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	NH_4^+
Vinegar like smell	CH_3COO^-
Smell like that of rotten eggs	S^{2-}

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.

Table : 2

	Observation	**Inference**
1.	**Gas evolved**	
	(a) Colourless and odourless gas	
	CO_2 gas – turns lime water milky	CO_3^{2-}
	(b) Colourless gas with odour	
	(i) H_2S gas – Smells like rotten eggs, turns lead acetate paper black.	Hydrated S^{2-} or S^{2-}
	(ii) SO_2 gas – Characteristic suffocating smell of burning sulphur turns acidified potassium dichromate solution or paper green.	SO_3^{2-}
	(iii) HCl gas – Pungent smell, white fumes with ammonia, white precipitate with silver nitrate solution.	Cl^-
	(iv) Acetic acid vapours–Characteristic vinegar like smell.	CH_3COO^-
	(v) NH_3 gas– Characteristic smell, turns Nessler's solution brown.	NH_4^+
	(c) Coloured gases – Pungent smell	
	(i) NO_2 gas – Reddish brown, turns ferrous sulphate solution brownish 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 red.	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.	**Fusion**	
	The mixture fuses.	Alkali metal salts or salt containing water of crystallisation.
4.	**Swelling**	
	The mixture swells up into voluminous mass.	PO_4^{3-}, BO_3^{3-} indicated
5.	**Residue**	
	(i) Yellow when hot, white when cold.	Zn^{2+}
	(ii) Brown when hot and yellow when cold.	Pb^{2+}
	(iii) Original salt blue becomes white on heating.	Hydrated $CuSO_4$ indicated
	(iv) Coloured salt becomes brown or black on indicated.	Co^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+} heating.

Note :

- 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.
- 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.

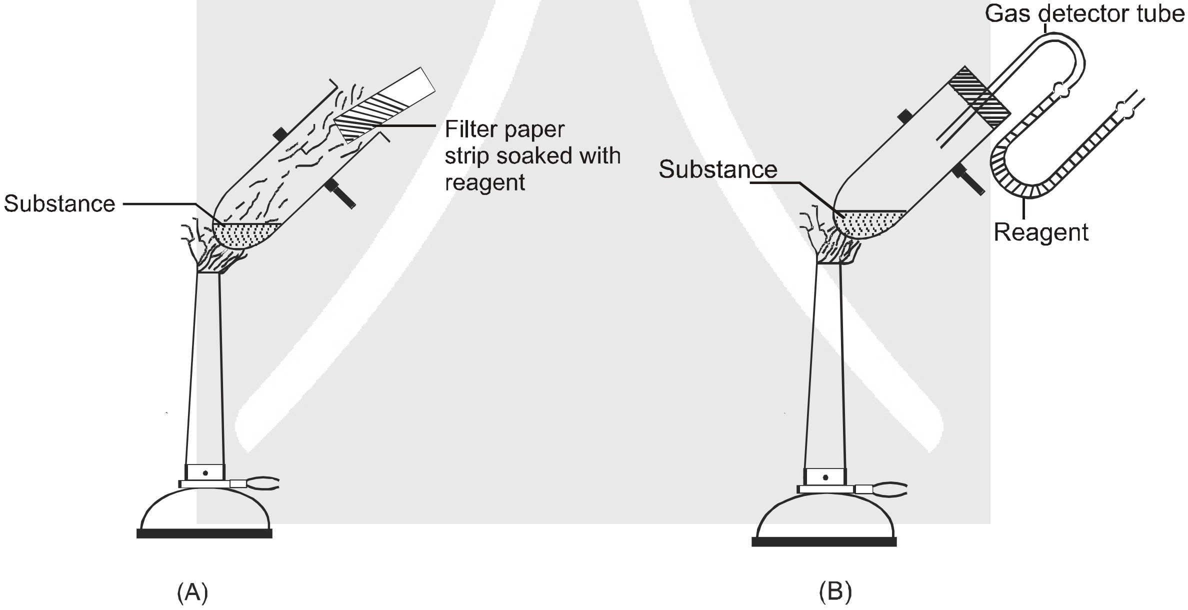


Figure : Detection of gas evolved.

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

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

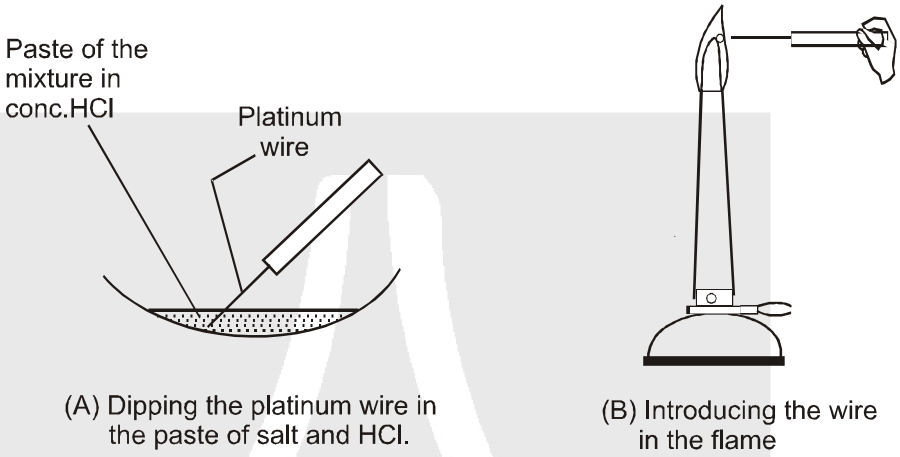


Figure : Flame test

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, Li, K, Sr, Rb, Cs, Be, Ca, Cu

Table : 4

Metal	Colour in oxidising flame		Colour in reducing flame	
	When Hot	When Cold	When Hot	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

☞ Non luminous flame is called oxidising flame. ☞ Luminous flame is called reducing flame.

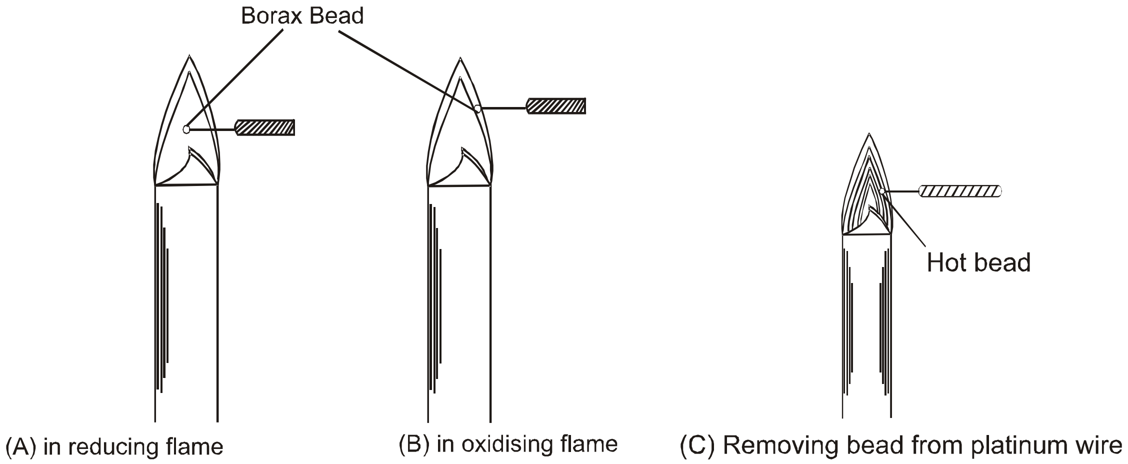


Figure : Borax bead test

☞ 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 :

(a) $ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$

$ZnCO_3 \longrightarrow ZnO$ (Yellow when hot, white when cold) $+ CO_2\uparrow$

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

$CuCO_3 \longrightarrow CuO + CO_2\uparrow$

$CuO + C \longrightarrow Cu$ (Reddish scales) $+ CO\uparrow$

Table : 5

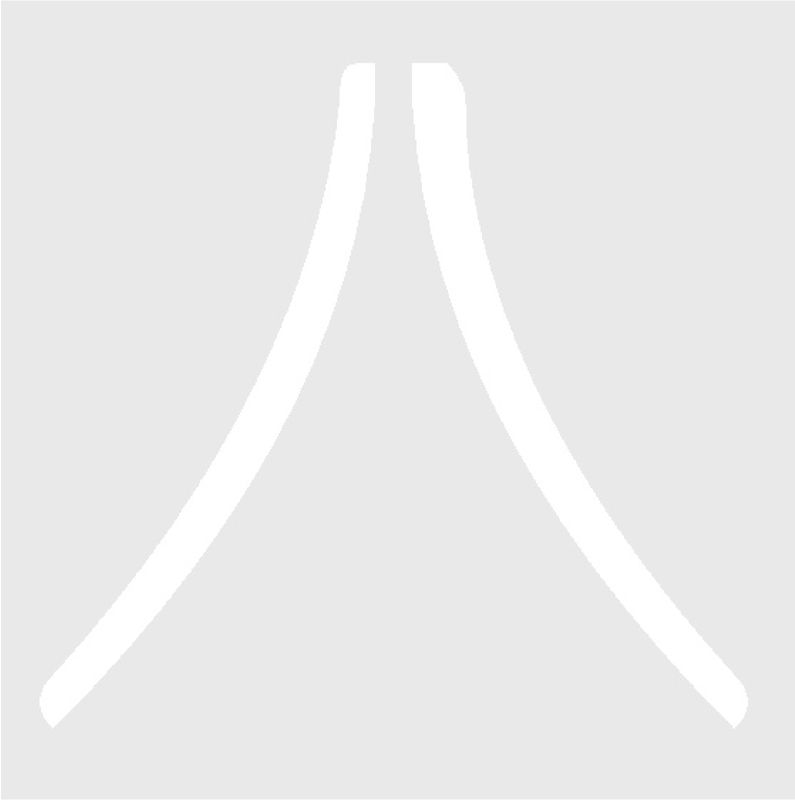
Observation		Inference
Incrustation or Residue	**Metallic bead**	
Yellow when hot, white when cold	None	Zn^{2+}
Brown when hot, yellow when cold	Grey bead which marks the paper	Pb^{2+}
No characteristic residue	Red beads or scales	Cu^{2+}
White residue which glows on heating	None	Ba^{2+},Ca^{2+}, Mg^{2+}
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 :

$ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$; $ZnCO_3 \longrightarrow ZnO + CO_2$

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



(i) $FeSO_4$ solution brownish-black and	NO_2	NO_2^-
(ii) wet starch –iodide paper blue. Colourless gas having smell of vinegar.	HAC(g)	CH_3COO^-
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_2SO_4.

Table : 9

Observation	**Inference**	
	Gas	**Radical**
Colourless gas with pungent smell which gives dense white fumes with a glass rod dipped in NH_4OH.	HCl	Cl^-
Reddish brown gas with pungent smell, intensity of reddish brown fumes increases on addition of a pinch of solid MnO_2. Also it turns starch paper orange red.	Br_2	Br^-
Evolution of violet vapours which turns starch paper blue.	I_2	I^-
Evolution of reddish brown fumes which intensifies on addition of copper turnings or bits of filter paper.	NO_2	NO_3^-
Starch iodide paper develops a blue–black spot due to the formation of a I_2–starch complex. (NO_2 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_2SO_4 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. + $BaCl_2(aq)$ White precipitate insoluble in dil. HCl and HNO_3	SO_4^{2-}
W.E or S.E + conc. HNO_3 (1–2 mL) + ammonium molybdate and boil $\rightarrow$ Canary yellow precipitate	PO_4^{3-}

☞ 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.

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

$$Cd_3\,(PO_4)_2 + 3Na_2CO_3 \longrightarrow 3CdCO_3 \downarrow + 2Na_3\,PO_4\,(aq)$$

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.

☞ 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.

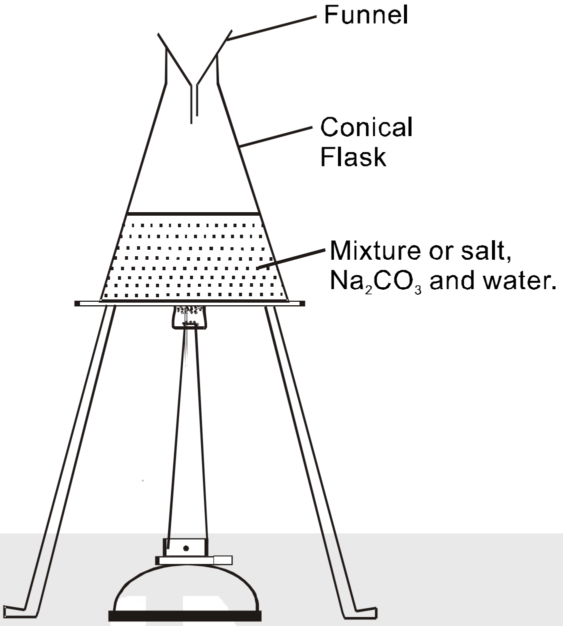


Figure : Preparation of sodium carbonate extract

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 (CO_3^{2-}) :

- Dilute H_2SO_4 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 ($Ba(OH)_2$) test : The liberated gas can be identified by its property of rendering lime water (or baryta water) turbid.

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

  On prolonged passage of CO_2 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) :

  $CO_3^{2-}\ (aq) + MgSO_4\ (aq) \longrightarrow \mathbf{MgCO_3\downarrow\ (white)} + SO_4^{2-}\ (aq)$

- Silver nitrate solution : **White precipitate** is formed

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

  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 ($3HgO.\ HgCO_3 = Hg_4O_3CO_3$) is formed.

$CO_3^{2-} + 4\,Hg^{2+} + 3\,H_2O \longrightarrow \mathbf{Hg_4O_3.CO_3}\downarrow + 6H^+$

Note: Lime water milky test is also shown by SO_2 but CO_2 does not turn the filter paper soaked in acidified $K_2Cr_2O_7$ green.

☞ Soluble bicarbonates give white precipitate with $MgSO_4$ (aq) / $MgCl_2$(aq) only on heating.

$Mg^{2+} + 2HCO_3^- \longrightarrow Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3\downarrow + H_2O + CO_2$

☞ **Action of heat :**

Bicarbonates : $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$

Carbonates : Except carbonates of Na, K, Rb, Cs ; the Li_2CO_3 and all alkaline earth metals decompose as given below :

$Li_2CO_3 \longrightarrow Li_2O + CO_2$; $MgCO_3 \longrightarrow MgO + CO_2$; $Ag_2CO_3 \longrightarrow 2Ag + CO_2$

☞ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

2. SULPHITE ION (SO_3^{2-}) :

- **Dilute H_2SO_4 test :** Decomposition of salt is more rapidly on warming, with the evolution of sulphur dioxide.

  $CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + \mathbf{SO_2} \uparrow$

  SO_2 has suffocating odour of burning sulphur.
- **Acidified potassium dichromate test :** The filter paper dipped in acidified $K_2Cr_2O_7$ turns green.

  $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow \mathbf{2Cr^{3+}}$ **(green)** $+ 3SO_4^{2-} + H_2O$.
- **Barium chloride/Strontium chloride solution :** White precipitate of barium (or strontium) sulphite is obtained.

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

☞ White precipitate dissolves in dilute HCl, when sulphur dioxide is evolved.

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

White precipitate ($BaSO_3$) 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.

$2\ BaSO_3 \downarrow + O_2 \longrightarrow 2\ BaSO_4 \downarrow$

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

Hence, reddish brown colour of bromine water is decolourised.

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

$BaSO_3 \downarrow + H_2O_2 \longrightarrow BaSO_4 \downarrow + H_2O$

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

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

  $SO_3^{2-} + 3Zn^{2+} + 8H^+ \longrightarrow \mathbf{H_2S} \uparrow + 3Zn^{2+} + 3H_2O$
- **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.

  $Ca(OH)_2 + SO_2 \longrightarrow \mathbf{CaSO_3}$**(milky)** $+ H_2O$

  $CaSO_3 \downarrow + SO_2 + H_2O \longrightarrow \mathbf{Ca(HSO_3)_2}$ **(soluble)**

☞ 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 $PbSO_3$ is obtained.

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

  White precipitate gets soluble in dil. HNO_3 on boiling. The precipitate is oxidized by atmospheric oxygen and $PbSO_4$ is formed.

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

3. SULPHIDE ION (S^{2-}) :

- **Dilute H_2SO_4 test :** Pungent smelling gas like that of rotten egg is obtained.

  $S^{2-} + 2H^+ \longrightarrow \mathbf{H_2S} \uparrow$
- **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.

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

  It is a ligand change reaction not a redox where NO^+ changes to $(NOS)^{-1}$.

  No reaction occurs with solution of H_2S or free gas. If however, filter paper moistened with a solution of the reagent is made alkaline with NaOH or NH_3 solution, a purple colouration is produced with free H_2S 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.

  $Na_2S + CdCO_3 \longrightarrow CdS \downarrow + Na_2CO_3$

☞ Filter paper moistened with cadmium acetate when brought in contact with evolving gas it turns **yellow.**

$S^{2-} + 2H^+ \longrightarrow H_2S$; $H_2S + Cd^{2+} \longrightarrow \mathbf{CdS} \downarrow$ **(yellow)** $+ 2H^+$.

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

  $Ag^+ + S^{2-} \longrightarrow \mathbf{Ag_2S} \downarrow$**(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_2SO_4 test :** Solid nitrite in cold produces a transient pale blue liquid (due to the presence of free nitrous acid, HNO_2 or its anhydride, N_2O_3) first and then evolution of pungent smelling reddish **brown vapours** of NO_2 takes place.

  $NO_2^- + H^+ \longrightarrow HNO_2$; ($2HNO_2 \longrightarrow H_2O + N_2O_3$);

  $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$; $2NO + O_2 \longrightarrow \mathbf{2NO_2}\uparrow$

- **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 $[Fe(H_2O)_5NO]SO_4$ at the junction of the two liquids. If the addition has not been made slowly and caustiously, a brown colouration results.

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

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

  $Fe^{2+} + SO_4^{2-} + NO \uparrow \longrightarrow \mathbf{[Fe(H_2O)_5NO]SO_4}$ **(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 HCl and $FeCl_3$ solution.

  $NaNO_2 + CH_3COOH \longrightarrow HNO_2 + CH_3COONa$

  $HNO_2 + H_2NCSNH_2(s)$ (thiourea) $\longrightarrow N_2 + HSCN + 2H_2O$

  $FeCl_3 + 3HSCN \xrightarrow{\text{dil. HCl}} \mathbf{Fe(SCN)_3}$ **(blood red colouration)** $+ 3HCl$

- **Acidified potassium permanganate solution : Pink colour of $KMnO_4$ is decolourised** by a solution of a nitrite, but no gas is evolved.

  $5\,NO_2^- + 2\,MnO_4^- + 6\,H^+ \longrightarrow 5\,NO_3^- + 2\,Mn^{2+} + 3\,H_2O$

- **Silver nitrate solution : White crystalline precipitate** of silver nitrite from concentrated solutions.

  $NO_2^- + Ag^+ \longrightarrow \mathbf{AgNO_2} \downarrow$ (white)

5. ACETATE ION (CH_3COO^-)

- With dilute H_2SO_4 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.

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

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

$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4H_2O \xrightarrow{\text{Boil}} 3Fe(OH)_2CH_3COO \downarrow + 3CH_3COOH + H^+$

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

  $CH_3COO^- + Ag^+ \rightleftharpoons \mathbf{CH_3COOAg} \downarrow$**(white)**

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

Section (D) : Conc. H_2SO_4 group

(b) CONC. H_2SO_4 GROUP :

1. CHLORIDE ION (Cl^-) :

- **Concentrated H_2SO_4 test : Colourless pungent smelling gas (HCl)** is evolved which gives fumes of NH_4Cl when a glass rod dipped in aq. ammonia is brought in contact with evolving gas.

$Cl^- + H_2SO_4 \longrightarrow \mathbf{HCl} + HSO_4^-$

- $NH_4OH + HCl \longrightarrow \mathbf{NH_4Cl} \uparrow$ **(white fumes)** $+ H_2O$.

☞ $2NaCl + MnO_2 + 2H_2SO_4$ (conc.) $\longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

- **Silver nitrate test :**

$Cl^- + Ag^+ \longrightarrow \mathbf{AgCl} \downarrow$ **(white)**

With sodium arsenite it is converted into **yellow precipitate** (distinction from AgBr and AgI) but insoluble in dilute nitric acid.

$3AgCl\downarrow + AsO_3^{3-} \longrightarrow \mathbf{Ag_3AsO_3}\downarrow$ **(yellow)** $+ 3Cl^-$.

☞ White precipitate is soluble in aqueous ammonia and precipitate reappears with HNO_3.

$AgCl + 2NH_4OH$ **$[Ag(NH_3)_2]Cl$ (Soluble)** $+ 2H_2O$

$[Ag(NH_3)_2]Cl + 2H^+ \longrightarrow AgCl \downarrow + 2NH_4^+$.

- **Chromyl chloride test :**

$4Cl^-(s) + Cr_2O_7^{2-}(s) + 6H^+$ (conc.) $\longrightarrow 2\mathbf{CrO_2Cl_2}$ **(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 **yellow precipitate of lead chromate**.

$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$

$CrO_4^{2-} + Pb^{+2} \longrightarrow \mathbf{PbCrO_4} \downarrow$ **(yellow)**

Note :

1. Heavy metal chlorides such as Hg_2Cl_2, $HgCl_2$, $SnCl_2$, AgCl, $PbCl_2$ and $SbCl_3$, CuCl do not respond to this test due to their high covalent character as a result of which sufficient free Cl^- are not available. This test is given generally by ionic chlorides.
2. Test should be carried out in a dry test tube otherwise chromic acid will be formed.

   $CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$
3. Br^- and I^- must be absent for this test because they are oxidized by $Cr_2O_7^{2-}$ into Br_2 (brown vapours) and I_2 (violet vapours) respectively. Both Br_2 and I_2 produce colourless solution with NaOH solution.
4. NO_2^-, NO_3^- and ClO_2^- radicals also interfere with this test and so should be absent.

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2. BROMIDE ION (Br^-) :

- **Concentrated H_2SO_4 test :** First a **reddish-brown solution** is formed, then reddish-brown bromine vapour accompanies the hydrogen bromide (fuming in moist air) is evolved.

$2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr$

$2HBr + H_2SO_4 \longrightarrow \mathbf{Br_2} \uparrow + 2H_2O + SO_2$

☞ $2KBr + MnO_2 + 2H_2SO_4 \longrightarrow Br_2\uparrow + K_2SO_4 + MnSO_4 + 2H_2O$

- **Silver nitrate test : Pale yellow precipitate** is formed

$NaBr + AgNO_3 \longrightarrow \mathbf{AgBr} \downarrow + NaNO_3$

☞ 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.

$2Br^- + Pb^{+2} \longrightarrow \mathbf{PbBr_2} \downarrow$ (white)

- **Chlorine water test (organic layer test) :** When to a sodium carbonate extract of metal bromide containing CCl_4, $CHCl_3$ or CS_2, chlorine water is added and the content is shaken and then allow to settle down reddish brown colour is obtained in organic layer.

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

$Br_2 + CHCl_3 / CCl_4 \longrightarrow \mathbf{Br_2}$ 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.

$Br_2 \uparrow + Cl_2 \uparrow \longrightarrow \mathbf{2BrCl}$

- **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_2SO_4 :** When a mixture of solid bromide, $K_2Cr_2O_7$ and concentrated H_2SO_4 is heated and evolved vapours are passed through water, a orange red solution is obtained.

  $6KBr + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Br_2\uparrow + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O$

3. IODIDE ION (I^-) :

- **Concentrated H_2SO_4 test : Pungent smelling violet vapours** are evolved.

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

  $2HI + H_2SO_4 \longrightarrow \mathbf{I_2\uparrow}$ **(dark violet)** $+ 2H_2O + SO_2$

☞ Evolution of dark violet fumes intensifies on adding a pinch of MnO_2.

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

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

  $3I^- + 2NO_2^- + 4H^+ \longrightarrow I_3^- + 2NO\uparrow + 2H_2O.$

- **Silver nitrate test :** Bright yellow precipitate is formed.

  $I^- + Ag^+ \longrightarrow \mathbf{AgI}\downarrow$ **(bright yellow)**

☞ 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 CS_2, $CHCl_3$ or CCl_4, it dissolves in organic layer forming a violet solution, which settles below the aqueous layer.

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

  $I_2 + CHCl_3 \longrightarrow$ **I_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.

  $2I^- + Pb^{+2} \longrightarrow \mathbf{PbI_2}\downarrow$**(yellow)**

- **Potassium dichromate and concentrated sulphuric acid : Violet vapours** are liberated, and no chromate is present in distillate.

  $6I^- + Cr_2O_7^{2} + 2H_2SO_4 \longrightarrow 3I_2 + Cr^{3+} + 7SO_4^{2-} + 7H_2O$

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

  $2FeCl_3 \longrightarrow 2FeCl_2 + Cl_2$; $MgCl_2.6H_2O \longrightarrow MgO + 2HCl + 5H_2O$

  $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$; $NH_4Cl \longrightarrow NH_3 + HCl$

  $2CuI_2 \longrightarrow CuI + I_2$ (without heating)

Solvent Precipitate	**NH_3**	**HNO_3**	**$Na_2S_2O_3$**	**NaCN/KCN**
AgCl	Completely soluble	Insoluble	Soluble	Soluble
AgBr	Partially soluble	Insoluble	Soluble	Soluble
AgI	Insoluble	Insoluble	Soluble	Soluble

Note : In NH_3, Ag^+ forms soluble complex of $[Ag(NH_3)_2]^+$

In $Na_3S_2O_3$, Ag^+ forms soluble complex of $[Ag(S_2O_3)_2]^{3-}$

In NaCN, Ag^+ forms soluble complex of $[Ag(CN)_2]^-$

4. NITRATE ION (NO_3^-) :

- **Concentrated H_2SO_4 test : Pungent smelling reddish brown vapours** are evolved.

  $4NO_3^- + 2H_2SO_4 \longrightarrow \mathbf{4NO_2}\uparrow + O_2 + 2SO_4^{2-} + 2H_2O$

☞ 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.

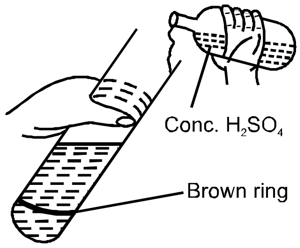

Figure : Brown ring test

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

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

or $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO \downarrow + 4SO_4^{2-} + 4H_2O$.

$Fe^{2+} + NO \uparrow + 5H_2O \longrightarrow$ **$[Fe^{I}(H_2O)_5\ NO^+]^{2+}$ (brown ring).**

Some important points related to brown ring test are :

Note :

1. Shaking and warming are not allowed for this test because on shaking and warming the mixture, NO 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.

   $H_2NHSO_3 + NO_2^- \longrightarrow N_2 \uparrow + SO_4^{2-} + H^+ + H_2O$

   $NO_2^- + H^+ \xrightarrow{HCl} HNO_2$

   $CO(NH_2)_2 + 2HNO_2 \longrightarrow 2N_2 \uparrow + CO_2 \uparrow + 3H_2O$
3. $FeSO_4$ solution must be freshly prepared because Fe^{2+} ion is very reactive towards aerial oxidation and gets converted to Fe^{3+}, 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)** $+ H_2O$.

☞ This test is also given by various oxidising agents like CrO_4^{2-}, $Cr_2O_7^{2-}$, ClO_3^-, BrO_3^-, IO_3^-, NO_2^- etc.

To distinguish Br_2 with NO_2 (both are reddish brown gases)

(a) Br_2 + starch–iodide paper → Blue black colour spots do not develop immediately as Br_2 is a weaker oxidising agent whereas NO_2 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_2SO_4 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_4^{2-}) :

- **Barium chloride test :**

  W.E. or S.E. + Barium chloride (aq) ⟶ White precipitate

  $Na_2SO_4 + BaCl_2 \longrightarrow$ **$BaSO_4 \downarrow$ (white)** + 2NaCl.

☞ White precipitate is insoluble in warm dil. HNO_3 as well as HCl but moderately soluble in boiling concentrated hydrochloric acid and conc. H_2SO_4.

$PbSO_4 + H_2SO_4 \longrightarrow$ **$PbHSO_4$(soluble)**

- **Lead acetate test :**

  W.E. or S.E. + Lead acetate ⟶ white precipitate

  $Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow$ **$PbSO_4 \downarrow$ (White)** $+ 2CH_3COONa$

☞ 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.** $+ (NH_4)_2SO_4$

$PbSO_4 + (NH_4)_2\,C_4H_4O_6 \longrightarrow (NH_4)_2SO_4 +$ **$(NH_4)_2\,[Pb(C_4H_4O_6)_2]$soluble**

- **Match stick test :**

  (a) W.E. or S.E. + Barium chloride ⟶ white precipitate

  $Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + \mathbf{BaSO_4} \downarrow$ **(white)**

  (b) White precipitate + Na_2CO_3(s) mix and apply the paste on the end of the carbonized match stick or a wooden splinter. Put it in the reducing flame.

  $BaSO_4 (s) + Na_2CO_3(s) \longrightarrow Na_2SO_4 + \mathbf{BaCO_3} \downarrow$ **(white)**

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

  (c) Now dip the match stick in sodium nitroprusside solution, purple colour near the fused mass is developed.

  $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \mathbf{Na_4[Fe(CN)_5NOS]}$ **(purple)**

- **Silver nitrate test : White precipitate** is obtained.

  $SO_4^{2-} + 2Ag^+ \longrightarrow \mathbf{Ag_2SO_4} \downarrow$ **(white ppt.)**

2. PHOSPHATE ION (PO_4^{3-}) :

- **Ammonium molybdate test :**

$Na_2HPO_4(aq) + 12(NH_4)_2MoO_4 + 23HNO_3 \rightarrow (NH_4)_3[P(Mo_3O_{10})_4]\downarrow$ **(canary yellow)** $+ 2NaNO_3 + 21NH_4NO_3 + 12H_2O$

☞ Some times ammonium phosphomolybdate is also represented by the formula $\mathbf{(NH_4)_3PO_4.12MoO_3}$

- **Magnesium nitrate or magnesia mixture test :** W.E. or S.E + Magnesium nitrate reagent (3-4 mL) and allows to stand for 4-5 minutes, white crystalline precipitate is formed.

  $Na_2HPO_4 (aq) + Mg(NO_3)_2 (aq) + NH_4OH(aq) \longrightarrow \mathbf{Mg(NH_4)PO_4} \downarrow$ **(white)** $+ 2NaNO_3 + H_2O$

  Magnesia mixture is a solution containing $MgCl_2$, NH_4Cl and a little aqueous NH_3.

☞ 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 i**s formed which is soluble in dilute ammonia and in dilute nitric acid.

  $PO_4^{3-} + 3Ag^+ \longrightarrow \mathbf{Ag_3PO_4} \downarrow$**(yellow)**

  $Ag_3PO_4 \downarrow + 6NH_3 \longrightarrow 3[Ag(NH_3)_2]^+ + PO_4^{3-}$;

  $Ag_3PO_4 \downarrow + 2H^+ \longrightarrow H_2PO_4^- + 3Ag^+$

- **Iron (III) chloride solution : Yellowish-white precipitate of $FePO_4$** is obtained

  $HPO_4^{2-} + Fe^{3+} \longrightarrow \mathbf{FePO_4} \downarrow$

3. BORATE ION (BO_3^{3-}) :

Salt (0.2 g) + conc. H_2SO_4 (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.

$2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$

$3C_2H_5OH + H_3BO_3 \longrightarrow \mathbf{(C_2H_5)_3BO_3}$ **or** $\mathbf{(C_2H_5O)_3B} + 3H_2O$

Note :

1. Use of methyl alcohol is preferred due to high volatility of the product formed is $B(OMe)_3$
2. 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 $KMnO_4$ is decolourised but there is no evolution of any gas. This may happen with the compound containing the following acid radical.
(A) SO_3^{2-} (B) NO_2^- (C) S^{2-} (D) All of these

Ans. **(D)**

Sol. (A) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$
(B) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
(C) $2MnO_4^- + H_2S + 6H^+ \longrightarrow 2Mn^{2+} + 5S\downarrow + 8H_2O$

2. Which of the following gives a precipitate with $Pb(NO_3)_2$ but not with $Ba(NO_3)_2$?
(A) Sodium chloride (B) Sodium acetate
(C) Sodium nitrate (D) Disodium hydrogen phosphate

Ans. **(A)**

Sol. (A) $Pb^{2+} + 2Cl^- \longrightarrow PbCl_2\downarrow$ (white) ; $Ba^{2+} + 2Cl^- \longrightarrow BaCl_2$ (water soluble)
(B) $(CH_3COO)_2$ Pb and $(CH_3COO)_2Ba$ both are water soluble salts.
(C) Nitrates are mostly soluble in water
(D) $3Pb^{2+} + 2HPO_4^{2-} \longrightarrow Pb_3(PO_4)_2\downarrow$ (white) + $2H^+$; $Ba^{2+} + HPO_4^{2-} \longrightarrow BaHPO_4\downarrow$ (white)

3. When H_2S gas is passed through an ammonical salt solution X, a slightly white precipitate is formed. The X can be :
(A) a cobalt salt (B) a lead salt (C) a zinc salt (D) a silver salt

Ans. **(C)**

Sol. $Zn^{2+} + H_2S \longrightarrow ZnS\downarrow$ (white) + $2H^+$

4. Which anion does not liberate any gas with dilute as well as conc. H_2SO_4.
(A) NO_2^- (B) NO_3^- (C) SO_3^{2-} (D) SO_4^{2-}

Ans. **(D)**

5. A salt having BO_3^{3-} on burning with alcohol and conc. H_2SO_4 gives, which colour edge flame.
(A) green (B) yellow (C) red (D) white

Ans. **(A)**

Sol. $3Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$
$3C_2H_5OH + H_3BO_3 \longrightarrow \underset{\text{(green)}}{(C_2H_5)_3BO_3} + 3H_2O$

6. When solution of KCl, KF and KBr are treated with I_2 ?
(A) Cl_2 and Br_2 are evolved (B) Cl_2 is evolved
(C) Cl_2, F_2 and Br_2 are evolved (D) None of these

Ans. **(D)**

Sol. I_2 is weak oxidising agent.
It does not oxidise the F^-, Cl^-, Br^-.

7. A mixture when rubbed with organic acid smells like vinegar. It contains :
(A) Sulphate (B) Nitrate (C) Nitrite (D) Acetate

Ans. **(D)**

8. Nitrate & Nitrite both give brown ring test, can be distinguish by –
(A) $HOSO_2NH_2$ (Sulphonic acid) (B) $NH_2HgO.HgI$ (Million base)
(C) $FeSO_4$ (D) None

Ans. **(A)**

9. Which reagent is used to remove SO_4^{2-} or Cl^- from water?
(A) NaOH (B) $Pb(NO_3)_2$ (C) $BaSO_4$ (D) KOH

Ans. **(B)**

Sol. $Pb^{2+} + SO_4^{2+} \longrightarrow PbSO_4\downarrow$ (ppt)
$Pb^{2+} + Cl^- \longrightarrow PbCl_2\downarrow$ (ppt)
Others does not from precipitate with both anions.

10.* Which of the following statements is/are correct for chromyl chloride test?

(A) Formation of chromyl chloride vapour (B) Liberation of chlorine gas

(C) Formation of lead chromate (D) Formation of reddish-brown vapour

Ans. **(A,C,D)**

Sol. $Cl^- + K_2Cr_2O_7 + H^+ \longrightarrow \underset{\text{(Chromyl chloride)}}{CrO_2Cl_2}$ (red-brown vapour) $\xrightarrow{NaOH} \underset{\text{Yellow (sodium chromate)}}{Na_2CrO_4} \xrightarrow{(CH_3COO)_2Pb} \underset{\text{Lead chromate (Yellow)}}{PbCrO_4}$

11.* Which of the following statements are incorrect?

(A) In thiourea test for nitrite, a green coloured solution is obtained.

(B) It is not necessary to carried out the chromyl chloride test in a dry test tube.

(C) Suspension of $CdCO_3$ gives black precipitate with Na_2S solution.

(D) In $PbNO_3$, the brown ring test can be performed with its water extract.

Ans. **(A,B,C,D)**

Sol. It is deep red colouration due to the formation of $Fe(SCN)_3$.

In presence of moisture, $CrO_2Cl_2 + H_2O \longrightarrow H_2CrO_4 + HCl$.

CdS (Yellow precipitate).

White precipitate of $PbSO_4$ is formed and hence brown ring is not visible.

12.* Conc. H_2SO_4 will not give any gas with :

(A) $ZnSO_4$ (B) $Ba_3(PO_4)_2$ (C) $Mg_3(BO_2)_2$ (D) $NaNO_3$

Ans. **(A,B,C)**

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

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

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.