Testprep Kart

ASIA UAE EUROPE

Chemistry

Chemical Analysis

Table of Content

Analytical chemistry deals with qualitative and quantitative analysis of substances.
Qualitative analysis : In qualitative inorganic analysis, the given compound is analysed for the basic and acid radicals (i.e., the cations and the anions), that it contains. For example zinc blend is analysed for the Zn^{2+} and S^{2-} ions that it contains.

1. Test for Different Gases.

(1) **Colourless gases**

(i) **Tests for CO_2 :** It is colourless and odourless gas. It gives white ppt. with lime water which dissolves on passing excess of CO_2. $\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\text{White ppt.}}{CaCO_3}\downarrow + H_2O$; $\underset{\text{White ppt.}}{CaCO_3} + \underset{\text{Excess}}{CO_2} + H_2O \rightarrow \underset{\text{So luble}}{Ca(HCO_3)_2}$

(ii) **Test for CO :** It is colourless and odourless gas. It burns with a blue flame. $2CO + O_2 \rightarrow 2CO_2$

Note: CO is highly poisonous gas.

(iii) **Test for O_2 :** It is colourless and odourless gas. It rekindles a glowing splinter.

(iv) **Tests for H_2S :** It is a colourless gas with a smell of rotten eggs. It turns moist lead acetate paper black.

$(CH_3COO)_2Pb + H_2S \rightarrow 2CH_3COOH + \underset{\text{Black}}{PbS}$

(v) **Tests for SO_2 :** It is a colourless gas with a suffocating odour of burning sulphur. It turns acidified $K_2Cr_2O_7$ solution green. $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$

(vi) **Tests for NH_3 :** It is a colourless gas with a characteristic ammonical smell. It gives white fumes of NH_4Cl with HCl, $NH_3 + HCl \rightarrow \underset{\text{White fumes}}{NH_4Cl}$. With Nessler's reagents, it gives brown ppt.

$\underset{\text{Nessler's reagent}}{2K_2[HgI_4]} + NH_3 + KOH \rightarrow \underset{\text{Iodine of Millon's base (Brown ppt)}}{NH_2HgOHgI} + 7KI + 2H_2O$

It gives deep blue colour with $CuSO_4$ solution, $CuSO_4 + 4NH_3 \rightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]}SO_4$. NH_3 dissolves in water to give NH_4OH, which being basic, turns red litmus blue, $NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$.

(vii) **Tests for HCl gas :** It is colourless gas with a pungent irritating smell. It turns moist blue litmus paper red i.e., it is acidic in nature. It gives white ppt. with $AgNO_3$ solution. This white ppt. is soluble in NH_4OH. $HCl + AgNO_3 \rightarrow \underset{\text{White ppt.}}{AgCl} + HNO_3$; $AgCl + 2NH_4OH \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]} + 2H_2O$.

(viii) **Test for** CH_3COOH **vapours** : These vapours are colourless with a vinegar like smell.

(2) **Coloured gases**

(i) **Tests for Cl_2 :** It is a greenish yellow gas with a pungent smell. In small quantity it appears almost colourless. It bleaches a moist litmus paper, $Cl_2 + H_2O \rightarrow 2HCl + [O]; Colour + [O] \rightarrow Colourless$. Blue litmus paper first turns red and then becomes colourless.

(ii) **Tests for Br_2 :** Brown vapours with a pungent smell. It turns moist starch paper yellow.

(iii) **Tests for I_2 :** Violet vapours with a pungent smell. It turns moist starch paper blue.

(iv) **Tests for NO_2 :** Brown coloured pungent smelling gas. It turns moist starch KI paper blue

$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$; $I_2 + Starch \rightarrow Blue\ colour$.

It turns ferrous sulphate solution black, $3FeSO_4 + NO_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + \underset{\text{Black brown}}{FeSO_4.NO} + H_2O$

2. Systematic Procedure for Qualitative Analysis of Inorganic Salts.

It involves the following steps : (1) Preliminary tests (2) Wet tests for acid radicals and (3) Wet tests for basic radicals.

(1) **Preliminary tests**

(i) **Physical examination** : It involves the study of colour, smell, density etc.

(ii) **Dry heating :** Substance is heated in a dry test tube.

Observation	**Result**
(a) A gas or vapour is evolved.	Compounds with water of crystallisation
Vapour, evolved, test with litmus paper.	Ammonium salts, acid salts, and hydroxides. (usually accompanied by change of colour)
The vapour is alkaline.	Ammonium salts.
The vapour is acidic.	Readily decomposable salts of strong acids.
Oxygen is evolved	Nitrates,chlorates and certain oxides.
Dinitrogen oxide	Ammonium nitrate or nitrate mixed with an ammonium salt.
Dark-brown or reddish fumes (oxides of nitrogen), acidic in reaction.	Nitrates and nitrites of heavy metals.
CO_2 is evolved, lime water becomes turbid.	Carbonates or hydrogen carbonates.
NH_3 is evolved which turns red litmus blue.	Ammonium salts.
SO_2 is evolved, which turns acidified $K_2Cr_2O_7$ green, decolourises fuschin colour.	Sulphates and thiosulphates.
H_2S is evolved, turns lead acetate paper black, or cadmium acetate yellow.	Hydrates, sulphides or sulphides in the prescnce of water.
Cl_2 is evolved, yellowish green gas, bleaches litmus paper, turns KI – starch blue, poisonous.	Unstable chlorides e.g., copper chlorides in the presence of oxidising agents.

Br_2 is evolved (reddish brown, turns fluorescent paper red).	Bromides in the presence of oxidising agents.
I_2 is evolved, violet vapours condensing to black crystals	Free iodine and certain iodides
(b) A sublimate is formed	Ammonium and mercury salts.
White sublimate	As_2O_3, Sb_2O_3
Grey sublimate	Hg
Steel grey, garlic odour	As
Yellow sublimate	$S, As_2S_3\ HgI_2(\text{Red})$

Action of heat on different compounds **:** Many inorganic salts decomposes on heating, liberating characteristic gases. A few such reactions are as follows.

$\underset{(\text{Red})}{2HgO} \xrightarrow{\Delta} \underset{(\text{Silvery deposit})}{2Hg} + O_2$	$\underset{(\text{Red})}{2Pb_3O_4} \xrightarrow{\Delta} \underset{(\text{Yellow})}{6PbO} + O_2$	$\underset{(\text{Brown})}{2PbO_2} \xrightarrow{\Delta} 2PbO + O_2$
$\underset{(\text{Green})}{CuCO_3} \xrightarrow{\Delta} CuO + CO_2$	$\underset{(\text{White})}{ZnO_3} \xrightarrow{\Delta} \underset{\substack{\text{Yellow (hot)}\\ \text{White (cold)}}}{ZnO} + CO_2$	$\underset{(\text{Blue})}{CuSO_4.5H_2O} \xrightarrow{\Delta} \underset{(\text{White})}{CuSO_4} + 5H_2O$
$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$	$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$	$2Ag_2O \rightarrow 4Ag + O_2$
$\underset{(\text{White})}{2Zn(NO_3)_2} \xrightarrow{\Delta} 2ZnO + \underset{(\text{Brown})}{4NO_2} + O_2$	$2AgNO_3 \xrightarrow{450^\circ C} 2Ag + 2NO_2 + O_2$	$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$
$2Ag_2CO_3 \rightarrow 4Ag + 2CO_2 + O_2$	$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$	$\underset{(\text{Orange})}{(NH_4)_2Cr_2O_7} \rightarrow N_2 + \underset{(\text{Green})}{Cr_2O_3} + 4H_2O$
$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$	$CaCO_3 \rightarrow CaO + CO_2$
$2NaNO_3 \rightarrow 2NaNO_2 + O_2$	$MgCO_3 \rightarrow MgO + CO_2$	$2NH_3 \xrightarrow{\text{Red hot}} N_2 + 3H_2$
$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$	$Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} Al_2O_3 + 3SO_3$
$2CaSO_4.2H_2O \rightarrow \underset{(\text{Plaster of Paris})}{2CaSO_4.H_2O} + 2H_2O$	$2AlCl_3.6H_2O \rightarrow Al_2O_3 + 6HCl + 9H_2O$	$2BeSO_4 \xrightarrow{\Delta} 2BeO + 2SO_2 + O_2$
$2AgNO_3 \xrightarrow{350^\circ C} 2AgNO_2 + O_2$	$2MgSO_4 \xrightarrow{\Delta} 2MgO + 2SO_2 + O_2$	$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$
$(COO)_2Sn \xrightarrow{\Delta} SnO + CO_2 + CO$	$CaC_2O_4 \rightarrow CaCO_3 + CO$	$NH_4NO_2 \rightarrow N_2 + 2H_2O$
$NH_4NO_3 \rightarrow N_2O + 2H_2O$	$2KClO_3 \rightarrow 2KCl + 3O_2$	$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$

$Li_2CO_3 \rightarrow Li_2O + CO_2$	$(COO)_2Fe \rightarrow FeO + CO + CO_2$	$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
$MgCl_2.6H_2O \rightarrow HgCl_2 + Hg$	$NH_4Cl \rightarrow NH_3 + HCl$	$2LiNO_3 \rightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$
$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$	$2CuCl_2 \xrightarrow{\Delta} Cu_2Cl_2 + Cl_2$	$2Co(NO_3)_2 \xrightarrow{\Delta} 2CoO + 4NO_2 + O_2$
$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$	$2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + H_2O + 2NH_3$	
$2Zn(NH_4)PO_4 \xrightarrow{\Delta} Zn_2P_2O_7 + H_2O + 2NH_3$	$K_4Fe(CN)_6 \xrightarrow{\Delta} 4KCN + Fe + 2C + N_2$	
$ZnCl_2.2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$	$2(ZnCl_2.H_2O) \xrightarrow{\Delta} Zn_2OCl_2 + 2HCl + H_2O$	
$2[FeCl_3.6H_2O] \xrightarrow{\Delta} Fe_2O_3 + 9H_2O + 6HCl$	$2ZnSO_4 \xrightarrow{800^oC} 2ZnO + 2SO_2 + O_2$	
$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{(Glassy bead)}}{2NaBO_2} + B_2O_3$		
$H_3BO_3 \xrightarrow{100^oC} HBO_2 \xrightarrow{160^oC} H_2B_4O_7 \xrightarrow{\text{Red hot}} B_2O_3$		
$ZnSO_4.7H_2O \xrightarrow[-H_2O]{70^oC} ZnSO_4.6H_2O \xrightarrow[-5H_2O]{100^oC} ZnSO_4.H_2O \xrightarrow{450^oC} ZnSO_4$		

(iii) **Flame test**

Characteristic flame colour : Certain metals and their salts impart specific colours to Bunsen burner flame.

- Pb imparts pale greenish colour to the flame.
- Cu and Cu salts impart blue or green colour to the flame.
- Borates also impart green colour to the flame.
- Ba and its salts impart apple green colour to the flame.
- Sr imparts crimsen red colour to the flame.
- Ca imparts brick red colour to the flame.
- Na imparts yellow colour to the flame.
- K imparts pink-violet (Lilac) colour to the flame.
- Li imparts crimsen-red, Rb imparts violet and Cs imparts violet colours to the flame.
- Livid- blue flame is given by As, Sb and Bi.

(iv) **Borax bead test :** The transparent glassy bead $(NaBO_2 + B_2O_3)$ when heated with inorganic salt and the colour produced gives some idea of cation present in it.

Colour of bead in oxidising flame	**Colour of bead in reducing flame**	**Basic radical present**
Greenish when hot, blue in cold.	Red and opaque	Cu
Dark green in hot and cold	Same	Cr
Deep – blue	Deep blue	Co
Yellow when hot	Green	Fe
Violet in hot and cold	Colourless	Mn
Brown in cold	Grey or black or opaque	Ni

Microcosmic salt bead test : Microcosmic salt, $Na(NH_4)HPO_4.4H_2O$ is also used to identify certain cations just like borax. When microcosmic salt is heated in a loop of platinum wire, a colourless transparent bead of sodium metaphosphate is formed.

$Na(NH_4)HPO_4.4H_2O \rightarrow Na(NH_4)HPO_4 + 4H_2O$; $Na(NH_4)HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$

Now $NaPO_3$ reacts with metallic oxides to give coloured orthophosphates.

$NaPO_3 + CuO \rightarrow NaCuPO_4$ (Blue); $NaPO_3 + CoO \rightarrow NaCoPO_4$ (Blue); $NaPO_3 + Cr_2O_3 \rightarrow NaPO_3.Cr_2O_3$ (Green)

(v) **Charcoal cavity test**

(a) **Compound fused in cavity directly**	
Nature and colour of bead	**Cation**
Yellow, brittle bead	Bi^{3+}
Yellow, soft bead which marks on paper	Pb^{2+}
White, brittle	Sb^{3+}
White yellow when hot	ZnO
White garlic odour	As_2O_3

Brown	CdO
Grey metallic particles attracted by magnet	Fe, Ni, CO
Maleable beads	Ag and Sn (White),Cu (Red flakes)

(b) **Compound mixed with Na_2CO_3 Crystalline**

Sustance Decrepitates — Salts, NaCl, KCl; — Substance deflagrates — Oxidising agents like NO_3^-, NO_2^- chlorates ; Substance infusible, perform test

(a)

(vi) **Cobalt Nitrate test**

Colour	**Composition**	**Result**
Blue residue	$CoO.Al_2O_3$	Al
Green residue	$CoO.ZnO$	ZnO
Pink dirty residue	$CoO.MgO$	MgO
Blue residue	$NaCoPO_4$	PO_4^{3-} in absence of Al.

(2) **Wet tests for acid radicals :** Salt or mixture is treated with dil. H_2SO_4 and also with conc. H_2SO_4 separately and by observing the types of gases evolved. Confirmatory tests of anions are performed.

Observations with Dilute H_2SO_4

Observations	**Acid Radical**	**Confirmatory test**
Brisk effervescence with evolution of colourless and odourless gas.	CO_3^{2-} (carbonate)	Gas turns lime water milky but milkyness disappears on passing gas inexcess, $Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$; $\underset{\text{lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$; $CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$

Brown fumes	NO_2^- (Nitrite)	Add KI and starch solution blue colour $2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$; $HNO_2 \longrightarrow NO$ (colourless); $2NO + O_2(\text{air}) \longrightarrow 2NO_2$ (brown); $2KI + H_2SO_4 + 2NHO_2 \longrightarrow K_2SO_4 + 2H_2O + 2NO + I_2$; I_2 + starch $\longrightarrow$ blue colour
Smell of rotten eggs (H_2S smell) on heating	S^{2-} (sulphide)	Gas turn lead acetate paper black Sodium carbonate extract $(SE)^*$ + sodium nitroprusside – purple colour, $Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4$; $H_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{(black)}}{PbS} + 2CH_3COOH$; $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$ sodium nitroprusside (purple)
Colourless gas with pungent smell of burning sulphur	SO_3^{2-} (sulphite)	Gas turns acidified $K_2Cr_2O_7$ solution green [different from CO_3^{2-}] since gas also turns lime water milky $Na_2SO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_2$; $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^2 + H_2O$; $Ca(OH)_2 + SO_2 \longrightarrow \underset{\text{(milky)}}{CaSO_3}$
Solution gives smell of vinegar	CH_3COO^- (acetate)	Aq. Solution + neutral $FeCl_3 \rightarrow$ blood red colour $3CH_3COONa + \underset{\text{neutral}}{FeCl_3} \longrightarrow \underset{\text{(red)}}{Fe(CH_3COO)_3} + 3NaCl$
White or yellowish white turbidity on warming	$S_2O_3^{2-}$ (thiosulphate)	Aq. Solution + $AgNO_3 \rightarrow$ white ppt. changing to black (viii) on warming, $Na_2S_2O_3 + 2AgNO_3 \longrightarrow \underset{\text{white ppt.}}{Ag_2S_2O_3} + 2NaNO_3$; $Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{black ppt.}}{Ag_2S} + H_2SO_4$

Observation with concentrated H_2SO_4

Observation	Acid Radical	Confiramatory Test
Colourless pungent gas giving white fumes with aq. NH_4OH	Cl^- (chloride)	Add MnO_2 in the same test tube and heat–pale green Cl_2 gas (i) S.E.+ $HNO_3 + AgNO_3$ solution –white ppt. soluble in aq. NH_3 (ii) Chromyl chloride test (iii)
Reddish brown fumes	Br^- (bromide)	Add Mn_2O and heat –yellowish brown Br_2 gas (iv) S.E.+ $HNO_3 + AgNO_3$ solution –pale yellow ppt. partially soluble aq. NH_3 (v) Layer test (vi)
Violet pungent vapours turning starch paper blue.	I^- (iodide)	S.E.+ $HNO_3 + AgNO_3 \rightarrow$ yellow ppt. insoluble in aq. NH_3 (vii) Layer test (viii)
Brown pungent fumes intensified by the addition of Cu- turnigs.	NO_3^- (nitrate)	Ring test (viii)
Colourless gases turning lime water milky and burning with blue flame.	$C_2O_4^{2-}$ (oxalate)	Acidified $KMnO_4$ solution is decolorised (ix) $S.E. + CH_3COOH + CaCl_2$ solution–white ppt. decolorising acidified $KMnO_4$ solution (x)

Reactions

Chloride : (i) $KCl + \text{conc.}H_2SO_4 \longrightarrow KHSO_4 + HCl$; $HCl + NH_3 \longrightarrow \underset{\text{(white fumes)}}{NH_4Cl}$

$4HCl + MnO_2 \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$

(ii) $KCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + KNO_3$; $AgCl + aq.2NH_3 \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl}$

(iii) Chromyl- chloride test : Chloride + $K_2Cr_2O_7(\text{solid}) + \text{conc. } H_2SO_4 \xrightarrow{\text{heat}}$ reddish brown vapours of chromyl-chloride (CrO_2Cl_2). Pass these vapours into $NaOH$, when yellow Na_2CrO_4 solution is formed. On adding CH_3COOH and $(CH_3COO)_2$ Pb, yellow ppt. of lead chromate $(PbCrO_4)$ is formed.

$KCl + \text{conc.}H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HCl$; $K_2Cr_2O_7 + 2H_2SO_4 \xrightarrow[\text{conc.}]{\Delta} 2KHSO_4 + 2CrO_3 + H_2O$

$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + 2H_2O$; $CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\text{yellow ppt.}}{PbCrO_4}\downarrow + 2CH_3COONa$

Bromide : (iv) $KBr + \text{conc.}H_2SO_4 \xrightarrow{\Delta} KHSO_4 + H$ **;** $4HBr + MnO_2 \xrightarrow{\Delta} Br_2 + 2H_2O + MnBr_2$

(v) $NaBr + AgNO_3 \longrightarrow \underset{\text{pale yellow ppt.}}{AgBr}\downarrow + NaNO_3$ **;** $AgBr + \text{aq. } 2NH_3 \longrightarrow \underset{\text{partially soluble}}{[Ag(NH_3)_2]Br}$

(vi) Layer Test : $S.E. + Cl_2$ water + $CHCl_3 \xrightarrow{\text{shake}}$ yellowish orange colour in $CHCl_3$ layer (CS_2 or CCl_4 can be taken instead of $CHCl_3$); $2NaBr + Cl_2 \longrightarrow 2NaCl + \underset{\substack{\text{orange yellow}\\(\text{soluble in } CHCl_3)}}{Br_2}$

In case of I^-, violet colour of I_2 in $CHCl_3$ layer, $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$ (violet)

Iodide : (vii) $KI + \text{conc.}H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HI$ **;** $2HI + H_2SO_4 \longrightarrow \underset{\text{(violet)}}{I_2} + 2H_2O + SO_2$

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

$4HNO_3 \longrightarrow \underset{\text{brown fumes}}{4NO_2} + O_2 2H_2O$ **;** $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(viii) Ring test : To water extract (all NO_3^- are water soluble) add freshly prepared $FeSO_4$ solution and then conc. H_2SO_4 carefully by the side of the test- tube. A dark brown ring of $[Fe(H_2O)_5\,NO]^{2+}\,SO_4^{2-}$ at the interface between the two liquids is formed.

$2NaNO_3 + H_2SO_4 \longrightarrow 2NaHSO_4 + 2HNO_3$;

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

$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5\,NO]^{2+}\,SO_4^{2-} + H_2O$

Oxalate : $Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO + CO_2$

CO burns with blue flame and CO_2 turns lime water milky.

(ix) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10\,CO_2 + 2Mn^{2+} + 8H_2O$
(violet) colourless

(x) $CaCl_2 + NaC_2O_4 \longrightarrow CaC_2O_4 \downarrow + 2NaCl$ CaC_2O_2 decolourises acidified $KMnO_4$.
white ppt.

Specific test in solution :

(i) **Sulphate :** S.E. add dil. (to decompose CO_3^{2-} until reaction ceases). Add $BaCl_2$ solution. White ppt. insoluble in conc. HNO_3, $BaCl_2 + NaSO_4 \longrightarrow BaSO_4 \downarrow + 2NaCl$
white ppt.

(ii) **Borate :** Ignite the mixture containing borate, conc. H_2SO_4. And ethanol in a china-dish with a burning splinter –green edged flame of ethyl borate.

$2Na_3BO_3 + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3Na_2SO_4$; $H_3BO_3 + 3C_2H_5OH \xrightarrow{\Delta} (C_2H_5O)_3B + 3H_2O$
(conc.) *ethanol* burns with green flame (volatile)

In presence of Cu^{2+}, perform this test in a test tube since Cu^{2+} salts are not volatile.

(iii) $S.E. + HNO_3 +$ ammonium molybdate solution. Heat, yellow crystalline ppt. confirms

$Na_3PO_4 + 12(NH_4)_2MoO_4 + 24HNO_3 \xrightarrow{\Delta} (NH_4)_3PO_4 . 12MoO_3 + 21NH_4NH_3 + NaNO_3 + 12H_2O$
yellow ppt.

Arsenic also gives this test. Hence presence of phosphate should also be checked after group II.

(iv) **Fluoride :** Sand +salt (F^-) +conc. H_2SO_4; heat and bring a water wetted rod in contact with vapours at the mouth of the test tube. A white deposit on the rod shows the presence to F^-

$NaF + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HF$; $SiO_2 + 4HF \xrightarrow{\Delta} SiF_4 + 2H_2O$;

$3SiF_4\,4H_2O \longrightarrow 2H_2SiF_6 + H_4SiO_4$
white

(3) **Wet tests for basic radicals :** Analysis of Basic Radicals

Group	Group reagent	Basic radical	Composition and colour of the precipitate
I	Dilute HCl	Ag^{+} Pb^{2+} Hg^{2+}	$AgCl$: white $PbCl_2$: white $HgCl_2$: white } Chloride insouble cold dilute HCl
II	H_2S in presence of dilute HCl	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+} As^{3+} Sb^{3+} Sn^{2+}	HgS : black PbS : black Bi_2S_3 : black CuS : black CdS : yellow As_2S_3 : yellow Sb_2S_3 : orange SnS : brown SnS_2 : yellow } Sulphides insoluble in dilute HCl
III	NH_4OH in presence of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	$Fe(OH)_3$: reddish brown $Cr(OH)_3$: green $Al(OH_3$: white } Hydroxides are insoluble in NH_4OH
IV	H_2S in presence of NH_4OH	Zn^{2+} Mn^{2+} Co^{2+} Ni^{2+}	ZnS : greenish white MnS : buff CoS : black NiS : black } Sulphides are insoluble in NH_4OH
V	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	$BaCO_3$: white $SrCO_3$: white $CaCO_3$: white } Carbonates are insoluble
VI	$NaHPO_4$	Mg^{2+}	$Mg(NH_4)PO_4$: White
VII	$NaOH$	NH_4^{+}	Ammonia gas is evolved

Chemical reactions involved in the tests of basic radicals

Group I : When dil. HCl is added to original solution, insoluble chlorides of lead, silver mercurous mercury are precipitated.

$Pb(NH_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$; $AgNO_3 + HCl \longrightarrow AgCl + HNO_3$

$Hg(NO_3)_2 + 2HCl \longrightarrow HgCl_2 + 2HNO_3$

Pb^{2+} (lead)

(i) $PbCl_2$ is soluble in hot water and on cooling white crystals are again formed.

(ii) The solution of $PbCl_2$ gives a yellow precipitate with potassium chromate solution which is insoluble in acetic acid but soluble in sodium hydroxide.

$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{yellow ppt.}}{PbCrO_4} + 2KCl$; $PbCrO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$

(iii) The solution of $PbCl_2$ forms a yellow precipitate with potassium iodide solution.

$PbCl_2 + 2KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2} + 2KCl$

(iv) White precipitate of lead sulphate is formed with dilute H_2SO_4. The precipitate is soluble in ammonium acetate, $PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HCl$;

$PbSO_4 + 2CH_3COONH_4 \longrightarrow Pb(CH_3COO)_2 + (NH_4)_2SO_4$

Ag^{+}(silver)

(i) $AgCl$ dissolves in ammonium hydroxide, $AgCl + 2NH_4OH \longrightarrow \underset{\substack{\text{Diammine silver(I)}\\ \text{chloride}}}{Ag(NH_3)_2Cl} + 2H_2O$

(ii) On adding dilute HNO_3 to the above solution, white precipitate is again obtained

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

(iii) On adding KI to the complex solution, yellow precipitate is obtained.

$Ag(NH_3)_2Cl + KI \longrightarrow AgI + KCl + 2NH_3$

Hg_2^{2+} (mercurous)

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

(ii) The black residue dissolves in aqua-regia forming mercuric chloride.

$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$; $2Hg(NH_2)Cl + 6Cl \longrightarrow 2HgCl_2 + 4HCl + N_2$

$Hg + 2Cl \longrightarrow HgCl_2$

(iii) The solution of $HgCl_2$, forms white or slate-coloured precipitate with stannous chloride.

$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{white ppt.}}{Hg_2Cl_2} + SnCl_4$; $Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey ppt.}}{2Hg} + SnCl_4$

(iv) The solution of $HgCl_2$ with copper turning forms a grey deposit.

$HgCl_2 + Cu \longrightarrow \underset{\text{Grey ppt.}}{Hg} + CuCl_2$

Group II : When hydrogen sulphide is passed in acidified solution, the radicals of second group are precipitated as sulphides. The precipitate is treated with yellow ammonium sulphide. The sulphides of IIB are first oxidised to higher sulphides which then dissolve to form thio-compounds.

$Ag_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + As_2S_5$; $Sb_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + Sb_2S_5$

$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2S + SnS_2$

$As_2S_5 + 3(NH_4)S \longrightarrow \underset{\text{Ammonium thioarsenate}}{2(NH_4)_3AsS_4}$; $Sb_2S_5 + 3(NH_4)_2S \longrightarrow \underset{\text{Ammonium thioantimonate}}{2(NH_4)_2SbS_4}$; $SnS_2 + (NH_4)_2S \longrightarrow \underset{\text{Ammonium thiostannate}}{(NH_4)_2SnS_3}$

All the three are soluble.

In case, the precipitate does not dissolve in yellow ammonium sulphide, it may be either HgS or PbS or Bi_2S_3 or CuS or CdS. The precipitate is heated with dilute HNO_3. Except HgS, all other sulphides of IIA are soluble.

$3PbS + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 3S + 4H_2O$;

$Bi_2S_3 + 8HNO_3 \rightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$

$3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$;

$3CdS + 8HNO_3 \rightarrow 3Cd(NO_3)_2 + 2NO + 3S + 4H_2O$

Hg^{2+} (mercuric)

HgS is dissolved in aqua-regia, $3HgS + 2HNO_3 + 6HCl \rightarrow 3HgCl_2 + 3S + 2NO + 4H_2O$

The solution is divided into two parts:

Part I **:** Stannous chloride solution reduces $HgCl_2$ first into white Hg_2Cl_2 and then to grey metallic mercury.

Part II **:** Copper displaces Hg from $HgCl_2$ which gets coated on copper turnings as a shining deposit.

Pb^{2+} (lead)

In case the sulphide dissolves in dilute HNO_3, a small part of the solution is taken. Dilute H_2SO_4 is added. If lead is present, a white precipitate of lead sulphate appears,

$$Pb(NO_3)_2 + H_2SO_4 \rightarrow \underset{\text{(White ppt.)}}{PbSO_4} + 2HNO_3$$

In absence of lead, the remaining solution is made alkaline by the addition of excess of NH_4OH. Bismuth forms a white precipitat of $Bi(OH)_3$, copper forms a deep blue coloured solution while cadmium forms a colourless soluble complex,

$$Bi(NO_3)_3 + 3NH_4OH \longrightarrow \underset{\text{White ppt.}}{Bi(OH)_3} + 3NH_4NO_3;$$

$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\substack{\text{Tetrammine cupric nitrate}\\ \text{(deep blue solution)}}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O;$$

$$Cd(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\substack{\text{Tetrammin e cadmium nitrate}\\ \text{(colourles s solution)}}}{[Cd(NH_3)_4](NO_3)_2} + 4H_2O$$

Bi^{3+} (bismuth) : The precipitate dissolves in dilute HCl, $Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$

Part I **:** Addition of excess of water to $BiCl_3$ solution gives a white precipitate due to hydrolysis.

$$BiCl_3 + H_2O \longrightarrow \underset{\text{Bismuth Oxychloride (White ppt.)}}{BiOCl} + 2HCl$$

Part II **:** The solution of $BiCl_3$ is treated with sodium stannite when a black precipitate of metallic bismuth is formed, $2BiCl_3 + 3\underset{\text{Sod. stannite}}{Na_2SnO_2} + 6NaOH \longrightarrow \underset{\text{Sod. stannate}}{3Na_2SnO_3} + 2Bi + 6NaCl + 3H_2O$

Cu^{2+} (copper) : Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added a chocolate coloured precipitate is formed,

$$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_4COONH_4$$

$$2Cu(NO_3)_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate ppt.}}{Cu_2[Fe(CN)_6} + 4KNO_3$$

Cu^{2+} (cadmium) : H_2S is passed through colourless solution. The appearance of yellow precipitate confirms the presence of cadmium, $Cd(NH_3)_4(NO_3)_2 + H_2S \longrightarrow \underset{\text{Yellow ppt.}}{CdS} + 2NH_4NO_3 + NH_3$

Group IIB : In case the precipitate dissolves in yellow ammonium sulphide, the tests of the radicals arsenic, antimony and tin are performed. The sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphide dissolve while arsenic sulphide remains insoluble.

As^{3+} (arsenic) : The insoluble sulphide is treated with concentrated nitric acid which is then heated with ammonium molybdate. Yellow precipitate of ammonium arsenomolybdate is formed.

$$As_2S_5 + 10HNO_3 \longrightarrow \underset{\text{Arsenic acid}}{2H_3AsO_4} + 10NO_2 + 2H_2O + 5S$$

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

Sn^{2+} or Sn^{4+} (tin) : Solution of sulphide in concentrated HCl is reduced with iron fillings or granulated zinc.

$$\underset{\text{White ppt.}}{SnS_2 + 4HCl \longrightarrow SnCl_4\,2H_2S}\ ;\quad SnCl_4 + Fe \longrightarrow \underset{\text{Grey}}{SnCl_2} + FeCl_4$$

$HgCl_2$ solution is added to above solution which gives first a white precipitate that turns to grey.

$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White ppt.}}{HgCl_2} + SnCl_4$; $Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + \underset{\text{Grey}}{SnCl_4}$

Sb^{2+} (antimony) : Filtrate of sulphide in concentrated HCl is divided into two parts.

Part I : On dilution with excess of water, a white precipitate of antimony oxychloride is obtained.

$SbCl_3 + H_2O \longrightarrow \underset{\text{White ppt.}}{SbOCl} + 2HCl$

Part II : H_2S is circulated. Orange precipitate is formed, $2SbCl_3 + 3H_2S \longrightarrow \underset{\text{Orange ppt.}}{Sb_2S_3} + 6HCl$

Group III : Hydroxides are precipitated on addition of excess of ammonium hydroxide in presence of ammonium chloride.

$AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{Gelatinous ppt.}}{Al(OH)_3} + 3NH_4Cl$; $CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{Green ppt.}}{Cr(OH)_3} + 3NH_4Cl$

$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{Brownish red ppt.}}{Fe(OH)_3} + 3NH_4Cl$

Fe^{3+} (iron) : The brownish red precipitate dissolves in dilute HCl. The solution is divided into two parts.

Part I : $K_4[Fe(CN)_6]$ solution is added which forms deep blue solution or precipitate.

$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$; $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$

Part II : Addition of potassium thiocyanate solution gives a blood red colouration.

$FeCl_3 + 3KCNS \longrightarrow \underset{\text{Blood red colour}}{Fe(CNS)_3} + 3KCl$

Cr^{3+}(chromium) : The green precipitate is fused with fusion mixture $(Na_2CO_3 + KNO_3)$. The fused product is extracted with water or the precipitate is heated with $NaOH$ and bromine water.

$2Cr(OH)_3 + 3KNO + 2Na_2CO_3 \longrightarrow 2Na_2CrO_4 + 3KNO_2 + 2CO_2 + 3H_2O$

or $2NaOH + Br_2 \longrightarrow NaBrO_4 + NaBr + H_2O$; $NaBrO \longrightarrow NaBr + [O]$

$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2NaCrO_4 + 5H_2O$

The solution thus obtained contains sodium chromate. The solution is acidified with acetic acid and treated with lead acetate solution. A yellow precipitate appears.

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

Al^{3+}(aluminium) : The gelatinous precipitate dissolves in $NaOH$, $Al(OH)_3 + NaOH \longrightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$

The solution is boiled with ammonium chloride when $Al(OH)_3$ is again formed.

$$NaAl_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 + NaCl + NH_3$$

Group IV : On passing H_2S through the filtrate of the third group, sulphides of fourth group are precipitated. NiS and CoS are black and insoluble in concentrated HCl while MnS (buff coloured), ZnS (colourless) are soluble in conc. HCl.

Zn^{2+} (zinc) : The sulphide dissolves in HCl. $ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$

When the solution is treated with $NaOH$, first a white precipitate appears which dissolves in excess of $NaOH$

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2} + 2NaCl\ ;\ Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{(Soluble)}}{Na_2ZnO_2} + 2H_2O$$

On passing H_2S, white precipitate of zinc sulphide is formed

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

Mn^{2+} (manganese) : Manganese sulphide dissolves in HCl $MnS + 2HCl \longrightarrow MnCl_2 + H_2S$

On heating the solution with $NaOH$ and Br_2-water, manganese dissolne gets precipitated.

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl\ ;\ Mn(OH)_2 + O \longrightarrow MnO_2H_2O$$

The precipitate is treated with excess of nitric acid and PbO_2 or Pb_3O_4 (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.

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

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

Note: The above test fails in presence of HCl.

Ni^{2+} (nickel) and Co^{2+} (cobalt)

The black precipitate is dissolved in aqua- regia.

$$3Nis + 6HCl + 2HNO_3 \longrightarrow 2NiCl_2 + 2NO + 3S + 2H_2O$$

$$3CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$

The solution is evaporated to dryness and residue extracted with dilute HCl. It is divided into three parts.

Part I : Add NH_4OH (excess) and dimethyl glyoxime. A rosy red precipitate appears, if nickel is present,

$$NiCl_2 + 2\begin{array}{l} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{array} + 2NH_4OH \longrightarrow \begin{array}{l} CH_3 - C = N \\ | \\ CH_3 - C = N \end{array} \quad \begin{array}{l} OH \\ | \\ \downarrow \\ O \end{array} \quad \begin{array}{l} O \\ \uparrow \\ N = C - CH_3 \\ | \\ N = C - CH_3 \\ | \\ OH \end{array} \quad Ni + 2NH_4Cl + 2H_2O$$

Part II : Add CH_3COOH in excess and KNO_2. The appearance of yellow precipite confirms the presence of cobalt.

$$KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2;\ CoCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + 2KCl$$

$$Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2)_3 + NO + H_2O;\ \ Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$$

Part III : Solution containing either nickel or cobalt is treated with $NaHCO_3$ and bromine water. Appearance of apple green colour is observed, the solution is heated when black precipited is formed, which shows the presence of nickel, $CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3H_2O + 3CO_2;\ \ Br_2 + H_2O \longrightarrow 2HBr + O$$

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

$$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2;\ 2NiCO_3 + O \longrightarrow \underset{\text{(Black)}}{Ni_2O_3} + 2CO_2$$

Group V : Ammonium carbonate precipitates V group radicals in the form of carbonates are soluble in acetic acid.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$$

$$SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Sr + CO_2 + H_2O$$

$$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$$

Ba^{2+} (barium) : Barium chromate is insoluble and precipitated by the addition of potassium chromate solution, $Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2CH_3COOK$

Sr^{2+} (Strontium) : Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution, $Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow \underset{\text{White ppt.}}{SrSO_4} + 2CH_3COONH_4$

Ca^{2+} (calcium) : Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.

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

Group VI : In the filtrate of V group, some quantity of ammonium oxalate is added as to remove Ba, Ca and Sr completely from the solution. The clear solution is concentrated and made alkaline with NH_4OH. Disodium hydrogen phosphate is now added, a white precipitate is formed.

$$MgCl_2 + Na_2HPO_4 + NH_4OH \longrightarrow \underset{\substack{\text{Megnesium ammonium phosphate} \\ \text{(White ppt.)}}}{Mg(NH_4)PO_4} + 2NaCl + H_2O$$

NH_4^+ (ammonium) : The substance (salt or mixture) when heated with $NaOH$ solution evolves ammonia.

$$NH_2Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

When a rod dipped in HCl is brought on the mouth of the test tube, white fumes of ammonia chloride are formed, $NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl}$

To the aqueous solution of ammonium salt when Nessler's reagents is added, brown coloured precipitate is formed.

$$2K_2HgI_4 + NH_4Cl + 4KOH \longrightarrow \underset{\substack{\text{Iodide of Millon's base} \\ \text{(Brown ppt.)}}}{\begin{matrix} & & NH_2 \\ & Hg & \diagup \\ & \diagdown & O \\ & Hg & \diagdown \\ & & I \end{matrix}} + 7KI + KCl + 3H_2O$$