In NH<sub>3</sub>, Aq<sup>+</sup> forms soluble complex of [Aq(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> In Na<sub>3</sub>S<sub>2</sub>O<sub>3</sub>, Ag<sup>+</sup> forms soluble complex of [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>3-</sup> In NaCN, Ag<sup>+</sup> forms soluble complex of [Ag(CN)<sub>2</sub>]<sup>-</sup>

#### 4. NITRATE ION $(NO_3^-)$

Ē

Concentrated H<sub>2</sub>SO<sub>4</sub> test : Pungent smelling reddish brown vapours are evolved.

$$4NO_3^- + 2H_2SO_4 \longrightarrow 4NO_2^+ + O_2^- + 2SO_4^{2-} + 2H_2O_2^-$$

Addition of bright copper turnings or paper pellets intensifies the evolution of reddish brown gas.  $2NO_3^- + 4H_2SO_4 + 3Cu \longrightarrow 3Cu^{2+} + 2NO \uparrow + 4SO_{4^2-} + 4H_2O; 2NO \uparrow + O_2 \longrightarrow 2NO_2 \uparrow$ 

4 C (paper pellet) + 
$$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + 4CO_2$$
.

Brown ring test : When a freshly prepared saturated solution of iron (II) sulphate is added to nitrate solution and then concentrated  $H_2SO_4$  is added slowly from the side of the test tube, a **brown ring** is obtained at the junction of two layers.

Qualitative Analysis (Anion) Conc. H<sub>2</sub>SO<sub>4</sub> Brown ring Figure : Brown ring test  $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$  $6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O_3$  $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO \downarrow + 4SO_4^{2-} + 4H_2O.$ or  $Fe^{2+} + NO \uparrow + 5H_2O \longrightarrow [Fe^{I}(H_2O)_5 NO^+]^{2+}$  (brown ring). Some important points related to brown ring test are : Note : Shaking and warming are not allowed for this test because on shaking and warming the mixture, NO 1. escapes and a yellow solution of iron(III) ions is obtained. 2. Bromides and iodides interfere in brown ring test as liberated halogens obscure the brown ring. Nitrites also interfere the brown ring test and can be removed by adding a little sulphamic acid, or urea.  $H_2NHSO_3 + NO_2^- \longrightarrow N_2 \uparrow + SO_4^{2-} + H^+ + H_2O_3$  $NO_2^- + H^+ \xrightarrow{HCI} HNO_2$  $CO(NH_2)_2 + 2HNO_2 \longrightarrow 2N_2 \uparrow + CO_2 \uparrow + 3H_2O$ 3. FeSO<sub>4</sub> solution must be freshly prepared because Fe<sup>2+</sup> ion is very reactive towards aerial oxidation and aets converted to Fe<sup>3+</sup>, which does not give this test. Diphenyl amine test : Blue ring is formed at the junction of two liquids (reagent and nitrate salt solutions).  $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$  $2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$  $2C_6H_5NHC_6H_5 + [O] \longrightarrow (C_6H_5)_2 N - N (C_6H_5)_2 (blue ring) + H_2O.$ P This test is also given by various oxidising agents like CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, ClO<sub>3</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, IO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> etc. To distinguish Br<sub>2</sub> with NO<sub>2</sub> (both are reddish brown gases) (a)  $Br_2$  + starch-iodide paper  $\rightarrow$  Blue black colour spots do not develop immediately as  $Br_2$  is a weaker oxidising agent whereas NO<sub>2</sub> being strong oxidising agent develops the blue black colour immediately. (b) Bromine develops orange-red colour spots on starch paper. Section (E): Precipitation Reactions (B) GROUP 'B' RADICALS : Group of anions which do not give any gas with dilute as well as concentrated H<sub>2</sub>SO<sub>4</sub> in cold but give precipitate with certain reagents : These acid radicals are identified in inorganic salts by their individual tests as given below 1. SULPHATE ION (SO<sub>4</sub><sup>2–</sup>) : Barium chloride test : W.E. or S.E. + Barium chloride (aq)  $\longrightarrow$  White precipitate Na<sub>2</sub>SO<sub>4</sub> + BaCl<sub>2</sub>  $\longrightarrow$  **BaSO<sub>4</sub>**  $\downarrow$  (white) + 2NaCl. æ White precipitate is insoluble in warm dil. HNO<sub>3</sub> as well as HCl but moderately soluble in boiling concentrated hydrochloric acid and conc. H<sub>2</sub>SO<sub>4</sub>.  $PbSO_4 + H_2SO_4 \longrightarrow PbHSO_4(soluble)$ Lead acetate test : W.E. or S.E. + Lead acetate  $\longrightarrow$  white precipitate Na<sub>2</sub>SO<sub>4</sub> + (CH<sub>3</sub>COO)<sub>2</sub>Pb  $\longrightarrow$  PbSO<sub>4</sub>  $\downarrow$  (White) + 2CH<sub>3</sub>COONa Ē White precipitate soluble in excess of hot ammonium acetate and ammonium tartrate.  $PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2 [Pb(CH_3COO)_4]$  soluble. +  $(NH_4)_2SO_4$  $PbSO_4 + (NH_4)_2 C_4 H_4 O_6 \longrightarrow (NH_4)_2 SO_4 + (NH_4)_2 [Pb(C_4 H_4 O_6)_2] soluble$ 

•	Match stick test :
	(a) W.E. or S.E. + Barium chloride $\longrightarrow$ white precipitate
	$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + BaSO_4 \downarrow (white)$
	(b) White precipitate + $Na_2 CO_3(s)$ mix and apply the paste on the end of the carbonized match stick or
	a wooden spinnter. Put it in the reducing name. $BaSO_4(s) + Na_2O_2(s) \longrightarrow Na_2SO_4 + BaCO_2 \sqrt{(white)}$
	Na <sub>2</sub> SO <sub>4</sub> + 4C $\longrightarrow$ Na <sub>2</sub> S + 4CO
	(c) Now dip the match stick in sodium nitroprusside solution, purple colour near the fused mass is developed.
	Na <sub>2</sub> S + Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO] $\longrightarrow$ Na <sub>4</sub> [Fe(CN) <sub>5</sub> NOS] (purple)
•	Silver nitrate test : White precipitate is obtained. $SO_4^{2-} + 2Ag^+ \longrightarrow Ag_2SO_4 \downarrow$ (white ppt.)
•	2. PHOSPHATE ION (PO4 <sup>3-</sup> ) : Ammonium molybdate test :
Na <sub>2</sub> HF	$PO_4(aq) + 12(NH_4)_2MOO_4 + 23HNO_3 \rightarrow (NH_4)_3[P(MO_3O_{10})_4] \downarrow (canary yellow) + 2NaNO_3 + 21NH_4NO_3 + 12H_2O_3)$
Ĩ	Some times ammonium phosphomolybdate is also represented by the formula (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> .12MoO <sub>3</sub>
•	<b>Magnesium nitrate or magnesia mixture test :</b> W.E. or S.E + Magnesium nitrate reagent (3-4 mL) and allows to stand for 4-5 minutes, white crystalline precipitate is formed.
	Na <sub>2</sub> HPO <sub>4</sub> (aq) + Mg(NO <sub>3</sub> ) <sub>2</sub> (aq) + NH <sub>4</sub> OH(aq) $\longrightarrow$ Mg(NH <sub>4</sub> ) PO <sub>4</sub> $\downarrow$ (white) + 2NaNO <sub>3</sub> + H <sub>2</sub> O Magnesia mixture is a solution containing MgCl <sub>2</sub> , NH <sub>4</sub> Cl and a little aqueous NH <sub>3</sub> .
(F	$PO_4^{3-}$ also gives $BaCl_2$ test due to the formation of white precipitate of $Ba_3 (PO_4)_2$ . So phosphate test should be carried out first and then conclude if $PO_4^{3-}$ is present or absent before proceeding with the test for $SO_4^{2-}$ .
•	Silver nitrate solution : Yellow precipitate is formed which is soluble in dilute ammonia and in dilute nitric acid.
	$PO_4^{3-} + 3Ag^+ \longrightarrow Ag_3PO_4 \downarrow (yellow)$
	$Ag_{3}PO_{4} \downarrow + 6NH_{3} \longrightarrow 3[Ag(NH_{3})_{2}]^{+} + PO_{4}^{3-};$
	$Ag_{3}PO_{4} \downarrow + 2H^{+} \longrightarrow H_{2}PO_{4}^{-} + 3Ag^{+}$
•	Iron (III) chloride solution : Yellowish-white precipitate of FePO <sub>4</sub> is obtained HPO <sub>4</sub> <sup>2-</sup> + Fe <sup>3+</sup> $\longrightarrow$ FePO <sub>4</sub> $\downarrow$
	3. BORATE ION (BO <sub>3</sub> <sup>3-</sup> ) : Salt (0.2 g) + conc. H <sub>2</sub> SO <sub>4</sub> (1 mL) + Ethyl alcohol (4-5 mL) mix in a test tube and then heat. Ignite the evolved vapours with the help of Bunsen flame, green edged flame is obtained. 2Na <sub>3</sub> BO <sub>3</sub> + 3H <sub>2</sub> SO <sub>4</sub> → 3Na <sub>2</sub> SO <sub>4</sub> + 2H <sub>3</sub> BO <sub>3</sub>
	$3C_2H_5OH + H_3BO_3 \longrightarrow (C_2H_5)_3BO_3 \text{ or } (C_2H_5O)_3B + 3H_2O$
Note :	
1. 2.	Use of methyl alcohol is preferred due to high volatility of the product formed is B(OMe) <sub>3</sub> Copper and barium salts also interfere with this test because they give similar green flame and so should be absent.
	MISCELLANEOUS SOLVED PROBLEMS (MSPs)
1.	Pink colour of acidified KMnO <sub>4</sub> is decolourised but there is no evolution of any gas. This may happen

ny g ay with the compound containing the following acid radical. (C) S<sup>2-</sup>

(A) SO<sub>3</sub><sup>2-</sup> (B)  $NO_{2}^{-}$  (D) All of these

Ans. (D)

Sol.

- (A)  $5SO_{3^{2-}} + 2MnO_{4^{-}} + 6H^{+} \longrightarrow 2Mn^{2+} + 5SO_{4^{2-}} + 3H_{2}O$ (B)  $2MnO_{4^{-}} + 5NO_{2^{-}} + 6H^{+} \longrightarrow 2Mn^{2+} + 5NO_{3^{-}} + 3H_{2}O$
- (C)  $2MnO_4^- + H_2S + 6H^+ \longrightarrow 2Mn^{2+} + 5S \downarrow + 8H_2O$

Qualita	tative Analysis (Anion)				
2. Ans. Sol.	Which of the following gives a precipitate with Pb(NO (A) Sodium chloride (B) (C) Sodium nitrate (D) (A) (A) $Pb^{2+} + 2Cl^- \longrightarrow PbCl_2 \downarrow$ (white) ; $Ba^{2+} + 2Cl^-$ (B) $(CH_3COO)_2$ Pb and $(CH_3COO)_2Ba$ both are wate (C) Nitrates are mostly soluble in water (D) $3Pb^{2+} + 2HPO_4^{2-} \longrightarrow Pb_3(PO_4)_2 \downarrow$ (white) + $2H^+$	nich of the following gives a precipitate with Pb(NO <sub>3</sub> ) <sub>2</sub> but not with Ba(NO <sub>3</sub> ) <sub>2</sub> ? ) Sodium chloride (B) Sodium acetate ) Sodium nitrate (D) Disodium hydrogen phosphate ) ) Pb <sup>2+</sup> + 2Cl <sup>-</sup> → PbCl <sub>2</sub> ↓ (white) ; Ba <sup>2+</sup> + 2Cl <sup>-</sup> → BaCl <sub>2</sub> (water soluble) ) (CH <sub>3</sub> COO) <sub>2</sub> Pb and (CH <sub>3</sub> COO) <sub>2</sub> Ba both are water soluble salts. ) Nitrates are mostly soluble in water ) 3Pb <sup>2+</sup> + 2HPO4 <sup>2-</sup> → Pb <sub>3</sub> (PO4) <sub>2</sub> ↓ (white) + 2H <sup>+</sup> ; Ba <sup>2+</sup> + HPO4 <sup>2-</sup> → BaHPO4 ↓ (white)			
3. Ans. Sol. 4.	When H2S gas is passed through an ammonical sat The X can be :(A) a cobalt salt(B) a lead salt(C)(C) $Zn^{2+} + H_2S \longrightarrow ZnS \downarrow$ (white) + 2H+Which anion does not liberate any gas with dilute as (A) NO2 <sup>-</sup> (B) NO3^-(C)	alt solution X, a slight ) a zinc salt () s well as conc. $H_2SO_4$ . ) $SO_3^{2-}$ ()	ly white precipitate is formed. (D) a silver salt (D) SO4 <sup>2-</sup>		
Ans. 5. Ans. Sol.	(D) A salt having $BO_3^{3-}$ on burning with alcohol and con- (A) green (B) yellow (C) (A) $3Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$ $3C_2H_5OH + H_3BO_3 \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$ (green)	c. H₂SO₄ gives, which ) red (	colour edge flame. (D) white		
6. Ans. Sol.	When solution of KCI, KF and KBr are treated with (A) $CI_2$ and $Br_2$ are evolved(B) (C) $CI_2$ , $F_2$ and $Br_2$ are evolved(D)(D)I2is weak oxidising agent.It does not oxidise the F <sup>-</sup> , CI <sup>-</sup> , Br <sup>-</sup> .	$I_2$ ? Cl <sub>2</sub> is evolved None of these			
7. Ans.	A mixture when rubbed with organic acid smells like (A) Sulphate (B) Nitrate (C) (D)	vinegar. It contains : ) Nitrite	(D) Acetate		
8. Ans.	Nitrate & Nitrite both give brown ring test, can be dis(A) HOSO2NH2 (Sulphonic acid)(B)(C) FeSO4(D)(A)	stinguish by – NH₂HgO.HgI (Million I ) None	base)		
9. Ans. Sol.	Which reagent is used to remove $SO_4^{2-}$ or $CI^-$ from v (A) NaOH (B) Pb(NO <sub>3</sub> ) <sub>2</sub> (C) <b>(B)</b> Pb <sup>2+</sup> + SO <sub>4</sub> <sup>2+</sup> $\longrightarrow$ PbSO <sub>4</sub> $\downarrow$ (ppt) Pb <sup>2+</sup> + CI <sup>-</sup> $\longrightarrow$ PbCI <sub>2</sub> $\downarrow$ (ppt) Others does not from precipitate with both anions.	water? ) BaSO₄	(D) KOH		
10.* Ans. Sol.	Which of the following statements is/are correct for c (A) Formation of chromyl chloride vapour (B) (C) Formation of lead chromate (D) (A,C,D) $Cl^- + K_2Cr_2O_7 + H^+ \longrightarrow CrO_2Cl_2 (red-brown vapour) + CrO_2Cl_2 (red-brown vapour) + Cromyl (chromyl chloride)$	chromyl chloride test? Liberation of chlorine Formation of reddished $\xrightarrow{\text{NaOH}} \text{Na}_2\text{CrO}_4$ Yellow (sodium chromate)	gas -brown vapour $\xrightarrow{(CH_3COO)_2Pb} PbCrO_4$ Lead chromate (Yellow)		
11.* Ans.	<ul> <li>Which of the following statements are incorrect?</li> <li>(A) In thiourea test for nitrite, a green coloured solution is obtained.</li> <li>(B) It is not necessary to carried out the chromyl chloride test in a dry test tube.</li> <li>(C) Suspension of CdCO<sub>3</sub> gives black precipitate with Na<sub>2</sub>S solution.</li> <li>(D) In PbNO<sub>3</sub>, the brown ring test can be performed with its water extract.</li> <li>(A,B,C,D)</li> </ul>				

- 12.\*Conc. H2SO4 will not give any gas with :<br/>(A) ZnSO4(B) Ba3(PO4)2

(C) Mg<sub>3</sub>(BO<sub>2</sub>)<sub>2</sub> (D) NaNO<sub>3</sub>

Ans. (A,B,C)

**Sol.** Only  $NO_3^-$  belong to conc.  $H_2SO_4$  anion group.

Ans. Both  $Br_2$  and  $I_2$  are covalent. They have preference for organic layer.

- **14.** What will happen when free bromine, iodine and chlorine separately react with a yellow dye stuff, fluorescein?
- **Ans.** With free bromine it will convert into red tetra bromo fluorescein and with iodine into the red violet coloured iodoeosin. But chlorine tends to bleach the reagent.

**<sup>13.</sup>** Why does only the organic layer assure colour and not the aqueous layer when the tests for halides are done ?