# Qualitative Inorganic Analysis

Radicals Included in Syllabus

Cation Radicals: $Na^{+}$, $K^{+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Co^{3+}$, $Ni^{3+}$, $Cu^{2+}$, $Zn^{2+}$.

Anion Radicals: $F^{-}$, $Cl^{-}$, $Br^{-}$, $BrO_3^{-}$, $I^{-}$, $SCN^{-}$, $S^{2-}$, $SO_4^{2-}$, $S_2O_3^{2-}$, $NO_3^{-}$, $NO_2^{-}$, $PO_4^{3-}$, $BO_3^{3-}$, $CrO_4^{2-}$/ $Cr_2O_7^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$

Insoluble Materials: $Al_2O_3$, $Fe_2O_3$, $Cr_2O_3$, $SnO_2$, $SrSO_4$, $BaSO_4$, $CaF_2$.

# Preliminary Tests for Basic Radicals

Experiment [A]: Heating in a dry fusion tube

| Experiment | Observations | | Inference |
|---|---|---|---|
| | At hot condition | At cold condition | |
| A pinch of sample is taken in a dry fusion tube and it was heated in flame until red-hot.<br><br>N.B. For colour and black sample this test is generally non-conclusive | Yellow | White | $Zn^{2+}$ may be present |
| | Red to Black | Brown | $Fe^{2+}$ may be present |
| | White | White | $Na^{+}$, $K^{+}$, $Cu^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Al^{3+}$ may be present |
| | Brown / reddish vapour | | $NO_2^{-}$, $NO_3^{-}$ (of heavy metal) and/or $Br^{-}$ may be present |
| | Violet vapour | | $I^{-}$ may be present |

Experiment [B]: Flame test

| Experiment | Observation | | Inference |
|---|---|---|---|
| | Colour of flame | Colour through double blue glass | |
| A platinum wire was touched with conc. HCl as well as with the sample and it was kept in the flame | Golden yellow | Colourless | $Na^{+}$ may be present |
| | Violet | Crimson red | $K^{+}$ may be present |
| | Brick red | | $Ca^{2+}$ may be present |
| | Crimson red | | $Sr^{2+}$ may be present |
| | Apple green | | $Ba^{2+}$ may be present |
| | Green | | $Cu^{2+}/BO_3^{3-}$ may be present |
| | Bluish green with bifurcation like snake tongue | | $Sn^{2+}$ may be present |

** Some times $Ca^{2+}$ e.g. $CaF_2$ gives flame like $Sr^{2+}$ but the colour is not persistent.
*** $MnCl_2$ also imparts a green colouration.
**** Sulfates of $Ca^{2+}$,$Ba^{2+}$,$Sr^{2+}$ are at first reduced to sulfides by heating in a small filter paper in the reducing flame then the flame test is performed because sulfates are insoluble in conc. HCl.

- Modified Flame Test

Phosphates give a yellow flame like sodium and musk the colour of $K^{+}$, $Ca^{2+}$, $Ba^{2+}$, and $Sr^{2+}$. So in presence of $PO_4^{3-}$ modified flame test is to be performed.
Test: 0.5 gm. of solid sample was boiled with 5 ml. of conc. $H_2SO_4$ and then it is cooled to room temperature. 2ml. of $C_2H_5OH$ was added and allowed to stand. Now the liquid is decanted off and the residue was washed with water. Now flame test was performed as before.

Experiment [C]: Borax bead test
(Only for colour samples)

| Experiment | Observation<br>Colour of the bead (In oxidizing flame & in cold) | Inference |
|---|---|---|
| A transparent bead of borax was made in the platinum ring by heating. The red-hot bead was touched to the sample and was heated vigorously in oxidizing flame. Then it was cooled | Sapphire blue | $Co^{2+}$ may be present |
| | Blue | $Cu^{2+}$ may be present |
| | Yellow | $Fe^{3+}$ may be present |
| | Emerald green | $Cr^{3+}$ may be present |
| | Violet | $Mn^{2+}$ may be present |
| | Reddish brown | $Ni^{2+}$ may be present |

Experiment [D]: Fusion test
(Only if Expt. C is positive & only for $Mn^{2+}$ and $Cr^{3+}$)

| Experiment | Observation | Inference |
|---|---|---|
| i) A pinch of sample was fused with solid NaOH and fusion mixture ($KNO_3$+$Na_2CO_3$) on a mica foil vigorously | Colour of the mass: Green | $Mn^{2+}$ may be present |
| | Colour of the mass: Yellow | $Cr^{3+}$ may be present |
| ii) Now the fused mass was dissolved in dil. $CH_3COOH$ and then $(CH_3COO)_2Pb$ was added | Pink colouration before adding $(CH_3COO)_2Pb$ | $Mn^{2+}$ may be present |
| | Yellow ppt. after adding $(CH_3COO)_2Pb$ | $Cr^{3+}$ may be present |

# When both are present, the green colour will mask the yellow
Then $CH_3COOH$ was added and a pink colour was obtained: Indicates $Mn^{2+}$. Now the colour was discharged by $NaNO_2$ and then $(CH_3COO)_2Pb$ was added: yellow ppt. was obtained: $Cr^{3+}$ present.

Experiment [E]: Fluorescence test
(Only for $Sn^{2+}$)

| Experiment | Observation | Inference |
|---|---|---|
| A paste was made with 0.2gm. of sample; tin free zinc dust and few drops of conc. HCl in a beaker. The outer surface of a test tube, half filled with cold water, was moist with the paste and was held near to the flame | Blue fluorescence was observed | $Sn^{2+}$ may be present |

# Preliminary Tests for Acid Radicals

Experiment [A]: Test for sulfur group (except $SO_4^{2-}$)

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was heated with Zn-dust and dil. $H_2SO_4$ | Smell of evolved $H_2S$ gas (detected by $(CH_3COO)_2Pb$ paper) / rotten egg smell | $S^{2-}$, $SCN^-$, $S_2O_3^{2-}$ (and/or) present |

Experiment [B]: Test with dil. $H_2SO_4$
(Only if Expt. A is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was heated with dil. $H_2SO_4$ | $H_2S$ gas evolved | Acid decomposable $S^{2-}$ |
| | $SO_2$ gas with yellowish white turbidity | $S_2O_3^{2-}$ may be present |
| | Pale reddish brown vapour | $NO_2^-$ may be present |

Experiment [C]: Iodine azide test (in spot plate)
(Only if Expt. A is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was stirred along with iodine azide ($I_2$ + $NaN_3$) and one drop of starch in a spot plate | Deep blue colour due to $I_2$ discharged | $S^{2-}$, $SCN^-$, $S_2O_3^{2-}$ (and/or) may be present |

Experiment [D]: Test with Cu-turnings & conc. $H_2SO_4$

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was heated with Cu-turnings and conc. $H_2SO_4$ | Red or brown vapour | $BrO_3^-$, $Br^-$, $NO_3^-$, $NO_2^-$ (and/or) may be present |
| | Violet vapour | $I^-$ may be present |
| | Oily liquid | $F^-$ may be present |

Experiment [E]: Test with conc. $H_2SO_4$
(Only if Expt. D is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was heated with few drops of conc. $H_2SO_4$ | Violet vapour | $I^-$ may be present |
| | Red or reddish vapour | $BrO_3^-$, $Br^-$, $NO_2^-$ (and/or) may be present |
| | Oily liquid | $F^-$ present & confirmed |

Experiment [F]: Special spot test

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was added to the mixture of $FeCl_3$ and $FeSO_4$ taken in a spot plate and was stirred | Blood red colour | $SCN^-$ may be present |
| | Deep blue colour | $Fe(CN)_6^{3-}$ and/or $Fe(CN)_6^{4-}$ may be present |

Experiment [G]: Ammonium molibdate test

Preparation of $HNO_3$ Extract

A small amount of sample was heated with conc. $HNO_3$ (2-3ml.) in a test tube till evolution of reddish brown vapour ceases (it also indicates that reducing agent is present).

If necessary filter or centrifuge...the filtrate is the desired extract.

| Experiment | Observation | Inference |
|---|---|---|
| To a little amount of the extract ammonium molibdate reagent was added and was heated for some time | Canary yellow ppt. | $PO_4^{3-}$ present & confirmed |

**** Preserve the extract for future use in the tests for $Mn^{3+}$ & $Cr^{3+}$ during wet tests of basic radicals.

Experiment [H]: Test for $BO_3^{3-}$

| Experiment | Observation | Inference |
|---|---|---|
| A pinch of sample was heated with a few drops of conc. $H_2SO_4$ and methanol ($CH_3OH$). The vapour coming through the mouth of the test tube was ignited | Vapour burns with green flame | $BO_3^{3-}$ present & confirmed |
| A paste of the sample was made using 1-2 drops of conc. $H_2SO_4$ and $CaF_2$. The paste was taken on a platinum wire and was held nearer to the oxidizing flame (not into the flame) | A green flame*,# originated | $BO_3^{3-}$ present & confirmed |

* If the flame is noticed without using $CaF_2$ then $BO_3^{3-}$ & $F^-$ both are present.
# The green flame is due to formation of $BF_3$

# Wet Tests for Acid Radicals

Solution preparation: If the sample is completely soluble in water and if there is no ppt. with $Na_2CO_3$ solution then proceed with aqueous solution.

If the sample is partly or completely insoluble in water prepare $Na_2CO_3$ extract.

(Preparation of $Na_2CO_3$ extract for each sample is recommended)

***** $Na_2CO_3$ Extract Preparation *****

To one part of sample add five times of $Na_2CO_3$ by weight. Then add 10-15 ml. of water and boil for 15-20 min. (use conical flask & glass funnel). Occasional addition of water is needed to maintain the amount of water. After complete boiling filter it and collect the $Na_2CO_3$ extract as filtrate.

N.B.: Preserve the residue for the tests of basic radicals.

[It is advised to start $Na_2CO_3$ extract preparation at the beginning of your new work and to perform the preliminary tests for both basic and acid radicals during the extract preparation. It saves the time.]

Experiment [A]: $AgNO_3$ test

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $HNO_3$ and few drops of $AgNO_3$ were added | White ppt. soluble in dil. $NH_3$ solution | $Cl^-$ present |
| | White ppt. soluble in conc. $NH_3$ solution | $Br^-$ present |
| | Yellowish white ppt. insoluble in liquor $NH_3$ | $I^-$ present |

Experiment [B]: $BaCl_2$ test

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $CH_3COOH$ and few drops of $BaCl_2$ were added | White ppt. insoluble in conc. HCl | $SO_4^{2-}$ present & confirmed |

Experiment [C]: Test for oxidizing anions

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $H_2SO_4$ and few drops of KI were added followed by two drops of starch | The solution became deep blue / blue / black | Oxidizing anions are present. [$NO_2^-$, $CrO_4^{2-}$, $BrO_3^-$, $Fe(CN)_6^{3-}$, $NO_3^-$ (very slow to react)] |

Experiment [D]: Test for reducing anions

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $H_2SO_4$ and two drops of $KMNO_4$ were added | The pink colour of was discharged | Reducing anions are present. [$Br^-$, $I^-$, $S_2O_3^{2-}$, $Fe(CN)_6^{4-}$,$S^{2-}$, $SCN^-$, $NO_2^-$, $Cl^-$ (slow to react)] |

**Tests for Oxidizing Anions**
*(Only if Expt. C is positive)*

Experiment [E]: Sulphanilic acid test
(Only if Expt. C is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract (also water extract) was acidified with dil. $CH_3COOH$ and taken in a spot plate, then one drop each of sulphanilic acid and α-napthyl amine was added in succession and was stirred | A pink colouration | $NO_2^-$ present & confirmed |
| If $NO_2^-$ is absent add Zn-dust to the resultant solution and stir | A pink colouration | $NO_3^-$ present & confirmed |
| If $NO_2^-$ is present add sulphamic acid / urea to discharge the pink colour then add Zn-dust to the resultant solution and stir | A pink colouration | $NO_3^-$ present & confirmed |

Experiment [F]: Test for $BrO_3^-$
(Only if Expt. C is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $H_2SO_4$ and few drops of manganese sulphate ($MnSO_4$) were added and heated | A dark brown ppt. with intermediate red brown colouration | $BrO_3^-$ present & confirmed |
| For detection of trace amount of $BrO_3^-$ To one drop of reaction mixture add excess of sodium acetate ($CH_3COONa$) or ammonium acetate followed by benzidiene reagent | A deep blue colouration | $BrO_3^-$ present & confirmed |

Experiment [G]: Test for $CrO_4^{2-}$ / $Cr_2O_7^{2-}$
(Only if Expt. C is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $CH_3COOH$ and few drops of $(CH_3COO)_2Pb$ were added | A yellow precipitate | $CrO_4^{2-}$ / $Cr_2O_7^{2-}$ present & confirmed |

N.B.: If the colour of extract is yellow: indicates $CrO_4^{2-}$ / $Cr_2O_7^{2-}$

Experiment [H]: Test for $Fe(CN)_6^{3-}$
(Only if Expt. C is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. HCl and a pinch of fresh solid Mohr's salt was added | A deep blue colouration | $Fe(CN)_6^{3-}$ present & confirmed |

**Tests for Reducing Anions**
(*Only if Expt. D is positive*)

Experiment [I]: Test for $S^{2-}$
(Only if Expt. D is positive)

| Experiment | Observation | Inference |
|---|---|---|
| To a part of $Na_2CO_3$ extract few drops of sodium nitropruside was added | A pink / violet colouration | $S^{2-}$ present & confirmed |

Experiment [J]: Test for $S_2O_3^{2-}$
(Only if Expt. D is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. $CH_3COOH$ and $AgNO_3$ solution was added quickly. | White ppt. turned yellow to brown to black | $S_2O_3^{2-}$ present & confirmed |

Experiment [K]: Test for $Br^-$ / $I^-$
(Only if Expt. D is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. HCl; little $CCl_4$ was added then chlorine water was added drop wise with shaking | Colour of the $CCl_4$ layer turned Violet | $I^-$ present & confirmed |
| | Colour of the $CCl_4$ layer turned Orange | $Br^-$ present & confirmed |

Experiment [L]: Test for $SCN^-$ / $[Fe(CN)_6]^{4-}$ / $[Fe(CN)_6]^{3-}$
(Only if Expt. D is positive)

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. HCl and few drops of $FeCl_3$ solution were added. | Blood red colour | $SCN^-$ present & confirmed |
| | Deep blue ppt. | $[Fe(CN)_6]^{4-}$ present & confirmed |
| | Brown / green colour | $[Fe(CN)_6]^{3-}$ indicated |

Experiment [M]: Test for $F^-$

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. HCl and added to few drops of Zr(IV)-Alizarin-S reagent. | Red colour of reagent was discharged. | $F^-$ present & confirmed |

In Presence of One Another

Experiment [N]: $Cl^-$, $Br^-$, $I^-$ in presence of one another

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was acidified with dil. HCl; little $CCl_4$ was added then chlorine water was added drop wise with shaking. | Colour of the $CCl_4$ layer turned Violet | $I^-$ present & confirmed |
| Reaction with $Cl_2$ water was continued until violet colour is discharged. Then few more drops of $Cl_2$ water were added. | Colour of the $CCl_4$ layer turned Orange | $Br^-$ present & confirmed |
| $Br^-$ and $I^-$ were removed from the extract by boiling the $Na_2CO_3$ extract with conc. $HNO_3$ and $AgNO_3$ solution was added. | White ppt. was obtained which is soluble in dil. $NH_3$ | $Cl^-$ present & confirmed |

Additionally, chromyl chloride test is recommended for $Cl^-$ (only if Expt. A is positive)

Experiment [O]: Chromyl Chloride Test

| Experiment | Observation | Inference |
|---|---|---|
| A part of $Na_2CO_3$ extract was evaporated to dryness. Little amount of solid $K_2Cr_2O_7$ and few drops of conc. $H_2SO_4$ were added and heated. | Reddish orange vapour obtained. | $Cl^-$ present |
| The orange vapour was absorbed in a drop of NaOH solution on a glass rod and transferred to spot plate. It was acidified with drop of $H_2SO_4$ and diphenyl carbazide reagent was added. | Violet colouration was obtained | $Cl^-$ present & confirmed |

# Wet Tests for Basic Radicals

**Preparation of Solution:**

Aqueous solution: Sample was heated with water with shaking. If necessary, it was filtered to collect filtrate as desired aqueous solution.

HCl extract: The residue (if obtained above) was heated with conc. HCl with shaking and filtered.
Residue: Insoluble or aqua rigia soluble or Gr-I cations (not in current syllabus)
Filtrate: Desired HCl extract.

HCl extract from the residue of $Na_2CO_3$ extract preparation: The residue was washed thoroughly with water and dissolved in conc. HCl with heating. It was filtered and filtrate was collected.

If Interfering acid radicals, *viz*. a) $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ b) $F^-$ and $BO_3^{3-}$ c) $PO_4^{3-}$ present:

a) Removal of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$:
   Residue from $Na_2CO_3$ extract preparation was fumed with a few drops of conc. $H_2SO_4$ over a low flame to decompose $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ completely. After cooling it was further heated with a little water and then filtered.
   Residue: It may contain sulfates of $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$ : may be confirmed by flame test.
   Filtrate: It was used for analyses of basic radicals as usual.

b) Removal of $F^-$ and $BO_3^{3-}$:
   Residue from $Na_2CO_3$ extract preparation was heated with a few drops of conc. HCl and ethanol (if $BO_3^{3-}$ present) several times to dryness and finally conc. HCl extract was prepared by heating.

Experiment [A]: Group II [$Cu^{2+}$]

| Experiment | Observation | Inference |
|---|---|---|
| For aqueous solution dil. HCl was added and for HCl extract, it was diluted with water. The solution was heated and to warmed solution $H_2S$ was passed. | Black ppt. obtained | $Cu^{2+}$ present |
| If ppt. obtained, it was filtered and $H_2S$ was boiled off from the filtrate. The solution was neutralized with $NH_4OH$ and 8 drops of dil. HCl per 5 ml of solution were added. It was warmed and $H_2S$ was passed. If ppt. obtained, it was filtered. Filtrate was diluted with water and $H_2S$ was passed. The process was continued to ensure complete precipitation. | Black ppt. obtained | $Cu^{2+}$ present |

| | | |
|---|---|---|
| **Confirmatory Test:** The ppt. obtained was boiled with dil. NaOH and filtered. Obtained ppt. was then dissolved with dil. $HNO_3$ by boiling. To the clear solution obtained excess $NH_4OH$ was added. It was filtered and filtrate was collected. | Deep blue filtrate obtained | $Cu^{2+}$ present |
| The filtrate was acidified with dil. acetic acid and $K_4[Fe(CN)_6]$ was added. | Chocolate ppt. obtained | $Cu^{2+}$ present & confirmed |

Experiment [B]: Group IIIA [$Fe^{3+}$, $Al^{3+}$, $Cr^{3+}$ and $Mn^{2+}$]

| Experiment | Observation | Inference |
|---|---|---|
| $H_2S$ was boiled off from the filtrate of group II filtrate completely. It was boiled with 1 ml conc. $HNO_3$ till no brown fumes.* 1 g. $NH_4Cl$ and excess $NH_4OH$ were added. | White / green / brown ppt. obtained | $Fe^{3+}$, $Al^{3+}$, $Cr^{3+}$ and / or $Mn^{2+}$ present |

**If $PO_4^{3-}$ present, it must be removed at this point by $FeCl_3$ method. So, follow the following method.*

c) Removal of $PO_4^{3-}$:
If $PO_4^{3-}$ is confirmed by ammonium molibdate test, then it is to be confirmed whether $PO_4^{3-}$ separation is required or not.
To few drops of solution excess $NH_4OH$ was added. If ppt. obtained, $PO_4^{3-}$ separation is mandatory.

Test for $Fe^{3+}$: To few drops of solution $NH_4SCN$ reagent was added. If deep red colour, $Fe^{3+}$ confirmed.

To the solution, dil. $NH_4OH$ was added drop wise to neutralize the acid. Minimum drops of dil. HCl were added just to dissolve the ppt. 2 – 3 ml. of conc. ammonium acetate per 10 ml. of solution was added. It was boiled and filtered.

Residue: Residue was washed with water and used for group IIIA treatment. [For $Fe^{3+}$,$Al^{3+}$, $Cr^{3+}$ and / or $Mn^{2+}$]

Filtrate: To the filtrate neutral $FeCl_3$ solution was added drop wise till a light TEA colour was attained. $NH_4OH$ was added to it till ammoniacal. Then it was heated and filtered. Residue obtained was discarded and to the filtrate $H_2S$ was passed to complete precipitation. It was filtered and the residue was used for treatment for group IIIB [See Expt. C, Treatment] and the filtrate was used for group IV [See Expt. D] analysis.

Treatment of Group IIIA

The ppt. was washed with water. Strong and fresh NaOH was added followed by a few drops of $H_2O_2$ solution and was shaken in the cold and then $H_2O_2$ was decomposed by heating. It was filtered.

Residue: *if available*

| Experiment | Observation | Inference |
|---|---|---|
| Residue was divided into two parts<br>1. It was dissolved in dil. HCl and $NH_4SCN$ reagent was added | Blood red colouration | $Fe^{3+}$ present & confirmed |
| 2. The remaining part was dissolved in dil. $H_2SO_4$ containing a pinch of $Na_2SO_3$. $SO_2$ was boiled off completely. Then it was cooled down and a pinch of sodium bismuthate was added and shaken. It was allowed to settle. | Pink colouration | $Mn^{2+}$ present & confirmed |

Filtrate:

| Experiment | Observation | Inference |
|---|---|---|
| Filtrate was divide into three parts<br>1. If yellow, one part was acidified with acetic acid and lead acetate reagent was added. | Yellow ppt. obtained | $Cr^{3+}$ present & confirmed |
| 2. Solid NH4Cl was added to the second part of the filtrate and heated to dissolve. | A white gelatinous ppt. obtained | $Al^{3+}$ present & confirmed |
| 3. To the third part on a spot plate, Alizarin-S reagent was added followed by dil. acetic acid drop wise to just discharge the violet color of the reagent. | Red colouration or ppt. obtained. It was compared to a blank. | $Al^{3+}$ present & confirmed |

Experiment [C]: Group IIIB [$Mn^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Zn^{2+}$]

| Experiment | Observation | Inference |
|---|---|---|
| To the filtrate from group IIIA, $H_2S$ was passed till complete precipitation. It was filtered. | Black / white / flesh colour ppt. obtained | $Mn^{2+}$, $Ni^{2+}$, $Co^{2+}$ and/or $Zn^{2+}$ present |

Treatment of Group IIIB

The ppt. obtained was stirred with cold 1(N) HCl and filtered.

Residue: It was dissolve in aqua regia by heating and was evaporated nearly to dryness. Then it was dissolved in hot dil. HCl and was divided into two parts.

| Experiment | Observation | Inference |
|---|---|---|
| 1. To one part DMG reagent was added followed by $NH_4OH$ till ammoniacal. | Rosy red ppt. obtained | $Ni^{2+}$ present & confirmed |
| 2. To other part equal amount of conc. HCl and conc. $NH_4SCN$ was added followed by acetone | Deep blue colour obtained | $Co^{2+}$ present & confirmed |

Filtrate: $H_2S$ was boiled off completely. 1-2 drops of $H_2O_2$ solution were added followed by excess NaOH. Then $H_2O_2$ was decomposed by heating and it was filtered.

Residue:

| Experiment | Observation | Inference |
|---|---|---|
| The ppt. was dissolved in dil. $H_2SO_4$ containing a pinch of $Na_2SO_3$. $SO_2$ was boiled off completely. Then it was cooled down and a pinch of sodium bismuthate was added and shaken. It was allowed to settle. | Pink colouration obtained | $Mn^{2+}$ present & confirmed |

Filtrate:

| Experiment | Observation | Inference |
|---|---|---|
| To the filtrate $H_2S$ was passed | White ppt. obtained | $Zn^{2+}$ present |
| The ppt. was dissolved in minimum drops of dil. $H_2SO_4$. $H_2S$ was boiled off completely. 1 drop of 0.1% $CuSO_4$ solution was added followed by few drops of ammonium mercuri thiocyanate reagent and it was scratched with a glass rod. | Violet ppt. obtained | $Zn^{2+}$ present & confirmed |

Experiment [D]: Group IV [$Ba^{2+}$, $Sr^{2+}$ and $Ca^{2+}$]

| Experiment | Observation | Inference |
|---|---|---|
| Filtrate from group IIIB was acidified with dil. HCl and $H_2S$ was boiled off completely. Excess $NH_4OH$ was added followed by saturated $(NH_4)_2CO_3$ solution. | White ppt. obtained | $Ba^{2+}$, $Sr^{2+}$ and/or $Ca^{2+}$ present |

Treatment of Group IV

| Experiment | Observation | Inference |
|---|---|---|
| The ppt. was dissolved in hot dil. acetic acid. To a few drops of solution, $K_2CrO_4$ was added. | Yellow ppt. obtained *(collect ppt.)* | $Ba^{2+}$ present & confirmed |
| *If $Ba^{2+}$ absent, proceed to the next stage with the rest of the solution*<br><br>*If $Ba^{2+}$ present, add the $K_2CrO_4$ reagent to the rest of the solution to precipitate out $Ba^{2+}$ and filter. Then proceed to the next stage with the filtrate.* | | |
| To the solution/filtrate solid $(NH_4)_2SO_4$ was added and dissolved. It was filtered. | White ppt. obtained *(collect ppt.)* | $Sr^{2+}$ present & confirmed |
| To the filtrate saturated $(NH_4)_2C_2O_4$ was added followed by $NH_3$ solution drop wise and the walls of test tube was scratched with glass rod. | White ppt. obtained *(collect ppt.)* | $Ca^{2+}$ present & confirmed |

Experiment with the collected ppt.:

| Experiment | Observation | Inference |
|---|---|---|
| With the ppt. collected from the above experiment the Flame test was performed as usual. | Apple green flame obtained | $Ba^{2+}$ present & confirmed |
| | Crimson red flame obtained | $Sr^{2+}$ present & confirmed |
| | Transient brick red flame obtained | $Ca^{2+}$ present & confirmed |

---

## Alternative Ways to Tests for Basic Radicals

All Experiments are Confirmatory

| # | Experiment | Observation | Inf. |
|---|---|---|---|
| | Conc. HCl extract | | |
| A | Extract + $NH_4SCN$ | Blood red colour | $Fe^{3+}$ |
| B | Extract + $NH_4SCN$ + if red colour discharge with $SnCl_2$ + acetone | Deep blue colour | $Co^{2+}$ |
| C | Extract + $NH_4OH$ (slight excess): if ppt., filer + DMG | Rosy red ppt. | $Ni^{2+}$ |
| D | Extract + 2-3 iron nails: heat to reduce: filter to drops of cacotheline | Violet colour | $Sn^{2+/4+}$ |
| | Conc. $HNO_3$ extract | | |
| E | Extract + $NaBiO_3$ (a pinch): shake & settle | Purple colour | $Mn^{2+}$ |
| F | Extract + $NaBiO_3$ (a pinch): shake & settle: [if pink colour: add dil. HCl: heat] | Orange colour | $Cr^{3+}$ |
| G | Extract + $NH_4OH$ (excess): Discard ppt. if any: deep blue colour: acidify with acetic acid + $K_4[Fe(CN)_6]$ | Chocolate brown ppt. | $Cu^{2+}$ |
| | Dil. $CH_3COOH$ extract<br>To be prepared from the residue of $Na_2CO_3$ extract preparation after thorough washing with water | | |
| H | Extract + $H_2S$: if ppt., discard ppt.: boil off $H_2S$ completely: follow treatment of group IV | | |
| | NaOH extract<br>If $S^{2-}$ is present, heat the sample / residue from the residue of $Na_2CO_3$ extract preparation with a few drops of dil. HCl to remove $H_2S$ completely. Add excess of fresh dil. NaOH, heat carefully and filter, if necessary (if $S^{2-}$ is absent, treat sample directly with NaOH) | | |
| I | Extract + $H_2S$: if ppt., filter: White ppt. ($Zn^{2+}$): little dil. $H_2SO_4$: heat (till no $H_2S$ evolves): filter, if required: few drops of solution in spot plate + 1 drop 0.1% $CuSO_4$ + few drops ammonium mercurithiocyanate: stir with a glass rod | Violet ppt. | $Zn^{2+}$ |
| J | Extract + $H_2S$: if ppt., filter: filtrate + dil. HCl (acidify): if ppt.: filter and boil off $H_2S$ from filtrate: divide into two part.<br>1. Part 1 + excess $NH_4OH$<br>2. Part 2 + Fresh aq. NaOH (excess): to few drops of this solution + 2 drops of Alizarin-S reagent + dil. acetic acid drop-wise just to discharge the violet colour of the reagent. | 1. White gelatinous ppt.<br><br>2. Red colour / ppt. | $Al^{3+}$ |

# Analysis of Insoluble Part

**Analysis of Aqua Regia Soluble Part:**

Aqua regia soluble salts and their colours: NiS (black), CoS (black).

If the residue after HCl extract is of above colour, react with minimum drops of aqua regia, evaporate nearly to dryness. Finally extract with dil. HCI and test for $Ni^{2+}$ and $Co^{2+}$ (Group IIIB or Alternative tests #B or #C).

**Analysis of Insoluble Part:**

List of insoluble compounds:

Coloured: Ignited $Cr_2O_3$ : Deep Green
Ignited $Fe_2O_3$ : Rusty Brown

White: $BaSO_4$, $SrSO_4$, $CaF_2$ (also grey), $Al_2O_3$, $SnO_2$

**Isolation of Insoluble Part:** After conc. HCI (aqua regia when required) extract, wash the residue several times by hot water containing a little dil. $HNO_3$ and finally dry it.

**Preliminary Tests for Insoluble Part**

| No. | Test | Condition | Observation | Inference |
|---|---|---|---|---|
| A | Flame test | White insoluble | Apple green flame | $BaSO_4$ |
| | | | Persistent crimson red flame | $SrSO_4$ / $CaF_2$ |
| B | Borax bead test | Coloured insoluble | Green bead | $Cr_2O_3$ |
| | | | Yellow bead | $Fe_2O_3$ |
| C | Fusion test | Green insoluble & if Expt. B positive | Yellow mass | $Cr_2O_3$ |
| D | Fluorescence test | White insoluble | Blue fluorescence | $SnO_2$ |
| E | Test for $F^-$ | White insoluble & if Expt. A shows crimson red flame | Oily liquid and the issuing vapour solidifies water drop | $CaF_2$ |

**Wet Tests for Insoluble Part**

A. For coloured compounds ($Fe_2O_3$ and $Cr_2O_3$):

Dissolution: The insoluble part was fused on a mica foil with fusion mixture, NaOH beads and crystals of $KNO_3$. The melt was cooled and extracted with water and filtered, if necessary.

Residue: It must be brown (if available)

| Experiment | Observation | Inference |
|---|---|---|
| Residue: It was dissolved in dil. HCl and $NH_4SCN$ was added. | Blood red colouration | $Fe_2O_3$ present & confirmed |
| Filtrate: Filtrate was acidified with dil. acetic acid and lead acetate solution was added. | Yellow ppt. obtained | $Cr_2O_3$ present & confirmed |

B. For white compounds ($BaSO_4$, $SrSO_4$ and $CaF_2$)

Dissolution: The insoluble part was fused on a mica foil with fusion mixture, NaOH beads and crystals of $KNO_3$. The melt was cooled and extracted with water and filtered.

| Experiment | Observation | Inference |
|---|---|---|
| Residue: The residue was dissolved in dil. acetic acid and with the solution treatment of group IV was followed. | As per treatment of group IV | $Ba^{2+}$, $Sr^{2+}$ or $Ca^{2+}$ present & confirmed |
| Filtrate: Filtrate was acidified with dil. $HNO_3$ and $Ba(NO_3)_2$ was added. | White ppt. obtained | $SO_4^{2-}$ present & confirmed |

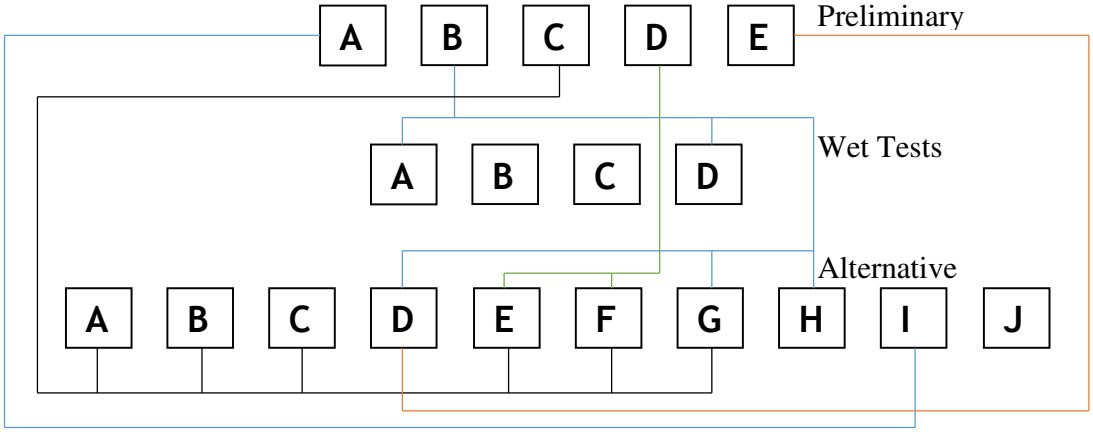
C. For white compounds ($Al_2O_3$ and $SnO_2$)

Dissolution: The insoluble part was fused with $KHSO_4$ for few minutes, cooled and extracted by heating with dil. HCl. With the solution following tests were performed in the given order

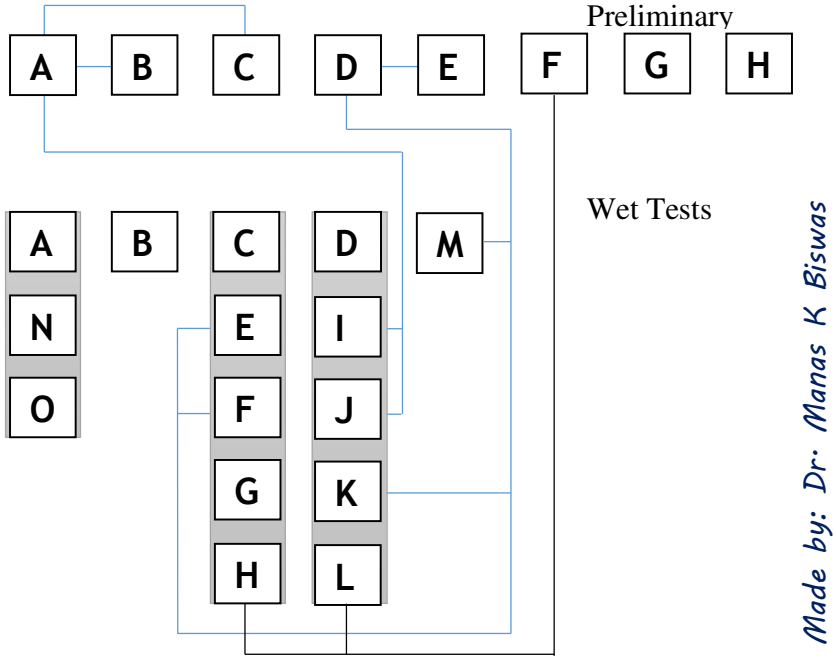
| Experiment | Observation | Inference |
|---|---|---|
| One part of the solution was heated with a little conc. HCl and iron nails for 1-2 minutes and was filtered directly to cacotheline or $HgCl_2$ reagent. | Purple colouration or white/ grey ppt. obtained | $SnO_2$ present & confirmed |
| Excess of fresh NaOH was added to the second part to make it alkaline.<br>If $SnO_2$ absent:<br>Alizarin-S test for $Al^{3+}$ was performed.<br>If $SnO_2$ present:<br>$H_2S$ was passed through the alkaline solution and then it was acidified with dil. HCl and filtered to remove the ppt. The filtrate was heated to boil off $H_2S$, made alkaline with excess of NaOH and with the solution the alizarin-S test for $Al^{3+}$ was performed. | Red ppt. or colouration compared to a blank | $Al_2O_3$ present & confirmed |

## LOGIC GATES

### For Analyses of Basic Radicals




### For Analyses of Acid Radicals






### For Analyses of Insoluble Part