# QUALITATIVE ANALYSIS

## Qualitative Inorganic Analysis

Qualitative inorganic analysis involves the detection of cations (basic radicals) and anions (acid radicals) present in an inorganic compound or a mixture of inorganic comopounds. For a systematic study, qualitative analysis may be studied in the following parts :

(A) Dry tests for inorganic compounds

(B) Confirmatory tests for basic radicals

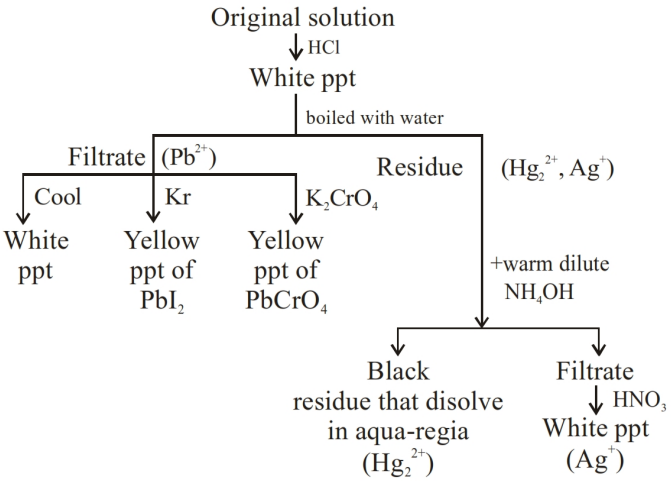
(C) Confirmatory tests for acid radicals

## Calssification of Basic Radicals

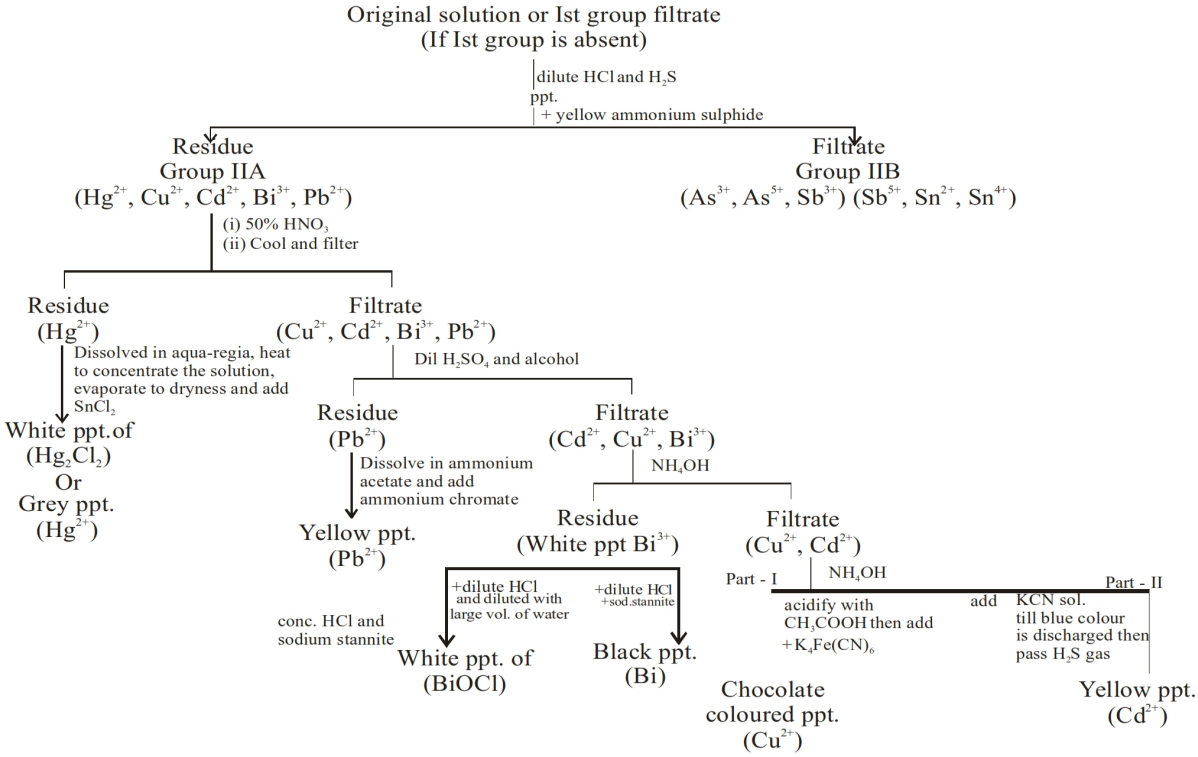
The qualitative analysis of basic radicals is based on the concept of solubility product, solubility and common ions. These concpets play very important role even in the classification of radicals in six groups and their group reagents.The common occuring cations have been divided into six groups.

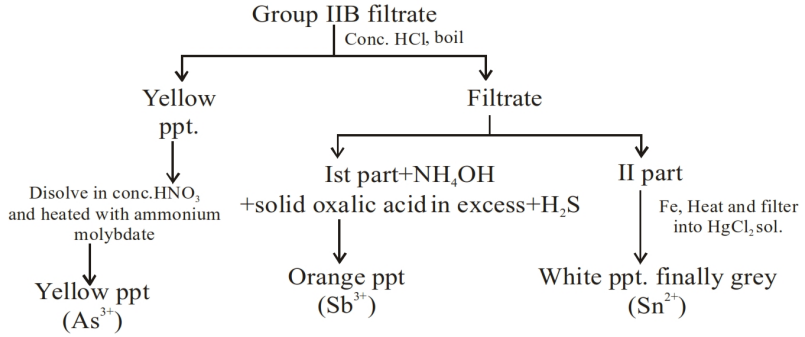
| Group | Group reagent | Basic radical | Composition and colour of the ppt. |
|---|---|---|---|
| I. | Dil. HCl | $Ag^{+}$<br>$Pb^{2+}$<br>$Hg_2^{2+}$ | AgCl……White<br>$PbCl_2$……White<br>$Hg_2Cl_2$……White |
| II.A | $H_2S$ in the presence of dil. HCl | $Hg^{2+}$<br><br>$Pb^{2+}$<br>$Bi^{3+}$<br>$Cu^{2+}$<br>$Cd^{2+}$ | HgS……Black<br><br>PbS……Black<br>$Bi_2S_3$……Black<br>CuS……Black<br>CdS……Yellow |
| II.B | $H_2S$ in the presence of dil. HCl | $As^{3+}$<br>$Sn^{4+}$<br>$Sb^{3+}$<br>$Sn^{2+}$ | $As_2S_3$……Yellow<br>$SnS_2$……Yellow<br>$Sb_2S_3$……Orange<br>SnS……Brown |
| III. | $NH_4OH$ in the presence of excess of $NH_4Cl$ | $Fe^{3+}$<br><br><br>$Cr^{3+}$<br>$Al^{3+}$ | $Fe(OH)_3$……Reddish brown<br><br>$Cr(OH)_3$……Dirty green<br>$Al(OH)_3$……White gelatinous ppt. |
| IV. | $H_2S$ in presence of $NH_4OH$ | $Co^{2+}$<br>$Ni^{2+}$<br>$Zn^{2+}$<br>$Mn^{2+}$ | CoS……Black<br>NiS……Black<br>ZnS……Bluis white<br>MnS…Buff (flesh) coloured |
| V. | $(NH_4)_2CO_3$ in the presence of $NH_4OH$ | $Ba^{2+}$<br>$Sr^{2+}$<br>$Ca^{2+}$ | $BaCO_3$……White<br><br>$SrCO_3$……White<br>$CaCO_3$……White |
| VI. | No specific group reagent | $Mg^{2+}$<br>Na+<br>K+ | $Mg(NH_4)PO_4$……White |
| Zero | NaOH | $NH_4^{+}$ | $NH_3$ gas is evolved |

1. Ist Group Basic Radicals : ($Ag^{+}$, $Pb^{2+}$, $Hg_2^{2+}$)

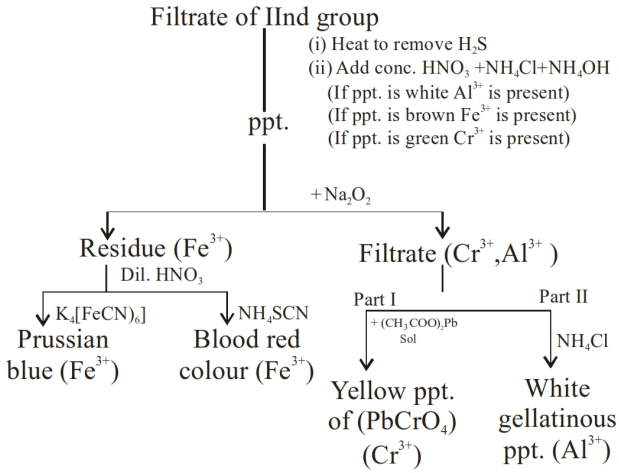



2. IInd Group Basic Radicals : Original solution or Ist group filtrate

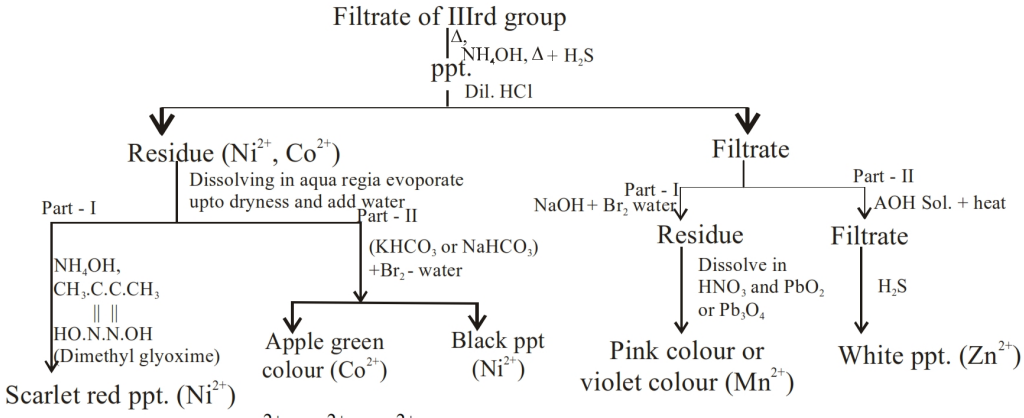


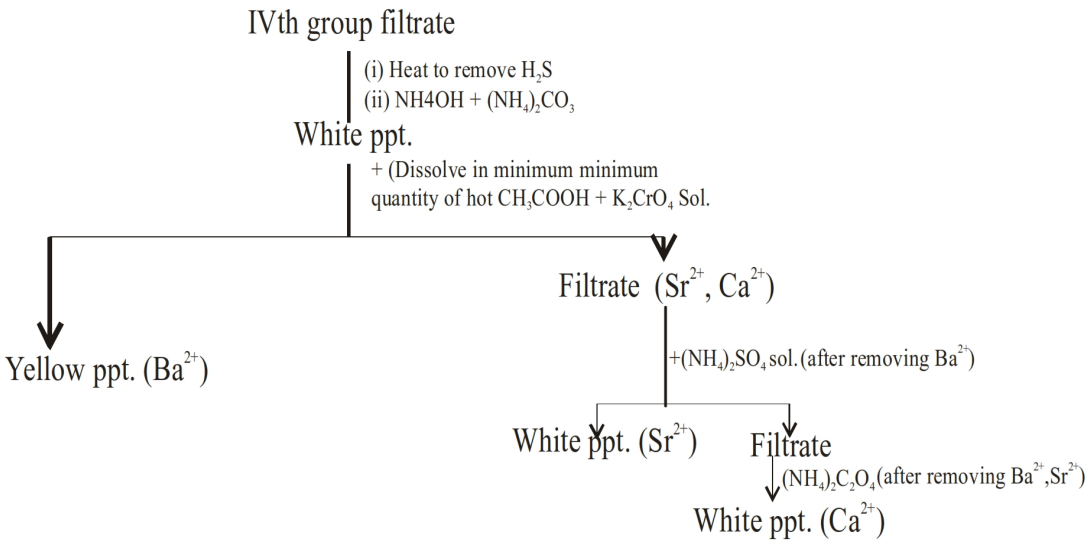
IIIrd Group Basic Radicals :




4. IV Group Baisc Radicals : ($Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Zn^{2+}$) :




5. Vth Group Basic Radicals : ($Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$)



6. VI Group Basic Radical

Filtrate of Vth group

↓ Heat and add $(NH^4)_2C_2O_4$. If any ppt. is obtained. Now add $NH_4OH$ and $Na_2HPO_4$ skretch with glass rod.

White crystalline ppt.

7. Zero Group Basic Radical : It contains $NH_4^{\oplus}$ ion.

(a) The salt is heated with NaOH, ammonia is evolved. The ammonia gives white fumes with HCl.

(b) $NH_4^+$ gives brown ppt. with Nessler's reagent.

Reactions :

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$NH_4Cl + 2K_2HgI_4 + 3KOH \longrightarrow NH_2HgOHgI + 7KI + 2H_2O$$

Reaction involve :

$Pb^{2+}$

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4} + 2KCl$$

$$PbCrO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

$Ag^+$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Diamine silver(I) chloride}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl} + 2NH_4NO_3$$

$Hg_2^{2+}$

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black}} + NH_4Cl + 2H_2O$$

$Hg^{2+}$

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$

$$2Hg(NH_2)Cl + 6Cl \longrightarrow 2HgCl_2 + 4HCl + N_2$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$3HCl + HNO_3 \longrightarrow 2H_2O + NOCl + 2Cl$$

$$3HgS + 2NOCl + 4Cl \longrightarrow 3HgCl_2 + 2NO + 3S$$

$Pb^{2+}$

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow Pb(CH_3COO)_{2+}(NH_4)_2SO_4^-)$$

$$Pb(CH_3COO)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2CH_3COOK$$

$Bi^{3+}$

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

$$BiCl_3 + H_2O \longrightarrow \underset{\text{White ppt.}}{BiOCl} + 3HCl$$

$$BiCl_3 + 3NaOH \longrightarrow Bi(OH)_3 + 3NaCl$$

$$2Bi(OH)_2 + \underset{\text{Sod.s tan nite}}{3Na_2SnO_2} \longrightarrow \underset{\text{Black}}{2Bi(OH)_3} + 3H_2O$$

$Cu^{2+}$

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

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

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

$Cd^{2+}$

$$[Cd(NH_4)_4]SO_4 + 4KCN \longrightarrow K_2[Cd(CN)_4] + K_2SO_4 + 4NH_3$$

$$K_2[Cd(CN)_4] + H_2S \longrightarrow \underset{\text{Yellow ppt.}}{CdS} + 2KCN + 2HCN$$

$As^{3+}$

$$As_2S_6 + 10HNO_3 \longrightarrow \underset{\text{Aresenic acid (So lub le)}}{2H_3AsO_4} + 10NO_2 + 5S + 2H_2O$$

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

$Ie^{3+}$

$$Fe(OH)_3 + 3HCl \longrightarrow \underset{\text{Soluble}}{FeCl_3} + 3H_2O$$

$$FeCl_3 + 3NH_4CNS \longrightarrow \underset{\text{Blood red}}{Fe(CNS)} + 3NH_4Cl$$

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

$Cr^{3+}$

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4} + 2CH_3COONa$$

$Al^{3+}$

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3} + NH_4 + NaCl$$

$Zn^{2+}$

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

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

$$Na_2ZnO_2 + H_2S \longrightarrow \underset{\text{White ppt.}}{ZnS} + 2NaOH$$

$Mn^{2+}$

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl$$

$$Mn(OH)_2 + O \longrightarrow MnO_2 + H_2O$$

$$2MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$$

$$2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 \longrightarrow \underset{\substack{\text{Permanganic} \\ \text{acid (pink)}}}{2HMnO_4} + 15Pb(NO_3)_2 + 12H_2O$$

$Ni^{2+}$

$$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3H_2O + 3CO_2$$

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

$$2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow \underset{\substack{\text{Sod. cobalti carbonate} \\ \text{(Green colouration)}}}{2Na_3Co(CO_3)_3} + 2NaOH$$

$$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2$$

$$2NiCO_3 + O \longrightarrow \underset{\text{(Black)}}{Ni_2O_3} + 2CO_2$$

$Ba^{2+}$ (barium)

$$Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2CH_3COOK$$

$Sr^{2+}$ (strontium)

$$Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow \underset{\text{White ppt.}}{SrSO_4} + 2CH_3COONH_4$$

$Ca^{2+}$ (calcium)

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

## DRY TEST

Dry tests are of great importance as these tests give clear indications of the presence of certain radicals. The following tests are performed in dry state:

(i) Flame test
(ii) Borax bead test
(iii) Micro-cosmic salt bead test
(iv) Charcoal cavity test
(v) Cobalt nitrate charcoal test

### Flame Test

Alkali and Alkaline earth Metals Salts give characteristic colour when introduced in Bunsen flame. The colour produced by them are given below.

| | | | |
|---|---|---|---|
| Li | Grimson red | Ca | Brick red |
| Na | Golden yellow | Sr | Crimson |
| K | Violet | Ba | Apple green |

### Note :

Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form alloy with platinum and hence, the wire is spoiled.

### Borax bead test

On heating borax the colourless glassy bead formed consists of sodium metaborate and boric anhydride.

$$Na_2B_4O_7K.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame.

$$CuSO_4 \longrightarrow CuO + SO_3$$

$$CuO + B_2O_3 \longrightarrow \underset{\substack{\text{Copper metaborate}\\(\text{Blue})}}{Cu(BO_2)_2}$$

| Metal | Colour of the bead in | | | |
|---|---|---|---|---|
| | Oxidising-flame | | Reducing-flame | |
| | Hot | Cold | Hot | Cold |
| Copper | Green | Blue | Colourless | Brown-red |
| Iron | Brown-yellow | Pale-yellow | Bottle green | Bottle green |
| Chromium | Green | Green | Green | Green |
| Cobalt | Blue | Blue | Blue | Blue |
| Manganese | Violet | Amethyst red | Grey | Grey |
| Nickel | Violet | Brown | Grey | Grey |

Microcosmic salt bead test

This test is similar to borax bead test. When microcosmic salt is heated, a colourless transparent bead of sodium metaphosphate is formed.

$$Na(NH_4)HPO_4 \longrightarrow \underset{\text{Sodium metaphosphate}}{NaPO_3} + NH_3 + H_2O$$

Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured. The shade of the colour gives a clue regarding the presence of metal.

| Metal | Colour of the bead in | | | |
|---|---|---|---|---|
| | Oxidising-flame | | Reducing-flame | |
| | Hot | Cold | Hot | Cold |
| Copper | Green | Blue | Colourless | Red |
| Iron | Yellow or reddish-brown | Yellow | Yellow | Colourless |
| Chromium | Green | Green | Green | Green |
| Manganese | Violet | Violet | Colourless | Colourless |
| Cobalt | Blue | Blue | Blue | Blue |
| Nickel | Brown | Brown | | Grey |

Test for acid radicals : Add dil. HCl or $H_2SO_4$ to a small amount of substanceand warm gently, observe.

Carbonate or $CO_3^{2-}$ :

(i) Brisk effervescences of colourless gas $CO_2$; may be carbonate.

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

(ii) The gas turns lime water milky

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

(iii) Excess of passage of gas through lime water is milkyness disappears

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2 \text{(Soluble)}$$

Sulphite or $SO_3^{2-}$ :

(i) Colourless gas with suffocating odour of burning sulphur; may be sulphite.

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

(ii) The gas turns orange colour of acidic $K_2Cr_2O_7$ to green

$$\underset{\text{Orange}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

Note : $CO_2$ does not turns orange colour of acidic $K_2Cr_2O_7$ to green

Sulphide $(S^{2-})$ :

(i) The sulphide salts from $H_2S$ which smells like rotten eggs.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S \uparrow$$

(ii) On exposure to this gas, the lead acetate paper turns black due to the formationof lead sulphide.

$$Pb(CH_3COO)_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COOH$$

(iii) The sulphides also turn sodium nitroprusside solution violet (use sodium carbonate extract for this rest).

$$Na_2S + Na_2[FeNO(CN)_5] \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COOH$$

Note : Sulphide of lead, calcium, nickel, cobalt antimony and stannic are not decomposed with dil. $H_2SO_4$. Conc. HCl should be used for their test. However, brisk evolution of H2S takes place even by use of dil. H2SO4 if a pinch of zinc dust is added.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

$$HgS + 2H \longrightarrow Hg + H_2S$$

Acetate $(CH_3COO^-)$

(i) Acetates decompose to give acetic acid vapours having characteristic smell of vinegar.

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

(ii) All acetates are soluble in water and their aqueous solution on addition to neutral $FeCl_3$ solution develops a blood red colour due to the formation of ferric acetate.

$$FeCl_3 + 3CH_3COONa \longrightarrow \underset{\text{Blood red colour}}{(CH_3COO)_3 Fe} + 3NaCl$$

Note :

1. The ferric chloride solution supplied in the laboratory is always acidic due to hydrolysis. It is made neutrla by the addition of dil. solution of $NH_4OH$ drop by drop with constant stirring till the precipitate formed does not dissolve. The filtrate is called neutral ferric chloride solution.
2. Before testing acetate inthe aqueous solution by $FeCl_3$, it must be made sure that the solution does not contain,

(i) $CO_3^{2-}$ (ii) $SO_3^{2-}$ (iii) $PO_4^{3-}$ (v) $I^-$

since these also combine will $Fe^{+3}$. Therefore the test of acetate should be performed by neutral ferric chloride solution only after the removal of these ions by $AgNO_3$ solution.

Chloride $(Cl^-)$

(i) Colourless pungent fumes of hydrogen chloride are evolved.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

(ii) The gas evolved forms white fumes of ammonium chloride with $NH_4OH$.

$$NH_4OH + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl} + H_2O$$

(iii) The gas evolved or solution of chloride salt forms a curdy precipitate of silver chloride with silver nitrate solution.

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$

(iv) Yellowish-green chlorine gas with suffocating odour is evolved on addition of $MnO_2$ to the above reaction mixture.

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

Note : The curdy precipitate of AgCl dissolves in ammonium hydroxide forming a complex salt.

$$AgNO_3 + 2NH_4OH \longrightarrow AgCl(NH_3)_2Cl + 2H_2O$$

(v) Chromyl chloride test : When solid chloride is heated with conc. $H_2SO_4$ in presence of $K_2Cr_2O_7$, deep red vapours of chromyl chloride are evolved.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$CrO_3 + 2HCl \longrightarrow \underset{\text{Chromyl chloride}}{CrO_2Cl_2} + H_2O$$

These vapours on passing through NaOH solution, form the yellow solution due to the formation of sodium chromate.

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Yellow colour}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

The yellow solution neutralized with acetic acid gives a yellow solution due to the formation of sodium chromate.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4} + 2CH_3COONa$$

Note :

1. This test is not given by the chloride of mercury, tin, silver lead and antimony.
2. The chromyl chloride test is a always to be performed in a dry test tube otherwise the chromyl chloride vapours will be hydrolysed in the test tube.

$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$$

3. Bromides and iiodies do not give this test.

2. Bromide ($Br^-$)

(i) Reddish-brown fumes of bromine are formed.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

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

(ii) More reddish-brown fumes of bromine are evolved when $MnO_2$ is added

$$2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2$$

(iii) The aqueous solution of bromide or sodium carbonate extract gives pale yellow precipitate of silver bromide which partly dissolves in excess of $NH_4OH$ forming a soluble complex.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr\downarrow} + NaNO_3$$

$$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2\,Br + 2H_2O$$

3. Iodide ($I^-$)

(i) Violet vapours of iodine are evolved.

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

(ii) Violet vapours with starch produce blue colour.

$$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$$

(iii) More violet vapours are evolved when $MnO_2$ is added.

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

4. Nitrate $(NO_3^-)$

(i) Light brown fumes of nitrogen dioxide are evolved.

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

$$2HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$$

(ii) These fumes intensify when copper turnings are added.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iii) Brown ring test : An aqueous solution of salt containing nitrate is mixed with freshly solution of salt solution and conc. $H_2SO_4$ is poured in test tube from sides, a brown ring is formed an account of the formation of a complex at the junction of two liquids.

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

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

$$\underset{\text{Ferrous sulphate}}{[Fe(H_2O)_6]SO_4.H_2O} + NO \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + 2H_2O$$