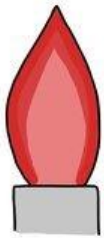


CHM 111 lab

Experiments for basic radicals

***Flame test**

| Experiment | Observation | Inference |
|--|--|---|
| The mixture is made into a paste with con. HCl on a watch glass. A little of this paste is taken at the end of a glass rod and shown very near a non-luminous Bunsen flame. The color imparted, if any, to the flame is noted. | a) Blue/Bluish green colour b) Pale green colour c) Brick red colour d) Crimson red colour e) Lilac colour f) Golden yellow colour g) Carmine red colour | Copper may be present Barium may be present Calcium may be present Strontium may be present Potassium may be present Sodium may be present Lithium may be present |



LITHIUM



SODIUM



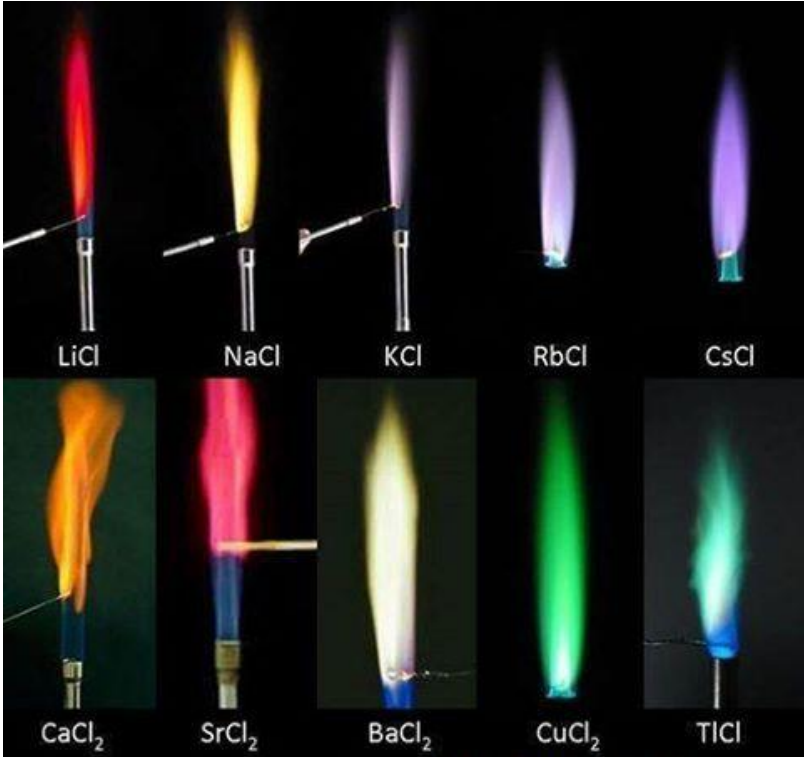
POTASSIUM



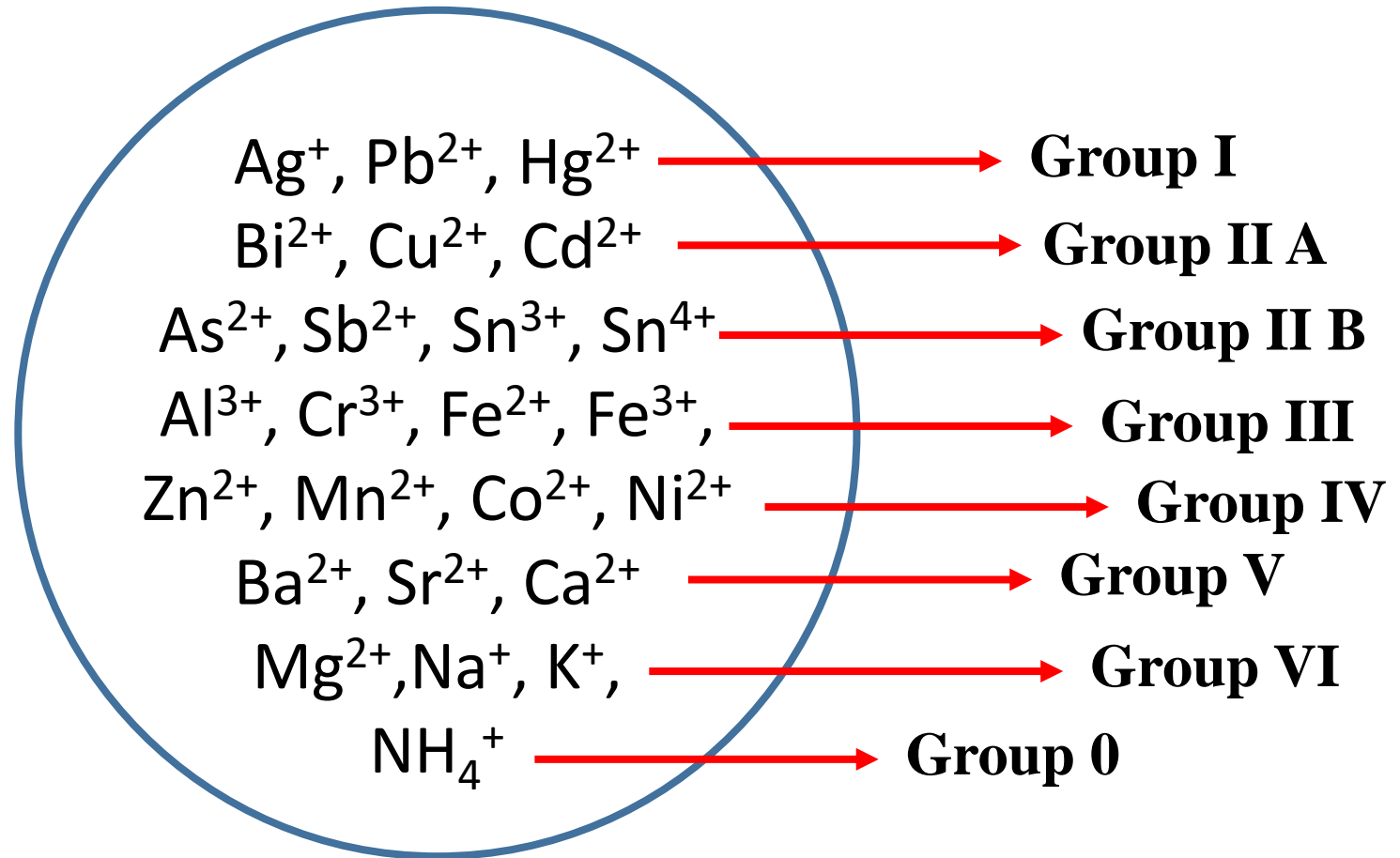
CALCIUM



COPPER



The complete qualitative analysis of any inorganic mixture covers the identification of both, the cations and anions. The analysis of cations is simple as it is systematic in approach, unlike acidic radicals. Once the original solution is prepared various radicals from it are precipitated GroupWise in the form of suitable compounds.

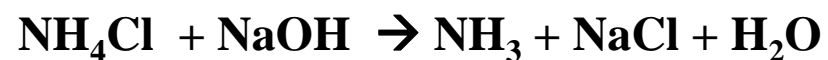


Take a pinch of substance + 2 test tube distilled water, stir, heat if necessary. Filter only if solutions is turbid i.e. not clear. Use it as original solution (O.S.)

Analysis of Group 0

Radical --- NH_4^+

| Experiment | Observation | Inference |
|--|---|----------------------------|
| 1) O. S. + 2ml dil NaOH shake well and warm gently | NH_3 gas evolved recognized by its smell turning moist red litmus paper blue or moist Turmeric Paper brown or Evolution of dense white fumes when a glass rod dipped in conc.HCl is held over the mouth of the test tube | NH_4^+ is present |
| Further treat with 1ml of Nessler's reagent | Brown ppt or colouration | NH_4^+ is present |



With Nessler's reagent



Oxydimercuric ammonium Iodide

Intergroup Separation

Dil. HCl is added to the original solution and filtered

**Residue: (white)→
Presence of Group I cation**

No residue →
Absence of Group I cation

Filtrate: It is diluted, heated and then H_2S is passed through it. (Filtered)
(Note: If a precipitate is formed, after separating it, H_2S should again be passed through the filtrate and these processes repeated till no more precipitate is formed.)

**Residue:
(Black/Brownish**

black/Yellow/Orange/Brown)→ Presence of Group II cation

No residue →
Absence of Group II cation

Filtrate: H_2S is boiled off. It is then treated with NH_4Cl and excess of NH_4OH . (Filtered)

**Residue:
(White/Green/Reddish brown)→**

Presence of Group III cation

No residue →
Absence of Group III cation

Filtrate: It is concentrated. Excess of NH_4OH is added and H_2S is passed. (Filtered)

(Note: If a precipitate is formed, completeness of precipitation must be ensured by continued passing of H_2S .)

**Residue
(Black/Flesh colored dirty white) →**

Presence of Group IV cation

No residue →
Absence of Group IV cation

Filtrate: H_2S is boiled off and concentrated. Excess of NH_4OH and excess of $NH_4(CO_3)_2$ are added and warmed. (Filtered)

**Residue (White) →
Presence of Group V cation**

No residue →
Absence of Group V cation

Filtrate: Tested for Group VI cations

Analysis of Group I Residue

Radicals --- Ag^+ , Pb^{2+} , Hg^{2+}

The Group I residue is boiled with water and filtered

Residue: A white residue \rightarrow Presence of Ag^+ and Hg^{2+}
Wash the residue with hot water to remove PbCl_2 if any. Now shake the residue with dil. NH_4OH , warm and filter.

Residue: It gradually turns black. Dissolve this in aqua regia (1 part conc. HNO_3 + 3 parts conc. HCl) and add SnCl_2 soln \rightarrow A white precipitate turning to grey colour \rightarrow **Presence of Hg_2^{2+}**

Filtrate: Divide into three portions:
a) I portion+ dil. $\text{HNO}_3 \rightarrow$ A white precipitate \rightarrow **Presence of Ag^+**
b) II portion+ KI soln \rightarrow A pale yellow precipitate \rightarrow **Presence of Ag^+**
c) III portion + $\text{K}_2\text{CrO}_4 \rightarrow$ A brick red precipitate \rightarrow **Presence of Ag^+ is confirmed.**

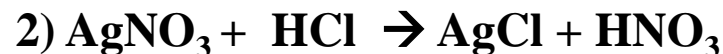
Filtrate: The hot solution is divided into three portions:

- a) I portion+ KI soln \rightarrow A yellow precipitate which dissolved on heating with water, but reappears on cooling in the form of golden spangles \rightarrow **Presence of Pb^{2+}**
- b) II portion + $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow$ A yellow precipitate soluble in $\text{NaOH} \rightarrow$ **Presence of Pb^{2+}**
- c) III portion + dil. $\text{H}_2\text{SO}_4 \rightarrow$ A white precipitate \rightarrow **Presence of Pb^{2+} is confirmed.**

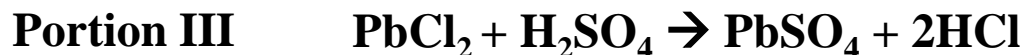
Reactions of specific tests

Analysis of Group I Radicals --- Ag^+ , Pb^{2+} , Hg^{2+}

Chemical Reactions involved in 1 Group Analysis: Ag^+ , Pb^{2+} and Hg^{2+} ions present in the solution react with Cl^- ions from HCl , to give white precipitate.



Separation and identification of Pb (filtrate): On boiling the ppt with water, PbCl_2 becomes soluble thus separated by filtration. This when treated with KI , K_2CrO_4 and H_2SO_4 separately, following reactions take place.



Treatment of residue with NH_4OH : i) AgCl dissolves in NH_4OH forming a soluble complex.



(diamine silver chloride)

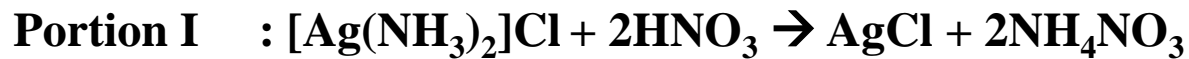
NH_4OH converts Hg_2Cl_2 to black residue which consists of white amino-mercuric chloride and black finely divided Hg .



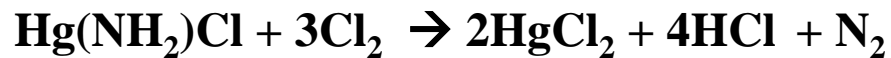
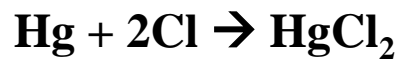
(white) (black)

(black)

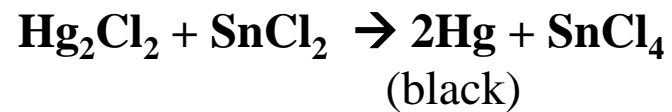
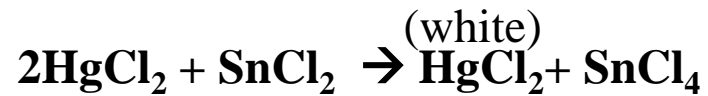
Reactions of Ag: The filtrate containing soluble silver complex is treated in three ways separately



Reactions of Hg_2^{2+} :



Addition of SnCl_2 reduces HgCl_2 to white Hg_2Cl_2 . Further addition of SnCl_2 reduces white Hg_2Cl_2 to black finely divided Hg. .



Analysis of Group II

The Group II residue is boiled with NaOH soln and a few drops of ammonium sulphides soln and filtered.

Residue:

- a) A Black/brownish black/yellow residue → Presence of Group IIA cation. (Bi^{2+} , Cu^{2+} , Cd^{2+})
- b) No residue: Absence of Group IIA cation.

Filtrate: It is acidified with dil.HCl and warmed

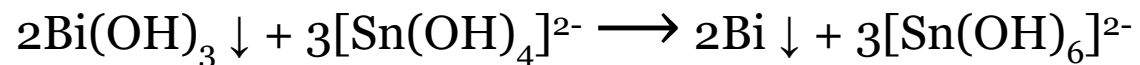
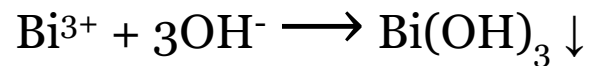
- a) An orange/yellow residue → Presence of Group IIB cation. (As^{2+} , Sb^{2+} , Sn^{3+} , Sn^{4+})
- b) No residue: Absence of Group IIB cation.

Analysis of Group IIA

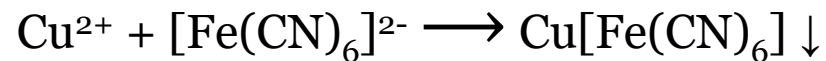
Radicals --- Bi^{2+} , Cu^{2+} , Cd^{2+}

| | | |
|--|--|---|
| Filtrate: The group IIA residue is boiled with dil HNO_3 and filtered. | | |
| Residue: Hg^{2+} | Filtrate: It is treated with excess of dil. H_2SO_4 and filtered. | |
| | Residue: A white residue: Presence of Bismuth (Bi^{3+}) The residue is collected and dissolved in minimum quantity of dil. HCl . The solution is divided into two portions a) A portion is added to large excess of water (taken in a boiling test tube or a beaker) → <i>A white turbidity</i> → Presence of Bi^{3+} b) The second portion is treated with sodium stannite solution → <i>A black precipitate</i> → Presence of Bi^{3+} is confirmed. | Filtrate: It is concentrated and then treated with excess of NH_4OH solution |
| | Filtrate: The color is noted. a) Blue : Presence of Cu^{2+} b) Colourless : Absence of Cu^{2+} It is divided into two portions: a) One portion is acidified with CH_3COOH and treated with $\text{K}_4\text{Fe}(\text{CN})_6$ solution → <i>A brown precipitate</i> → Presence of Cu^{2+} is confirmed. <u>Test for Cadmium (Cd^{2+})</u> The second portion is again divided into two parts : a) To one part, add KCN soln drop by drop until blue colour disappears and then H_2S is passed through it → <i>A yellow precipitate</i> → Presence of Cd^{2+} is confirmed. b) To second part, add excess of dil. H_2SO_4 to make soln strongly acidic. Now, add Zn dust, boil and filter. To the filtrate add NH_4OH to neutralize excess acid, then add 1ml. Dil. HCl and pass H_2S → <i>A yellow precipitate</i> → Presence of Cd^{2+} is confirmed. | |

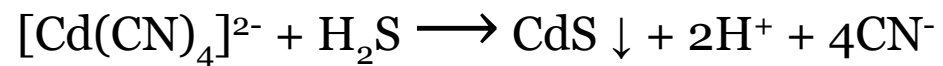
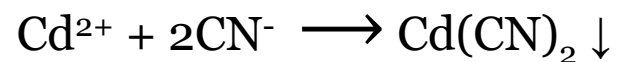
Reactions of Ba³⁺:



Reactions of Cu²⁺:



Reactions of Cd²⁺:



Analysis of Group IIB

Radicals: As^{2+} , Sb^{2+} , Sn^{3+} , Sn^{4+}

Filtrate: Warm the filtrate with dil HCl. If white precipitate comes, filter it off. Now add 10ml of conc. HCl and boil it for 2-3 minutes. Dilute it with about 5ml of hot water and filter.

Residue:

A yellow residue \rightarrow Presence of Arsenic As^{3+}

Divide and dissolve the residue separately in

a) Con HNO_3 and add excess of ammonium molybdate and heat \rightarrow A yellow precipitate \rightarrow **Presence of As^{3+} .**

b) The residue is gently warmed with ammonium carbonate solution and acidified with dil. HCl \rightarrow A yellow precipitate with or without passing $\text{H}_2\text{S} \rightarrow$ **Presence of As^{3+} is confirmed.**

Filtrate: Boil the filtrate to remove H_2S completely and divide the solution in two portions:

a) I Portion+ NH_4OH till alkaline. Add solid oxalic acid, boil and pass $\text{H}_2\text{S} \rightarrow$ An orange precipitate \rightarrow **Antimony**

b) II Portion + 1-2 iron nails. Boil and filter .

i) If black residue \rightarrow **Antimony**

ii) Filtrate + HgCl_2 soln \rightarrow A white precipitate \rightarrow **Tin**



Analysis of Group III Radicals --- Al^{3+} , Cr^{3+} , Fe^{2+} , Fe^{3+}

The Group III residue is mixed with NaOH and few drops of Br_2 water. Boil it for 2-3 minutes and filter.

Residue : The color is noted.

- a) Black residue → **Presence of Mn**
- b) Reddish brown → **Presence of Ferric only**

Wash the residue with hot water. Reject the washing. Dissolve in conc. HNO_3 . Divide solution into two portions:

- a) I Portion + $\text{K}_4[\text{Fe}(\text{CN})_6]$ soln → *A deep blue precipitate/coloration* → **Presence of iron**
- b) II Portion + pinch of PbO_2 . It is then diluted with water and allowed to stand for a while → *Violet or purple colour in upper layer of solution* → **Presence of Mn^{2+} is confirmed.**

To test whether Ferrous(Fe^{2+}) or Ferric (Fe^{3+}) (Note: These tests need to be done only if iron is found to be present)

- a) O.S. + $\text{K}_3[\text{Fe}(\text{CN})_6]$ is added → *A deep blue ppt/colour* → **Presence of Ferrous(Fe^{2+})**
- b) O.S. + dil. H_2SO_4 + dil. KMnO_4 is added in drops → *The KMnO_4 soln is decolourised* → **Presence of Ferrous(Fe^{2+})**
- c) O.S. + $\text{K}_4[\text{Fe}(\text{CN})_6]$ soln is added → *A deep blue ppt/colour* → **Presence of Ferrous(Fe^{3+})**
- d) O.S. + KCNS soln is added → *A blood red colouration* → **Presence of Ferrous (Fe^{3+})**

Filtrate: The color is noted.

- a) Yellow → **Presence of Cr^{3+}**
- b) Colourless → **Absence of Cr^{3+}**

It is divided into two portions:

One portion is acidified with CH_3COOH and again divided into two parts:

- i) Part I treated with lead acetate solution → *A yellow precipitate soluble in NaOH and reappears* → **Presence of Cr^{3+}**
- ii) Part II + AgNO_3 soln → *Brownish red precipitate* → **Presence of Cr^{3+} is confirmed.**

The second portion is boiled with solid NH_4Cl → *A white gelatinous precipitate* → **Presence of Al^{3+} .**

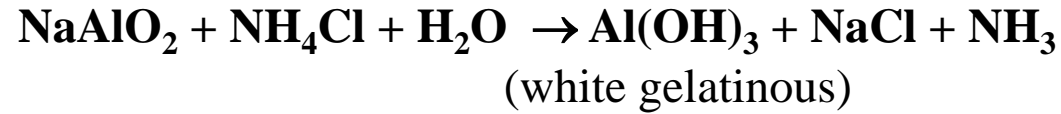
The above ppt is collected and dissolved in conc. HNO_3 . This soln is boiled with a few drops of cobalt nitrate solution. A piece of filter paper is moistened with this soln and the burned to ashes → *A blue tinted ash* → **Presence of Al^{3+} is confirmed.**

Analysis of Group III Radicals --- Al^{3+} , Cr^{3+} , Fe^{2+} , Fe^{3+}

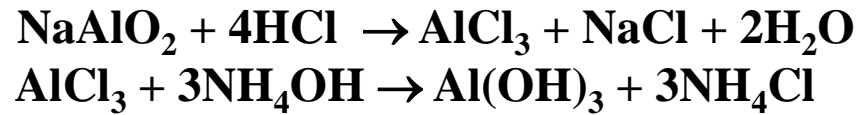
Radicals --- Al^{3+} , Cr^{3+} , Fe^{2+} , Fe^{3+}

Reactions of Al^{3+} :

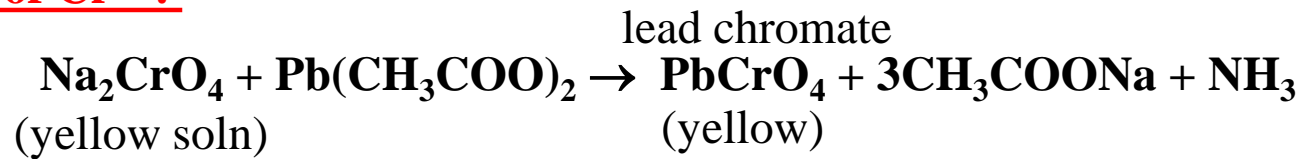
i) In presence of NH_4Cl :



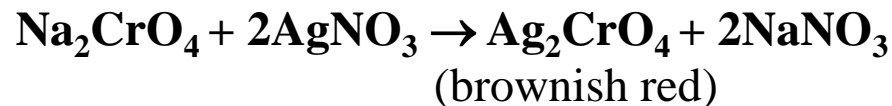
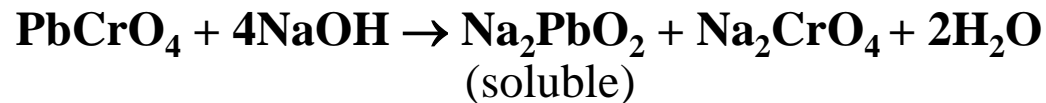
ii) In presence of HCl and NH_4OH :



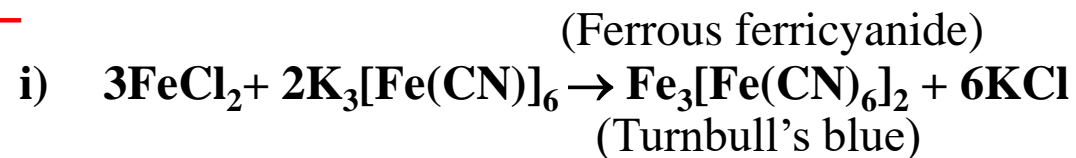
Reactions of Cr^{3+} :



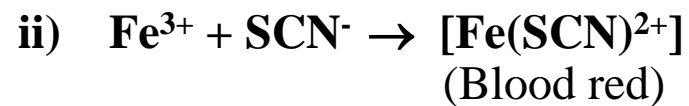
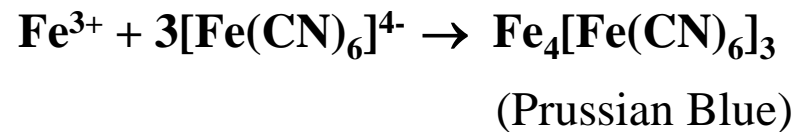
PbCrO₄ is soluble in NaOH but insoluble in CH₃COOH



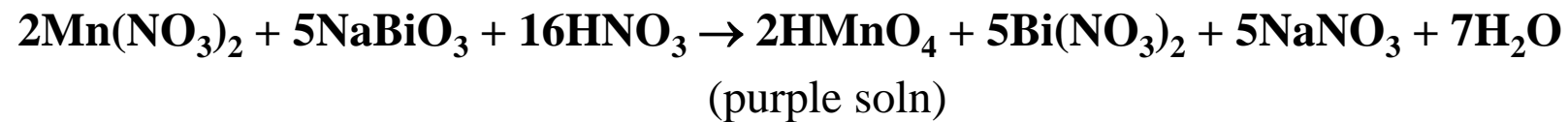
Reactions with Fe²⁺:



Reactions with Fe³⁺:



Reactions with Mn³⁺:



Analysis of Group IV Radicals --- Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+}

Filtrate: The group IV residue is shaken with dil HCl and filtered.

A Black residue $\rightarrow \text{Co}^{2+}$ or Ni^{2+} are present.

The residue is dissolved in aquaregia by heating in a porcelain dish and then the soln is evaporated nearly to dryness.

a) A yellow residue \rightarrow **Presence of Ni^{2+}**

b) A blue residue \rightarrow **Presence of Co^{2+}**

This residue is dissolved in water and the solution is divided into three portions:

i) I portion + solid NH_4Cl + excess NH_4OH + $\text{K}_3[\text{Fe}(\text{CN})_6]$ soln is added \rightarrow A reddish brown precipitate \rightarrow **Presence of Co^{2+}**

ii) II portion + solid ammonium thiocyanate is added and then shaken well with a mixture of amyl alcohol and ether \rightarrow A Blue organic layer \rightarrow **Presence of Co^{2+} is confirmed.**

iii) III portion + NH_4Cl + excess NH_4OH + dimethyl glyoxime reagent are added \rightarrow A Rose red precipitate \rightarrow **Presence of Ni^{2+} is confirmed.**

Filtrate: Boil off H_2S . Cool. Excess of NaOH soln is added. Boil for 3 minutes and filter.

Residue: Wash the residue and add con. HNO_3 . Boil, cool and divide in two parts.

i) I part, dilute and cool. Add sodium bismuthate. Stir well and wait \rightarrow *supernatant liquid purple coloured* \rightarrow **Presence of Manganese (Mn^{2+})**

ii) II part + pinch of PbO_2 , boil for some time and then allow to stand \rightarrow *purple color in upper liquid* \rightarrow **Presence of (Mn^{2+}) is confirmed.**

Filtrate:

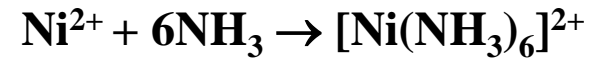
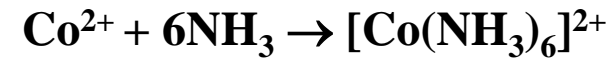
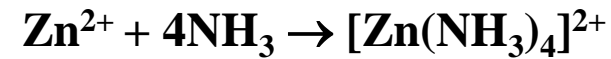
It is divided into two portions:

i) H_2S is passed through the first portion \rightarrow A white precipitate \rightarrow **Presence of Zinc (Zn^{2+})**

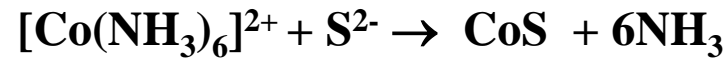
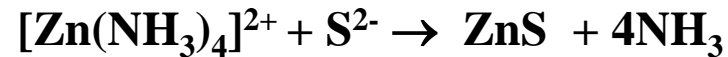
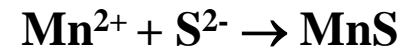
ii) II portion + CH_3COOH + $\text{K}_4[\text{Fe}(\text{CN})_6]$ \rightarrow A white precipitate \rightarrow **Presence of (Zn^{2+}) is confirmed.**

Analysis of Group IV Radicals --- Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+}

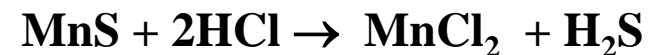
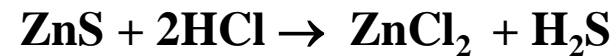
Chemical Reactions involved in IV Group Analysis: The addition of NH_4OH converts these cations except Mn into soluble amino complexes.



The ammoniacal solution containing Mn^{2+} and these amino complexes gets converted into sulphides when H_2S is passed.

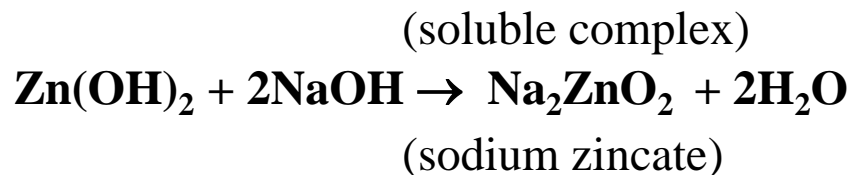
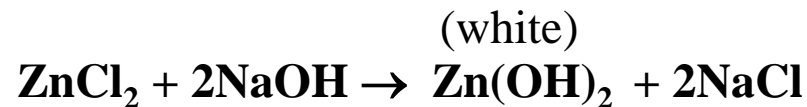


Addition of very dil. HCl , dissolves only Zn and Mn sulphides

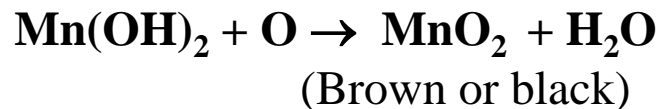


Reactions with Zn²⁺ and Mn²⁺

Zn forms a white precipitate of Zn(OH)₂ but it dissolves in excess of NaOH forming a soluble complex sodium zincate.

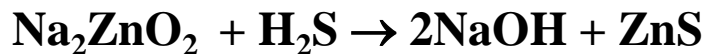


Mn is converted to a white ppt of Mn(OH)₂ which is oxidized to black MnO₂ and finally becomes hydrated as MnO₂.xH₂O

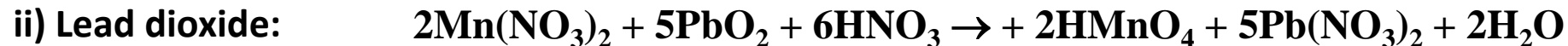


Thus filtrate contains Na₂ZnO₂ and residue contains MnO₂.xH₂O

Test for Zn²⁺ : On passing H₂S into the filtrate, a white ppt of ZnS is produced.



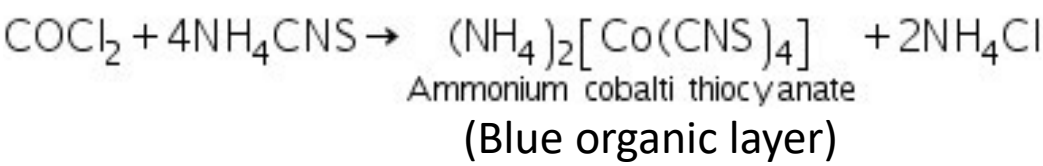
Test for Mn²⁺ Mn(OH)₂ with con.HNO₃ changes to Mn(NO₃)₂



Confirmatory test for Co²⁺

Ammonium thiocyanate ether test:

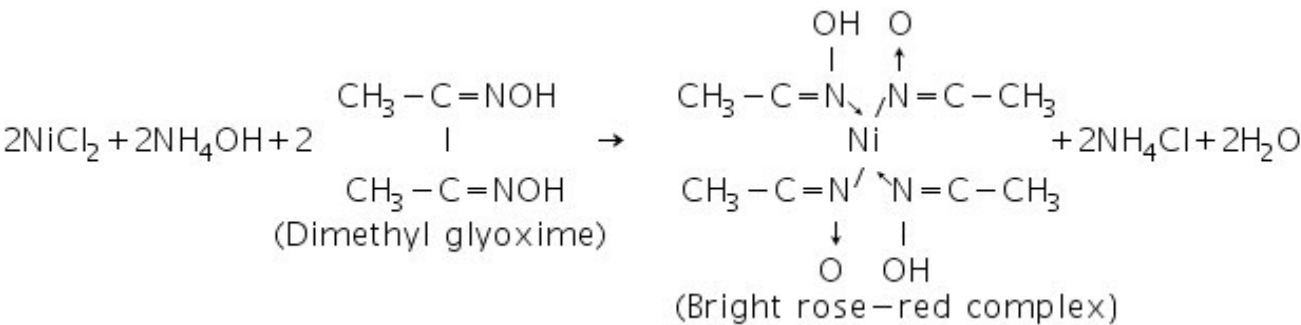
On addition of ether and a crystal of ammonium thiocyanate, a blue colour is obtained in the ethereal layer due to the formation of ammonium cobalti thiocyanate.



Confirmatory test for Ni²⁺

Dimethyl glyoxime test

Ni²⁺ ions react with dimethyl glyoxime to form bright rose-red coloured Nickel-dimethyl glyoxime complex, Ni(dmgH)₂.



Analysis of Group V

Radicals --- Ba^{2+} , Sr^{2+} , Ca^{2+}

Filtrate: The group V residue is washed with a little hot water and dissolved in minimum quantity of hot acetic acid. The dissolved CO_2 is boiled off. To the nearby boiling solution, a slight excess of K_2CrO_4 solution is added dropwise with constant stirring and filtered.

Residue:

Yellow Residue \rightarrow **Ba^{2+} is present.**

The residue is collected, washed well with hot water and dissolved in a little con. HCl. The solution is divided into two portions.

- i) To one portion, dil. H_2SO_4 is added \rightarrow A white precipitate \rightarrow **Presence of Ba^{2+} is confirmed.**
- ii) The second portion is evaporated in a porcelain dish to a paste and flame test is conducted with it \rightarrow A pale green flame \rightarrow **Presence of Ba^{2+} is further confirmed.**

Filtrate: It is concentrated by evaporation and $(\text{NH}_4)_2\text{SO}_4$ solution is added in excess, boiled and filtered.

Residue: Test for Sr^{2+}

A white precipitate \rightarrow **Presence of Sr^{2+}**

Flame test is conducted on the original mixture \rightarrow A crimson red flame \rightarrow **Presence of Sr^{2+} is further confirmed.**

Filtrate: Test for Ca^{2+}

To filtrate, ammonium oxalate solution is added \rightarrow A white precipitate \rightarrow **Presence of Ca^{2+}**

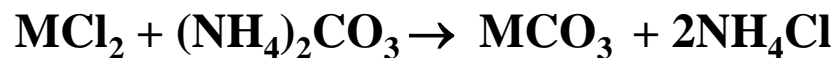
*Flame test is conducted on the original mixture \rightarrow Brick red Flame \rightarrow **Ca^{2+} is confirmed.**

*Flame test: The mixture is made into a paste with con. HCl on a watch glass. A little of this paste is taken at the end of a glass rod and shown very near a non-luminous Bunsen flame. The color imparted, if any, to the flame is noted.

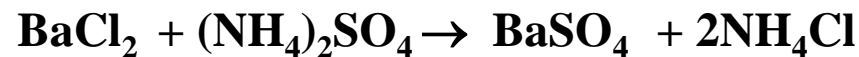
Analysis of Group V Radicals --- Ba²⁺, Sr²⁺, Ca²⁺

The fifth group radicals are precipitated as their carbonates. The function of NH₄Cl is to suppress the ionization of NH₄OH and (NH₄)₂CO₃ (common ion effect) which will otherwise precipitate Mg.

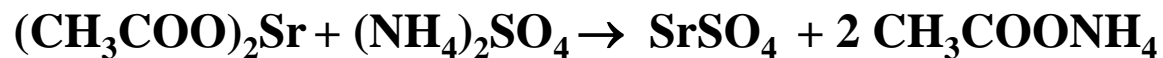
The precipitation reaction takes place as follows:



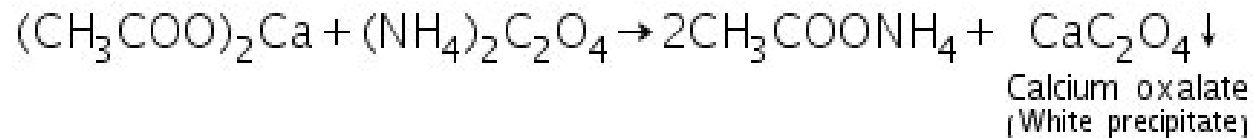
Reactions of Ba²⁺



Confirmatory test for Sr²⁺



Confirmatory test for Ca²⁺



Analysis of Group VI

Radicals --- Mg^{2+} , Na^+ , K^+

The filtrate left after the removal of Group V cations is evaporated nearly to dryness in a porcelain dish. About 5ml of con. HNO_3 is added to the paste and then evaporated cautiously to dryness. Heating is continued cautiously until the evolution of white fumes stops. The major portion of the residue is dissolved in minimum amount of water.

A) Tests for Magnesium Mg^{2+}

1 a) Portion I + saturated NH_4Cl and NH_4OH till alkaline (in slight excess) and then add ammonium phosphate solution and shaken well (The inner sides of the test tube below the liquid level are scratched using a glass rod) → *A white crystalline precipitate* → **Presence of Mg^{2+}**

b) The above ppt is collected and dissolved in con. HNO_3 . This soln is boiled with a few drops of cobalt nitrate solution. A piece of filter paper is moistened with this soln and the burned to ashes → A pink tinted ash → **Presence of Mg^{2+} is confirmed.**

2. Portion II + excess of NH_4OH is added followed by oxine reagent → *A yellow precipitate* → **Presence of Mg^{2+} is confirmed.**

3. Portion III of the solution is treated with a few drops of magneson reagent is added followed by excess of NaOH soln → *A Blue precipitate* → **Presence of Mg^{2+} is further confirmed.**

B) Test for Na and K

1. Take the filtrate of Group V, precipitate off magnesium by Na_2HPO_4 . Now evaporate this filtrate to dryness to remove NH_4^+ . Lixivate it with water and add sodium reagent (magnesium acetate and uranyl acetate). The inner sides of the test tube below the liquid level are scratched using a glass rod and kept for a while. → *A crystalline yellow precipitate* → **Presence of Na^+ is confirmed**

2. Lixivate it with water and add some acetic acid and finally sodium cobaltinitrite in excess → *A yellow precipitate* → **Presence of K^+**

C) Flame test is conducted with the initial residue:

a) Golden yellow color flame → **Presence of Na^+ is confirmed.**

b) A lilac flame → **Presence of K^+ is confirmed.**

Confirmatory test for Mg⁺

Ammonium Phosphate test

Mg²⁺ ions react with ammonium phosphate in presence of NH₄Cl and NH₄OH to form white precipitate of magnesium ammonium phosphate.



Confirmatory test for Na⁺



Confirmatory test for K⁺

