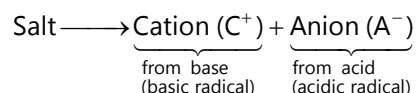


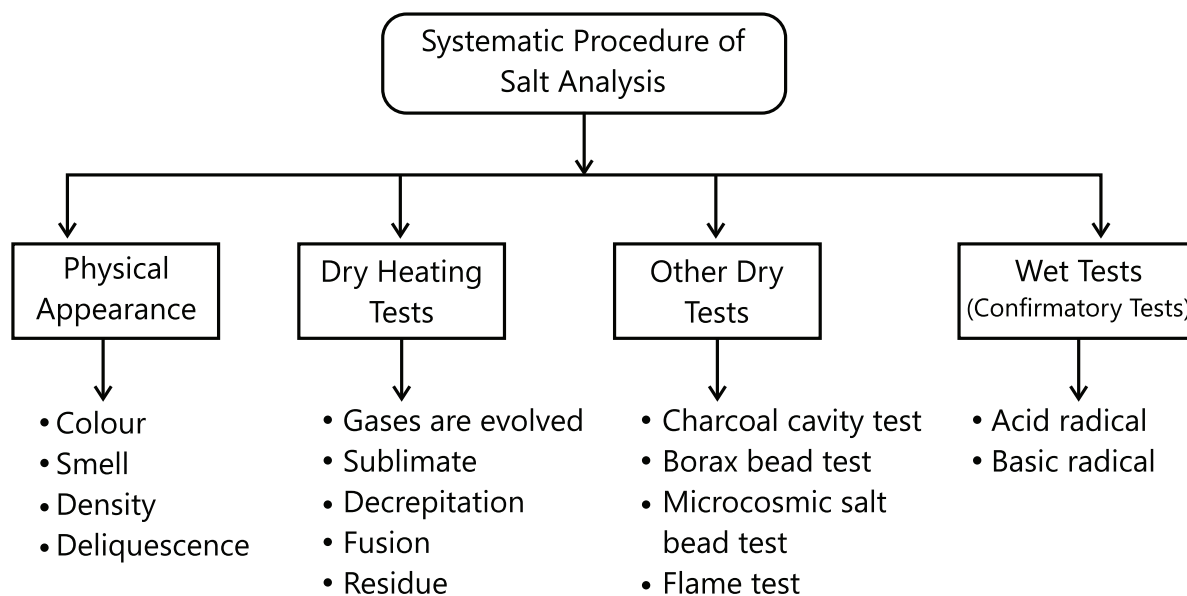
30.

QUALITATIVE ANALYSIS

1. INTRODUCTION



Determination of quality of any salt mixture is called **Qualitative analysis** or **Salt analysis**.



Flowchart 30.1: Procedure of salt analysis

2. PHYSICAL APPEARANCE

Table 30.1: Physical properties

Experiment	Observation	Inference
Color (due to d-d transition of e^- in d-block elements and f-f transition of e^- in f-block elements)	Blue or bluish green Green Reddish brown Pink violet Light pink White	Cu^{2+} or Ni^{2+} Ni^{+2} Fe^{+2} Fe^{+3} Co^{+2} Mn^{+2}
		Absence of above transition metals ions $[\text{Ba}^{+2}, \text{Sn}^{+2}, \text{Ca}^{+2}, \text{Mg}^{+2}, \text{Al}^{+3}, \text{Zn}^{+2} \text{ etc}]$
Smell	Rotten egg Vinegar Ammonical	S^{2-} CH_3COO^- NH_4^+
Density	Heavy Light powder	$\text{Pb}^{+2}, \text{Ba}^{+2}$ can be CO_3^{2-}

Deliquescence: Colorless $\rightarrow \text{Mg}^{+2}, \text{Al}^{+3}, \text{Zn}^{+2}$

Colored $\rightarrow \text{Cu}^{+2}, \text{Fe}^{+3}$

[Deliquescence \rightarrow Substance absorbs moisture from the atmosphere until it dissolves in the absorbed water and forms a solution]

[Hygroscopic \rightarrow Substance absorbs and hold water molecules from the surroundings]
(Water of crystallisation)

3. DRY HEATING TESTS

Table 30.2: Dry tests

Observation	Inference
1. Gas evolved: Colorless + odorless Colorless Rotten egg ($\text{H}_2\text{S} \uparrow$) Vinegar like CH_3COOH Burning sulphur Ammonical	$\text{CO}_3^{2-}, \text{HCO}_3^-$ S^{2-} CH_3COO^- $\text{SO}_3^{2-}, \text{S}_2\text{O}_3^{2-}, \text{S}^{2-}$ NH_4^+
Colored (Pungent Smell) Reddish brown ($\text{NO}_2 \uparrow$) Yellowish green Reddish brown ($\text{Br}_2 \uparrow$) Violet black ($\text{I}_2 \uparrow$)	$\text{NO}_3^-, \text{NO}_2^-$ Cl^- Br^- I^-

Observation	Inference
2. Sublimate: Decomposition of solid substance and deposition in the upper portion of test-tube.	White → NH_4Cl , Hg(I) , Hg(II) chlorides As(III) , Sb(III) or Se(IV) Yellow → S (free sulphur), As_2S_3 (exception to above), Hg(I) / Hg(II) iodides
3. Decripitation: Decomposition with crackling sound on heating. Salts not having water of crystallization.	{halides of alkali metals, $\text{Pb}(\text{NO}_3)_2$ }
4. Fusion: Salts with water of crystallization will fuse generally.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
5. Swelling:	PO_4^{3-} , BO_3^{3-}
6. Residue: Yellow when hot and white when cold Brown when hot and yellow when cold White residue which glows on heating Original salt is blue in color, becomes white on heating Colored salts become brown or black on heating	ZnO PbO Ba^{+2} , Sr^{+2} , Ca^{+2} , Mg^{+2} Cu^{2+} or CuSO_4 Co^{+2} , Fe^{+3} , Fe^{+2} , Cr^{+3} , Cu^{+2} , Ni^{+2} , Mn^{+2} , etc

4. OTHER DRY TESTS

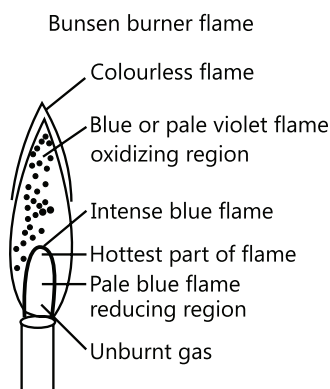


Figure 30.1: Different regions of flame

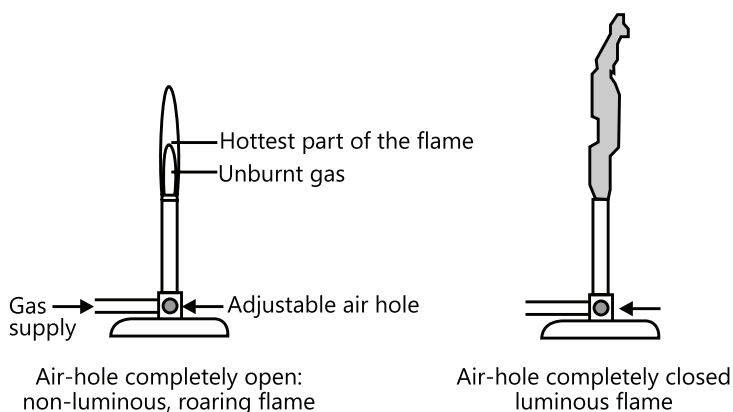
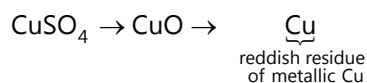
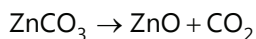
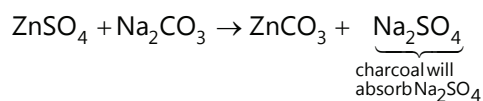


Figure 30.2: Diagram showing non luminous and luminous flame

5. CHARCOAL CAVITY TEST



Metal carbonate decompose on heating to form metal oxides and may further get reduced to metal especially if metals are less reactive (e.g Ag, Cu, gold).

Charcoal absorbs the anion formed by Na.

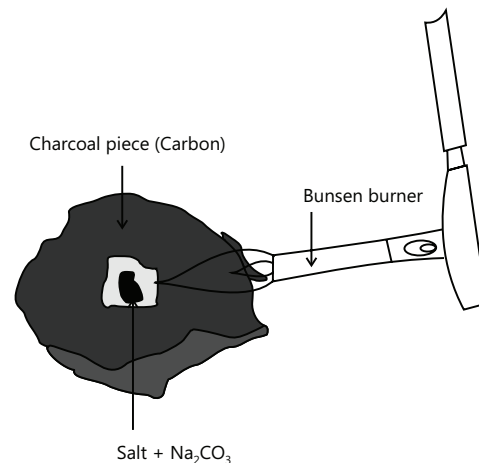


Figure 30.3: Set up for charcoal cavity test

6. COBALT NITRATE TEST

Residue of charcoal cavity test + cobalt nitrate.

If residue in charcoal cavity test is white, then this test is performed.

Table 30.3: Charcoal cavity test

Test	Inference
Residue + $\text{Co}(\text{NO}_3)_2 + \Delta$ E.g. $2\text{Co}(\text{NO}_3)_2 \rightarrow 2\text{CoO} + 4\text{NO}_2 + \text{O}_2$ $\text{ZnO} + \text{CoO} \rightarrow \underbrace{\text{ZnO} \cdot \text{CoO}}_{\left\{ \begin{array}{c} \text{CoZnO}_2 \\ \text{Rinman's green} \end{array} \right\}}$ $\text{ZnO} \cdot \text{CoO}$	Distinct colour residue is obtained for different metal cations. They are mixed cobalt-metal oxides.
$\text{Al}_2\text{O}_3 \cdot \text{CoO}$	Green
$\text{MgO} \cdot \text{CoO}$	Blue
$\text{SnO} \cdot \text{CoO}$	Pink
$\text{SnO} \cdot \text{CoO}$	Bluish

7. FLAME TEST

Generally, alkali and alkaline earth metal salts impart characteristic color to the flame. For this metals only, the electronic de-excitation will be in visible range. To perform this test, the metal salts are converted into their corresponding chlorides [generally, these metal chlorides are volatile] (volatile \rightarrow vaporizes easily)

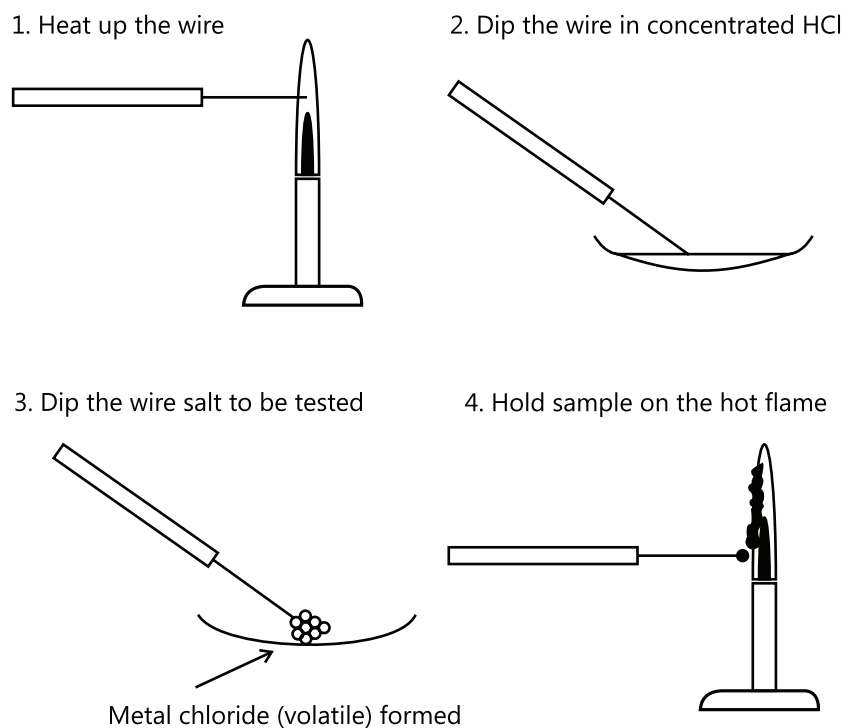


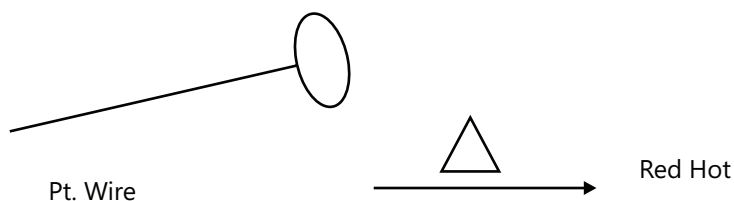
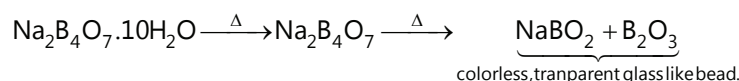
Figure 30.4: Steps to perform flame test

Table 30.4: Flame test for transition metals

Sr. No.	Metals	Color of flame
1	Sr , Li	Crimson Red
2	Ca	Brick Red
3	Ba	Apple Green
4	K	Violet (lilac)
5	Cu	Blue Green
6	Na	Golden Yellow
7	Ni	Brown

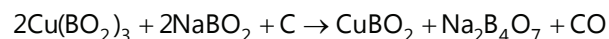
8. BORAX BEAD TEST

Borax \rightarrow salt of boric acid $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$. The free end of Pt wire is coiled into a small loop. This loop is heated in Bunsen flame until it is red hot and then is quickly dipped into powdered form of solid. The adhering solid is held in the hottest part of the flame. At first, salt loses water of crystallization and shrinks on the loop forming a colorless, transparent glass like bead consisting of mixture of sodium meta borate and boric anhydride.

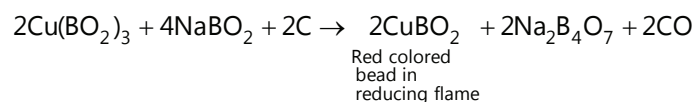
**Figure 30.5:** Heating a Pt wire

The bead is moistened and dipped into the finely powdered subs. (salt) so that a minute of it sticks to the bead and this bead is heated in lower reducing flame, is allowed to cool and the color is observed. This is then heated in an oxidizing flame, allowed to cooled and color is observed again.

Coloured beads are due to the formation of various coloured transition metal borates. The Bead "R" and Bead "O" is due to the variable oxidation states of the metal ions.



Copper(I) metaborate \rightarrow Colorless

**Table 30.5:** Colour of flame of different ions during borax bead test

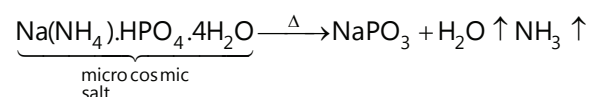
Metal	Color in oxidizing flame		Color in reducing flame	
	When Hot	When Cold	When Hot	When Cold
Copper	Green	Blue	Colorless	Brown red

	Color in oxidizing flame		Color in reducing flame	
Metal	When Hot	When Cold	When Hot	When Cold
Iron	Brown yellow	Pale yellow	Bottle green	Bottle green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Red	Grey	Grey
Nickel	Violet	Brown	Grey	Grey

Non luminous flame = Oxidizing flame.

Luminous flame = Reducing flame.

9. MICROCOSMIC SALT BEAD TEST



(Ammonium sodium phosphate)

$\text{Na}(\text{NH}_4)_2\text{HPO}_4$ when heated first, colorless transparent bead of sodium metaphosphate is obtained.

This combines with metallic oxide to form orthophosphate which are of characteristic colors.

It will have color similar to borax bead test.



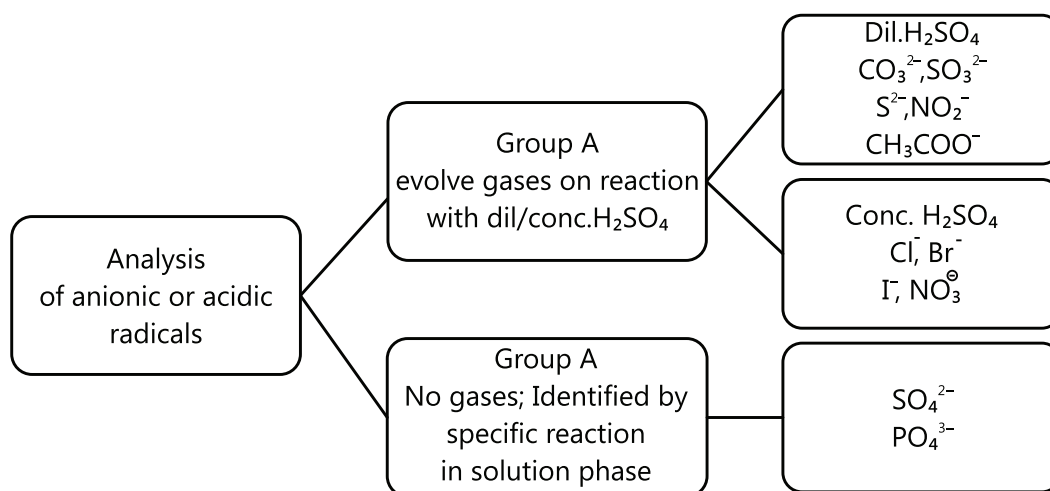
10. CONFIRMATORY TESTS (WET TESTS)

Table 30.6: Wet tests

Sr. No.	Acid radical	Characteristics
1	CO_3^{2-}	All carbonates are ppt. except $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$
2	HCO_3^-	All bicarbonates are soluble (i.e. are found in soln. phase only). Only alkali metals NH_4^+ bicarbonate can be obtained in solid form or can be isolated.
3	SO_3^{2-}	All sulphides are insoluble except group I- NH_4^+
4	S^{2-}	The acid, bisulphide, polysulphides of alkali metal & NH_4^+ are soluble, rest are ppt. Generally S^{2-} ppt are common. $\left. \begin{array}{l} \text{Sn}^{2+} \\ \text{HS}^- \end{array} \right\}$ are normally soluble
5	$\text{NO}_2^-, \text{NO}_3^-, \text{CH}_3\text{COO}^-$	All are soluble except $\text{AgNO}_2, \text{CH}_3\text{COOAg}, \text{CH}_3\text{COOHg}$

Sr. No.	Acid radical	Characteristics
6	Cl^-	All soluble except $\text{Ag}^+, \text{Hg}_2^{2+}, \text{Cu}^+, \text{BiO}^+, \text{SbO}^+, \text{Pb}^{+2}$ soluble in hot water
7	Br^-	All except $\text{Ag}^+, \text{Pb}^{+2}, \text{Cu}^+, \text{Hg}_2^{+2}$ soluble in hot water
8	I^-	All soluble except $\text{Ag}^+, \text{Hg}_2^{2+}, \text{Hg}^{+2}, \text{Cu}^+, \text{Bi}^{+3}, \text{Pb}^{+2}$
9	SO_4^{2-}	All soluble except $\text{Pb}^{+2}, \text{Ba}^{+2}$ $\text{Sr}^{+2}, \text{Ca}^{+2}$ or Hg(II) slightly soluble Basic sulphates of Hg, Bi and Cr are insoluble but these dissolves in dil.HCl or dil. HNO_3 E.g. $\text{HgO} \cdot \text{HgSO}_4 \rightarrow$ insoluble (basic) (neutral salt)
10	PO_4^{3-}	All phosphates are ppt except $\text{Grp I} + \text{NH}_4^+$ slightly soluble Primary phosphates of alkaline earth metals are also soluble (dihydrogen phosphate) E.g. $\text{Mg}(\text{H}_2\text{PO}_4)_2$

11. ANALYSIS OF ANIONIC OR ACIDIC RADICAL

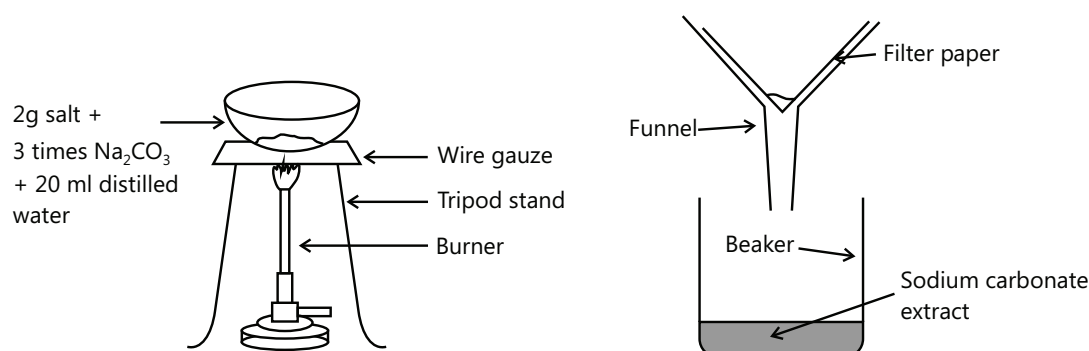


Flowchart 30.2: Analysis of anionic or acidic radical

Table 30.7: Analysis of group A and group B radicals

Group A (dil H_2SO_4)			
Sr. No.	Observation	Gases	Inference
1	Effervescence of a colorless & odorless gas, which turns lime water milky	CO_2	CO_3^{2-} , HCO_3^{2-}
2	Evolution of colorless, suffocating gas with burning sulphur smell which turns $\text{K}_2\text{Cr}_2\text{O}_7$ paper green $\text{Cr}_2\text{O}_7^{2-} + \text{SO}_2 \rightarrow \text{Cr}^{3+}(\text{green})$	SO_2	SO_3^{2-}
3	Evolution of colorless gas with rotten egg smell which turns lead acetate paper black (PbS)	H_2S	S^{2-}
4	Evolution of pungent smelling reddish brown gas which turns starch iodide paper blue $\text{I}^- + \text{NO}_2 \rightarrow \text{I}_2$ (I_2 + starch-blue complex)	NO_2	NO_2^-
5	Evolution of colorless gas having vinegar like smell	CH_3COOH	CH_3COO^-
Group A (conc. H_2SO_4)			
1	Colorless, pungent smelling gas which gives white fumes with rod dipped in NH_3 (conc. H_2SO_4 can't oxidise Cl^- to Cl_2)	HCl	Cl^-
2	Reddish brown gas with pungent smell and intensity of these fumes/vapours increase on addition of a pinch of MnO_2 & these also turn starch iodide paper orange red.	Br_2	Br^-
3	Evolution of violet vapours which turn starch paper blue	I_2	I^-
4	Evolution of brown fumes, intensity of which increase on addition of Cu pieces/turnings and turns starch iodide paper blue.	NO_2	NO_3^-
Group B		Ppt.	
1	Water extract (WE) + sodium carbonate extract + soda extract (SE) + $\text{BaCl}_2(\text{aq})$	White insoluble ppt.	SO_4^{2-}
2	WE + SE + conc. HNO_3 (1N or 2N) + ammonium molybdate	Canary yellow ppt.	PO_4^{3-}

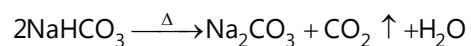
12. SODIUM CARBONATE EXTRACT

**Figure 30.6:** Set up for preparation of sodium carbonate extract

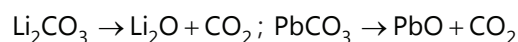
Sodium carbonate reacts with other inorganic salts to form water soluble salt of acid radical and the cation of salt will be ppt. in the form of CO_3^{2-} . SE is used when given salt is partially soluble or insoluble in water. Cation of the salt interfere with the test of acid radical.

Dil. H₂SO₄ grp (CO₃²⁻, CO₂)**Table 30.8:** Sodium carbonate extract test

Sr. No.	Reagent	Observation	Remarks
1	Dil. H ₂ SO ₄ $\text{CO}_3^{2-} + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_4^{2-} + \underbrace{\text{H}_2\text{O} + \text{CO}_2}_{\text{H}_2\text{CO}_3}$	Colorless, Odourless, brisk Effervescence gas	Some carbonates like FeCO ₃ , MgCO ₃ and CaCO ₃ should be powdered for appreciable reaction.
2	Lime water Ca(OH) ₂ $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow$ $\text{Ba(OH)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 \downarrow$	White turbidity (For CaCO ₃ , prolonged passage of CO ₂ dissolves the turbidity) $\text{CaCO}_3 + \text{CO}_2 \rightarrow \text{Ca(HCO}_3)_2$	White turbidity dissolves in dil. acid liberating CO ₂ gas. $\text{CaCO}_3 \downarrow + \underbrace{\text{HCl}}_{\text{dil.}} \rightarrow \text{CaCl}_2 + \text{CO}_2 \uparrow + \text{H}_2\text{O}$
3	MgSO ₄ /BaCl ₂ soln (colorless) $\text{Mg}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MgCO}_3$ $\text{Mg}^{2+} + 2\text{HCO}_3^- \rightarrow \text{Mg(HCO}_3)_2$ $\text{Mg(HCO}_3)_2 \xrightarrow{\Delta} \text{MgCO}_3 \downarrow + \text{CO}_2 + \text{H}_2\text{O}$	White	
4	AgNO ₃ soln. $2\text{Ag}^+ + \text{CO}_3^{2-} \rightarrow \text{Ag}_2\text{CO}_3$ $\text{Ag}_2\text{CO}_3 \xrightarrow[\text{standing}]{\Delta} \text{Ag}_2\text{O} + \text{CO}_2$ $\xrightarrow{\Delta} 2\text{Ag} + \frac{1}{2}\text{O}_2$	White ppt(dissolves in NH ₃ or HNO ₃) Yellow/brown ppt.	Carbonates are more easily polarized Metal carbonates are generally constant and not stable to heat.
5	HgCl ₂ /Hg(NO ₃) ₂ $\text{Hg}^{2+} + \text{HCO}_3^- \rightarrow \text{No reaction}$ $\text{Hg}^{2+} + 3\text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightarrow 3\text{HgO} \cdot \text{Hg(CO}_3)_2 \cdot \text{Hg(CO}_3)_2$ (basic mercuric carbonate)	Reddish brown ppt	
6	Phenolphthalein (HPh)	CO ₃ ²⁻ + HPh = Pink HCO ₃ ⁻ + HPh = Colorless	

ACTION OF HEATBicarbonates $\xrightarrow{\Delta}$ Carbonates

Carbonates $\xrightarrow{\Delta}$ $\underbrace{\text{metal oxide} + \text{CO}_2}_{\left(\text{exception Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+\right)}$



Carbonates of less reactive metals

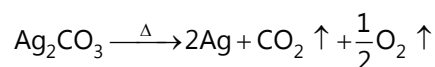
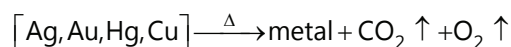


Table 30.9: Confirmatory test for sulphite radical

S. No.	Reagent	Observation	Remarks
SO₃²⁻			
1	Dil. H ₂ SO ₄ $\text{SO}_3^{2-} + \text{H}_2\text{SO}_4 (\text{aq}) \rightarrow \text{SO}_2 \uparrow + \text{H}_2\text{O} + \text{SO}_4^{2-}$	Colorless, suffocating burning sulphur smelling gas.	
	Above gas + lime/baryta water $\text{Ca}(\text{OH})_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 \downarrow + \text{H}_2\text{O}$	Milkiness	If both SO ₃ ²⁻ , CO ₃ ²⁻ are present, then SO ₃ ²⁻ will be oxidized to SO ₄ ²⁻ by K ₂ Cr ₂ O ₇
	On prolonged passage, milkiness disappears $\text{CaSO}_3 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{Ca}(\text{HSO}_3)_2$	No milkiness	(a) and (b) not given by CO ₃ ²⁻
	a) $\underbrace{\text{acidified K}_2\text{Cr}_2\text{O}_7}_{\text{moist filter paper}} + \text{SO}_2 \longrightarrow \underbrace{\text{Cr}^{3+}}_{\text{green}} + \text{SO}_4^{2-}$	Green	
	b) $\text{SO}_2 + \underbrace{\text{IO}_3^-}_{\substack{\text{starch iodate} \\ \text{filter paper}}} \rightarrow \underbrace{\text{I}_2}_{\text{(blue)}} + \text{SO}_4^{2-}$	Blue	
2	BaCl ₂ Soln. $\text{Ba}^{2+} + \text{SO}_3^{2-} \rightarrow \text{BaSO}_3 \downarrow$ On exposure to air, changes to BaSO ₄ . Oxidising agents show such changes. $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}; \text{Br}_2 \rightarrow \text{Br}^-$ $\text{HNO}_3 \rightarrow \text{NO}; \text{MnO}_4^- \rightarrow \text{Mn}^{+2}$	White ppt.	BaSO ₃ dissolves in- (i) Dil. HCl BaSO ₃ + HCl → SO ₂ + H ₂ O + BaCl ₂ (ii) Dil. H ₂ SO ₄ $\text{BaSO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_3^{2-}$
	Sodium nitroprusside $\text{Na}[\text{Fe}(\text{CN})_5\text{NO}] + \text{SO}_3^{2-} \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}]\text{SO}_3$	Rosy-red coloration	If both SO ₃ ²⁻ and S ²⁻ are present, this test is not used.
3	AgNO ₃ Soln. $\text{Ag}^+ + \text{SO}_3^{2-} \longrightarrow \underbrace{[\text{Ag}(\text{SO}_3)]^-}_{\substack{\text{soluble} \\ \text{sulphito argentate}}}$	No Visible change	
	On adding more AgNO ₃ to the above complex $[\text{Ag}(\text{SO}_3)]^- + \text{Ag}^+ \rightarrow \text{Ag}_2\text{SO}_3$	White ppt.	
	Dissolves in excess of SO ₃ ²⁻ $\text{Ag}_2\text{SO}_3 + \text{SO}_3^{2-} \rightarrow 2[\text{Ag}(\text{SO}_3)]^-(\text{aq})$ $2[\text{Ag}(\text{SO}_3)]^- \xrightarrow{\Delta} 2\text{Ag} \downarrow + \text{SO}_4^{2-} + \text{SO}_2$	Dissolves in NH ₃ and dil. HNO ₃	

S. No.	Reagent	Observation	Remarks
4	$\text{Pb}(\text{NO}_3)_2 / \text{Pb}(\text{CH}_3\text{COO})_2$ $\text{Pb}^{+2} + \text{SO}_3^{2-} \rightarrow \text{PbSO}_3 \xrightarrow{\text{O}_2} \text{PbSO}_4$	White	
5	$\text{Zn} + \text{H}_2\text{SO}_4 (\text{aq})$ $\text{Zn} + \text{SO}_3^{2-} + \text{H}^+ \rightarrow \text{Zn}^{+2} + \text{H}_2\text{S} \uparrow + \text{H}_2\text{O}$		

Illustration 1: $\text{M}_2\text{X} \cdot 7\text{H}_2\text{O}(\text{A})$ has water and M_2X (M is monovalent alkaline cation and X is divalent anion) in 1:1 ratio by wt. (A). On reaction with dil. H_2SO_4 gives a gas that turns $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ soln green. Identify (A) and explain.

Sol: Anion $\rightarrow \text{SO}_3^{2-}$ M_2SO_3

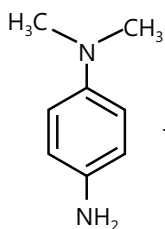
$$2x + 32 + 48 = 18 \times 7 = 126$$

$$2x = 46 \Rightarrow x = 23$$

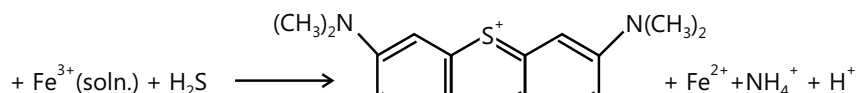


Table 30.10: Confirmatory tests for sulphide and nitrite ion

S^{2-}	Reagent	Observation	Reaction
1	Dil H_2SO_4 $\text{S}^{2-} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S} + \text{SO}_4^{2-}$	Colorless, rotten egg smell.	
	(i) Above gas + $\text{Pb}(\text{NO}_3)_2 / \text{Pb}(\text{CH}_3\text{COO})_2 \xrightarrow{\text{moist filter paper}} \text{PbS} \downarrow$	Black	
	(ii) $\text{Cd}^{+2} + \text{H}_2\text{S} \rightarrow \text{CdS} \downarrow$	Yellow	
	(iii) $\text{Pb}^{+2} \xrightarrow{2\text{OH}^-} \text{Pb}(\text{OH})_2 \downarrow + 2\text{OH}^-$ $\text{PbS} + 2\text{H}_2\text{O} + 2\text{OH}^- \xrightarrow{\text{H}_2\text{S}} [\text{Pb}(\text{OH})_4]^{2-}$	All sulphide One ppt except $\text{Al}_2\text{S}_3 (\text{aq.})$ $\text{H}_2\text{S} + \text{Al}(\text{OH})_3$	
2	Oxidising agent (i) $\text{MnO}_4^- \xrightarrow{\text{H}_2\text{S}} \text{S} \downarrow + \text{Mn}^{+2}$ (ii) $\text{Cr}_2\text{O}_7^{2-} \xrightarrow{\text{H}_2\text{S}} \text{S} \downarrow + \text{Cr}^{3+}$ (iii) $\text{I}_3^- \xrightarrow{\text{H}_2\text{S}} 3\text{I} + \text{S}$	Yellow/white ppt.	
3	Sodium Nitroprusside $\text{S}^{2-} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}]$	Purple colour	
4	Methylene blue test	Methylene blue	



N, N-Dimethyl phenyl diamine



NO_2^-	Reagent	Observation	Reaction
1	Dil. H_2SO_4 Dil. H_2SO_4 + solid nitrites	Pale blue liquid (contains $\text{HNO}_2 + \text{N}_2\text{O}_3$) gives reddish brown NO_2 fumes-Pungent smell)	
2	BaCl_2 soln. $\text{Ba}^{2+} + \text{NO}_3^- \rightarrow$ No Reaction		
3	Conc. AgNO_3 $\text{Ag}^+ + \text{NO}_2^- \longrightarrow \text{AgNO}_2$	White ppt	
4	KI Sol ⁿ (excess) $2\text{NO}_2^- + 3\text{I}^- + 4\text{H}^+ \Rightarrow \text{I}_3^- + 2\text{NO} \uparrow + \text{H}_2\text{O}$	Yellow brown vapours	
5	MnO_4^- (acidic) $\text{NO}_2^- + \text{MnO}_4^- \rightarrow \text{NO}_3^- + \text{Mn}^{+2}$ (Nogas)	Decolourised by a soln. of nitrite	
6	Solid urea $\text{NO}_2^- + \text{urea} \rightarrow \text{N}_2 \uparrow + \text{CO}_2 \uparrow$ acidified		
7	Solid thiourea $(\text{NH}_2)_2\text{CS} + \text{NO}_2^- \rightarrow \text{H}^+ + \text{N}_2 \uparrow + \text{SCN}^- + \text{H}_2\text{O}$ acidified		SCN^- ions can be confirmed by reaction with $\text{FeCl}_3 + \text{HCl}$
	$\text{Fe}^{3+} + 3\text{SCN}^- \longrightarrow \downarrow \text{Fe}(\text{SCN})_3$ (aq.)	Blood red colour	

13. BROWN RING TEST

When nitrite solution is added carefully along the sides of test tube to a saturated solution of FeSO_4 , acidified with acetic acid or dil. H_2SO_4 , a brown ring is formed due to formation of complex of variable composition best represented as

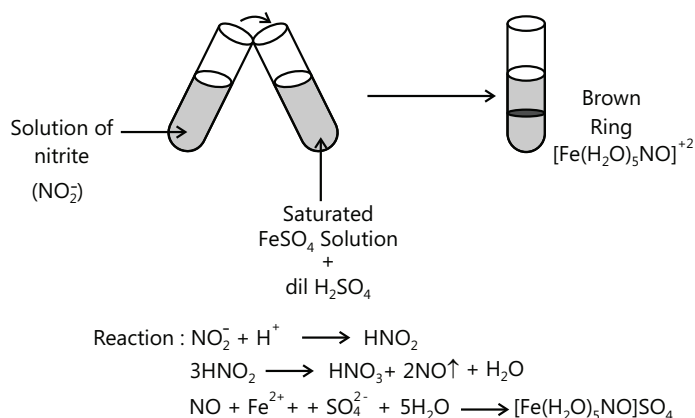
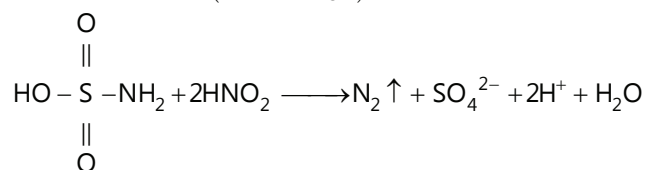


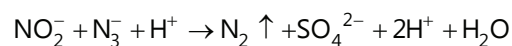
Figure 30.7: Brown ring test for estimation of unsaturation

NO_3^- will also give similar test if NO_2^- and NO_3^- both are present, then NO_2^- can be selectively decomposed by using

Sulphamic acid ($\text{NH}_2 - \text{SO}_3\text{H}$)



Sodium oxide (NaN_3)



Boil the mixture with NH_4Cl

NO_2^- is decomposed to N_2

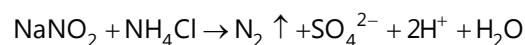


Table 30.11: Confirmatory test for acetate ion

CH_3COO^-	Test	Observation	Remarks
1	$\text{Dil. H}_2\text{SO}_4$ $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$	Vinegar like smell	All acetate are soluble except. CH_3COOAg and CH_3COOHg
2	AgNO_3 Soln: $\text{CH}_3\text{COO}^- + \text{Ag}^+ \rightarrow \text{CH}_3\text{COOAg}$	White ppt.	
3	BaCl_2 soln: $\text{BaCl}_2 + \text{CH}_3\text{COO}^- \rightarrow$ No reaction		
4	$\text{C}_2\text{H}_5\text{OH} + \text{conc. H}_2\text{SO}_4$ (2 – 3ml) (1ml) + 1gm acetate salt + heat	Fruity smell of an ester	
5	Neutral FeCl_3 $6\text{CH}_3\text{COO}^- + 3\text{Fe}^{+3} + 2\text{H}_2\text{O} \rightarrow [\text{Fe}_3(\text{H}_2\text{O})_2](\text{CH}_3\text{COO})_6$	Red blood sol ⁿ	
	Above redblood soln. $\xrightarrow{\Delta} 4\text{H}_2\text{O}$	Reddish brown	

Illustration 2: An aqueous solution of salt containing an anion X^{n-} gives the following reactions: It gives the purple or violet coloration with sodium nitroprusside solution. It liberates a colorless, unpleasant smelling gas with dilute H_2SO_4 which turns lead acetate paper black. Identify the anion (X^{n-}) and write the chemical reactions involved.

Sol: X^{n-} is S^{2-} because

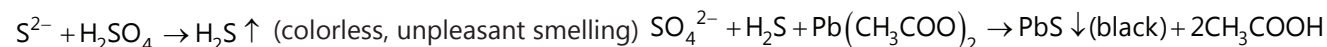
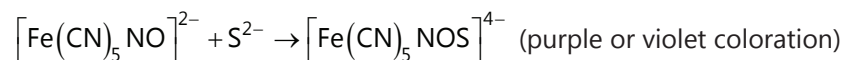


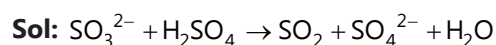
Illustration 3: Sulphite on treatment with dil H_2SO_4 liberates a gas which:

Turns lead acetate paper black

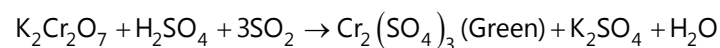
Turns with blue flame

Smells like vinegar

Turns acidified K solution green



SO_2 turns acidified $K_2Cr_2O_7$ solution green



Therefore, (iv) option is correct.

Illustration 4: A colorless pungent smelling gas (x) is obtained when a salt is reacted with dil. H_2SO_4 . The gas (X) responds to the following properties.

It turns lime water milky

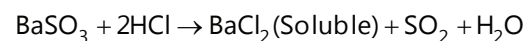
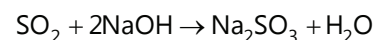
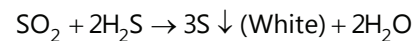
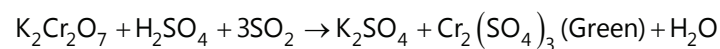
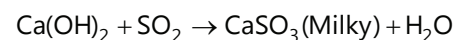
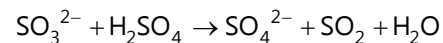
It turns acidified potassium dichromate solution green

It gives white turbidity when H_2S gas is passed through its aqueous solution.

Its aqueous solution in NaOH gives a white ppt. with barium chloride which dissolves in dil HCl liberating (X).

Identify (X) and write the chemical equations involved.

Sol: As gas X turns lime water milky it may be CO_2 or SO_2 . But CO_2 is colorless and odorless, so 'X' may be SO_2 . This is further confirmed by the following reactions:



Conc: H₂SO₄ group**Table 30.12:** Confirmatory test for chloride ion

[Cl ⁻]	Reagent	Observation	Remarks
1	$\text{Cl}^- \xrightarrow{\text{H}_2\text{SO}_4} \text{HCl} \uparrow + \text{HSO}_4^-$ $+ \text{H}_3\text{PO}_4$ \downarrow $\text{HCl} \uparrow + \text{H}_2\text{PO}_4^-$	Dipped rod of NH ₃ + HCl = white fumes of NH ₄ Cl	Being a stronger oxidizing agent, Cl ₂ is not produced.
2	$\text{MnO}(\text{OH})_2 + 2\text{H}_2\text{SO}_4 + 2\text{Cl}^- \rightarrow$ $\text{Mn}^{+2} + \text{Cl}_2 \uparrow + 2\text{SO}_4^{2-} + 3\text{H}_2\text{O}$	Yellowish green; turns iodide paper blue	Permanently bleaches dyes by oxidation
3	$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$ (AgNO_3)	White ppt soluble in NH ₃	
	$\text{AgCl} + \text{AsO}_3^{3-} \text{ (arsenite)} \rightarrow \text{Ag}_3\text{AsO}_3 \downarrow$	Yellow (distinct from AgBr/AgI)	
4	$\text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2$ $\text{Pb}(\text{CH}_3\text{COO})_2$	White ppt-soluble in hot water) conc.HCl/KCl	
5	Chromyl chloride test $\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4 + 4\text{Cl}^- \longrightarrow \text{CrO}_2\text{Cl}_2$	Red vapours	Cl ₂ & K ₂ Cr ₂ O ₇ have equal oxidizing power. Br & I don't give similar test since Cr ₂ O ₇ ²⁻ oxidises Br, I ⁻ to Br ₂ & I ₂
	$\text{CrO}_4^{2-} + \text{Pb}^{+2} \rightarrow \text{PbCrO}_4 \downarrow$	Bright yellow ppt.	

Illustration 5: Comp X imparts a golden yellow flame and shows following reaction

(1) Zn (powder) when boiled with conc. Ag. Solⁿ of X dissolves and H₂ gas is evolved .

(2) When Ag. Solⁿ of X is added to Ag Solⁿ of SnCl₂, a white ppt is obtained which dissolves in excess of X

When dissolved in Zn which is amphoteric, H₂O gas is evolved which signifies Basic nature

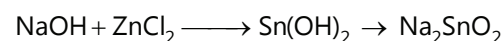
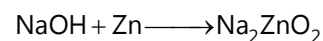
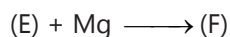
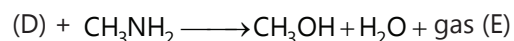
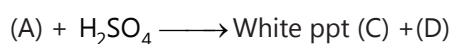
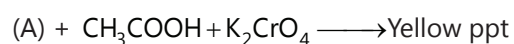
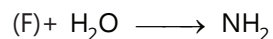


Illustration 6: A gaseous mixture of X, Y, Z when passed into acidified K₂Cr₂O₇, gas X was absorbed and solⁿ turned green. The remainder mixture was passed through lime which turned milky by absorbing gas Y. The residue gas when passed through alc. pyrogallol solution turned black.

Sol: K₂Cr₂O₇ and lime water to differentiate between SO₂ and CO₂ .pyrogallol is used to absorb O₂ gas Q.

Illustration 7: Colourless salt (A) gives apple green flame with conc. HCl, (A) or reaction with dil. H₂SO₄ gives brown fumes (D) turning KI starch paper blue





Identify A to F

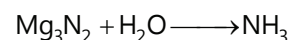
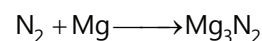
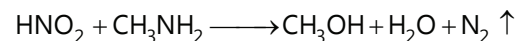
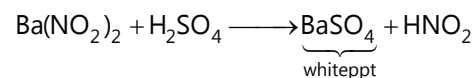


Table 30.13: Confirmatory test for bromide ion

Br ⁻	Reagent	Observation	Remarks
1	i) $2Br^- + SO_4^{2-} + 4H^+ \rightarrow Br_2 + SO_2 + 2H_2O$ ii) $Br^- + H_3PO_4 \rightarrow HBr + H_2PO_4^-$	Reddish brown Br ₂ vapours and pungent smell	
2	Pinch of MnO ₂ added to above test-tube. $Br^- + MnO_2 \rightarrow Br_2 + Mn^{2+} + H_2O$	Intensity of coloured fumes increases. Irritating pungent smell. Bleaches litmus paper. Filter paper dipped in fluorescein dye(yellow) turns red. Turns starch iodide paper blue.	Fluorescence Cl ₂ , Br ₂ , I ₂ , Colourless red violet
3	$Ag^+ + Br^- \rightarrow AgBr \downarrow$ (AgNO ₃)	Pale yellow ppt. Dissolves in conc. NH ₃ , KCN hypo soln.	
4	$Pb^{+2} + 2Br^- \rightarrow PbBr_2$ (Pb-acetate)	White ppt. Soluble in conc. HBr or conc. KBr	
5	$8HNO_3 + 6Br^- \rightarrow 3Br_2 \uparrow + NO \uparrow + 6NO_3^- + 4H_2O$		
6	$K_2Cr_2O_7 + H_2SO_4 + Br^- \longrightarrow Br_2 + Cr^{+3}$		
7	Layer test With Cl ₂ water. i) $\underbrace{Cl_2 \text{ water} + Br^-}_{\text{Dropwise}} \rightarrow Br_2 \uparrow$	Br ₂ vapours colours the sol ⁿ orange red.	
	ii) Above soln. + CHCl ₃ + shake	Upper layer: colourless Lower layer: Red brown Greater solubility of Br ₂ in organic solvent	
	iii) Excess of Cl ₂ water $Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$ $Br_2 + Cl_2 \rightarrow 2BrCl$	Yellow soln.	

Table 30.14: Confirmatory test for Iodide ion

I ⁻	Reagent	Observation	Remarks
1	$\begin{array}{ccc} \boxed{\text{HI} + \text{HSO}_4^-} & & \boxed{\text{I}_2 \uparrow + \text{SO}_2 \uparrow} \\ & \uparrow & \uparrow \\ & \boxed{\text{I} + \text{H}_2\text{SO}_4} & \\ & \downarrow & \downarrow \\ \boxed{\text{I}_2 \uparrow + \text{S} \downarrow} & & \boxed{\text{I}_2 \uparrow + \text{H}_2\text{S} \uparrow} \end{array}$ <p>Feasible only with I⁻, not with Br⁻ HI is a good reducing agent</p>	Violet coloured vapours	All are soluble except Ag ⁺ , Hg ⁺² , Cu ⁺ , Pb ⁺² , Pb ⁺² = soluble in hot water
2	$\text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{I}^- \rightarrow \text{I}_2 + \text{Mn}^{+2}$	Intensity of violet vapours increase	
3	$\underbrace{\text{Ag}^+}_{\text{AgNO}_3} + \text{I}^- \rightarrow \text{AgI} \downarrow$	Yellow. Soluble in KCN, Partially soluble in conc. NH ₃ .	
4	$\underbrace{\text{Pb}^{+2}}_{\text{Pb-acetate}} + 2\text{I}^- \rightarrow \text{PbI}_2 \downarrow$	Yellow	
5	$\text{I}^- + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{Cr}^{3+}$		
6	$\text{KNO}_2 + \text{I}^- + \text{H}_2\text{SO}_4 \rightarrow \text{I}_3^- + \text{NO} \uparrow + \text{H}_2\text{O}$		
7	$\text{HgCl}_2 + 2\text{I}^- \rightarrow \text{HgI}_2 \downarrow + 2\text{Cl}^-$ $\text{HgI}_2 + 2\text{I}^- \rightarrow [\text{HgI}_4]^{2-}$	Scarlet Red	$\text{K}_2[\text{HgI}_4] + \text{KOH}$ Nessler's reagent Used for detection of NH ₄ ⁺ and NH ₃
8	Iodometric Titrations i) $2\text{Cu}^{+2} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2$ ii) $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$		
9	$2\text{FeCl}_3 + 3\text{I}^- \rightarrow 2\text{Fe}^{+2} + \text{I}_3^-$		
10	Layer Test $\text{Cl}_2 \text{ water} + \text{I}^- \rightarrow \text{I}_2$	Brown soln.	
	Above solution. + CHCl ₃	Upper layer: Colourless lower layer: violet layer	
	Excess of Cl ₂ water i) $\text{Cl}_2 + \text{I}^- \rightarrow \text{Cl}^- + \text{I}_2$ $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$ ii) $\text{I}_3^- + 8\text{Cl}_2 + 9\text{H}_2\text{O} \rightarrow 3\text{IO}_3^- + 16\text{Cl}^- + 18\text{H}^+$	Colourless iodic acid formed	

Remark for HgCl_2

$\text{K}_2[\text{HgI}_4] + \text{KOH}$ as alkaline solution of K_2HgI_4 . Is called Nessler's reagent used for detection of NH_4^+ or NH_3

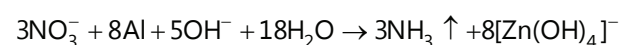
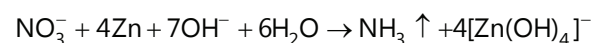
Table 30.15: Confirmatory test for nitrate ion

NO_3^-	Reagent	Observation	Remarks
1	i) $\text{NO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3 + \text{HSO}_4^-$		All nitrate are soluble
	ii) $2\text{HNO}_3 \rightarrow 2\text{NO}_2 \uparrow + \frac{1}{2}\text{O}_2 \uparrow + \text{H}_2\text{O}$	Reddish Brown	
2	Cu turnings + Above soln. \rightarrow $\text{Cu}^{+2} + 2\text{NO} \uparrow + 4\text{SO}_4^{2-} + 4\text{H}_2\text{O}$	Intensity of above colour increases	
3	Diphenyl /blue ring test $\text{NO}_3^- + (\text{C}_6\text{H}_5)_2\text{NH} \downarrow$ $\text{Ph}_2 - \text{N} - \text{N} - \text{Ph}_2$	Blue complex	
4	Brown Ring Test		

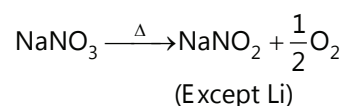
Brown ring Test

3 – 4 ml conc. H_2SO_4 + 2ml of NO_3^- solution + mix + cool the mixture under a stream of cold water + saturated solution of FeSO_4 from the side of the test tube to form a layer on the top of the liquid. A brown ring will formed at the junction of two liquids. This brown ring complex is unstable and decomposes on shaking or on heating into NO and a yellow colour solution of Fe^{+3} ion.

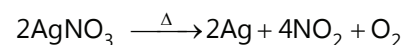
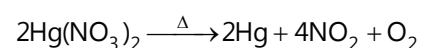
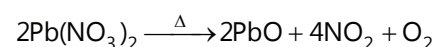
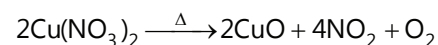
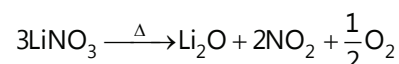
Reduction of NO_3^- or NO_2^- is alkaline medium into NH_4^+ or NH_3 can be done by Zn, Al, Devarda's Alloy (50% Cu, 45% Al, 5% Zn)

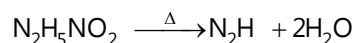
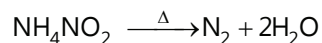
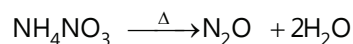
**Action of heat on nitrate**

Alkali metal nitrate $\xrightarrow{\Delta}$ Metal nitrate + O_2



Metal nitrate $\xrightarrow{\Delta}$ Metal oxide + NO_2 + O_2
(Except Na^+ , K^+ , Rb^+ , Cs^+)





Nitrogen oxides are supporter of combustion as these fumes in to N_2 and O_2 .

$\text{N}_2\text{O} \longrightarrow$ Supporter of combustion (better than air)

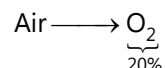
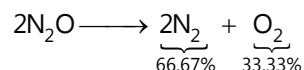


Table 30.16: Confirmatory test for sulphate ion

SO_4^{2-}	Reagent	Observation	Remarks
1	$\underbrace{\text{Ba}^{+2}}_{\text{BaCl}_2} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \downarrow$	White ppt. Insoluble in dil.HCl Soluble in hot, conc. H_2SO_4	All sulphates are soluble except $\text{Ba}^{+2}, \text{Pb}^{+2}, \text{Sn}^{+2}, \text{Ag}^+, \text{Ca}^{+2}$ which are partially soluble.
2	$\underbrace{2\text{Ag}^+}_{\text{AgNO}_3} + \text{SO}_4^{2-} \rightarrow \text{Ag}_2\text{SO}_4 \downarrow$	White ppt.	
3	$\underbrace{\text{Pb}^{+2}}_{\text{Pb}(\text{NO}_3)_2} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \downarrow$	White ppt	
4	$\underbrace{3\text{Hg}^{+2}}_{\text{Hg}(\text{NO}_3)_2} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \downarrow 2\text{HgO} \cdot \text{HgSO}_4$	Yellow ppt.	
5	Match Stick Test $\text{Ba}^{+2} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \downarrow$	White ppt	
	<p>Above ppt + Na_2CO_3</p> <p style="text-align: center;">(s)</p> <p style="text-align: center;">paste</p> <p>Apply paste on wooden piece of match stick+Burn in reducing flame+Dip in sodium nitroprusside soln.</p> <p>i) Paste $\rightarrow \text{BaCO}_3 + \text{Na}_2\text{SO}_4$</p> <p>ii) $\text{Na}_2\text{SO}_4 + 4\text{C} \rightarrow \text{Na}_2\text{S} + 4\text{CO} \uparrow$</p> <p>iii) $\underbrace{\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]}_{\text{S}^{2-}}$</p> <p style="text-align: center;">$\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$</p>	Purple coloration	

Table 30.17: Confirmatory test for phosphate ion

PO_4^{3-}	Reagent	Observation	Remarks
1	$\text{Ba}^{+2} + \text{PO}_4^{3-} \longrightarrow \text{Ba}_3(\text{PO}_4)_2 \downarrow$ BaCl_2	White ppt	
2	$3\text{Ag}^+ + \text{PO}_4^{3-} \longrightarrow \text{Ag}_3\text{PO}_4 \downarrow$ AgNO_3	White ppt Soluble in NH_3 , KCN, hypo, etc.	
3	Magnesia i) $\text{PO}_4^{3-} + \text{Mg}^{+2} + \text{NH}_4^+$ $\text{Mg}(\text{NO}_3)_2$ $\text{Mg}(\text{NH}_4)\text{PO}_4 \downarrow + \text{Mg}^+ \rightarrow \text{Mg}_3\text{PO}_4 \downarrow$	White ppt.	
	ii) $\text{AsO}_4^{3-} + \text{Mg}^{+2} + \text{NH}_4^+$ $\text{Mg}(\text{NH}_4)\text{AsO}_4 \downarrow + \text{Mg}^+ \rightarrow \text{Mg}_3\text{AsO}_4 \downarrow$	White ppt Brownish red ppt	
4	$\text{PO}_4^{3-} + \text{conc. HNO}_3 + \text{ammonium molybdate (excess)}$ $(\text{NH}_4)_2\text{MoO}_4 \triangle \downarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \downarrow$ $+ \text{H}_2\text{O} + \text{NH}_4\text{NO}_3 + \text{NaNO}_3$	Canary yellow ppt.	

Table 30.18: Confirmatory test for borate ion

BO_3^{3-}	Reagent	Observation	Remarks
	0.2g salt + Conc. H_2SO_4 (1ml) + $\text{C}_2\text{H}_5\text{OH}$ (4-5ml) + Ignite on a Bunsen flame. $2\text{Na}_3\text{BO}_3 \xrightarrow[-3\text{Na}_2\text{SO}_4]{3\text{H}_2\text{SO}_4} 2\text{H}_3\text{BO}_3$ $2\text{H}_3\text{BO}_3 \xrightarrow[-3\text{H}_2\text{O}]{3\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{BO}_3$	Green edged flame	
Group O			
1	$\text{NH}_4^+ + \text{dil. NaOH}$ \downarrow $\text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{Na}^+$	- Ammoniacal smell - White fumes (NH_4Cl) with HCl - HgNO_3 on filter paper becomes black (Hg) - Red litmus turns blue - ($\text{MnCl}_2 + \text{H}_2\text{O}_2$) on filter paper becomes brown black ($\text{MnO}_2[\text{MnO}(\text{OH})_2]$)	
2	$\text{NH}_4^+ + \text{K}_2[\text{HgI}_4]$ $\xrightarrow{+\text{OH}^-}$ Nessler's reagent \downarrow $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{I}$		

3	$3\text{NH}_4^+ + \text{Na}_3[\text{Co}(\text{NO}_2)_6]$ \downarrow $(\text{NH}_4)_3[\text{Co}(\text{NO}_2)_6] \downarrow + 3\text{Na}^+$	Yellow ppt	
4	$2\text{NH}_4^+ + \text{Na}_2[\text{PtCl}_6]$ \downarrow $(\text{NH}_4)_2[\text{PtCl}_6] \downarrow + 2\text{Na}^+$	Yellow ppt	NH_4^+ salts are insoluble

Illustration 8: A compound (A) of S, Cl and O has vapour density of 67.5 (approx). It reacts with water to form two acids and reacts with KOH to form two salts (B) and (C) while (B) gives white ppt. with AgNO_3 solution and (C) gives white ppt. with BaCl_2 solution. Identify (A), (B) & (C).

Sol: As mixture gives white ppt. with BaCl_2 and AgNO_3 , it should be SO_4^{2-} and Cl^- ions. As SO_2Cl_2 when dissolves in water gives, a mixture of H_2SO_4 & HCl which then reacts with KOH to form KCl and K_2SO_4 . Therefore (A) is SO_2Cl_2 and (B) & (C) are K_2SO_4 and KCl respectively.

Vapour density of SO_2Cl_2 = molecular weight/2.

Vapour density of SO_2Cl_2 = $135/2 = 67.5$.

Illustration 9: $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{NaI} + \dots\dots[\text{X}]$, [X] is:

(A) $\text{Na}_2\text{S}_4\text{O}_6$ (B) Na_2SO_4 (C) Na_2S (D) Na_3ISO_4

Sol: $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$

Therefore A is correct option.

Illustration 10: Column I and II contains four entries each. Entries of column I are to be matched with some entries of column II. Each entry of column I may have the matching with one or more than one entries of column II.

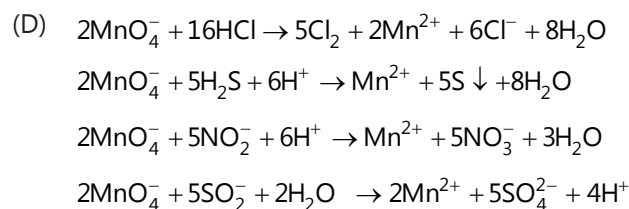
Column I	Column II
(A) Colourless gas evolved on addition of dil. H_2SO_4	(p) Cl^-
(B) White ppt. on addition of AgNO_3	(q) S^{2-}
(C) Ppt. with solution containing Pb^{+2} ions	(r) NO_2^-
(D) Its acidified salt solution decolourises pink KMnO_4 solution.	(s) SO_3^{2-}

Sol: A \rightarrow p, q, s; B \rightarrow p, r, s; C \rightarrow p, q, s; D \rightarrow p, q, r, s

(A) $\text{Cl}^- + \text{H}_2\text{SO}_4 \rightarrow \text{HCl} \uparrow$ (Colourless) + HSO_4^- ; $\text{S}^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} \uparrow$ (Colourless)
 $\text{NO}_2^- + 2\text{H}^+ \rightarrow \text{NO}_2 \uparrow$ (Redish brown) + H_2O ; $\text{SO}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 \uparrow$ (Colourless) + H_2O

(B) $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$ (White); $\text{Ag}^+ + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S} \downarrow$ (Black)
 $\text{Ag}^+ + \text{NO}_2^- \rightarrow \text{AgNO}_2 \downarrow$ (White); $2\text{Ag}^+ + \text{SO}_3^{2-} \rightarrow \text{Ag}_2\text{SO}_3 \downarrow$ (White)

(C) $\text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2 \downarrow$ (White); $\text{Pb}^{2+} + \text{S}^{2-} \rightarrow \text{PbS} \downarrow$ (Black)
 $\text{Pb}^{2+} + \text{NO}_2^- \rightarrow \text{PbNO}_2$ (Soluble); $\text{Pb}^{2+} + \text{SO}_3^{2-} \rightarrow \text{PbSO}_3 \downarrow$ (White)



Classification of Cation Radicals: For the purpose of systematic qualitative analysis, the cations are classified into various groups and the classification is based on whether the cation with the given group reagent and forms a ppt or not

Table 30.19: Classification of cation radicals

Group	Cation	Reagent	Observation
Zero	NH_4^+	NaOH or Ca(OH)_2 , heat if required	Ammonium gas is evolved.
I.	$\text{Ag}^+, \text{Hg}_2^{+2}, \text{Pb}^{+2}$	dil. HCl	$\left. \begin{array}{l} \text{AgCl} \\ \text{Hg}_2\text{Cl}_2 \\ \text{PbCl}_2 \end{array} \right\}$ White
II (A)	$\text{Cu}^{+2}, \text{Hg}^{+2}, \text{Pb}^{+2}, \text{Bi}^{+3}, \text{Cd}^{+2}$	H_2S gas in dil. HCl insoluble in YAS (Yellow Ammonium Sulphide) $(\text{NH}_4)_2\text{Sn}$	$\left. \begin{array}{l} \text{Cu}^{+2} \\ \text{Hg}^{+2} \\ \text{Pb}^{+2} \\ \text{Bi}^{+3} \end{array} \right\}$ $\left. \begin{array}{l} \text{CuS} \\ \text{HgS black} \\ \text{PbS} \\ \text{Bi}_2\text{S}_3 \end{array} \right\}$ $\text{CdS} \rightarrow$ yellow CdS
II (B)	$\text{Sn}^{+2}, \text{Sn}^{+4}, \text{As}^{+3}, \text{As}^{+5}, \text{Sb}^{+3}, \text{Sb}^{+5}$		$\text{SnS} \rightarrow$ Brown ppt. $\text{SnS}_2, \text{As}_2\text{S}_3 \rightarrow$ Yellow $\text{Sb}_2\text{S}_3 \rightarrow$ Orange $\text{As}_2\text{S}_5 \rightarrow$ Yellow solution $\text{Sb}_2\text{S}_5 \rightarrow$ Orange solution
III	$\text{Fe}^{+3}, \text{Al}^{+3}, \text{Cr}^{+3}$	NH_4OH in presence of NH_4Cl	$\text{Fe(OH)}_3 \rightarrow$ Reddish brown $\text{Al(OH)}_3 \rightarrow$ Gelatinous white $\text{Cr(OH)}_3 \rightarrow$ Dirty/ grey green
IV	$\text{Mn}^{+2}, \text{Co}^{+2}, \text{Zn}^{+2}, \text{Ni}^{+2}$	H_2S in presence of NH_4OH and NH_4Cl	$\text{NiS}, \text{CoS} \rightarrow$ Black $\text{ZnS} \rightarrow$ Dirty black $\text{MnS} \rightarrow$ Buff colored (light pink)
(V)	$\text{Ba}^{+2}, \text{Sr}^{+2}, \text{Ca}^{+2}$	$(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4OH and NH_4Cl Na_2HPO_4 in presence of NH_4OH and NH_4Cl	$\left. \begin{array}{l} \text{BaCO}_3 \\ \text{SrCO}_3 \\ \text{CaCO}_3 \end{array} \right\}$ White ppt $\text{Mg(NH}_4\text{)PO}_4 \downarrow$ (White)

Preparation of Original Solution (O.S): Original solution is used for the analysis if basic radicals except NH_4^+ . It is prepared by dissolving given salt or mixture in a suitable solvent as follows:

1. H_2O 2. Dil. HCl 3. Conc. HCl

Salt or Mixt. + $\text{H}_2\text{O} \xrightarrow{\Delta}$ Soluble (then H_2O is suitable solvent)

If given salt or mixture is insoluble in H_2O , then it is dissolved in dil. HCl.

Salt or Mixt. + dil. HCl $\xrightarrow{\Delta}$ Soluble (then dil HCl is taken as solvent)

If given salt or mixture is insoluble in dilute HCl, then it is dissolved in conc. HCl.

Salt or Mixt. + conc. HCl $\xrightarrow{\Delta}$ Soluble

In this way after selecting suitable solvent, given salt or mixture is dissolved in small quantity in the solvent and filtered. Obtained filtered is called as original solution (O.S.) and that is used for the detection of basic radicals except NH_4^+ .

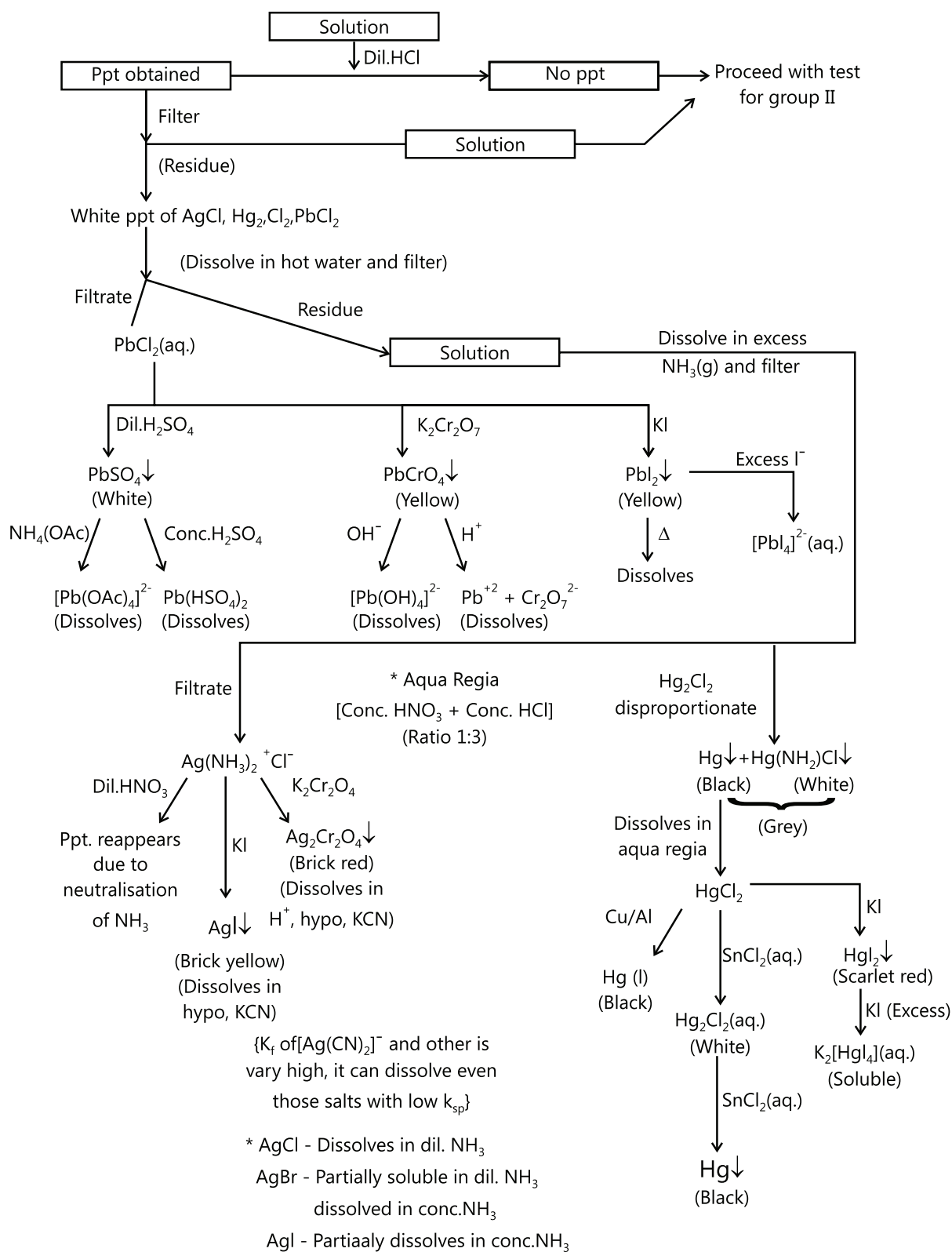
Remarks:

1. Pb^{+2} is placed in both group I and group II because PbCl_2 is soluble in water and all of Pb^{+2} is not separated by addition of HCl.
2. In group II, only those sulphides are ppt. which have very low values of K_{sp} for this. H_2S gas is added in acidic medium. Dil. HNO_3 can't be added to prevent oxidation of H_2S to sulphur. (It is yellow and may be confused with CdS). Dil. H_2SO_4 can't be added to prevent the formation of ppt. of sulphates.
3. Before proceeding with test of group III, the solution is boiled to remove dissolved H_2S gas to prevent ppt. of sulphides in group III. Then dil. HNO_3 is added as we don't have to perform tests with Fe^{+2} . HNO_3 oxidises Fe^{+2} to Fe^{+3} .
4. NH_4OH is added in presence of NH_4Cl to decrease the degree of dissociation of NH_4OH by common ion effect. So, only those salts are ppt. which have low values of K_{sp} . $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{CO}_3$ cannot be used in place of NH_4Cl to prevent the ppt of carbonates and sulphates.
5. For the test of group IV, H_2S is added in presence of NH_4OH to increase the degree of dissociation of H_2S resulting in increase of S^{2-} conc. So that sulphides of higher values of K_{sp} can be separated.
6. We can't use NaCO_3 in test of group V as Na_2CO_3 is highly soluble resulting in high conc. of CO_3^{2-} which may lead to ppt of group VI, Mg^{+2} ions.

Table 30.20: Classification of cation radicals

Group 0:		
Reagent	Observation	Remarks
1. Dil. NaOH	$\text{NH}_4^+ + \text{dil. NaOH} \longrightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{Na}^+$	Ammoniacal smell forms white fumes in presence of HCl. $\text{NH}_3(\text{g}) + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}(\text{g})$ (dense White fumes) Filter paper dipped in HgNO_3 (aq.) becomes black $\text{HgNO}_3 \xrightarrow{\text{NH}_3} \text{Hg} + \text{Hg}(\text{NH}_2)\text{NO}_3 \downarrow$ <div style="display: flex; justify-content: space-around; width: 100%;"><div>Black</div><div>white</div></div>
		Filter paper dipped in red litmus become blue Filter paper dipped in $\text{MnCl}_2 + \text{H}_2\text{O}_2$ (aq.) Becomes brown black due to formation of MnO_2 [$\text{MnO}(\text{OH})_2$]
2. Test with K_2HgI_4	$\underbrace{\text{NH}_4^+ + \text{K}_2[\text{HgI}_4] + \text{OH}^-}_{\text{Nessler's reagent}} \longrightarrow \underbrace{\text{Hg}(\text{NH}_2)\text{I} + 2\text{K}^+}_{\text{basic mercuric amido iodide}}$	Yellow / brown
3. Test with $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	$3\text{NH}_4^+ + \text{Na}_3[\text{Co}(\text{NO}_2)_6] \rightarrow (\text{NH}_4)_3[\text{Co}(\text{NO}_2)_6] + 3\text{Na}^+$ <div style="text-align: center;">Yellow</div>	Yellow ppt.
4. $\text{Na}_2[\text{PtCl}_6]$ or $\text{H}_2[\text{PtCl}_6]$ {sodiumchloroplatinate} or {chloroplatinate acid}	$2\text{NH}_4^+ + \text{Na}_2[\text{PtCl}_6] \longrightarrow (\text{NH}_4)_2[\text{PtCl}_6] \downarrow + 2\text{Na}^+$	Yellow ppt Generally, NH_4^+ salts are insoluble.

Group I



Flowchart 30.3: Systematic path for the analysis of group I radicals

Table 30.21: Analysis of group I and group II radical

Pb ²⁺	Test/Reagents	Observation
	Dilute HCl solution: $\text{Pb}^{2+} + \text{HCl} \rightarrow \text{PbCl}_2 \downarrow (\text{white}) + 2\text{H}^+$ $\text{PbCl}_2 \downarrow + 2\text{Cl}^- \rightarrow [\text{PbCl}_4]^{2-}$	White ppt is formed in cold solution. White ppt is soluble in hot water. White ppt is also soluble in concentrated HCl or concentrated KCl.
	Sodium hydroxide solution $\text{Pb}^{2+} + 2\text{OH}^- \rightarrow \text{Pb}(\text{OH})_2 \downarrow$; $\text{Pb}(\text{OH})_2 \downarrow + 2\text{OH}^- \rightarrow [\text{Pb}(\text{OH})_4]^{2-}$ $[\text{Pb}(\text{OH})_4]^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{PbO}_2 \downarrow + 2\text{H}_2\text{O} + 2\text{OH}^-$ $[\text{Pb}(\text{OH})_4]^{2-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{PbO}_2 \downarrow + 2\text{H}_2\text{O} + 2\text{SO}_4^{2-}$	White ppt is formed which is soluble in excess of the reagent. Black/brownish black
	Potassium iodide solution $\text{PbCl}_2 + 2\text{KI} \rightarrow \text{PbI}_2 \downarrow + 2\text{KCl}$; $\text{PbI}_2 + \text{KI} \longrightarrow \text{K}_2[\text{PbI}_4] \downarrow$	A yellow ppt is formed which is soluble in excess more conc.(6M) soln of the reagent. Yellow ppt of PbI ₂ is moderately soluble in boiling water to give a colourless solution. Yellow ppt reappears on dilution with water. Yellow ppt of PbI ₂ does not dissolve in excess of dilute solution of KI.
	Potassium chromate solution (in neutral, acetic or ammonia solution) $\text{PbCl}_2 + \text{K}_2\text{CrO}_4 \rightarrow \text{PbCrO}_4 \downarrow + 2\text{KCl}$ $2\text{PbCrO}_4 + 2\text{H}^+ \rightleftharpoons 2\text{Pb}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ $\text{PbCrO}_4 + 4\text{OH}^- \rightleftharpoons [\text{Pb}(\text{OH})_4]^{2-} + \text{CrO}_4^{2-}$	A yellow ppt is formed. Yellow ppt is soluble in sodium hydroxide and HNO ₃ (nitric acid). Both reversible reactions on buffering the solution with ammonia or acetic acid respectively, PbCrO ₄ reprecipitates.
	Ammonia solution $\text{Pb}^{2+} + 2\text{NH}_4\text{OH} \rightarrow \text{Pb}(\text{OH})_2 \downarrow + 2\text{NH}_4^+$	With ammonia solution, Pb ²⁺ gives a white ppt of lead hydroxide
	Dilute H₂SO₄: $\text{PbCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 \downarrow + 2\text{HCl}$ $\text{PbSO}_4 \downarrow + 4\text{CH}_3\text{COO}^- \rightarrow [\text{Pb}(\text{CH}_3\text{COO})_4]^{2-} + \text{SO}_4^{2-}$ $\text{PbSO}_4 \downarrow + 2\text{C}_4\text{H}_4\text{O}_6^{2-} \rightarrow [\text{Pb}(\text{C}_4\text{H}_4\text{O}_6)_2]^{2-} + \text{SO}_4^{2-}$ $\text{PbSO}_4 \downarrow + \text{H}_2\text{SO}_4 \rightarrow \text{Pb}^{2+} + 2\text{HSO}_4^-$	White ppt is formed which is soluble in more conc. ammonium acetate (6M) solution or ammonium tartrate in the presence of ammonia. Hot, conc. H ₂ SO ₄ dissolves the ppt due to the formation of PbHSO ₄ .

Hg_2^{2+}	Test/Reagents	Observation
	Dilute HCl solution $\text{Hg}_2^{2+} + 2\text{HCl} \rightarrow \text{Hg}_2\text{Cl}_2 \downarrow (\text{white}) + 2\text{H}^+$	White ppt is formed in cold solution.
	Ammonia solution $2\text{Hg}_2\text{Cl}_2 + 4\text{NH}_4\text{OH} \rightarrow \text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{Cl} \downarrow + \text{Hg} \downarrow + 3\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$	A mixture of mercury metal (black ppt) and basic mercury (II) amido chloride (white ppt) is formed.
	Dissolution of white ppt. Hg_2Cl_2 in aquaregia $3\text{Hg}_2\text{Cl}_2 + 2\text{HNO}_3 + 6\text{HCl} \rightarrow 6\text{HgCl} + 2\text{NO} + 4\text{H}_2\text{O}$ $2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{SnCl}_4$; $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \rightarrow 2\text{Hg} \downarrow (\text{black}) + 2\text{SnCl}_4$ $\text{HgCl}_2 + \text{KI} \rightarrow \text{HgI}_2 \downarrow + 2\text{KCl}$; $\text{HgI}_2 + \text{KI}(\text{excess}) \rightarrow \text{K}_2[\text{HgI}_4] (\text{soluble})$ $\text{HgCl}_2 + \text{Cu} \rightarrow \text{Hg} \downarrow + \text{CuCl}_2$	(a) Stannous chloride test: White ppt is formed which finally turns to black. (b) Potassium iodide test: Scarlet/red ppt is formed which is soluble in excess of the reagent. (c) Copper chips test: Shining grey deposition of mercury on copper chips is formed.
	Potassium iodide solution: A green ppt is formed. $\text{Hg}_2^{2+} + 2\text{I}^- \rightarrow \text{Hg}_2\text{I}_2 \downarrow$ $\text{Hg}_2\text{I}_2 + 2\text{I}^- \rightarrow [\text{HgI}_4]^{2-} + \text{Hg} \downarrow (\text{finely divided})$ $\text{Hg}_2\text{I}_2 \rightarrow \text{HgI}_2 \downarrow + \text{Hg} \downarrow$	Green ppt in excess of reagent undergoes disproportionation reaction and a soluble $[\text{HgI}_4]^{2-}$ ions and black mercury are formed. Boiling the mercury (I) iodide ppt with water, disproportionation takes place and a mixture of red mercury (II) iodide ppt and black mercury is formed.
	Potassium chromate solution $\text{Hg}_2^{2+} + \text{CrO}_4^{2-} \rightarrow \text{Hg}_2\text{CrO}_4 \downarrow$; $\text{Hg}_2\text{CrO}_4 + 2\text{OH}^- \rightarrow \text{Hg}_2\text{O} \downarrow + \text{CrO}_4^{2-} + \text{H}_2\text{O}$	A red crystalline ppt is formed which turns black when solution of sodium hydroxide is added.
	Potassium cyanide solution $\text{Hg}_2^{2+} + 2\text{CN}^- \rightarrow \text{Hg} \downarrow + \text{Hg}(\text{CN})_2 (\text{soluble})$	A black ppt of mercury is obtained
(Ag ⁺)	Dilute hydrochloric acid/soluble chlorides $\text{Ag}^+ + \text{HCl} \rightarrow \text{AgCl} \downarrow + \text{H}^+$ $\text{AgCl} + \text{Cl}^- \longrightarrow [\text{AgCl}_2]^-$ $\text{AgCl} + 2\text{NH}_3 \longrightarrow [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$ $[\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{HNO}_3 \rightarrow \text{AgCl} \downarrow + 2\text{NH}_4\text{NO}_3$	White ppt Soluble in conc.HCl On dilution with water, the equilibrium shifts back to the left and the ppt reappears. Dil.ammonia solution dissolves the ppt forming a soluble complex. Dil.HNO ₃ or HCl neutralizes the excess ammonia and the ppt reappears because the equilibrium is shifted backwards.
	Potassium iodide solution $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI} \downarrow$ $\text{AgI} + 2\text{CN}^- \rightarrow [\text{Ag}(\text{CN})_2]^- + \text{I}^-$; $\text{AgI} + 2\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + \text{I}^-$	A bright yellow ppt. is formed which is insoluble in dilute ammonia but partially soluble in concentrated ammonia. The yellow ppt. is soluble in KCN and in Na ₂ S ₂ O ₃ .

	Potassium chromate solution $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow$ $2\text{Ag}_2\text{CrO}_4 + 2\text{H}^+ \rightleftharpoons 4\text{Ag}^+ + \text{Cr}_2\text{O}_7^{2-}$ $2\text{Ag}_2\text{CrO}_4 + 4\text{NH}_3 \rightarrow 2[\text{Ag}(\text{NH}_3)_2]^+ + \text{CrO}_4^{2-}$	Red ppt. is formed which is soluble in dilute HNO_3 and in ammonia solution.
	Disodium hydrogen phosphate solution $3\text{Ag}^+ + \text{HPO}_4^{2-} \rightarrow \text{Ag}_3\text{PO}_4 \downarrow + \text{H}^+$	In neutral solution a yellow ppt. is formed with the reagent. The yellow ppt. is soluble in nitric acid and ammonia solution.
	Hydrazine sulphate (saturated) $4[\text{Ag}(\text{NH}_3)_2]^+ + \text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{SO}_4 \rightarrow$ $4\text{Ag} \downarrow + \text{N}_2 \uparrow + 6\text{NH}_4^+ + 2\text{NH}_3 + \text{SO}_4^{2-}$	With diammineargentate (I) reagent forms finely divided silver which adheres to the cleaned glass walls of the test tube forming an attractive mirror.
	Ammonia solution $2\text{Ag}^+ + 2\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} \downarrow + 2\text{NH}_4^+$ $\text{Ag}_2\text{O} \downarrow + 4\text{NH}_3 + \text{H}_2\text{O} \rightarrow 2[\text{Ag}(\text{NH}_3)_2]^+ + 2\text{OH}^-$	Brown ppt. is formed Ppt. dissolves in ammonia.
Hg²⁺	Test/Reagents	Observation
	Precipitation with H₂S in acidic medium $\text{Hg}^{2+} + \text{H}_2\text{S} \xrightarrow{\text{H}^+} \text{HgS} \downarrow + 2\text{H}^+$ $\text{HgS} + \text{S}^{2-} \rightarrow [\text{HgS}_2]^{2-}$ $3\text{HgS} + 6\text{HCl} + 2\text{HNO}_3 \rightarrow$ $3\text{HgCl}_2 + 3\text{S} \downarrow + 2\text{NO} \uparrow + 4\text{H}_2\text{O}$ $2\text{HNO}_3 + \text{S} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{NO} \uparrow$	Black ppt. is formed. Insoluble in water, hot dil HNO_3 , alkali hydroxides, or colourless ammonium sulphide. $\text{Na}_2\text{S}(2\text{M})$ dissolves the ppt. forming soluble complex. Aqua regia dissolves the ppt. HgCl_2 is undissociated. On heating, white ppt. of sulphur dissolves forming H_2SO_4 .
	Stannous chloride solution $2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 \downarrow$ $\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{Hg}_2 \downarrow$	When added in moderate amounts silky white ppt. is formed. If more reagent is added, Hg (I) chloride is reduced to black ppt. of mercury.
	Potassium iodide solution $\text{Hg}^{2+} + 2\text{I}^- \rightarrow \text{HgI}_2 \downarrow$ $\text{HgI}_2 + 2\text{I}^- \rightarrow [\text{HgI}_4]^{2-}$	On slow addition red ppt. is formed. Ppt. dissolves in excess of KI forming colourless soluble complex. KCN does not have any effect.
	Copper chips, sheet or coin $\text{Hg}^{2+} + \text{Cu} \rightarrow \text{Hg} \downarrow + \text{Cu}^{2+}$	A black ppt. of mercury is formed.
	Sodium hydroxide solution $\text{Hg}^{2+} + 2\text{OH}^- \rightarrow \text{HgO} \downarrow + \text{H}_2\text{O}$	When added in small quantity brownish-red ppt. of varying composition is formed and in stoichiometric amounts ppt. turns to yellow when Hg (II) oxide is formed. Ppt. is insoluble in excess reagent but dissolves readily in acids and this can be used to differentiate Hg (I) from Hg (II).

	Ammonia solution $2\text{Hg}^{2+} + \text{NO}_3^- + 4\text{NH}_3 + \text{H}_2\text{O} \rightarrow$ $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{NO}_3 \downarrow + 3\text{NH}_4^+$	White ppt. of mixed composition (Mercury (II) oxide+Mercury (II) amido nitrate) is formed with metal nitrate.
	Cobalt (II) thiocyanate test $\text{Hg}^{2+} + \text{CO}^{2+} + 4\text{SCN}^- \rightarrow \text{CO}^{+2}[\text{Hg}(\text{SCN})_4]^{2-} \downarrow$	When reagent is added to an aqueous solution of Hg^{2+} ions and the walls of the test tube is stirred with a glass rod, deep-blue crystalline ppt. is formed. In place of Cobalt (II) thiocyanate, $\text{Co}(\text{CH}_3\text{COO})$ and NH_4SCN can be added to the aqueous solution of Hg^{2+} ions.
Cu^{2+}	Test/Reagents	Observation
	Precipitation with H_2S in acidic medium $\text{Cu}^{2+} + \text{H}_2\text{S} \xrightarrow{\text{H}^+} \text{CuS} \downarrow + 2\text{H}^+$ $3\text{CuS} + 8\text{HNO}_3 \rightarrow$ $3\text{Cu}(\text{NO}_3)_2 \text{ (blue)} + 2\text{NO} + 4\text{H}_2\text{O} + 3\text{S}$ $2\text{CuS} \downarrow + 8\text{CN}^- \rightarrow 2[\text{Cu}(\text{CN})_4]^{3-} + \text{S}_2^{2-}$	Black ppt. is formed. Ppt. is insoluble in boiling dilute (M) H_2SO_4 (distinction from cadmium), in NaOH, Na_2S and $(\text{NH}_4)_2\text{S}$. Ppt. dissolves in hot conc. HNO_3 When boiled for longer, S is oxidized to H_2SO_4 and a clear solution of $\text{Cu}(\text{NO}_3)_2$ is obtained. KCN dissolves the ppt. forming a clear solution. (disulphide ion)
	Ammonia Solution $2\text{Cu}^{2+} + \text{SO}_4^{2-} + 2\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow$ $\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4 \downarrow + 2\text{NH}_4^+$ $\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4 + 8\text{NH}_3 \rightarrow$ $2[\text{Cu}(\text{NH}_3)_4]^{2+} + \text{SO}_4^{2-} + 2\text{OH}^-$	When added sparingly a blue ppt. of basic salt (basic copper sulphate) is formed with CuSO_4 . It is soluble in excess of reagent forming a deep blue colouration.
	Sodium hydroxide in cold solution $\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2 \downarrow$ $\text{Cu}(\text{OH})_2 \xrightarrow{\text{Heat}} \text{CuO} \downarrow \text{ (black)} + \text{H}_2\text{O}$	A blue ppt. is formed.
	Potassium iodide $2\text{Cu}^{2+} + 5\text{I}^- \rightarrow \text{Cu}_2\text{I}_2 \downarrow + \text{I}_3^-$ $\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$	It gives a white ppt. of Cu (I) iodide but the solution is intensely brown because of the formation of tri-iodide ions (or iodine). The soln becomes colourless and a white ppt. is visible when excess of sodium thiosulphate solution is added. These reactions are used in quantitative analysis for the iodometric determination of copper.
	Potassium ferrocyanide (Potassium hexacyanidoferrate (II) solution) $2\text{Cu}^{2+} + \text{K}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] \downarrow + 4\text{K}^+$	Cu^{2+} ions gives brown/chocolate brown ppt.
	$2[\text{Fe}(\text{CN})_6]^{3-} + 3\text{Cu}^{2+} \rightarrow \text{Cu}_3[\text{Fe}(\text{CN})_6]_2 \downarrow$	Green

	Potassium cyanide $\text{Cu}^{2+} + 2\text{CN}^- \rightarrow \text{Cu}(\text{CN})_2 \downarrow$ $2\text{Cu}(\text{CN})_2 \rightarrow 2\text{CuCN} \downarrow (\text{white}) + (\text{CN})_2 \uparrow (\text{highly poisonous})$ $\text{CuCN} + 3\text{CN}^- \rightarrow [\text{Cu}(\text{CN})_4]^{3-}$	<p>When added sparingly forms first a yellow ppt. which decomposes into CuCN and cyanogen.</p> <p>Excess reagent dissolves the ppt. forming a colourless soluble complex.</p> <p>Complex is so stable that H_2S cannot ppt. Cu(I) sulphide (distinction from cadmium).</p>
	Potassium thiocyanate solution $\text{Cu}^{+2} + 2\text{SCN}^- \rightarrow \text{Cu}(\text{SCN})_2 \downarrow$ $2\text{Cu}(\text{SCN})_2 \rightarrow 2\text{CuSCN} \downarrow + (\text{SCN})_2 \uparrow$ $2\text{Cu}(\text{SCN})_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow$ $2\text{CuSCN} + 2\text{SCN}^- + \text{SO}_4^{2-} + 4\text{H}^+$	<p>The Cu^{+2} ions solution initially gives a black ppt. which then slowly decomposes to give white ppt. of Cu (I) thiocyanate.</p> <p>Cu (II) thiocyanate can be immediately converted into Cu (I) thiocyanate by adding a suitable reducing agent like saturated solution of SO_2.</p>
Bi³⁺	Test/Reagents	Observation
	Precipitation with H_2S in acidic medium $2\text{Bi}^{3+} + 3\text{H}_2\text{S} \xrightarrow{\text{H}^+} \text{Bi}_2\text{S}_3 \downarrow (\text{black}) + 6\text{H}^+$ $\text{Bi}_2\text{S}_3 + 8\text{HNO}_3 \rightarrow 2\text{Bi}(\text{NO}_3)_3 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$ $\text{Bi}_2\text{S}_3 + 6\text{HCl}(\text{boiling, conc.}) \rightarrow 2\text{Bi}^{3+} + 6\text{Cl}^- + 3\text{H}_2\text{S}$	<p>Black ppt. is formed which is insoluble in cold dilute HNO_3 and yellow ammonium sulphide.</p>
	Sodium hydroxide $\text{Bi}^{3+} + 3\text{OH}^- \rightarrow \text{Bi}(\text{OH})_3 \downarrow$ $\text{Bi}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Bi}^{3+} + \text{H}_2\text{O}$ $\text{Bi}(\text{OH})_3 \rightarrow \text{BiO.OH} \downarrow + \text{H}_2\text{O}$ $\text{BiO.OH} + \text{H}_2\text{O}_2 \rightarrow \text{BiO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	<p>White ppt. is formed with the reagent, slightly soluble in excess reagent in cold solution but soluble in acids. Ppt. on boiling loses water and turns yellowish white which is oxidised to BiO_3^- by H_2O_2.</p>
	Ammonia solution $\text{Bi}^{3+} + \text{NO}_3^- + 2\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow \text{Bi}(\text{OH})_2 \text{NO}_3 \downarrow + 2\text{NH}_4^+$	<p>White basic salt of variable composition is formed.</p>
	Alkaline sodium stannite (Sodium tetrahydroxidoantimonate (II)) $\text{Bi}^{3+} + 3\text{OH}^- \rightarrow \text{Bi}(\text{OH})_3 \downarrow$ $2\text{Bi}(\text{OH})_3 + [\text{Sn}(\text{OH})_4]^{2-} \rightarrow 2\text{Bi} \downarrow + 3[\text{Sn}(\text{OH})_6]^{2-}$	<p>A black ppt. of metallic bismuth is obtained.</p> <p>The reagent must be freshly prepared and test must be carried out in cold solution.</p>
	Dilution with water $\text{Bi}^{3+} + \text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{BiO}(\text{NO}_3) \downarrow + 2\text{H}^+$ $\text{Bi}^{3+} + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \underbrace{\text{BiOCl}}_{\text{bismuthoxychloride or bismuthylchloride}} \downarrow + 2\text{H}^+$	<p>Solution of bismuth salts gives white ppt. when water is added in larger quantity. Soluble in mineral acids (dilute) but insoluble in tartaric acid (distinction from antimony) and in alkali hydroxide (distinction from tin).</p>

	Potassium iodide $\text{Bi}^{3+} + 3\text{I}^- \rightarrow \text{BiI}_3 \downarrow$ $\text{BiI}_3 + \text{I}^- \rightarrow [\text{BiI}_4]^-$ $\text{BiI}_3 \downarrow + \text{H}_2\text{O} \rightarrow \text{BiOI} \downarrow + 2\text{H}^+ + 2\text{I}^-$	When the reagent is added dropwise to a solution containing Bi^{3+} ions, a black ppt. is formed. The ppt. dissolves in excess KI forming orange coloured soluble complex. On dilution the reaction is reversed and black BiI_3 turns orange.
(Cd²⁺)	Test/Reagents	Observation
	Precipitation with H₂S in acidic medium $\text{Cd}^{2+} + \text{H}_2\text{S} \xrightarrow{\text{H}^+} \text{CdS} \downarrow + 2\text{H}^+$ $\text{CdS} + 8\text{HNO}_3 \rightarrow 3\text{Cd}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO} + 3\text{S}$	Yellow ppt. is formed which dissolves in hot dil. HNO_3 . Ppt. does not dissolve in KCN.
	Ammonia solution (Dropwise addition) $\text{Cd}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow \text{Cd}(\text{OH})_2 \downarrow + 2\text{NH}_4^+$ $\text{Cd}(\text{OH})_2 + 4\text{NH}_3 \rightarrow [\text{Cd}(\text{NH}_3)_4]^{2+} + 2\text{OH}^-$	Ammonium hydroxide first gives white ppt. of $\text{Cd}(\text{OH})_2$ which gets dissolve in excess of reagent forming a soluble complex.
	Potassium cyanide $\text{Cd}^{2+} + 2\text{CN}^- \rightarrow \text{Cd}(\text{CN})_2 \downarrow$ $\text{Cd}(\text{CN})_2 + 2\text{CN}^- \rightarrow [\text{Cd}(\text{CN})_4]^{2-}$ $[\text{Cd}(\text{CN})_4]^{2-} + \text{H}_2\text{S} \rightarrow \text{CdS} \downarrow + 2\text{H}^+ + 4\text{CN}^-$	White ppt. of $\text{Cd}(\text{CN})_2$ is formed which in excess of reagent dissolves forming a soluble complex. The colourless soluble complex is unstable, therefore, reacts with H_2S gas forming a yellow ppt. of CdS . KI forms no ppt. (distinction from Copper)
	Sodium hydroxide $\text{Cd}^{2+}(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Cd}(\text{OH})_2 \downarrow + 2\text{Na}^+$	White ppt. is obtained which insoluble in excess of NaOH

Illustration 11: When NaOH solution is mixed with aqueous solution of a salt 'A', and warmed, a black ppt. is formed. Black ppt. is filtered and dissolved in concentrated HNO_3 by boiling. The resulting solution gives a chocolate brown coloured ppt. with potassium ferrocyanide solution. The filtrate obtained after filtering off the black ppt., upon warming with Zn and NaOH evolves an alkaline pungent smelling gas. The resulting solution also responds to the brown ring test. The filtrate does not evolve N_2 gas when it is boiled with urea in the presence of H_2SO_4 . Identify the cation and anion present in the salt 'A'.

Sol: $\text{Cu}(\text{NO}_3)_2 + \text{NaOH} \rightarrow \text{Cu}(\text{OH})_2 \downarrow (\text{Blue}) + 2\text{NaNO}_3$
 $\text{Cu}(\text{OH})_2 \downarrow \xrightarrow{\Delta} \text{CuO} \downarrow (\text{Black}) + \text{H}_2\text{O}$
 $4\text{Zn} + \text{NaNO}_3 + 7\text{NaOH} \rightarrow 4\text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O} + \text{NH}_3 \uparrow (\text{Pungent smelling alkaline gas})$
 $\text{CuO} + 2\text{HNO}_3 \xrightarrow{\Delta} \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O}$
 $2\text{Cu}(\text{NO}_3)_2 + \text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] \downarrow (\text{Chocolate brown}) + 4\text{KNO}_3$

Illustration 12: A compound on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on exposure of HCl. The resultant alkaline solution thus obtained after heating again liberates the same gas (B) when heated with zinc powder. Compound (A) on heating alone gives a neutral oxide of nitrogen not nitrogen gas. Identify (A) and (B) and give the relevant chemical reactions.

Sol: As NH_3 gives white fumes with HCl, therefore, (B) should be NH_3 and (A) should be the salt of ammonium. Further we know that nitrite of ammonium gives a NH_3 with Zn and alkali and when heated alone gives neutral oxide (N_2O) not N_2 . Hence the salt should be ammonium nitrate not ammonium nitrite.

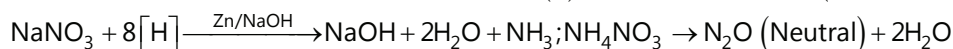
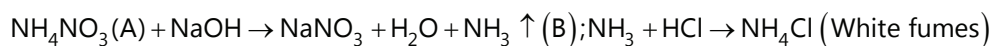


Illustration 13: A certain metal (A) is boiled with dilute HNO_3 to give a salt (B) and a neutral oxide of nitrogen (C). An aqueous solution of (B) gives a white ppt. (D) with brine which is soluble in ammonium hydroxide. An aqueous solution of (B) also gives red/brick red ppt., (E) with potassium chromate solution. Identify (A) to (E) and write the chemical reactions involved.

Sol: As solution of (B) gives white ppt. with NaCl (aq) ppt. is soluble in ammonium hydroxide, it may be of silver salt. Further it gives brick red ppt. with K_2CrO_4 , therefore, metal (A) may be silver.

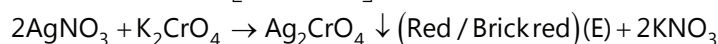
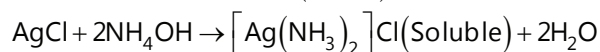
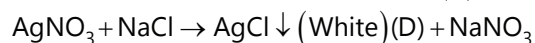
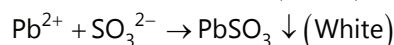
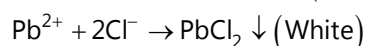
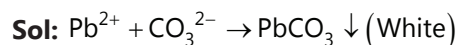


Illustration 14: Which of the following salt will give white ppt. with the solution containing Pb^{2+} ions?

- (A) Na_2CO_3 (B) NaCl (C) Na_2SO_3 (D) All of these



Therefore, (D) option is correct.

Table 30.22: Some important reactions of group III radicals

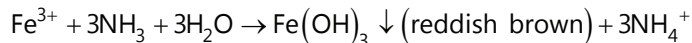
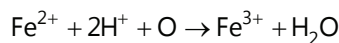
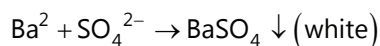
Fe^{+3}	Test/Reagents	Observation
	Potassium ferrocyanide (Potassium hexacyanidoferrate (II)) $4\text{Fe}^{+3} + 3[\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_8]_3 \downarrow$ $\text{Fe}_4[\text{Fe}(\text{CN})_8]_3 + 12\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3 \downarrow + 3[\text{Fe}(\text{CN})_6]^{4-}$	Intense blue ppt. (Prussian blue) of iron (III) hexacyanidoferrate (II) is formed. This is insoluble in dilute acids but decomposes in concentrated HCl . A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained. Sodium hydroxide turns the ppt. red. Oxalic acid also dissolves Prussian blue forming a blue-solution.
Important: If iron (III) chloride is added to an excess of potassium hexacyanidoferrate (II), a product with the composition of $\text{KFe}[\text{Fe}(\text{CN})_6]$ is formed. This tends to form colloidal solutions ('soluble Prussian blue') and can not be filtered.		

	<p>Potassium ferricyanide (Potassium hexacyanidoferrate (III))</p> $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \rightarrow \text{Fe}[\text{Fe}(\text{CN})_6]$ $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{3-} \rightarrow \text{Fe} + [\text{Fe}(\text{CN})_6]^{4-}$ $4\text{Fe}^{3+} + 3[\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{Fe}_4 + [\text{Fe}(\text{CN})_6]_3$	<p>A brown colouration is formed. Upon adding hydrogen peroxide or some tin (II) chloride solution, the hexacyanidoferrate (III) part of the compound is reduced and Prussian blue is ppt..</p> <p>Fe^{2+} gives dark blue ppt. with potassium ferricyanide. First hexacyanidoferrate (III) ions oxidise iron (II) to iron (III), when hexacyanidoferrate (II) is formed.</p> <p>And these ions combine to form a ppt. called Turnbull's blue.</p>
<p>Note: Composition of this ppt. is identical to that of Prussian blue. Earlier the composition suggested was $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, hence different name.</p> $3\text{Fe}^{2+} + 2\text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 \text{ (Ferrous ferric cyanide)} + 6\text{K}^+$ <p style="text-align: center;">Turnbull's blue</p> <p>Fe (II) in ammonical solution gives red solution with DMG-colouration fades on standing due to the oxidation of iron (II) complex. Fe (III) does not give such complex.</p> <p>In complete absence of air, Fe (II) ions produces white ppt. with potassium hexacyanidoferrate (II).</p> $\text{Fe}^{2+} + 2\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6] \downarrow$ <p>Under ordinary atmospheric conditions a pale-blue ppt. is formed.</p>		
Cr^{+3}	Test/Reagents	Observation
	<p>Acidified H_2O_2 test</p> $\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{CrO}_4;$ $\text{H}_2\text{CrO}_4 + 2\text{H}_2\text{O}_2 \xrightarrow{\text{Amyl alcohol}} \text{CrO}_5 + \text{H}_2\text{O}$ $4\text{CrO}_5 + 6\text{H}_2\text{SO}_4 \rightarrow 2\text{Cr}_2(\text{SO}_4)_3 + 7\text{O}_2 + 6\text{H}_2\text{O}$	<p>Blue colouration</p> <p>On acidifying the yellow solution with dil. H_2SO_4 + few drops of ether/amyl alcohol + H_2O_2 = Blue colouration, can be extracted into the organic layer by gently shaking.</p> <p>Blue colouration fades slowly due to the decomposition of perchromic acid (or chromium peroxide) with the liberation of oxygen.</p>
	<p>Tests for:</p> $\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$ $\text{NaAlO}_2 + \text{H}_2\text{O} + \text{NH}_4\text{Cl} \rightarrow \text{Al}(\text{OH})_3 + \text{NaCl} + \text{NH}_3$	<p>In excess of NaOH. Sodium meta-aluminate (soluble). White gelatinous ppt.</p>

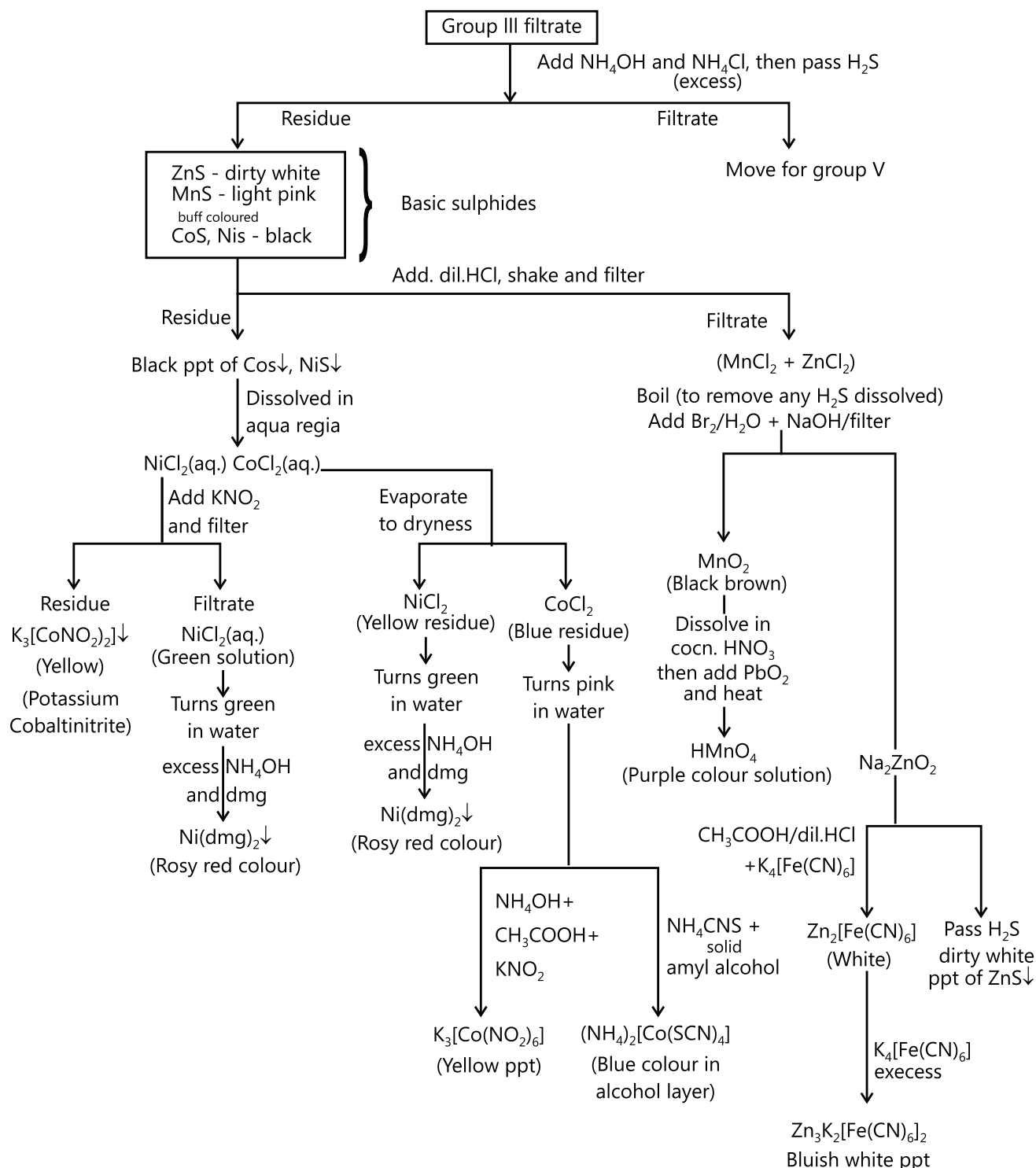
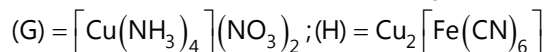
Fe^{3+}	Test/Reagents	Observation
	Tests for $\text{Fe}(\text{OH})_3 + 3\text{HCl} \rightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$ $4\text{FeCl}_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$ $\text{FeCl}_3 + \text{KSCN} \rightarrow \text{Fe}(\text{SCN})\text{Cl}_2 + \text{KCl}$	Red brown $\text{Fe}(\text{OH})_3$ dissolves in dil. HCl as Reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$: Ferric ferrocyanide (Dark Blue) Reaction with KCNS: Ferrithiocyanate (dark red colour)
Cr^{3+}	Test/Reagents	Observation
	Tests for $(\text{CH}_3\text{COO})_2\text{Pb} / \text{CH}_3\text{COOH}$ $2\text{NaOH} + \text{Br}_2 \rightarrow \text{NaOBr} + \text{NaBr} + \text{H}_2\text{O}$ $\text{NaOBr} \rightarrow \text{NaBr} + [\text{O}]$ $2\text{Cr}(\text{OH})_3 + 4\text{NaOH} + 3[\text{O}] \rightarrow 2\text{Na}_2\text{CrO}_4 + 5\text{H}_2\text{O}$ Yellow solution $\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \rightarrow \text{PbCrO}_4 \downarrow + 2\text{CH}_3\text{COONa}$ Yellowppt. $2\text{Cr}(\text{OH})_3 + 2\text{Na}_2\text{CO}_3 + 3\text{KNO}_3 \rightarrow 2\text{Na}_2\text{CrO}_4 + 3\text{KNO}_2 + 3\text{H}_2\text{O} + 2\text{CO}_2$ Yellow solution $\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \rightarrow \text{PbCrO}_4 \downarrow + 2\text{CH}_3\text{COONa}$ Yellowppt.	On boiling with $\text{NaOH} / \text{Br}_2$, $\text{Cr}(\text{OH})_3$ gives sodium chromate which gives yellow ppt. of PbCrO_4 with Yellow solution Yellow ppt. Yellow solution Yellow ppt.

Illustration 15: A black coloured compound (A) on reaction with dil. H_2SO_4 gives a gas (B) and a green colour solution. The gas (B) on passing in a solution of an acid (C) gives a white/yellow turbidity (D). Gas (B) when passed in acidified solution of (E) gives a ppt. (F) soluble in dil HNO_3 . After boiling this solution when excess of NH_4OH is added, a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous potassium ferrocyanide a chocolate coloured ppt. (H) is obtained. On addition of an aqueous solution of BaCl_2 to an aqueous solution of (E), a white ppt. insoluble in HNO_3 is obtained. Green colour solution on reaction with ammonium hydroxide in presence of air gives reddish brown ppt.. Identify (A) to (H).

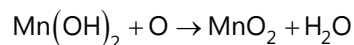
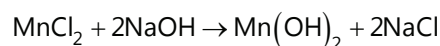
Sol: $\text{FeS}(\text{A}) + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{S}(\text{B})$
 $\text{HNO}_3(\text{C}) \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{O}; \text{H}_2\text{S} + \text{O} \rightarrow \text{H}_2\text{O} + \text{S} \downarrow (\text{D})$
 $\text{CuSO}_4(\text{E}) + \text{H}_2\text{S} \rightarrow \text{CuS} \downarrow (\text{F}) + \text{H}_2\text{SO}_4$
 $3\text{CuS} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} \uparrow + 4\text{H}_2\text{O} + 3\text{S} \downarrow$
 $\text{Cu}^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+} (\text{G})$
 $2\text{Cu}^{2+} + \text{K}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] \downarrow (\text{H}) + 4\text{K}^+$



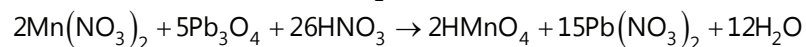
Hence, (A) = FeS ; (B) = H_2S ; (C) = HNO_3 ; (D) = S ; (E) = CuSO_4 ; (F) = CuS ;



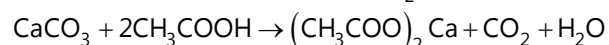
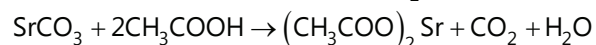
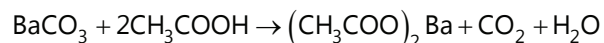
Flowchart 30.4: Systematic path for the analysis of group IV radicals



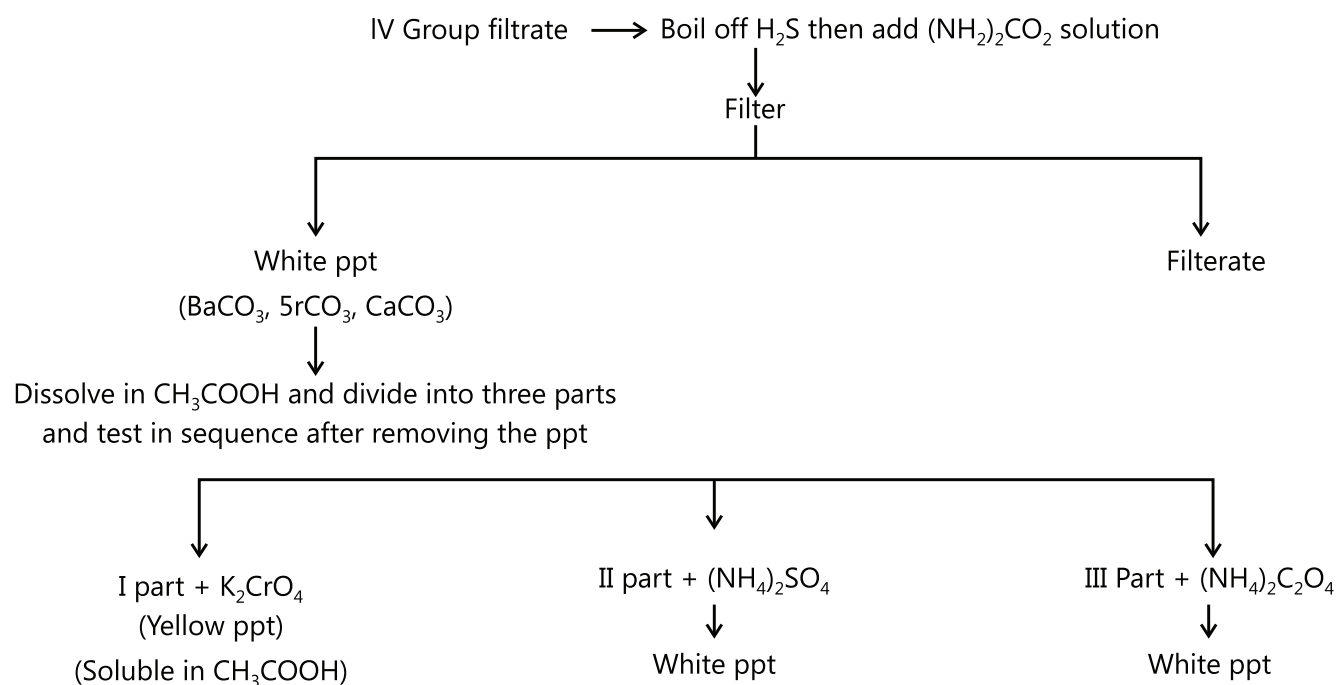
The ppt. is treated with excess of HNO_3 and PbO_2 or Pb_3O_4 (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.



Permanganic acid (pink)



V Group (Ba^{2+} , Sr^{2+} , Ca^{2+})



Flowchart 5: For the analysis of group V radical

GROUP V (Ba (II), Sr (II), Ca (II))

Ammonium carbonate ppt. V group radicals in the form of carbonates. These carbonates are soluble in acetic acid.

Table 30.24: Confirmatory test for group V radicals

Ba ²⁺	Test/Reagents	Observation
	$\text{Ba}(\text{CH}_3\text{COO})_2 + \text{K}_2\text{CrO}_4 \rightarrow \text{BaCrO}_4 \downarrow + 2\text{CH}_3\text{COOK}$ $\text{Ba}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2\text{CH}_3\text{COONH}_4$ $\text{Ba}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{BaC}_2\text{O}_4 \downarrow + 2\text{CH}_3\text{COONH}_4$	White ppt.
	$\text{Sr}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{SrSO}_4 \downarrow + 2\text{CH}_3\text{COONH}_4$ <p style="text-align: center;">White ppt.</p>	White ppt.
	$\text{Sr}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{SrC}_2\text{O}_4 \downarrow + 2\text{CH}_3\text{COONH}_4$ $\text{Ca}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + 2\text{CH}_3\text{COONH}_4$ <p style="text-align: center;">White ppt.</p>	<p>White ppt.</p> <p>Calcium chlorate and calcium sulphate are soluble.</p>

VITH GROUP**Table 30.25:** Confirmatory test for group VI radical

Mg ²⁺	Test/Reagents	Observation
	Disodium hydrogen phosphate solution $\text{Mg}^{2+} + \text{NH}_3 + \text{HPO}_4^{2-} \rightarrow \text{Mg}(\text{NH}_4)\text{PO}_4 \downarrow$ $\text{Mg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{MgHPO}_4 \downarrow$	<p>White crystalline ppt. is formed in presence of NH₄Cl prevent precipitation of Mg(OH)₂ and NH₃ soln</p> <p>white flocculent ppt.</p>
	Ammonia solution $\text{Mg}^{2+} + 2\text{NH}_4\text{OH} \rightarrow \text{Mg}(\text{OH})_2 \downarrow + 2\text{NH}_4^+$ $\text{Mg}(\text{OH})_2 \longrightarrow \text{Mg}^{+2} + 2\text{OH}^-$ $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-;$ $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_4\text{OH}(\text{weak base})$	<p>White gelatinous ppt is sparingly soluble in water but readily soluble in ammonium salts.</p> <p>NH₄⁺ ions 'remove' OH⁻ causing the hydroxide to dissolve more. Not possible with NaCl.</p>
	Ammonium carbonate solution $5\text{Mg}^{2+} + 6\text{CO}_3^{2-} + 7\text{H}_2\text{O} \rightarrow 2\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} \downarrow + 2\text{HCO}_3^-$ $\text{NH}_4^+ + \text{CO}_3^{2-} \longrightarrow \text{NH}_3 + \text{HCO}_3^-$	<p>Absence of NH₄⁺ salts.</p> <p>In the presence of NH₄⁺ salts no precipitation occurs, because the equilibrium is shifted towards the formation of HCO₃⁻ ions. K_{sp} of the ppt. being high (K_{sp} of pure MgCO₃ is 1 × 10⁻⁵), the concentration of carbonate ions necessary to produce a ppt. is not attained.</p>
	4-(4-Nitrophenyl azo resorcinol) or Magneson I $\text{MgCl}_2 + 2\text{NaOH} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{NaCl}$ <p>Magneson reagent = p-nitrobenzene-azo resorcinol, a dye stuff, absorbed over Mg(OH)₂ to give a blue coloured lake.</p>	<p>Ppt. is dissolved in dilute HCl (min.) + NaOH + 0.5ml magneson-I reagent = Blue lake</p>

	Titan yellow (a water soluble yellow dyestuff) It is adsorbed by $\text{Mg}(\text{OH})_2$	Deep red colour or ppt.
	Dissolve ppt. in dil.HCl(min.)+1 drop of NaOH soln (2M) + 1 drop titan yellow soln	Deep red colour solution or ppt. is obtained. Ba^{2+} and Ca^{2+} do not react but intensify the colour.

Table 30.26: Action of heat on different compounds

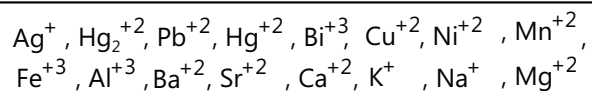
<p>(a) Some oxides liberate O_2:</p> $2\text{HgO} \xrightarrow{\text{Heat}} 2\text{Hg} + \text{O}_2 \uparrow$ <p>(Red) (Silvery deposit)</p> $2\text{Pb}_3\text{O}_4 \xrightarrow{\text{Heat}} 6\text{PbO} + \text{O}_2 \uparrow$ <p>(Red) (Yellow)</p> $2\text{PbO}_2 \xrightarrow{\text{Heat}} 2\text{PbO} + \text{O}_2 \uparrow$ $2\text{Ag}_2\text{O} \xrightarrow{\text{Heat}} 4\text{Ag} + \text{O}_2 \uparrow$ <p>(b) Some carbonates liberate CO_2:</p> $\text{CuCO}_3 \xrightarrow{\text{Heat}} \text{CuO} + \text{CO}_2 \uparrow$ <p>(Green) (black)</p> $\text{ZnCO}_3 \xrightarrow{\text{Heat}} \text{ZnO} + \text{CO}_2 \uparrow$ <p>(white) Yellow (hot) white(cold)</p> $2\text{Ag}_2\text{CO}_3 \xrightarrow{\text{Heat}} 4\text{Ag} + 2\text{CO}_2 \uparrow + \text{O}_2 \uparrow$ $\text{CaCO}_3 \xrightarrow{\text{Heat}} \text{CaO} + \text{CO}_2 \uparrow$ $\text{MgCO}_3 \xrightarrow{\text{Heat}} \text{MgO} + \text{CO}_2 \uparrow$ $\text{Li}_2\text{CO}_3 \xrightarrow{\text{Heat}} \text{Li}_2\text{O} + \text{CO}_2 \uparrow$ <p>(c) Some bicarbonates liberate CO_2:</p> $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ $\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$ <p>(d) Some sulphates liberate SO_3:</p> $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow[\text{-5H}_2\text{O}]{\text{Heat}} \text{CuSO}_4;$ $\xrightarrow{\text{Heat}} \text{CuO} + \text{SO}_3$ $2\text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$ $\text{Al}_2(\text{SO}_4)_3 \xrightarrow{\text{Red Hot}} \text{Al}_2\text{O}_3 + 3\text{SO}_3$	<p>(e) Some sulphates liberate SO_2:</p> $2\text{MgSO}_4 \xrightarrow{\text{Heat}} 2\text{MgO} + 2\text{SO}_2 + \text{O}_2$ $2\text{ZnSO}_4 \xrightarrow{\text{Heat (high temp)}} 2\text{ZnO} + 2\text{SO}_2 + \text{O}_2$ $2\text{BeSO}_4 \xrightarrow{\text{Heat}} 2\text{BeO} + 2\text{SO}_2 + \text{O}_2$ <p>(f) Some sulphates lose water of crystallization:</p> $2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) \xrightarrow{\text{Heat}} 2(\text{CaSO}_4 \cdot \text{H}_2\text{O}) + 2\text{H}_2\text{O}$ $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow[\text{-H}_2\text{O}]{70^\circ\text{C}} \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow[\text{-5H}_2\text{O}]{100^\circ\text{C}} \text{ZnSO}_4$ $\text{ZnSO}_4 \cdot \text{H}_2\text{O} \xrightarrow[\text{-H}_2\text{O}]{450^\circ\text{C}} \text{ZnSO}_4$ <p>(g) Some nitrates liberate NO_2 and O_2:</p> $2\text{Zn}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} 2\text{ZnO} + 4\text{NO}_2 + \text{O}_2$ <p>white Brown</p> $2\text{Cu}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$ $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$ $2\text{Mg}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} 2\text{MgO} + 4\text{NO}_2 + \text{O}_2$ $2\text{Ca}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$ $2\text{LiNO}_3 \xrightarrow{\text{Heat}} \text{Li}_2\text{O} + 2\text{NO}_2 + 1/2\text{O}_2$ $\text{Hg}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} \text{Hg} + 2\text{NO}_2 + \text{O}_2$ $2\text{AgNO}_3 \xrightarrow{\text{Heat}} 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$ $2\text{Co}(\text{NO}_3)_2 \xrightarrow{\text{Heat}} 2\text{CoO} + 4\text{NO}_2 + \text{O}_2$ <p>(h) Some nitrates liberate O_2:</p> $2\text{NaNO}_3 \xrightarrow{\text{Heat}} 2\text{NaNO}_2 + \text{O}_2$ $2\text{AgNO}_3 \xrightarrow{\text{Heat}} 2\text{AgNO}_2 + \text{O}_2$
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Black Coloured Compounds	Blue Coloured Compounds	Green Coloured Compounds	Yellow Coloured Compounds
5. NiS 6. CoS 7. HgS 8. FeS 9. NiO 10. MnO 11. FeO 12. CuO 13. PbO ₂ 14. MnO ₂ 15. Mn ₃ O ₄ 16. Fe ₃ O ₄ 17. Co ₃ O ₄ 18. Ni(OH) ₃ 19. Cu ₃ P ₂ 20. BiI ₃ 21. Hg+Hg(NH ₂)Cl	5. Zn ₂ [Fe(CN) ₆] (Bluish white ppt) 6. Co(OH) ₂ Deep Blue 1. [Cu(NH ₃) ₄]SO ₄ (Swizzer's reagent) 2. [Cu(NH ₃) ₄](NO ₃) ₂ 3. Fe ₄ [Fe(CN) ₆] ₃ (Prussian's blue) 4. Fe ₃ [Fe(CN) ₆] ₂ (Turnbull's blue) 5. Na ₄ [Fe(CN) ₅ (NOS)] (Violet)	5. CrCl ₃ 6. FeSO ₄ ·7H ₂ O 7. FeCl ₂ 8. FeSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O (Mohr's salt) 9. Na ₂ MnO ₄ 10. K ₂ MnO ₄ 11. B(OC ₂ H ₅) ₃ (Burns with green edge flame) 12. CoO.ZnO (Riemann's green)	5. FeS ₂ (Fool's gold) 6. (NH ₄) ₂ S _x (where X=2 to 5) 7. PbCrO ₄ 8. BaCrO ₄ 9. SrCrO ₄ 10. AgBr (light yellow) 11. AgI (Dark yellow) 12. PbI ₂ 13. PbO (in Cold) 14. ZnO (in Hot) 15. HgO (Yellow ppt.) 16. Na ₂ O ₂ (Pale yellow) 17. Ag ₃ PO ₄ 18. Ag ₂ CO ₃ 19. Ag ₃ AsO ₄ 20. Cu(CN) ₂ 21. K ₃ [Co(NO ₂) ₆] 22. (NH ₄) ₃ PO ₄ ·12MoO ₃ 23. (NH ₄) ₃ AsO ₄ ·12MoO ₃ 24. Na ₂ CrO ₄ 25. CrO ₄ ²⁻ (Yellow in solution)

Red Coloured Compounds	Brown Coloured Compounds	Orange Coloured Compounds	Pink Coloured Compounds
1. Ag ₂ CrO ₄ (Brick red) 2. Hg ₂ CrO ₄ (Brick red) 3. HgI ₃ (Scarlet red) 4. Pb ₃ O ₄ (2PbO + PbO ₂) 5. CrO ₂ Cl ₂ (Reddish Brown) 6. Fe(CH ₃ COO) ₃ (Blood red)	1. SnS 2. Bi ₂ S ₃ 3. CdO 4. PbO ₂ 5. Fe(OH) ₃ (Reddish Brown) 6. Fe ₂ O ₃ (Reddish Brown solid)	1. Sb ₂ S ₃ 2. Sb ₂ S ₅ 3. KO ₃ 4. CsO ₂ 5. Cr ₂ O ₇ ²⁻ (orange in aq. soln)	Mn(OH) ₂ MnS MnO ₄ ⁻ (pink or purple in aq.soln) Co(CN) ₂ (NH ₄) ₂ SnCl ₆ CoCl ₂ ·6H ₂ O
7. Fe(SCN) ₃ (Blood Red) 8. AsI ₃ 9. SbI ₃ 10. SnI ₂ 11. CuBr ₂ 12. [Ni(DMG) ₂] (Rosy red)	7. Fe ₂ (CO ₃) ₃ 8. Cu ₂ O (Reddish Brown) 9. Ag ₃ AsO ₄ (Reddish Brown) 10. Cu ₂ I ₂ + I ₃ ⁻ (Brown ppt.) 11. Cu ₂ [Fe(CN) ₆] (Chocolate Brown) 12. NO ₂ (Brown gas) 13. [Fe(H ₂ O) ₅ (NO)]SO ₄ (Brown ring)		

POINTS TO REMEMBER

An aqueous solution containing :

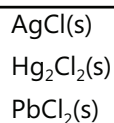


Add dilute HCl

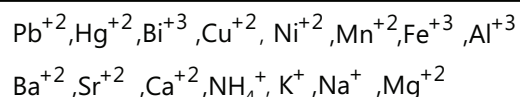
↓ Precipitate forms

↓ Ions remain in soln.

Group I:



Group II-V:

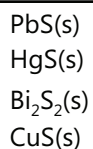


Add H_2S in 0.3 M HCl

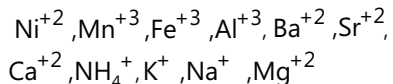
↓ Precipitate forms

↓ Ions remain in soln.

Group II:



Group III-V:

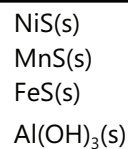


Add H_2S in basic soln.
($\text{NH}_3/\text{NH}_4\text{Cl}$ buffer).

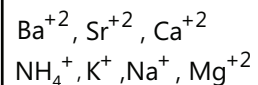
↓ Precipitate forms

↓ Ions remain in soln.

Group III:



Group IV-V:

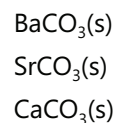


Add $(\text{NH}_4)_2\text{CO}_3$ in basic
soln. ($\text{NH}_3/\text{NH}_4\text{Cl}$ buffer).

↓ Precipitate forms

↓ Ions remain in soln.

Group IV:



Group V:

