

Section: Senior

Name of the student:

Qualitative Analysis (Cations)

Date: 18-06-2020

I.D.No: Sec:

Reactions of metal ions with important reagents

Group Separation

Group – I : cations : Ag^+ , Pb^{+2} , Hg_2^{+2}

Group reagent : dil . HCl

Precipitated : as their chlorides : AgCl or PbCl_2 or Hg_2Cl_2 (white ppt)

⇒ Ksp values of AgCl , PbCl_2 and Hg_2Cl_2 are low ($\text{Hg}_2\text{Cl}_2 < \text{AgCl} < \text{PbCl}_2$)

Hence low conc. Of Cl^- required for their precipitation.

∴ dil. HCl is used.

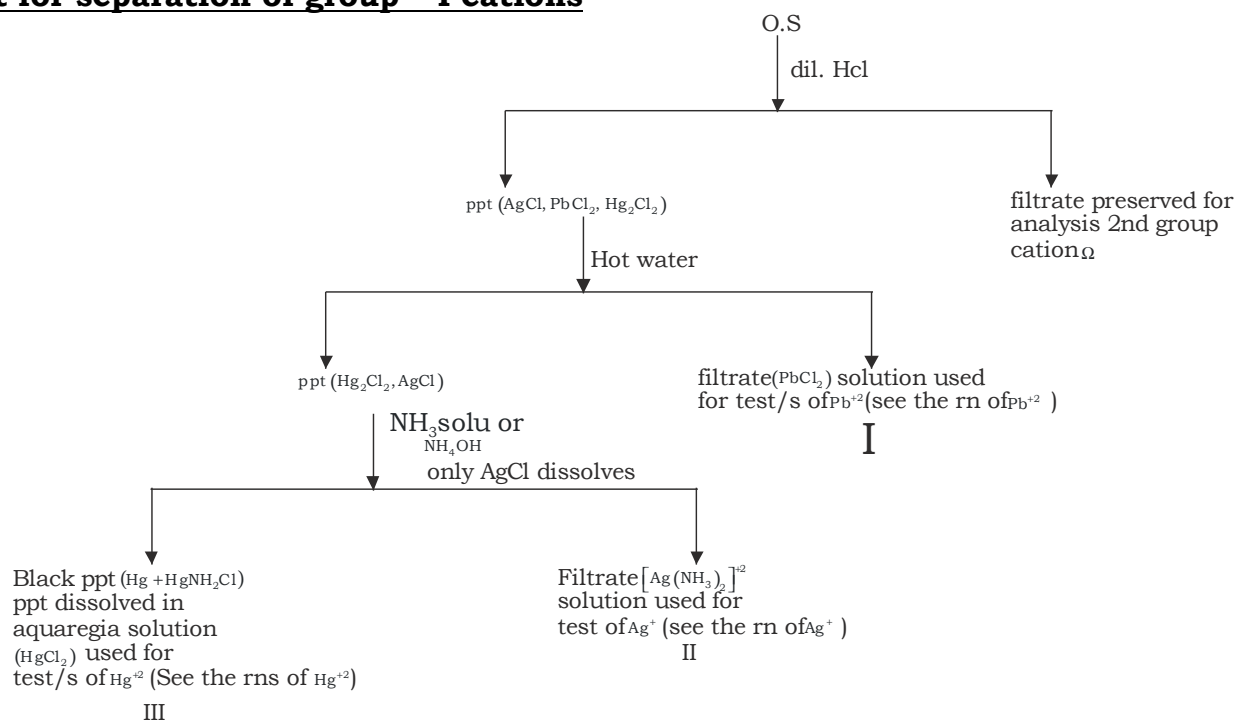
⇒ Solubility of chlorides of Group – I cations:

only PbCl_2 soluble in Hot water; AgCl soluble in NH_3 solution Hg_2Cl_2 insoluble in NH_3 solu. but changes to black ppt [$\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}$].

⇒ sometimes O.S on dilution forms white ppt which is due to presence of SbCl_3 BiCl_3

[$\text{SbCl}_3 + \text{H}_2\text{O} \rightarrow \text{SbOCl} + \text{HCl}$ $\text{BiCl}_3 + \text{H}_2\text{O} \rightarrow \text{BiOCl} + \text{HCl}$
white ppt white ppt]

Chart for separation of group – I cations



I. Reaction of Pb^{+2}

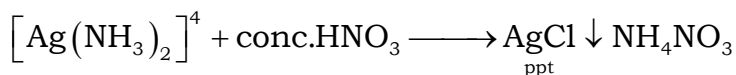
1. Solution (PbCl_2) + $\text{K}_2\text{CrO}_4 \longrightarrow$ yellow ppt (Pb CrO_4)

2. Solution (PbCl_2) + $\text{KI} \longrightarrow$ yellow ppt (PbI_2) $\xrightarrow{\text{H}_2\text{O}}$ C.L solutions $\xrightarrow{\text{Cooling}}$ yellow crystal (PbI_2)

3. Solution (PbCl_2) + $\text{H}_2\text{SO}_4 \longrightarrow$ white ppt (PbSO_4) soluble in amm. acetate.

II. Reaction of Ag^+

1. solution + conc. $\text{HNO}_3 \longrightarrow$ white ppt



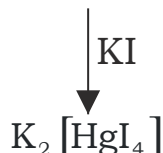
2. $\underset{(\text{Ag}^+)}{\text{solution}} + \text{KI} \longrightarrow \text{yellow ppt (AgI) (insoluble in excess of KI).}$

3. $\underset{(\text{Ag}^+)}{\text{solution}} + \text{K}_2\text{CrO}_4 \longrightarrow \text{Red ppt (Ag}_2\text{CrO}_4)$

III. Reaction of Hg_2^{+2}

1. $\text{Solution (HgCl}_2) + \text{SnCl}_2 \longrightarrow \text{white ppt (Hg}_2\text{Cl}_2) + \text{SnCl}_4 \xrightarrow{\text{excess SnCl}_2} \text{Hg (grey ppt)}$

2. $\underset{\text{HgCl}_2}{\text{solution}} + \text{KI} \longrightarrow \text{Red ppt HgI}_2 \text{ soluble in excess}$



Group – II

Cation : IIA : $\text{Pb}^{+2}, \text{Cu}^{+2}, \text{Cd}^{+2}, \text{Hg}^{+2}, \text{Bi}^{+3}$ } copper sub group

II B : $\text{As}^{+3}, \text{As}^{+5}, \text{Sb}^{+3}, \text{Sb}^{+5}, \text{Sn}^{+2}, \text{Sn}^{+4}$ } Arsenic sub group

Group reagent : dil HCl/ H_2S : precipitated as sulphides

IIA. $\text{PbS}, \text{CuS}, \text{HgS}$ } black Bi_2S_3 } CdS yellow.
Dark brown

IIB. As_2S_3 (yellow), As_2S_5 (yellow)

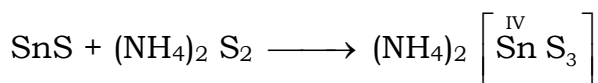
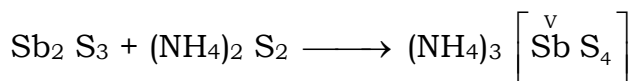
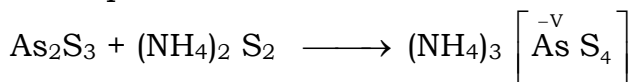
Sb_2S_3 Sb_2S_5 (Orange) Sns (brown) SnS_2 (yellow)

separation of IIA(copper sub group) II_B (Arsenic sub group)

\Rightarrow All the sulphides of II_B except Sn(II) sulphide are soluble in colour less ammonium sulphide.

\therefore ammonium poly sulphide is needed for separation. (which acts partly as an oxidizing agent)

II_B sulphides dissolves in YAS due to following soluble complexes.



\Rightarrow solubility of salts copper sub group cations :

\Rightarrow chlorides, sulphates, nitrates soluble except PbSO_4

\Rightarrow Hydroxides, carbonates are insoluble

\Rightarrow Solubility of sulphides ; IIA

\Rightarrow i) All are soluble in aquaregia \Rightarrow ii) $\text{CdS}, \text{CuS}, \text{PbS}, \text{Bi}_2 \text{S}_3$ soluble in 50% of HNO_3

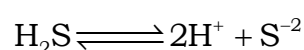
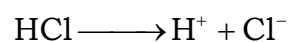
\Rightarrow iii) HgS soluble in aq. regia and $\text{Na}_2\text{S} \Rightarrow$ iv) CuS dissolves in $\text{KCN} \Rightarrow \text{K}_3[\text{Cu}(\text{CN})_4]$

\Rightarrow v) CdS insoluble in $\text{KCN} \Rightarrow$ distinction of CdS .

1. Why dil.HCl/ H_2S (group reagent)

KSP value of II group sulphides is very low

\therefore Low conc. of S^{-2} is required for their precipitation

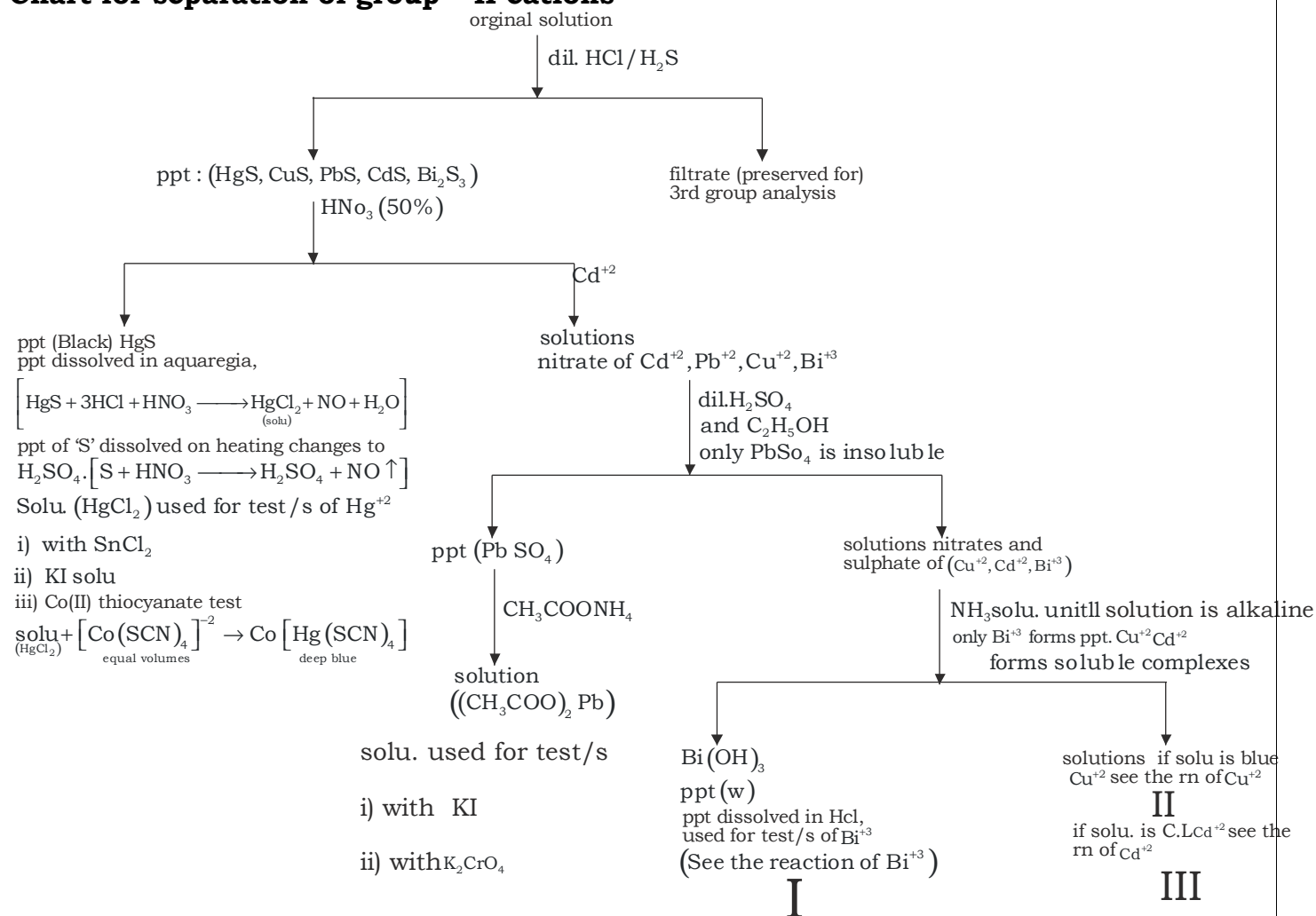


Due to common ion effect the conc. Of sulphide (\downarrow) the conc. of S^{2-} is just sufficient to ppt only 2nd group cation.

KSP value order :

2. With out di.HCl if H_2S is passed, 2nd group and some other group cation are precipitated.
3. If conc. HCl is used, to acidity O.S ionization of H_2S (\downarrow) to such an extent even 2nd group cations are not precipitated. To get the ppt. Proper acidity must be maintained. [0.25N – 0.5N HCl]
4. Some times yellow on white ppt appear by passing H_2S even though no cation of 2nd group is present. Which in due to oxidation of H_2S by oxidizing anions like NO_3^- , NO_2^- , SO_3^{2-} .
 \therefore Before passing H_2S O.S is boiled with dil.HCl to eliminate these oxidizing anions.

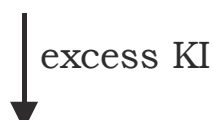
Chart for separation of group – II cations



I. Reactions of Bi^{+3}

i) NaOH:

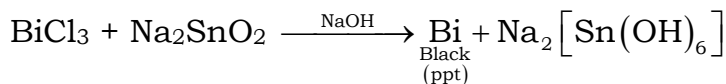
$solu(BiCl_3) + NaOH \rightarrow$ white ppt $Bi(OH)_3$ insoluble for excess reagent.



orange solu K [BiI₄]

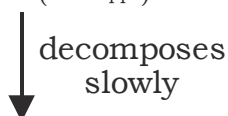
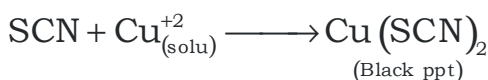
ii)

iii) solu + NaOH + sod. Stanrite \longrightarrow Black ppt



II. Reactions of Cu⁺² [reaction with KCN, KI, NH₄OH and NaOH are already given]

i) solution (Cu⁺²) + K₄ [Fe(CN)₆] \longrightarrow Cu₂ [Fe(CN)₆] (R.B) ppt



(Cu SCN) white ppt + (SCN)₂ thiocyanogen

ii)

II Reactions Cd⁺² : reaction with KCN, KI, NH₄OH, NaOH already discussed.

i) solu (cd⁺²) + KCN \longrightarrow $\underset{\substack{\text{white ppt}}}{\text{Cd}(\text{CN})_2} \downarrow \xrightarrow{\text{excess}} \underset{\substack{\text{solu}}}{\text{K}_2[\text{Cd}(\text{CN})_4]} \xrightarrow{\text{H}_2\text{S}} \text{CdS yellow ppt}$

Group III

Cations : Al⁺³, Fe⁺³, (Fe⁺²), Cr⁺³

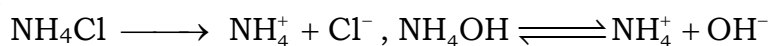
Group reagent : NH₄Cl / NH₄OH.

[K_{SP} of Fe(OH)₂ is high \therefore Fe⁺² not ppt by this group reagent]

Few drops of conc. HNO₃ is added to oxidised Fe⁺² to Fe⁺³ if excess of con. HNO₃ is added (3rd group cation are absent) Mn⁺² oxidised to Mn⁺³ (Brown)

Participated as : hydroxides Fe(OH)₃ (R.B) : Cr (OH)₃ (Green) Al(OH)₃ (white).

\Rightarrow KSP of these hydroxide is low, Hence low cone of OH⁻ is required for their precipitation.



\Rightarrow In presence of NH₄Cl ionization of NH₄OH (\downarrow) the OH⁻ produced is jus sufficient to precipitate only 3rd group cations.

\Rightarrow Without NH₄Cl if NH₄OH is added 3rd and 4th group cation are precipitated.

\Rightarrow Excess of NH₄Cl is avoided, otherwise Al⁺³ and Cr⁺³ are not precipitated.

\Rightarrow Solution should not be heated before adding NH₄OH (Cr forms coloured soluble comple $[\text{Cr}(\text{NH}_3)_6]^{+3}$ (pink).

Solubility of hydroxides:

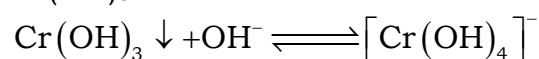
i) Fe(OH)₃ insoluble in NaOH

ii) Al(OH)₃ ppt dissolves in NaOH. $\left[\text{Al}(\text{OH})_3 \downarrow \text{OH}^- \rightleftharpoons \underset{\substack{\text{solu}}}{\text{Al}(\text{OH})_4} \right]$ equilibrium shifted

of L.H.S and ppt occurs in presence

i) NH₄Cl ii) slightly acidification [if excess acid ppt Al(OH)₃ redissolves].

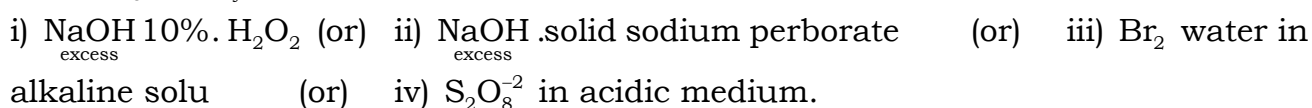
iii) Cr(OH)₃ dissolves in excess of NaOH.



i) Boiling solu.

ii) Slight acidification eq. state shifted to LHS and precipitation re occurs.

\Rightarrow Cr (iii) is oxidized to CrO₄⁻² chromate then identified.

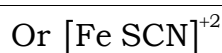


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graph TD
    A[original solu] -- NH4Cl / NH4OH --> B[ppt may contain  
Fe(OH)3, Al(OH)3, Cr(OH)3]
    A -- NH4Cl / NH4OH --> C[filtrate used  
for IV group]
    B -- "Fe(OH)3 insoluble in NaOH  
1) NaBO2 or H2O2 and NaOH  
Cr(OH)3 changes to Cr2O4^2-  
Al(OH)3 forms soluble [Al(OH)4-]" --> D[ppt Fe(OH)3  
dissolved in HCl  
[Fe(OH)3 + HCl + FeCl2 + H2O]  
Solution (FeCl2) used for test / s Fe^2+  
I]
    B -- "Fe(OH)3 insoluble in NaOH  
1) NaBO2 or H2O2 and NaOH  
Cr(OH)3 changes to Cr2O4^2-  
Al(OH)3 forms soluble [Al(OH)4-]" --> E[solution  
i) solution colourless => [Al(OH)4-]  
used for tests / s Al^3+ - II  
ii) yellow solution (Cr2O4^2-)  
used for test / s of cr^3+  
III]

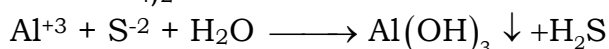
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Reagent	Fe ⁺³	Fe ⁺²
i) NH ₄ Cl / NH ₄ OH	Raidish brown ppt Fe(OH) ₃	NO ppt
ii) H ₂ S(gas) in acidic solu	$\text{Fe}^{+3} \xrightarrow{\text{H}_2\text{S}/\text{H}^+} \overset{\text{(II)}}{\text{Fe}}^{+2} + \text{S} + 2\text{H}^+$ <p style="text-align: center;">↓ milky white ppt</p>	NO ppt Ksp of FeS is large [S ⁻²] is not sufficient for precipitation. But partial ppt. Occurs in presence of CH ₃ COONa.
iii) (NH ₄) ₂ S	$\text{Fe}^{+3} \xrightarrow{(\text{NH}_4)_2\text{S}} \text{FeS} + \text{S} \downarrow$ <p style="text-align: center;">Black ppt</p>	$\text{Fe}^{+2} + (\text{NH}_4)_2\text{S} \rightarrow \text{FeS} \downarrow$ <p style="text-align: center;">Black ppt</p>
iv) H ₂ S / alkali	Black ppt of Fe ₂ S ₃	
v) K ₄ [Fe(CN) ₆]	Intense blue ppt Fe ₄ [Fe(CN) ₆] ₃ dissolves in H ₂ C ₂ O ₄	K ₂ Fe[Fe(CN) ₆] white ppt in absence of air
vi) K ₃ [Fe(CN) ₆]	Fe[Fe(CN) ₆] Brown coloration	Fe ⁺² + K ₃ [Fe(CN) ₆] → Fe ₄ [Fe(CN) ₆] dark blue ppt
NH ₄ SCN	Deep-red colouration [Fe(SCN) ₃] or [Fe(SCN) ₄] ⁻	No colouration (Distinction from Fe ⁺³).

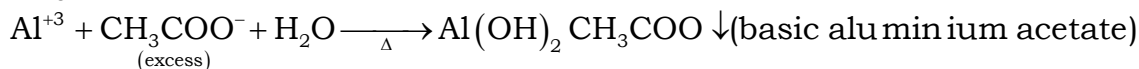


II. Reactions of Al^{+3}

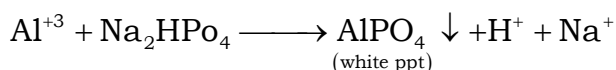
i) with $\text{NH}_4)_2\text{S}$ solution.



ii) CH_3COONa solution.

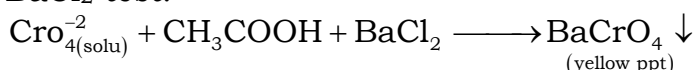


iii) $(\text{Na}_2\text{HPO}_4)$ disodium hydrogen phosphate

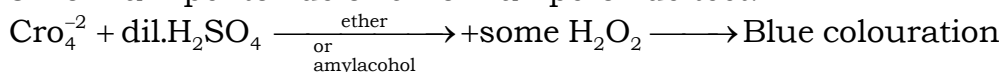


III Reaction of Cr after oxidation to CrO_4^{-2}

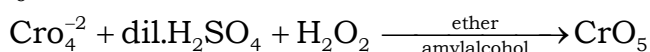
i) BaCl_2 test:



ii) Chromium pentoxide or chromiumperoxide test.



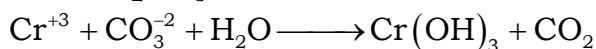
Which is extracted in to organic phase by gently shaking. Blue colouration is due to CrO_5 .



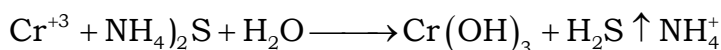
In aq. Solution blue colour fades rapidly due to decomposition of CrO_5 to $\text{Cr}^{+3} + \text{O}_2$

Reactions of Cr^{+3}

i) With Na_2CO_3 solution



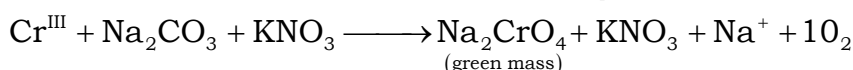
ii) $\text{NH}_4)_2\text{S}$ solution:



Note [similar to Al_2S_3 ; Cr_2S_3 undergoes hydrolysis and form hydroxide].

iii) Cr with Na_2CO_3 and KNO_3 .

When $\text{Cr}^{(\text{III})}$ salt + $\text{Na}_2\text{CO}_3 + \text{KNO}_3 \xrightarrow[\text{pt. foil}]{\text{Heated on}} \text{green mass.}$



IV Group

Cations : Mn^{+2} , Zn^{+2} , Co^{+2} , Ni^{+2}

\Rightarrow Group reagent : NH_4Cl / NH_4OH / H_2S

\Rightarrow Precipitated as : Sulphides MnS , ZnS Cos NiS
(light pink) (white) Black

Ksp values of these sulphides is higher than the 2nd group sluphide. \therefore higher concentration of $[\text{S}^{-2}]$ is required for their precipitation. Ionisation of H_2S (\uparrow) in slightly alkaline medium. The conc of S^{-2} is sufficient to precipitate IV group cations.

Note: the cations are not precipitated in neutral or acidic medium.

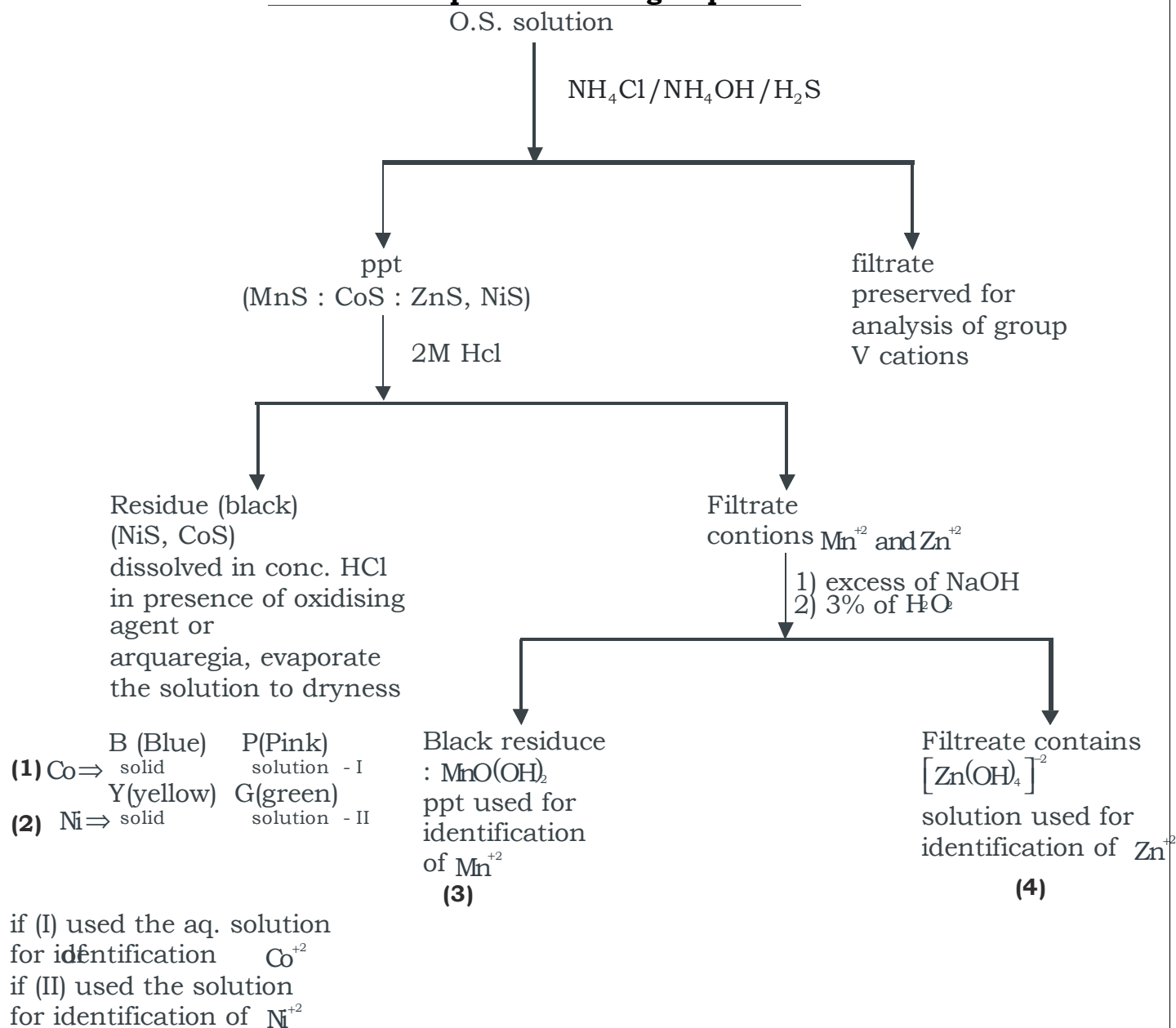
Solubility of sulphides : Ksp values

i) ZnS , MnS are soluble in mineral acids.

ii) CoS , NiS , insoluble in only mineral acids but dissolves in mineral acids in presence of oxidizing agent. i) KClO_3 ii) PbO_2 iii) NaOCl

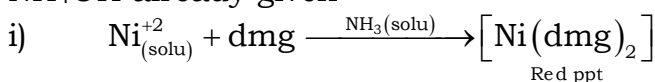
iii) CoS , NiS soluble in aquaregia and Hot conc. HNO_3

Chart for the separation of IV group cations



2. Reactions of Ni^{+2} : Dissolved Ni(II) salts are green owing to the $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$

\Rightarrow Reaction with NaOH , NaCN NH_4OH & KI already discussed
 NH_4OH already given



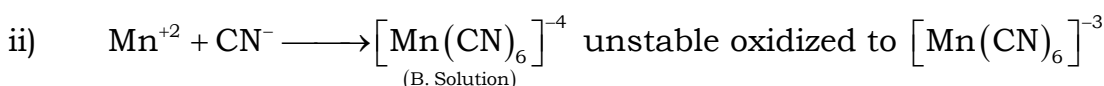
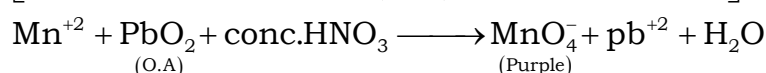
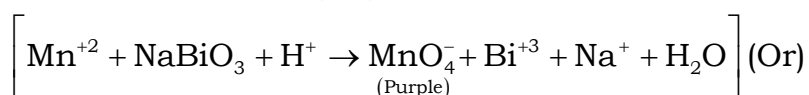
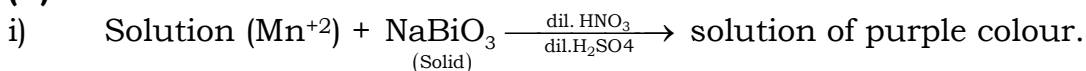
(Ni^{+2} : dsp^2 : square planar $n = 0$ $\mu = 0$ diamagnetic)

$\text{Fe}^{+2} + \text{dmg} \longrightarrow \text{Red colouration}$

$\text{Co}^{+2} + \text{dmg} \longrightarrow \text{Brown colouration}$

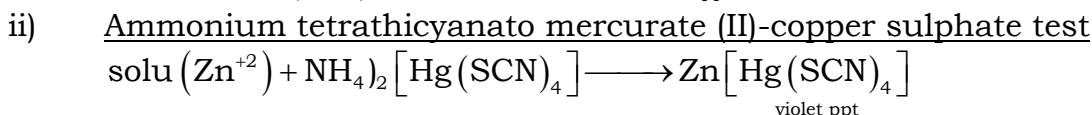
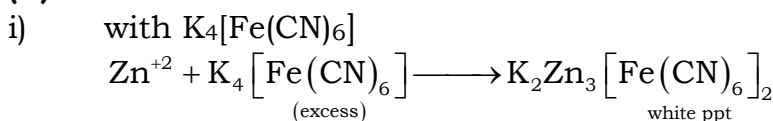
$\text{Bi}^{+3} + \text{dmg} \longrightarrow \text{yellow ppt}$

(3). Reaction of Mn^{+2}

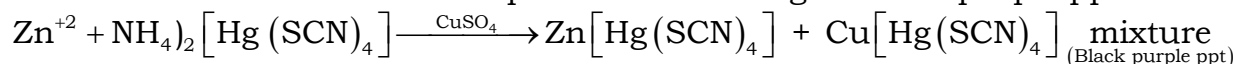


Note : Complexes of Mn^{+2} with NH_3 and H_2O $[\text{Mn}(\text{NH}_3)_6]^{+2}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$ are highly stable resist attack of oxidizing and reducing agents.

(4). Reactions of Zn^{+2}



Above reaction is carried out in present of CuSO_4 give Black purple ppt.



Group V

Cations : Ca^{+2} Sr^{+2} Ba^{+2}

Group reagent : NH_4Cl NH_4OH $(\text{NH}_4)_2\text{CO}_3$.

Precipitated as : Carbonates CaCO_3 : SrCO_3 , BaCO_3 (white)

Solubility of salts of V group. cation

CO_3^{-2} , SO_4^{-2} , PO_4^{-3} , $\text{C}_2\text{O}_4^{-2}$ are insoluble NO_3^- and Cl^- are soluble

Role of NH_4Cl is to 1) prevent the ppt of hydroxides by lowering the ionisation of NH_4OH .

ii) Lower the ionization of $(\text{NH}_4)_2\text{CO}_3$ other wise Mg^{+2} (VI gp) is precipitated
 solubility of carbonates : All are soluble in CH_3COOH .

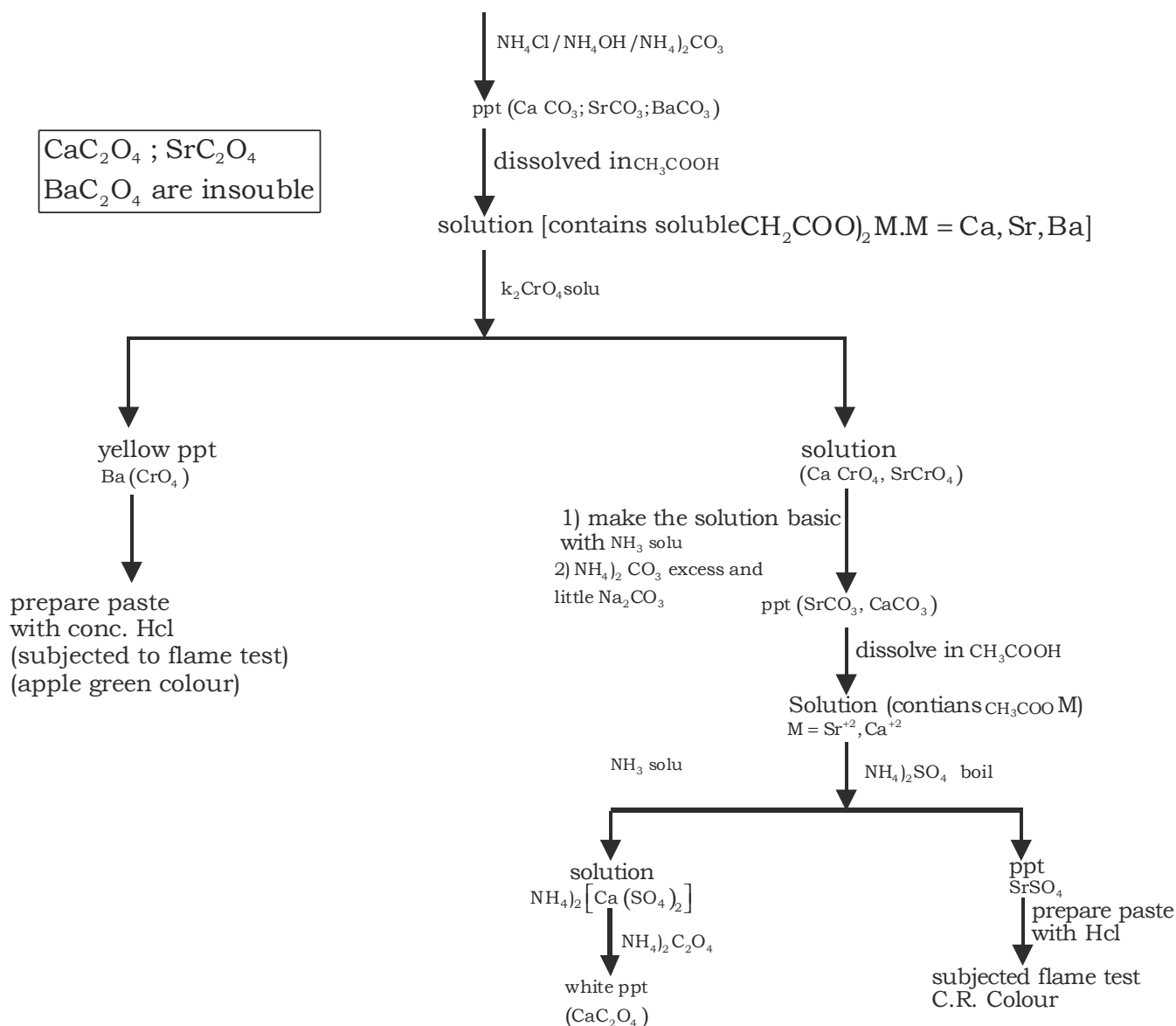
Solubility of chromates : $\text{Ba}(\text{CrO}_4)_2$ insoluble Ca , Sr chromate (are soluble)

Solubility of sulphates : BaSO_4 , CaSO_4 insoluble CaSO_4 dissolves in $(\text{NH}_4)_2\text{SO}_4$ due to formation of $(\text{NH}_4)_2[\text{Ca}(\text{SO}_4)_2]$

$(\text{NH}_4)_2\text{CO}_3$ has to be used in neutral or slightly alkaline medium (in acidic medium $(\text{NH}_4)_2\text{CO}_3$ decomposes) NH_4OH / NH_4Cl maintains slightly alkaline.

Chart of separation of V group cations

O.S or filtrate of IV group [If IV group cations are present]



Group VI

Cations : Mg⁺², K⁺, Na⁺

Test/s for Mg⁺²;

Slightly alkaline i) $\text{Na}_2\text{HPO}_4 + \text{Mg}^{+2} \xrightarrow[\text{NH}_4\text{OH}]{\text{NH}_4\text{Cl}} \text{Mg NH}_4\text{PO}_4$ white crystalline ppt

Role of NH₄Cl / NH₄OH : prevents ppt of Mg(OH)₂ by maintaining slightly alkaline

Alkaline ii) $\text{Mg}^{+2} + \text{NH}_4\text{OH} \rightleftharpoons \underset{\text{white ppt}}{\text{Mg(OH)}_2} + \text{NH}_4^+$

Ppt readily dissolves in NH₄⁺ salt solution

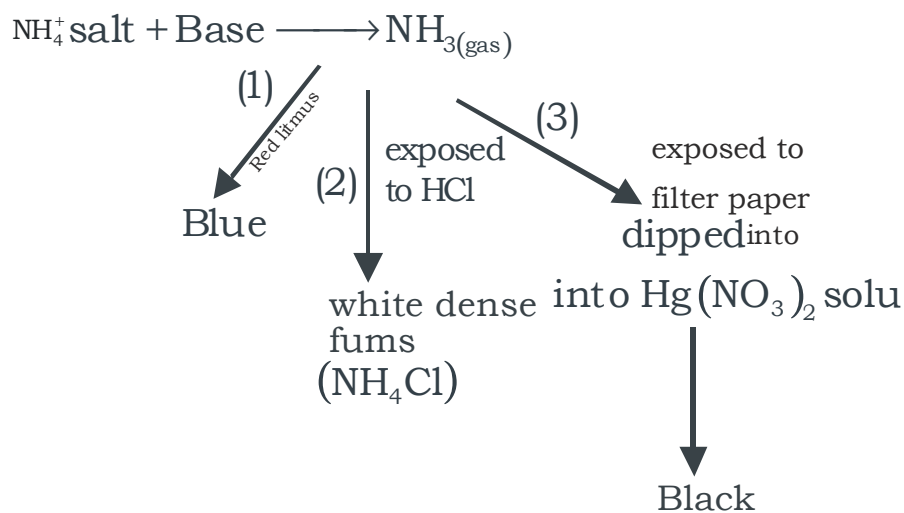
Neutral iii) $\text{Mg}^{+2} + \text{Na}_2\text{HPO}_4 \longrightarrow \underset{\text{(white ppt)}}{\text{MgHPO}_4}$

Zero group (NH₄⁺) ammonium

i) ammonium salts on reaction with base gives NH₃ gas. [NH₄ salt + OH⁻ → NH₃]

ii) Nessler's reagent alkaline solution of K₂[Hg I₄]

$\text{K}_2\text{Hg I}_4 + \text{NH}_4^+ + \text{OH}^- \longrightarrow [\text{HgOHg(NH}_2)_2\text{I}]^+ \text{I}^-$ (Iodide of millon's base). Brown ppt or solution depending on cone. Of NH₄⁺



Action of heat – Some salts change their colour when heated

Substance	Colour in Cold	Colour in Hot
HgO	Red	Black
HgS	Scarlet	Black
ZnO	White	Yellow
CuCl_2	Blue	Brown
CuSO_4	Blue	White
HgI_2	Crimson	Yellow

NaCl , KI , $\text{Pb}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ Decrepitate (Cracking sound)

Alums, borates and phosphate swell up on heating. HgCl_2 , Hg_2Cl_2 , Sb_2O_3 , AlCl_3 and NH_4X – are white and sublime on heating. As_2O_3 , HgI_2 yellow and sublime on heating.

Gas evolved on heating

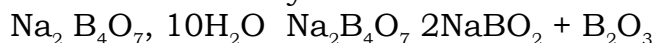
Gas evolved	Identified by	Possible compound
CO	Burns with blue flame	Oxalate $(\text{COO})_2\text{Ca} \rightarrow \text{CaO} + \text{CO} + \text{CO}_2$
CO_2	Turns lime water milky	Carbonate (except carbonate of alkali metals)
NH_3	White fumes with HCl	Ammonium salts $(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4 + \text{NH}_3$
SO_2	Smell of burning Sulphur turns $\text{K}_2\text{Cr}_2\text{O}_7$ Soln green	Sulphites $\text{CaSO}_3 \rightarrow \text{CaO} + \text{SO}_2$
H_2S	Smell of rotten egg	Sulphides $\text{Na}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{S}$
Br_2	Reddish brown	Bromide $2\text{CdBr}_2 + \text{O}_2 \rightarrow 2\text{CdO} + 2\text{Br}_2$
I_2	Violet vapours	Iodide $2\text{ZnI}_2 + \text{O}_2 \rightarrow 2\text{ZnO} + \text{I}_2$
NO_2	Reddish brown	Nitrate (except alkali metals)

Flame test – Salt 1–2 drops of Conc HCl Heat in a non luminous (oxidising) Bunsen flame using platinum wire.

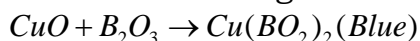
Note : Conc. HCl is used to convert non-volatile metal salt into volatile metal chloride.

Element	colour of the flame
Sodium	Golden yellow
Potassium	Lilac
Calcium	Brick red
Strontium	Crimson
Barium	Apple green
Copper	Bluish green

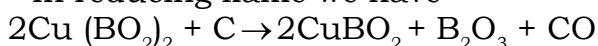
Borax bead test – Borax is heated on a loop of Pt. wire when colourless glassy bead of sodium metaborate anhydride is formed.



Coloured salts are then heated on the glassy bead when coloured metaborate is formed in the oxidising flame



In reducing flame we have

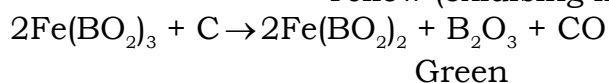
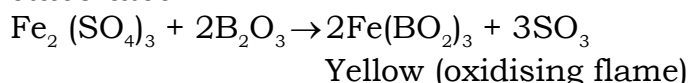


Hence different colour appears in different flames

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

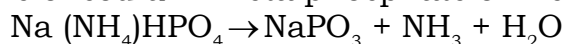
Note :

Metals undergoing change in oxidation state eg Fe^{2+} and Fe^{3+} and Cu^+ and Cu^{2+} form two metaborates

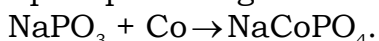


(reducing flame)

Microcosmic bead test – It is similar to borax bead test. Here microcosmic salt $\text{Na}(\text{NH}_4)\text{HPO}_4$ is used in place of borax which forms a colourless, transparent bead on a loop of Pt. wire of sodium meta phosphate on heating



The metallic oxides then combine with sodium metaphosphate to form coloured ortho phosphates eg

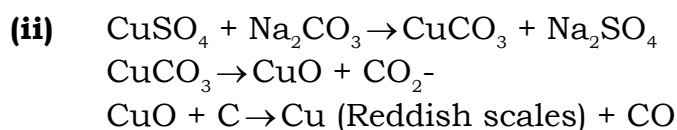
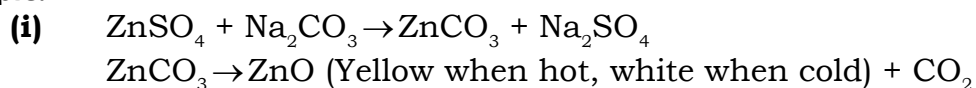


Cobalt orthophosphate (blue)

Colours of beads are similar to those obtained in borax bead test.

Charcoal Cavity Test :

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

Example:

Observation		Inference
Incrustation or Residue	Metallic bead	
Yellow when hot, white when cold	None	Zn^{2+}
Brown when hot, yellow when cold	Grey bead which marks the paper	Pb^{2+}
No characteristic residue	Red beads or scales	Cu^{2+}
White residue which glows on heating	None	$\text{Ba}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}$
Black	None	Nothing definite—generally coloured salt

(i) Cobalt Nitrate Test :

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

