3

Identification of Cationic Constituents

Dry Test Analysis for Cationic Constituents

The identification of cationic constituents (or basic radicals) is always started by carrying out the preliminary dry tests. Although these tests may not lead to very conclusive results, yet these afford certain valuable information which might be helpful for the correct identification of cationic constituents (basic radicals) by wet tests. Now we will discuss various dry tests which are :

1. Physical Examination

Examine the mixture carefully and draw inference if any, from the following table.

(a) Study of colour of the mixture

(i) **Black** → CuO, NiO, SnO, MnO_2, FeO, Fe_3O_4, FeS, CuS, Cu_2S, HgS, Hg_2S, Ag_2S, PbS, NiS, CoS, $CuBr_2$, $Co(OH)_3$, NiI_2, BiI_3, $Cu(SCN)_2$.

(ii) **Brown** → CdO, PbO_2, Bi_2O_5, SnS, Bi_2S_3, ferric ion, $MnCO_3$.

(iii) **Blue** → Some anhydrous cobaltous salts, some hydrated cupric salts, $[Cu(NH_3)_6]^{2+}$, $[Ni(NH_3]_6]^{2+}$.

(iv) **Green** → Some hydrated nickel salts, hydrated ferrous salts, Cr^{3+}, MnO_4^{2-}, $Cu(C_2H_3O_2)_2$, $CuCl_2$, MnO.

(v) **Yellow** → Bi_2O_3, HgO, PbO, CdS, SnS_2, As_2S_3, As_2S_5, $FeCl_3$, S, AgI, AlI_3, $K_3Co(NO_2)_6$, PbI_2, Hg_2F_2, Hg_2I_2, $Hg(NO_3)_2$, $AgBr$, Ag_2CO_3, AgF, Ag_3PO_4.

(vi) **Red** → Fe_2O_3, Cu_2O, HgO, Pb_3O_4, Sb_2S_3, HgI_2, AsI_3, $BiOI$, SbI_3, SnI_2, $[Co(NH_3)_6]^{2+}$,

(vii) **Orange** → Sb_2S_5, SnI_4.

(*viii*) **Pink** → Mn^{2+}, hydrated cobaltous salts.

(*ix*) **Purple** → Cr^{3+}, MnO_4^-.

(*x*) **White** → Cu, Ni, Fe, Cr, Mn and Co absent.

NOTE

1. The information obtained by studying the colour of a mixture is not always very reliable. This is because of the following reasons.
   - (*i*) When certain salts are mixed together, the mixture may have a different colour than either of the individual salts.
   - (*ii*) A dark coloured salt may mask the light coloured salt in the mixture.
   - (*iii*) If a light coloured salt is mixed with a white salt, the mixture may appear to be practically colourless.
2. If the mixture is completely colourless or white, the presence of coloured salts *i.e.*, salts containing Cu^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+} and Mn^{2+} can be definitely ruled out.

(*b*) Density

Observation	*Inference*
(*i*) Mixture is heavy	Slats of lead, mercury or barium
(*ii*) Light fluffy powder magnesium, etc.	Carbonates of bismuth, zinc,

(*c*) Study of the smell of mixture : Rub a pinch of the mixture between the fingers and smell it. Then, draw the inference from the following Table.

Observation	*Inference*
(i) Ammonia gas having characteristic ammonical smell.	Ammonium radical.
(ii) Vapours of acetic acid (vinegar like smell).	Acetate
(iii) Vapours of hydrogen sulphide gas having smell like that of rotten eggs.	Sulphide
(iv) No characteristic smell.	

NOTE

1. Many ammonium salts and sulphides do not give their characteristic smell. Therefore, the absence of any characteristic smell should not be taken as the absence of these radicals.
2. *Caution :* Wash your hands immediately after having touched the mixture. This is because many salts are corrosive to skin.

(d) On keeping it in air

Observation	*Inference*
(i) Deliquescent and becomes pasty.	If it is colourless, it may be $SbCl_3$, $ZnCl_2$, $CaCl_2$ or $Zn(NO_3)_2$. If it is coloured, it may be $Cu(NO_3)_2$, $FeCl_3$, $Fe(NO_3)_3$ or $MnCl_2$.
(ii) Colour changes from white to	
(a) Yellow	Cadmium salts.
(b) Black	Lead or bismuth salts.

NOTE Never touch or taste the mixture. Mercury and arsenic salts are highly poisonous and salts like animony chloride, silver nitrate are corrosive to action and cause ugly spots on the skin.

2. Dry Heating

Take a small quantity (0.5g) in a dry test tube. Hold the test tube in a horizontal position while its mouth slightly downwards. First heat the test tube gently and then strongly and make necessary observations given in tables 1, 2 and 3.

(a) **Colour of Residue** (Due to the formation of coloured oxides).

Table 1

Observation		*Inference*
In hot	*In Cold*	
(i) Orange yellow	White	Zinc
(ii) Brown	Yellow	Lead, Bismuth & Tin
(iii) Reddish brown	Reddish brown	Iron
(iv) Red or black	Brown	Cadmium

(b) **Colour of Residue (Due to the loss of water of crystallization).**

Table 2

Observation		*Inference*
Original Colour	*Colour after heating*	
(i) Blue	White	Copper sulphate
(ii) Blue	Brown	Copper Sulphide
(iii) Crimson	Blue	Cobalt chloride
(iv) Dark red	Green	Cobalt bromide
(v) Dark red	Violet	Cobalt iodide
(vi) Red	Pink	Cobalt sulphate
(vii) Red	Pink (liquid)	Cobalt nitrate
(viii) Yellow	Black	Ferric chloride
(ix) Violet	Green	Chromium salt
(x) Green	Yellow	Nickel Salt

(c) **Sublimate Formation**

Table 3

Observation	*Inference*
(i) White	Ammonium halides, Aluminium chloride, Mercury (ous or ic) chlorides.
(ii) Grey	Hg (oxides and cyanide)
(iii) Steel grey sublimate, garlic like oddur	As
(iv) Greyish-black	HgS
(v) Yellow	S, As_2S_3 and HgI_2 (red on being rubbed with a glass rod).
(vi) Blue black sublimate	Iodine.

Observation	*Inference*
(vii) The substance swells	Some borates, phosphate, alum
(viii) Decrepitation takes place	$Pb(NO_3)_2$, $Ba(NO_3)_2$, NaCl, KCl and KI.
(ix) Water of crystallization condenses	Salts containing water of crystallization, notably chlorides, and sulphates.
(x) The substances fuse	Alkali metal salts.

NOTE

(i) Keep the mouth of the test tube away from you as well as from your neighbour while heating the mixture.

(ii) Always smell the gas with a puff of your hand and not from the test tube direct.

(iii) While heating the test tube, watch all the changes which take place very carefully.

(iv) Use a perfectly dry test tube only for performing dry heating test.

(v) After the heating is over, keep the test tube in inverted position.

Definitions

(i) **Swelling :** Certain salts such as alums and phosphates when heated swell up to form voluminous mass. This phenomenon, known as **intumescences,** is due to loss of water of crystallization and change in molecular structure.

(ii) **Decrepitation :** Crystals of certain salts do not contain any water of crystallization. Yet they contain a small quantity of mother liquor entrapped in their crystals. When such salts are heated, the entrapped liquid vapourises and, thereby, causes the crystals to break. This produces a *crackling sound* known as **decrepitation**. For example, lead nitrate undergoes decrepitation.

3. Charcoal Cavity Test

Principal : On heating the salt or mixture with sodium carbonate or fusion mixture (Na_2CO_3+KNO_3), first the corresponding metal carbonates (if the salts are not originally in that form) are produced by double decomposition and these carbonates then decompose to the corresponding oxides. These metal oxides :

(i) are left as coloured residues, the colour of the residue being characteristic of the basic radical present, or

(ii) the metallic oxides undergo reduction to metallic state by the reducing action of carbon of charcoal resulting in the formation of metallic beads of easily fusible, or

(iii) the metal so formed volatilizes in the form of vapours which burn in air to form oxide. These get deposited in the form of the layer or crust around the cavity (incrustation).

Examples :

(a)

$$ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$$

$$ZnCO_3 \rightarrow ZnO + CO_2\uparrow$$

Yellow when hot
white when cold

(b)

$$CdCl_2 + Na_2CO_3 \rightarrow CdCO_3 + 2NaCl$$

$$CdCO_3 \rightarrow CdO + CO_2\uparrow$$

Reddish brown
residue

(c)

$$CuSO_4 + Na_2CO_3 \rightarrow CuCO_3 + Na_2SO_4$$

$$CuCO_3 \rightarrow CuO + CO_2\uparrow$$

$$CuO + C \rightarrow Cu + CO\uparrow$$

red

Procedure of Charcoal Cavity Test

(a) Make a small cavity in the clean charcoal black with the help of a borer.

(b) Fill the mixture of I part of salt and 2 parts of fusion mixture ($Na_2CO_3 + NaNO_3$) in the cavity.

(c) Press the mixture with a spatula and moisten the contents of cavity with a drop of water.

(d) Hold the charcoal back in the left hand and play upon it by reducing flame very gently with the help of a blow pipe for about two minutes.

(e) Observe the colour of residue (in hot and cold), the colour of incrustation (if any), and the bead formation. Make the inference as provided in table 4.

Table 4
Charcoal Cavity Test

Incrustation or Residue		*Bead*	*Inference*
In hot	*In cold*		
(i) Yellow residue and incrustation.	White residue and incrustation	–	Zinc
(ii) Reddish brown residue and incrustation	Reddish-Brown residue and incrustation	–	Cadmium
(iii) Reddish-brown residue and incrustation	Yellow residue and incrustation	White malleable metallic bead which marks paper	Lead
(iv) Orange residue and incrustation	Yellow residue or incrustation	White brittle bead	Lead
(v) Red residue	Red residue	Reddish scales	Copper
(vi) White residue	White incrustation	Shining white metallic hard bead which does not mark paper	Silver
(vii) Black residue	Black residue		
(viii) White residue	White residue	–	Iron, Cobalt, Nickel and Managanese Aluminium, Magnesium, Calcium, Barium, Strontium, and Zinc

NOTE

1. Do not bore a very deep cavity and while boring do not apply too much pressure as this may crack the charcoal.
2. Always bore a fresh cavity for a new salt.
3. Moisten the mixture in the cavity with a drop of water, otherwise it may be blown away.

4. Cobalt Nitrate Test

This test is to be performed if white infusible residue is obtained in charcoal cavity test.

Principle : The salts of aluminum, magnesium, zinc, calcium, etc., yield oxides which are white in colour. This residue is heated with cobalt nitrate solution in a reducing flame. Cobalt oxide, formed as result of decomposition of cobalt nitrate, combines with metallic oxides to form coloured compounds which are characteristic of cations.

(a) $2Co(NO_3)_2 \rightarrow 2CoO + 4\,NO_2\uparrow + O_2\uparrow$

$CoO + ZnO \rightarrow CoO.ZnO$
Green residue

(b) $CoO + Al_2O_3 \rightarrow Co(AlO_2)_2$
Blue residue

(c) $CoO + MgO \rightarrow CoO.MgO$
Pink

Procedure : In case the residue is white in colour, add a drop of cobalt nitrate solution over the white residue in the charcoal cavity. Heat it again in the oxidizing flame by means of blow pipe. Note the colour of residue and make the inference as given in. Table 5.

Table 5
Cobalt Nitrate Test

Observation	*Inference*
1. Bluish residue	Al^{3+}, PO_4^{3-}, BO_3^{3-}
2. Green	Zn^{2+}
3. Pink	Mg^{2+}
4. Black	No definite indication (The black colour is due to the formation of CoO).

NOTE

(*i*) Perform the test only if a white residue is left in the charcoal cavity test.

(*ii*) Add only a drop or two of cobalt nitrate to the white residue in the cavity otherwise a black mass will be produced.

Filter Ash Test : Cobalt nitrate test may be replaced by this test. Take a solution of the substance, add a few drops of cobalt nitrate. Dip a filter paper in the mixture and burn it. The colour of the ash will correspond to the Table V.

5. Borax Bead Test

When borax is heated, if first loses its water of crystallization and then decomposes to give a clear and transaparent bead consisting of boric anhydride and sodium metaborate.

$$\begin{array}{rcl} Na_2B_4O_7.10H_2O & \rightarrow & Na_2B_4O_7 + 10H_2O \\ Na_2B_4O_7 & \rightarrow & 2NaBO_2 + B_2O_3. \end{array}$$

Boric anhydride being less volatile, displaces more volatile acidic anhydrides from their salts to form metaborates which possess characteristic colours.

$$B_2O_3 + CuSO_4 \rightarrow Cu(BO_2)_2 + SO_3$$

In certain cases meteorites of two different colours are produced in oxidizing and reducing flames.

$$B_2O_3 + CuSO_4 \rightarrow Cu\,(BO_2)_2 + SO_3$$

Green when hot and blue when cold in oxidizing flame

$$2Cu\,(BO_2)_2 + C \rightarrow 2CuBO_2 + B_2O_3 + CO$$

Colourless

In some cases, the bead becomes even opaque in the reducing flame. This happens too much if the metal metaborate is there and its reduction to metallic state is possible.

$$2CuBO_2 + C \rightarrow 2Cu + B_2O_3 + CO$$

Residue-brown in hot

Procedure of Borax Bead Test

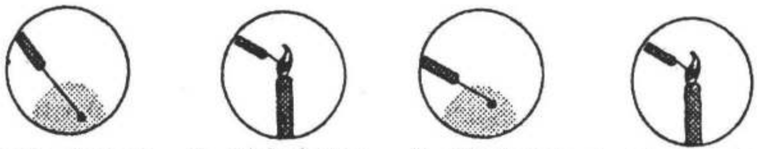
(*a*) Make a loop at the free end of the platinum wire.

(*b*) Heat the wire red hot and dip it in to powdered borax and again heat to get small transparent bead in the loop of the wire. Ensure that the bead is clear and transparent. In case the bead is opaque, it is removed and the process is repeated to get transparent glassy bead.

(*c*) Touch the hot bead with a little of the mixture. Heat it again in the oxidizing flame, cool and examine the colour.

(*d*) Observe the colour when hot and also when cold.

(*e*) Heat it again in the reducing flame and examine the colour of the bead when hot and also when cold (Table 6).



1. Dip the cleaned platinum wire needle in borax powder.
2. Make borax bead in the flame.
3. Dip borax bead in unknown salt or mixture
4. Head gently borax bead in the flame and observe the colour of the bead.

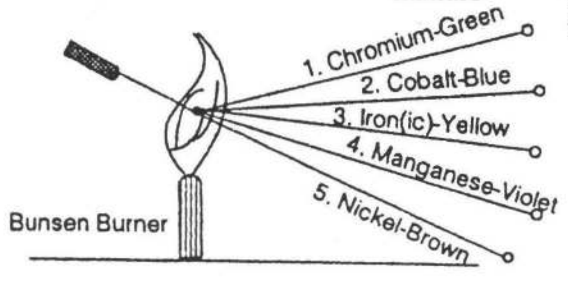


Fig. 3.1.

Table 6

Basic Radical	*Oxidising flame (non-luminous)*	*Reducing flame (luminous)*
Cobalt (Co)	Deep blue	Deep blue
Nickel (Ni)	Light brown	Black
Manganese (Mn)	Amethyst violet	Colourless
Chromium (Cr)	Green	Green
Iron (Fe)	Yellow	Bottle green
Copper (cu)	Light blue or green	Colourless or green

NOTE

(i) Borax bead test is applicable only to coloured salts. It needs not to be performed, if the substance is white or colourless.

(ii) The borax bead prepared to perform the test must be colourless and transparent. In case it is not, it should be removed and a fresh bead is prepared.

(iii) The borax bead should be touched with only a particle or two of the given substance otherwise an opaque bead mass would be obtained.

6. Microcosmic Salt (Phosphate) Bead Reactions

Similar to borax bead, phosphate bead is obtained when microcosmic salt ($NaNH_4HPO_4.4H_2O$) is made to heat in a loop of platinum wire. The salt loses water and ammonia, forming first NaH_2PO_4 and then sodium metaphosphate ($NaPO_3$) as a colourless transparent bead.

$$NaNH_4HPO_4 \rightarrow NaPO_3 + H_2O + NH_3$$

This substance, sodium metaphosphate, like sodium metaborate will combine with metallic oxides. But the borate beads have been more viscous than phosphate bends. They also stick to the platinum wire loop better than phosphate beads.

The metallic oxides form characteristic colour with phosphate beads and in general they have been similar to borate beads, *e.g.*,

$$NaPO_3 + CuO \rightarrow \underset{\text{blue bead}}{NaCuPO_4}$$

$$NaPO_3 + CoO \rightarrow \underset{\text{deep blue bead}}{NaCoPO_4}$$

But one advantage with phosphate bead is that it shows little tendency to combine with acidic oxides, particularly silica is not dissolved by the phosphate bead, whereas it gets dissolved in borate bead. When strongly heated, silica gets separated and does not react with phosphate bead and the so called *silica skeleton* (floating silica particles) is seen during and after fusion. This reaction is used for detecting silicates.

$$CaSiO_3 + NaPO_3 \rightarrow NaCaPO_4 + \underset{\text{silica particles}}{SiO_2}$$

It is to be noted that many silicates dissolve completely in the bead and so the absence of silica particles does not conclusively prove the absence of silicates. The various colours of the phosphate bead with metallic oxides are given as follows :

S.N. Metal	*Oxidizing flame*		*Reducing flame*	
	Hot	*Cold*	*Hot*	*Cold*
1. Copper	Green	Blue	Colourless	Red
2. Iron	Yellowish or Reddish Brown	Yellow	Yellow	Colourless
3. Chromium	Green	Green	Green	Green
4. Manganese	Violet	Violet	Colourless	Colourless
5. Cobalt	Blue	Blue	Blue	Blue
6. Nickel	Brown	Brown	Grey	Grey

7. Flame Test

There are certain metallic salts (specially chlorides) which when heated strongly in non-luminous oxidizing flame, get thermally ionized. The ions become excited by promoting electrons to higher energy levels. On coming back to the ground state, they emit radiations which fall in the visible region of the spectrum giving characteristic colour to the flame; the colour being characteristic of the cationic constituent present in the vapourised salt.

In a mixture, where more than one colour are given, ***cobalt blue glass*** acts as a filter. For example, if there is a mixture of sodium and potassium, blue cobalt glass will absorb yellow light due to sodium but transmits violet due to potassium.

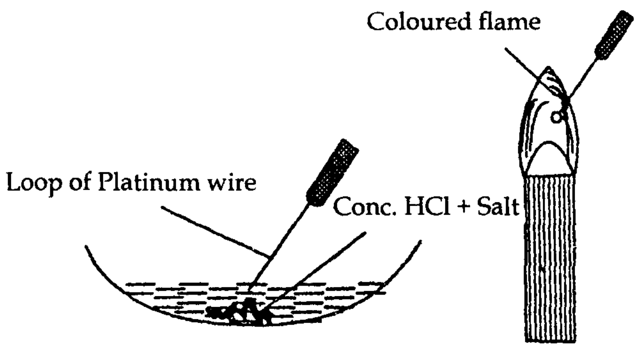


Fig. 3.2.

Procedure of Flame Test :

(*a*) Make a circular loop at the end of platinum wire. Clean the platinum wire by dipping its loop in concentrated HCl and heating it in non-luminous oxidizing flame. Repeat it several times.]

(*b*) Prepare a paste of mixture in HCl on a watch glass.

(*c*) Take small quantity of the paste on the loop of the platinum wire and put it in the base of non-luminous flame and keep it for sometime.

(*d*) Observe the colour imparted to the flame.

(*e*) Again observe the colour of the flame using cobalt blue glass.

Refer to the following table for inference

Observations		*Inference*
Through naked eye	*Through cobalt blue glass*	
Golden yellow	Invisible	Sodium
Pale violet (Lilac)	Crimson	Potassium
Bluish green or blue	Visible	Copper
Crimson red	Purple	Strontium
Brick red	Light yellow	Calcium
Grassy green	Visible	Barium
(Heat for longer time)		
Bright green	Visible	Borate

⏭ NOTE

1. Always use pure concentrated hydrochloric acid both for cleaning the platinum wire and for preparing a paste of the mixture.
2. Never dip the platinum wire in the bottle of hydrochloric acid. Always take the acid in a place of glass watch.
3. Clean the platinum wire very thoroughly before performing the test.
4. For viewing the colour of the flame through blue glass, preferably a double layer of blue glasses may be used.

WET TESTS FOR CATIONIC CONSTITUENTS

Preparation of Solution

The first step before proceeding for the identification of cationic constituents by wet test analysis is to prepare a clear and transparent solution of the mixture under investigation. The following noted solvents are tried one by one in a systematic order taking a small pinch of the mixture each time, heating if needed for 1-2 minutes before trying the next solvent : *(i)* distilled water, *(ii)* pure dil. HCl, *(iii)* pure conc. HCl, *(iv)* pure dil. HNO_3, *(v)* conc. HNO_3, (vi) Aqua regia (3 parts of conc. HCl and 1 part of conc. HNO_3).

If a gas is liberated on adding a solvent, let the reaction be over, add more of solvent and heat. A clear solution may be formed when no gas comes out.

After finding out the appropriate solvent, prepare the stock solution by taking about 0.20 to 0.30 g of mixture in 10 ml of the solvent.

Important Points

(i) *If the original solution has been prepared in conc. HCl, the excess must be evaporated off and the solution is considerably diluted before proceeding for analysis.*

(ii) *Avoid the use of dil. or conc.* HNO_3 *or aqua regia. In case of using any of them then evaporate the solution in a china dish, till it becomes almost dry. Extract the residue in dil. HCl. If* HNO_3 *is not removed,* H_2S *gets oxidized to colloidal sulphur during the analysis of II group.*

$$H_2S + HNO_3 \rightarrow 2H_2O + 2NO_2 + S$$

(iii) *In case thiosulphate is present in the mixture, add a crystal of NH_4NO_3 to the solution of mixture in dil. HCl. Heat until evolution of SO_2 ceases, centrifuge and proceed with the centrifugate.*

$$Na_2S_2O_3 + 2\,HCl \rightarrow 2NaCl + SO_2 + H_2O + S$$

(iv) *If the solution is made in conc. HCl and on dilution a white precipitate or milkiness appears, it may be due to Bi^{3+}, Sn^{2+} or Sb^{3+}. Dissolve the precipitate in dil. HCl before proceeding for group examination.*

(v) *From the colour of original solution, one can draw the useful inference about the presence of certain cations.*

Colour	*Inference*
1. Pink	Manganese and cobalt
2. Blue	Copper (II)
3. Green	Nickel, iron (II), and chromic salts
4. Yellow	Iron (III)

(vi) *If sulphite and nitrate have been detected then it is essential to boil the solution with dil. HCl before proceeding for group I.*

(vii) *Sulphuric acid is not used to prepare original mixture. The reason for this is that if the solution is prepared in H_2SO_4, the fifth group cations viz. Ba^{2+}, Sr^{2+}, Ca^{2+}, if present would precipitate as corresponding sulphates. Also, H_2SO_4 is an oxidizing agent and oxidizes H_2S into sulphur.*

$$H_2SO_4 + H_2S \rightarrow 2H_2O + SO_2 + S$$

Identification of Cationic Constituents

Before proceeding for the separation of cations into various groups one should perform a test for ammonium radical (zero group) and then proceed as outlined in the blow sheet diagram given below :

Separation of Cationic Constituents into Various Groups of Analysis

To the clear solution (1ml) add 3-4 drops of dil. HCl. If the mixture becomes turbid, boil for ½ minute. Thoroughly cool under tap water and centrifuge.

Table 1

<table>
<tr>
<td rowspan="2">Residue. 1.
White $PbCl_2$, AgCl, Hg_2Cl_2</td>
<td colspan="2">Centrifugate. If sulphide and nitrite, have been identified in the mixture, transfer the solution into a beaker. Add to it 3-4 drops of H_2O_2 and boil for two minutes. Transfer the solution into test tube.
If arsenate has been identified in mixture, transfer the solution into a beaker, add to it 2 mg of NH_4I and boil until all the liberated iodine has been removed as vapour, dilute to 2 ml and transfer the solution in test tube.
Boil the solution and pass H_2S. Add 1 ml of water, boil and again pass H_2S. Centrifuge.</td>
</tr>
<tr>
<td>Residue. Wash the residue with 2ml of NH_4NO_3 solution, centrifuge and reject the washing.
Add to the residue 2ml of KOH or NaOH plus a few drops of yellow ammonium sulphide. Boil and centrifuge.</td>
<td>Centrifugate. Transfer the solution in a beaker and boil off H_2S completely.
Test 3-4 drops of solution with a crystal of ammonium molybdate and warm. Yellow precipitate indicates the presence of phosphate.
Take rest of the solution in a test tube and add to this a solid NH_4Cl. Stir and add NH_4OH dropwise with stirring until the solution is alkaline. Add 1ml of water, boil and centrifuge.</td>
</tr>
</table>

				Centrifugate : Pass H_2S boil and then centrifuge.		
	Residue 2 HgS, PbS, CuS - black Bi_2S_3 - Dark brown CdS - Yellow	**Centrifugate** Add dil. HCl dropwise until the mixture is just *acidic*. If an *orange yellow* or *orange-red* precipitate is formed, warm and centrifuge. Reject solution. **Residue 3** As_2S_3- Yellow Sb_2S_3 – Orange red SnS-Brown SnS_2-Yellow	**Residue 4** $Fe(OH)_3$ -Reddish brown $Al(OH)_3 \rightarrow$ White gelatinous $Cr(OH)_3$- Green $MnO_2 \cdot xH_2O$ -Brown	**Residue 5** NiS-Black CoS-Black MnS-Buff ZnS-White	**Centrifugate.** Take the solution in a beaker and boil the solution to remove H_2S. Transfer the solution in a test tube, add to it 1 ml of ammonium carbonate solution and then add 2 drops of NH_4OH. Warm gently.	
					Residue 6 White $BaCO_3$, $SrCO_3$, $CaCO_3$	**Centrifugate** Test Mg, Na and K
Group I	**Group IIa**	**Group IIb**	**Group III**	**Group Iv**	**Group V**	**Group VI**

Identification of Zero Group Cation

(Ammonium Radical)

Tests :

(i) Take 10-20mg mixture and heat it with 10 drops of NaOH solution, NH_3 is evolved. The vapours will turn filter paper moistened with mercurous nitrate black.

(ii) Take 10-20mg of mixture and to this add 10 drops of dilute NaOH. Warm the solution and pass the vapours through Nessler's reagent. A brown coloration or ppt. confirms the presence of NH_4^+ ion.

(iii) Take 10-20mg of mixture. Warm this with 10 drops of dil. NaOH. Bring a drop of conc. HCl carried at the top of a glass rod to the mouth of the tube. Dense white fumes of NH_4Cl will be formed if NH_3 is evolved. This confirms the presence of NH_4^+ ion.

Identification of Group I Cations (Pb^{2+}, Hg_2^{2+} and Ag^+)

To 1mg of original solution add 3-4 drops of dil. HCl; centrifuge if a white precipitate is formed. Preserve the centrifugate for subsequent groups.

Residue : White will be due to $PbCl_2$, Hg_2Cl_2, AgCl.

Wash the residue with few drops of cold water. Centrifuge while hot.

Table 2

<table>
<tr>
<td rowspan="2"><i>Centrifugate :</i>
Divide it in four parts.
<i>(i)</i> To part I add a drop of conc. H_2SO_4 and alcohol each. Formation of white ppt. of $PbSO_4$ confirms Pb^{2+}.
<i>(ii)</i> To Part II add one drop of K_2CrO_4 Solution. Yellow precipitate soluble in NaOH solution but insoluble in dil. CH_3COOH confirms Pb^{2+}.
<i>(iii)</i> To part III add one drop of KI solution. Yellow precipitate of PbI_2 soluble in excess of KI solution confirms Pb^{2+}.
<i>(iv)</i> To part IV add dithizone reagent and shake. A red coloration confirms Pb^{2+}.
Pb^{2+}</td>
<td colspan="2">Residue : May have Hg_2Cl_2 and AgCl. Wash it with hot water and treat it with 0.5ml of NH_4OH. Shake and centrifuge.</td>
</tr>
<tr>
<td>Residue : Black which dissolves in aqua regia. Evaporate off aqua regia. Dissolve the residue in water. Divide it in 4 parts.
<i>(i)</i> Add 2 drops of KI solution to part I of the solution. The red precipitate of HgI_2 confirms Hg_2^{2+}.
<i>(ii)</i> To part II add 2 drops of NaOH solution. Black precipitate confirms Hg_2^{2+}.
<i>(iii)</i> To part III add 2 drops of $SnCl_2$ solution and heat. A grey precipitate confirms Hg_2^{2+}.
<i>(iv)</i> To part IV add 2 drops of gallic acid. Formation of an orange colour confirms Hg_2^{2+}.
Hg_2^{2+}</td>
<td><i>Centrifugate :</i> Add very dil. HCl dropwise to neutralise the solution and then add NH_4OH to redissolve any precipitate formed. Add a drop of KI solution. If any precipitate appears then complete it. Centrifuge.
<i>Residue.</i> Pale yellow. It is due to AgI. This confirms Ag^+ Take 3-4 drops of the centrifugate after the separation of Pb and Hg and add a drop of K_2CrO_4 a red precipitate indicates Ag^+.
Ag^+</td>
</tr>
</table>

Identification of Group II Cations

(Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+} and Sn^{2+})

Dilute the centrifugate from group I to 2 ml. Pass H_2S gas in a test portion of this. If a ppt. is formed, it indicates the presence of group II. Then pass H_2S gas in the remaining solution slowly and steadily until the precipitation is complete. Centrifuge.

Note : If no ppt. comes in the test portion, there is no need of passing H_2S gas and it is advisable to proceed to group III.

Table 3

Residue : IF it is coloured; this may contain HgS, PbS, Bi_2S_3, CdS, As_2S_3, and SnS_2. Wash the residue twice and reject the washings. Treat this residue with 3 ml of yellow ammonium sulphide. Heat the contents for 3 minutes and then centrifuge.		*Centrifguate* : Keep it for analysis of subsequent groups.
Residue : If it is coloured, this may contain group II A sulphides. This residue may be tested according to Table 4.	*Centrifugate* : Add dil. HCl dropwise until it is just acidic. If a coloured ppt. is obtained, test this residue for group IIB according to Table 5.	

Table 4

Analysis of Group IIA

Treat the residue for group IIA according to Table 3 with 1.5 ml of dil. HNO_3.
Boil it for 2 minutes and centrifuge it.

<table>
<tr>
<td rowspan="4"><i>Residue</i> : Black due to HgS.
Dissolve it in aqua-regia and evaporate off aqua regia. Dilute it with water. Divide it into 3 parts.
(<i>i</i>) To a drop of the solution add a drop each of amm. thiocyanate and sod. acetate followed by a drop of $Co(NO_3)_2$ solution. A deep blue colur or precipitate confirms mercury.
(<i>ii</i>) To a drop of solution add a drop of NaOH solution. A yellow precipitate confirms Hg^{2+}.
(<i>iii</i>) To 5 drops of solution add 3 drops of $SnCl_2$ solution. A white or grey precipitate confirms Hg^{2+}.
Hg^{2+}</td>
<td colspan="4"><i>Centrifugate</i> : To a portion add a drop of dil. H_2SO_4 and alcohol. If a white precipitate appears, add alcohol and H_2SO_4 to the whole and boil till white fumes appear. Cool and add a drop of water and centrifuge.</td>
</tr>
<tr>
<td rowspan="3"><i>Residue</i> : White due to $PbSO_4$. Dissolve in minimum amount of ammonium acetate solution. Now add 2 drops of K_2CrO_4 solution. A yellow precipitate of $PbCrO_4$ confirms Pb^{2+}.
Pb^{2+}</td>
<td colspan="3"><i>Centrifugate</i> : Add ammonia solution dropwise till the solution is alkaline. If precipitate appears, centrifuge.</td>
</tr>
<tr>
<td rowspan="2"><i>Residue</i> : White. Dissolve the residue in 2-3 drops of conc. HCl and heat. Add to this 1/2 ml of water. Now test this solution as follows :
(<i>i</i>) To 3 drops of solution add 2 drops of sodium stannite reagent. A white precipitate confirms Bi^{3+}.
(<i>ii</i>) To 3 drops of solution add 2 drops of thiourea solution. A yellow colouration appears if Bi^{3+} is present.
Bi^{3+}</td>
<td colspan="2"><i>Centrifugate</i> : Divide it in two parts.</td>
</tr>
<tr>
<td>(<i>i</i>) Acidify 3 drops of solution with acetic acid. Add two drops of $K_4Fe(CN)_6$. A brown precipitate confirms Cu^{2+}.
(<i>ii</i>) To a drop of solution add 2 drops of rubeanic acid reagent and a few drops of ammonia solution. A deep blue coloration confirms Cu^{2+}.
Cu^{2+}</td>
<td>If Cu^{2+} is present, add KCN solution drop by drop till the solution is colorless. Pass H_2S. A yellow precipitate of CdS confirms Cd^{2+}.
If KCN solution is not available, acidify the filtrate with 6(N) HCl, passH_2S and filter.
<i>Residue</i> : Black Cu^{2+} present.
<i>Centrifugate</i>: Saturate with sodium acetate, pass H_2S yellow ppt. Cd^{2+} present.
If Cu^{2+} is absent : Add dilute HCl to the centrifugate until it just acidic (test with litmus), pass H_2S, yellow ppt. Cd^{2+} present.
Cd^{2+}</td>
</tr>
</table>

Table 5
Analysis of Group IIB

Wash the residue for Group IIB (See Table 3) with 1ml of hot water. Centrifuge and reject the washings. To the residue, add 1ml of conc. HCl and boil gently for 2 minutes. Add 1 ml of water, stir and then centrifuge.

Residue : Dissolve the residue by boiling it with 1ml of conc. HNO_3. Divide it into three parts. (*i*) To I part of the solution, add ammonium molybdate solution and heat. A yellow precipitate confirms As^{3+}. (*ii*) Make II part alkaline with NH_4OH and add ½ ml of magnesia mixture. A white precipitate confirms As^{3+}. (*iii*) To part III, add a pinch of zinc dust and 4 drops of dil. H_2SO_4. Hold a paper of $HgBr_2$ over the mouth of the test tube. Yellow or orange colour confirms As^{3+}. **As^{3+}**	*Centrifugate* : It may have $SnCl_4$ and $SbCl_3$. Boil off H_2S. Add NH_4OH to make the centrifugate alkaline. Add 3-4 crystals of oxalic acid, boil and pass H_2S Centrifuge.	
	Residue : Orange. Dissolve the residue in conc. HCl. Boil off H_2S. Divide it in two parts. (*ii*) To one part add NH_4OH in order to neturalise the large excess of acid. A white residue or turbidity soluble in tartaric acid confirms Sb^{3+}. (*iii*) To another part of the solution, add small tin piece and wait for some time. A grey spongy deposit indicates Sb^{3+} **Sb^{3+}**	*Centrifugate* : It may contain $SnCl_4$. Boil off H_2S and add Zn dust and dil. HCl. Keep it for some time. Centrifuge and divide it into three portions. (*i*) To one part add ammonium molybdate solution. A deep blue coloration or residue indicates Sn^{2+}. (*ii*) To second portion add 5mg of Mg powder + 2 drops of $FeCl_3$ + 2 drops of 5% tartaric acid + 1 - 2 drops of dimethly glyoxime solution and then add dil. NaOH solution. A red colour confirms Sn^{2+}. (*iii*) To part III add 0.1 M $HgCl_2$ solution. A silky white ppt. confirms Sn^{2+}. **Sn^{2+}**

Identification of Group III Cations
(Fe^{3+}, Al^{3+}, Cr^{3+})

Boil of H_2S form the centrifgugate. Add 1 drop of conc. HNO_3 and boil. Add about 200mg of NH_4Cl and boil. Cool and add NH_4OH drop by drop until the solution is ammonical, Centrifuge. Residue may have $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ and MnO_2xH_2O. Wash the residue with 1 ml of NH_4Cl solution. Centrifuge and reject washings. To the residue add 7 or 8 drops of H_2O_2 (3%) solution and 1ml of NaOH or 50mg of Na_2O_2. Warm and then boil for 1minute.

Residue : Brown. Dissolve the residue in 1ml dil. HNO_3 and divide it into 5 parts. (*i*) To part 1 add 2 drops of $K_4Fe(CN)_6$ solution. A deep blue precipitate confirms Fe^{3+}. (*ii*) To part II add 2 drops of KCNS solution. A blood red colouration confirms Fe^{3+}. (*iii*) To part III add 2 drops of sulphosalicylic acid reagent. Formation of a violet colour confirms Fe^{3+}. **Fe^{3+}** (*iv*) To part IV add 10mg of sodium bismuthate and shake. A purple violet precipitate confirms Mn^{2+}. (*v*) Boil the residue with 1-2 ml of conc. nitric acid and 0.1 to 0.5g of PbO_2. Cool and dilute. A purple colour confirms Mn^{2+}. **Mn^{2+}**	Centrifugate : If colourless, Al is present and/or is absent; if yellow Cr is definitely present. Divide the centrifugate in two portions.	
	Tests for Cr^{3+} (*i*) Acidify a part of this portion, with acetic acid and add lead acetate solution. A bright yellow precipitate soluble in, NaOH confirms Cr^{3+}. (*ii*) Acidify another part with dil. H_2SO_4 and add ether. Add 2-3 drops of H_2O_2 and shake. A Blue colour in ethereal layer confirms Cr^{3+}. **Cr^{3+}**	(*i*) Add few crystals of NH_4Cl to second part and boil. A white gelatinous precipitate confirms Al^{3+}, (*ii*) Acidify another part with acetic acid. To this add 5 drops of amm. acetate, 5 drops of aluminon reagent, 8 drops of NH_4OH and 10 drops of $(NH_4)_2CO_3$ solution. A bright red ppt. or colour confirms Al^{3+}. **Al^{3+}**

NOTE Before proceeding for group III, remove the interfering radicals.

Identification of Group III Cations in the Presence of Interfering Radicals

When interfering radicals are present in a mixture, it becomes necessary to remove these interfering radicals before we proceed for the third group. The various interfering radicals are : borates, oxalates, fluorides, phosphates. Let us discuss their removal one by one.

1.Removal of borate

Transfer the centrifugate from group II into a small crucible. Heat it to expel H_2S gas. After cooling the crucible, add 3-5 drops of conc. HCl and 5–8 drops of ethyl alcohol. Evaporate to dryness. Repeat this process of addition of conc. HCl and ethyl alcohol and, again, evaporate it to dryness. When borate has gone out as ethyl borate, extract the residue with 2 ml of 0.3 N HCl and start the systematic cation analysis of group III.

2. Removal of oxalate and fluoride

If borate is present, evaporate the centrifugate from group II with conc. HCl to dryness in a similar manner as discussed above. After removing borate, add 1 ml of conc. HCl and 0.5 ml of conc. HNO_3. Evaporate the solution to dryness. Again, add 1 ml of conc. HCl and 1 ml of conc. HNO_3 and evaporate it to dryness. Repeat the process three or four times. Then dissolve the residue in 2 ml of 0.3 N HCl and proceed with the analysis of cations of group III.

3. Removal of Phosphate

Before eliminating phosphate, it becomes necessary to confirm the presence of phosphate in the centrifugate from II group with ammonium molybdate and conc. nitric acid. If a yellow ppt. is obtained, it confirms phosphate. There are two methods for the removal of phosphate.

(*a*) **Zirconyl nitrate method** : If borate, oxalate and fluoride are present, remove them by the above methods. Extract the residue with 0.3 N HCl (If these are not present, take the centrifugate from group II and treat with 2 drops of conc. HNO_3 and boil gently for one minute and use this solution for removal of phosphate). Transfer the solution into a semic-micro test tube. To this add 2 drops of NH_4Cl solution and 4 drops of zirconium nitrate reagent. Heat the tube on a water bath for 3 minutes. Centrifuge and remove the clear centrifugate and reject the residue. To the clear centrifugate add 1 drop of zirconium nitrate. If a ppt. is again produced, repeat the process of addition of zirconium nitrate until there is no ppt. Finally heat the tube on a boiling water bath for 1minute and centrifuge again.

Residue is zirconium phosphate Reject it.	*Centrifugate.* To this add 50mg of NH_4Cl. Heat it on water bath, followed by addition of NH_4OH to make it alkaline. Heat it on a boiling water bath for 4 minutes. Centrifuge the solution.	
	Residue may have hydroxides of III group. Analyse it in a similar manner as discussed in III group.	Examine for cations of groups IV, V and VI by tables discussed at appropriate places.

(b) Ferric chloride acetate buffer method : It involves the following steps :

First step : (Tests for iron). Take a small portion of (filtrate) centerifugate from group II. To this add 2-3 drops of conc. nitric acid and boil the solution. Divide it in two parts :

(i) To one part add a few drops of ammonium thiocyanate. Formation of blood red colouration indicates Fe^{3+}.

(ii) To second part add a few drops of $K_4Fe(CN)_6$. If a Prussian ppt. or solution is obtained, it conirms Fe^{3+}.

Second step : To the rest of the centrifugate from group II, add NH_4OH solution dropwise with shaking till a slight turbidity persists. To this add 2-3 ml of glacial acetic acid and 100 mg of solid CH_3COONH_4. Now add netural $FeCl_3$ solution dropwise till the solution of the colour becomes red. Boil it for 2 minutes. Centrifuge.

<table>
<tr><td rowspan="2"><i>Residue</i> : may contain phosphates of Fe, Al and Cr. Test for Al and Cr in a similar manner as discussed in Group III.
(No need of testing iron as it is coming from FeCl$_3$).</td><td colspan="2"><i>Centrifugate</i> : To this add 50mg of solid NH_4Cl and slight excess of NH_4OH to make it alkaline. Boil it and centrifuge.</td></tr>
<tr><td><i>Reside</i> : Mix it with earlier residue and test for Cr and Al in it.</td><td><i>Centrifiugate</i> : Proceed for analysis with it for groups IV, V and VI in the usual manner.</td></tr>
</table>

Identification of Group IV Cations

(Co^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+})

Add 2-3 drops of NH_4OH to the centrifugate from group III, heat and pass H_2S until the precipitation is complete.

Centrifuge. Preserve the centrifugate for the subsequent groups. Residue may contain CoS, NiS, MnS, and ZnS.

Wash the residue with 1 ml of NH_4Cl. Centrifuge and reject washings. To the residue add 2 ml of water followed by 1 ml of dil. HCl. Stir the mixture and then centrifuge. Now proceed as on p. 52.

<table>
<tr>
<td colspan="2"><i>Residue</i> : Black residue may have NiS, CoS. Dissolve the residue in aqua regia (6 drops of HCl + 2 drops of HNO_3). Evaporate it to dryness. Note the colour of the residue. If it is blue, it indicates cobalt. If it is yellow, it indicates nickel. If green, both cobalt and nickel may be present.
Extract the residue with 2 ml of water and divide into five parts.</td>
<td colspan="2"><i>Centrifugate</i> : may contain $ZnCl_2$ and $MnCl_2$. Boil off H_2S. Add NaOH solution in excess 0.5-1 ml and 3-4 drops of 3% H_2O_2. Boil and centrifugate.</td>
</tr>
<tr>
<td>(<i>i</i>) To 5drops of solution, add 0.5ml of NH_4OH and 1 drop of dimethyl glyoxime solution. A bright red precipitate confirms Ni^{2+}.
(<i>ii</i>) Take 5 drops of the solution. Add 5 drops of NaOH and 2 drops of Br_2 water. Black precipitate confirms Ni^{2+}.
Ni2+</td>
<td>(<i>i</i>) To 3 drops of solution add 5 drops of dil. HCl and 0.5 ml of amyl alcohol and 5 drops of amm. thiocyanate solution and shake. A blue colour of amyl alcohol layer confirms Co^{2+}
(<i>ii</i>) To 5 drops of solution add acetic acid (3 drops) followed by 3 drops of α-nitroso β-naphthol. A red-brown precipitate confirms the presence of Co^{2+}
Co^{2+}</td>
<td rowspan="2"><i>Residue</i> : Brown to black due to $Mn(OH)_2$ or MnO.OH. Divide it in 4 parts.
(<i>i</i>) To part I add 2 drops of Br_2 water and 3 drops of NaOH. Boil. A black precipitate conforms Mn^{2+}.
(<i>ii</i>) To part II add 5 mg of PbO_2 and ½ ml of conc. HNO_3. Boil, cool and dilute the contents. A pink colouration confirms Mn^{2+}.
(<i>iii</i>) To part III, add a pinch of solid sodium bisumthate. Formation of a purple colour confirms Mn^{2+}.
(<i>iv</i>) To part IV, add 2 drops of dil. NaOH and 1 drop of benzidine reagent. A blue colour confirms Mn^{2+}.
Mn^{2+}</td>
<td rowspan="2">Centrifugate may contain Na_2ZnO_2. Divide it into four parts :
(<i>i</i>) Acidify part I with dil. acetic acid and pass H_2S. A white or dirty white precipitate confirms Zn^{2+}.
(<i>ii</i>) Acidify part II with dil. HCl and add $K_4Fe(CN)_6$ solution. A bluish white precipitate confirms Zn^{2+}.
(<i>iii</i>) To part III, add 5 drops of amm. tetrathiocyanato mercurate (II) solution and 5 drops of cobalt chloride or cobalt acetate or cobalt nitrate solution. Formation of blue colour or ppt. confirms Zn^{2+}.
(<i>iv</i>) Acidify part IV with dilute H_2SO_4, add 5 drops of 0.1 percent $CuSO_4$ solution and 5 drops of ammonium tetrathiocyanato mercurate (II) ragent and stir. Violet ppt. confirms Zn^{2+}.
Zn^{2+}</td>
</tr>
<tr>
<td colspan="2"><i>Test for Co^{2+} and Ni^{2+} if present together.</i>
Take 5 drops of the solution in a dish. To this add $NaHCO_3$ and Br_2 water dropwise. Shake the dsh. If an apple green colour is obtained in cold, it confirms Co^{2+}. If on heating a black colour appears, it confirms Ni^{2+}</td>
</tr>
</table>

Identification of Group V Cations
(Ba^{2+}, Sr^{2+} and Ca^{2+})

Transfer the centrifugate after precipitation of IV group to a semimicro boiling tube or crucible. Boil off H_2S completely and concentrate to 1 ml. Centrifuge if a residue. appears. Transfer the clear solution to another tube. To this add four drops of NH_4OH solution and 0.5 ml of $(NH_4)_2CO_3$ solution. Heat the tube for about 3 minutes in a water bath. Stir and centrifuge. Analyse the residue for group V and keep the centrifugate for group VI.

Wash residue with 1ml of water, centrifuge and reject the washings. To residue add dropwise dil. acetic acid and warm the clear solution. Boil to drive off CO_2. Take 3-4 drops of this solution. To this add 2 drops of K_2CrO_4 solution. The formation of a yellow ppt. of $BaCrO_4$ indicates Ba^{2+}. If it is present, K_2CrO_4 is added to the remaining solution. Separate the ppt. by centrifugation. If Ba^{2+} is absent, the test solution having K_2CrO_4 is discarded and then the tests for Ca^{2+} and Sr^{2+} solution should be done with the solution of the group V.

<table>
<tr>
<td rowspan="2">Residue : Pale yellow residue indicates the presence of Ba^{2+}. Wash the residue with hot water, confirm the residue for Ba^{2+} as follows :
(*i*) Dissolve a portion of the precipitate in least quantity of conc. HCl and apply the flame test. An apple green coloration confirms Ba^{2+}.
(*ii*) Dissolve the residue in minimum amount of conc. HCl. Take 2-3 drops of this solution, and add 2 drops of H_2O_2, 1 drop of NH_4Cl solution followed by 2 drops of NH_4OH and finally 1 drop of sod. rhodizonate solution. A red brown precipitate confirms Ba^{2+}.
Ba^{2+}</td>
<td colspan="2">Centrifugate. Add a few drops of $(NH_4)_2SO_4$ solution followed byNH_4OH dropwise until mixture is a lkaline. Warm and keep it for one minute and centriuge.</td>
</tr>
<tr>
<td>*Residue*. White due to $SrSO_4$. Wash with water. Dissolve a portion in least volume of HCl and apply flame test. A crimson colour confirms Sr^{2+}.
Sr^{2+}</td>
<td>*Centrifugate*-Ca^{2+}.
(*i*) To the solution add 1 ml of ammonium oxalate and warm. A while precipitate indicates Ca^{2+}. (*ii*) Carry out the flame test on the residue. A brick-red coloration confirms Ca^{2+}.
Ca^{2+}</td>
</tr>
</table>

Identification of Group VI Cations

[Na^+, K^+ and Mg^{2+}]

Evaporate the centrifugate from group V with 0.5 ml of conc. HNO_3 to almost dryness. In a crucible continue heating of the dry mass until fumes of ammonium salt cease to come Treat the residue with 1 ml of water. Stir and transfer to a semi-micro tube, centrifuge and separate the clear liquid.

Residue : Dissolve the residue in a few drops of dil. HCl and divide the solution into four parts.	*Centrifugate* : Divide it into equal parts	
(*i*) Take 3-4 drops of solution, add 4 drops of magneson reagent, and add 2 drops of NaOH solution. A blue precipitate (lake) in the clear liquid confirms Mg^{2+}. (*ii*) To 3 drops of the solution add 1 drop of sodium hydrogen phosphate solution. Scratch walls of the test tube with a glass rod. A white crystalline precipitate confirms Mg^{2+}. (*iii*) To 3 drops of the solution, add 4 drops of Titan yellow reagent and then add a few drops of 0.1 NaOH solution red colour or ppt. confirms Mg^{2+}. (*iv*) Treat 0.25 ml of 2% oxine solution in 2 M acetic acid with 1ml of 2 M ammonia solution. Add a little NH_4Cl to the 4 drops of test solution followed by the ammoniacal oxine reagent and heat in a water bath for 1-2 minutes (the odour of NH_3 should be apparent). Pale-yellow ppt. of Mg oxinate confirms Mg^{2+}.	(*i*) To 3-4 drops of the solution add 4 drops of zinc uranylacetate solution. Shake and wait. A yellow crystalline precipitate confirms Na^+. (*ii*) To 3-4 drops of the test solution, add 5-10 drops of uranyl magnesium acetate reagent, shake or stir and allow to stand for 5 minutes. Yellow crystalline ppt. confirms Na^+. (*iii*) To 3 drops of solution add 2 drops of potassium antimonate solution. A white precipitate confirms Na^+. (*iv*) Apply flame test. A golden yellow flame confirms Na^+.	(*i*) To ½ ml of the solution add 3 drops of perchloric acid. A white crystalline precipitate confirms K^+. (*ii*) Dissolve 10 mg of sod. Cobalti-nitrite in 3 drops of dil. acetic acid and add to this 3 drops of test solution. A yellow precipitate confirms K^+. (*iii*) Also apply flame test. A violet flame confirms K^+. When viewed through two thicknesses of cobalt glass, red (crimson) flame (usually transient) confirms K^+.
Mg^{2+}	**Na+**	**K^+**

5.10 Analysis of Insolubles

Substances which are found insoluble in conc. HCl or conc. HNO_3 or even in aqua regia are termed as insolubles. Such acid, resistant insoluble substances require special treatment for bringing them into solution.

Insoluble substances have been classified according to their colour.

1. White : AgCl, $PbSO_4$, $BaSO_4$, SnO_2, Al_2O_3, CaF_2, Sb_2O_4
2. Yellow : AgBr, AgI
3. Green : Cr_2O_3, $Cr_2(SO_4)_3$
4. Violet : $CrCl_3$
5. Black : HgS
6. Red : Fe_2O_3
7. Brown : Fused $PbCrO_4$, MnO_2 (Mineral).

All these insoluble substances are treated in a number of ways :

Scheme I :This involves the following steps :

First Step : This step involves the treatment for silver compounds AgCl, AgBr and AgI. Here two methods are used for analyzing such insolubles :

(i) The insoluble material is boiled with granulated zinc and dil. H_2SO_4. Here zinc displaces silver from solution.

$$2AgCl + Zn \rightarrow 2Ag + ZnCl_2$$

The black ppt. of silver thus separated is dissolved in dil. HNO_3 and identified by adding dil. HCl. A white ppt. soluble in NH_4OH confirms silver. The anion may be confirmed from the centrifugate.

(ii) In this method the insoluble is treated with a concentrated solution of KCN and then warmed when silver goes into solution as $[Ag(CN)_2]^-$ while anions form the soluble potassium salts.

The solution is diluted and saturated with H_2S where silver sulphide is precipitated which confirms silver. The solution can be tested for Cl^-, Br^- or I^-.

Second step : Here $PbSO_4$ (white residue) is brought into the soluble form by treating it with concentrated ammonium acetate solution. Now acidify with acetic acid, boil. Centrifuge and add K_2CrO_4 solution to the filtrate. Formation of yellow ppt. confirms Pb^{2+}.

Third step : The insolubles that are not brought into solution by above treatments are fused with 6 times its bulk with the fusion mixture (Na_2CO_3 + K_2CO_3 + a crystal of KNO_3) on a piece of porcelain tile till a tranquil melt is obtained.

The mass is extracted with boiling water.

A systematic scheme of analysis of insoluble substance is given in the table 6.

Table 6

Boil the insoluble portion of the mixture in aqua-regia. Dilute with water and centrifuge if necessary.

Wash the residue and boil it with zinc and dil. H_2SO_4 when silver halides will be attacked. Centrifuge if necessary :

<table>
<tr><td rowspan="4">**Centrifugate** may contain halides of zinc.</td><td colspan="4">Residue may contain *(a)* silver produced in the above treatment, and *(b)* other insolubles. Extract with dil. HNO_3. Centrifuge.</td></tr>
<tr><td rowspan="3">**Centrifugate** may have $AgNO_3$. Add HCl. A white ppt. soluble in NH_4OH confirms silver.</td><td colspan="3">Residue : Fuse it with 6 times its weight of residue weight (Na_2CO_3 + K_2CO_3 and a crystal of KNO_3.) Cool it, boil with wter. Centrifuge.</td></tr>
<tr><td rowspan="2">**Centrifugate** may contain sulphate, ferrocyanide and antimonite. Test it for acid and basic radicals in the usual manner.</td><td colspan="2">**Residue** may contain carbonates of alkaline earth metals and lead. Digest with dil. HNO_3. Centrifgue.</td></tr>
<tr><td>Centrifugate : Test for Ba, Sn, Ca and Pb.</td><td>Residue may consist of Fe_2O_3 and SiO_2. Confirm the former by borax-bead test.</td></tr>
</table>

Scheme II : A complete scheme involving all the insoluble substances has been outlined in table II.

Table 7 : Separation and Identification of Insoluble Substances

Heat the insoluble substance so as to burn away C and S completely. Treat 0.25g of the residue with 5ml of concentrated ammonium acetate (slightly acidified with acetic acid). Now heat the solution to nearly boiling. Centrifuge it.

<table>
<tr>
<td rowspan="5">Centrifugate : It may possess Pb^{2+}, SO_4^{2-}, Cl^-, Br^- and I^-. Test for these radicals in the usual manner. The silver nitrate test for halogens must be conducted in the presence of large quantity of nitric acid.</td>
<td colspan="5">Residue : If lead salts are found in the centrifugate, repeat the extraction of residue with amm. acetate solution and wash the residue with hot water until the washings give no colour with dilute amm. sulphide solution. Now warm the residue with concentrated KCN solution (if lead salts are present). Centrifuge.</td>
</tr>
<tr>
<td rowspan="4">Centrifugate : may contain AgCl, AgBr, AgCN and AgI. Now pass H_2S through the filtrate. If a black ppt. is obtained, dissolve it in dil. HNO_3 and add dil. HCl. A white ppt. confirms the presence of Ag^+. If Ag^+ is present, take a little of original substance. To this add Zn and dil. H_2SO_4. Keep it for 10-15 min. Filter the solution and test for Cl^-, Br^-, I^- in the filtrate by the usual tests.</td>
<td colspan="4">Residue : Mix with 5-6 times its weight of Na_2CO_3 and KNO_3 (3 : 1) and heat on a Pt foil or in nickel until a melt is produced. Cool, extract the residue with wter and centrifuge</td>
</tr>
<tr>
<td colspan="2" rowspan="2">Centrifugate : May contain Cr, Al, Sn, SO_4^{2-} and F^-. To the filtrate add conc. HCl and evaporate to dryness. Treat the residue with conc. HCl, followed by addition of water. Warm the solution and Centrifuge.</td>
<td colspan="2">Residue : May have $BaCO_3$, $CaCO_3$, $SrCO_3$, and unattacked CaF_2, SnO_2, Sb_2O_4, Al_2O_3 and Fe_2O_3. Extract the residue with dil. HNO_3 and filter it.</td>
</tr>
<tr>
<td rowspan="2">Centrifugate : May have nitrates of Ba, Sr and Ca. Evaporate it to drynes and extract it with dil. HCl. Test for V group radicals in this extract as we do in the V group of qualitative analysis.</td>
<td rowspan="2">Residue : If it is white, it may contain CaF_2, SnO_2, Sb_2O_4, Al_2O_3, SiO_2 etc. If it is brown, Fe_2O_3 may be present. Confirm iron in it by borax bead test when a brown bead in oxidising and green in reducing flame is produced. In order to confirm the remaining radicals present in it, fuse the residue with NaOH, cool and extract with water and filter. The filtrate may contain sodium stannate, sodium anti-monite and aluminate. Confirm these by their usual tests.</td>
</tr>
<tr>
<td>Centrifugate : May have Sn, Al and Cr. Test for these cations in the usual manner as done in II and III groups of qualitative analysis.</td>
<td>Residue : May have SiO_2. Confirm by microcosmic bead test when silica is visible as white opaque mass of skeleton in both the fused and cold bead.</td>
</tr>
</table>

Special Tests for Some Basic Radicals

The students may also perform the following special tests and they may have some idea about some of the basic radicals which can be confirmed in the regular analysis describing in preceding sections.

Copper

Prepare clear solution of mixture in HCl and add slowly NH_4OH solution → *Bluish ppt.* The ppt. dissolves by adding excess of NH_4OH→ *Deep blue solution* shows the presence of copper.

Arsenic

1. Fleitmann's Test : The basis of this test is that AsH_3 is easily produced by treating an arsenic compound with nascent hydrogen. AsH_3 easily reduces a salt of Ag and Hg. Do not smell AsH_3 as it is *highly poisonous.* This test is performed as under :

All reagents used in this test must be free from arsenic. Take about 6-10 ml of NaOH solution in a test tube and add about 2 g of granulated zinc. Introduce loose cotton plug in the mouth of this test tube and put over mouth of test tube a piece of filter paper moistened with $AgNO_3$ or $Hg_2(NO_3)_2$ solution. Heat the test tube and if there is *no stain* on filter paper, it is clear that reagent is free form arsenic. Now the substance under test is introduced and cotton plug is again fitted in. If any *black stain* appears on $AgNO_3$ or $Hg_2(NO_3)_2$ paper it indicates presence of arsenic.

⏭ NOTE As there would be fast and energetic evolution of hydrogen throughout the experiment, it is better to take the substance in soluble form.

Antimony salts do not respond to this test. Stain on $Hg_2(NO_3)_2$ paper is more dependable.

2. Gutzeit's Test : The experimental details are same as in Fleitmann's test except when dil. H_2SO_4 is taken in place of NaOH solution. *Similar black stain* will be obtained on $AgNO_3$ paper.

⏭ NOTE Antimony salts also respond Guzeit's Test. Hence this test is useful only where either Sb or As is present.

Antimony

Perform Gutzeit's test (see above) in *absence of arsenic* and if black stain on $AgNO_3$ paper is obtained → Sb is indicated.

Tin

Herbert-Meissner Test : In a porcelain dish take zinc powder and the substance under test and add to it conc. HCl and let the reaction go on for some time and simultaneously stir the mixture with a test tube filled with water. When the bottom of this test tube is brought very near to the non-luminous Bunsen flame, a bluish flame or fluorescence is seen at the bottom of the test tube to show that tin is present in the mixture. Probably the bluish flame is produced due to burning of unstable tin hydride (probably SnH_4).

Iron (ferric)

1. Take the mixture, add to it dil. HCl and a few drops of conc. HNO_3 and boil for 2 minutes. To it, add a solution of $K_4Fe(CN)_6$→Deep blue colouration also called Prussian blue indicates presence of Fe^{3+}.
2. Take the mixture, add to it dil. HCl and a few drops of conc. HNO_3 and boil well. Dilute the solution by adding water. Now add to it KCNS solution. Deep blood red colour indicates the presence of Fe^{3+}.

NOTE In KCNS test, a pink colour will be given by it in any solution. Only deep blood red colouration confirms the presence of Fe^{3+}.

Chromium and Manganese

Excess of Na_2CO_3 + KNO_3 is mixed with the substance under examination. This powdered mixture is fused on a piece of broken porcelain and then cooled.

If fused solid mass on cooling is

1. Green → Mn is indicated.
2. Yellow → Cr is indicated.

If both Mn and Cr are present, the green colour of manganate will mask yellow colour of chromate. Reactions during fusion are :

$$Cr_2(SO_4)_3 + 5Na_2CO_3 + 3KNO_3 \rightarrow 2Na_2CrO_4 \text{ (yellow)} + 3KNO_2 + 3Na_2SO_4 + 5CO_2$$

$$MnSO_4 + 2KNO_3 + 2Na_2CO_3 \rightarrow Na_2MnO_4 \text{ (green)} + 2KNO_2 + Na_2SO_4 + 2CO_2$$

The fused mass is extracted with boiling water. Acidify this extract with dil. H_2SO_4 → pink colour shows presence of Mn. Boil this pink solution with alcohol → pink colour is destroyed and yellow or orange-yellow colour becomes distinct → Cr is present. When yellow solution is treated with acetic acid and lead acetate, a yellow ppt. confirms the presence of chromium.

Cobalt

Take the mixture in a test tube and add 1-2 ml. of conc. HCl and boil → Dark green solution. To it add excess of water and boil → Light pink solution. Put a drop of this pink solution on a filter paper and dry it on low flame. Green spot on the paper shows presence of *cobalt.*

NOTE Most of the cobalt compounds respond to this test.

Nickel

As in dimethyl glyoxime test of nickel, Fe^{+2} and cobalt interfere, perform the dimethyl glyoxime test for Ni as follows :

Prepare the solution of mixture in HCl and boil it with 1-2 drops of conc. HNO_3. Cool and make solution alkaline by NH_4OH and filter out if any green ppt. Add dimethyl glyoxime to the filtrate → rosy-red ppt. shows the presence of nickel.

Manganous Salts

The salt free from chlorides is boiled with a little of conc. HNO_3 in presence of a little lead peroxide diluted with water and then allowed to stand for 5-10 minutes. If supernatant liquid is purple (violet) in colour Mn^{2+} is indicated. The purple colour is due to permanganic acid.

Since Pb_3O_4 on continued boiling with conc. HNO_3 changes to PbO_2, hence in the above test Pb_3O_4 (red lead) may also be used in place of lead peroxide (PbO_2).

Some Clues Regarding Mixture Analysis

In some cases by carrying out the direct tests, observing the physical state of the mixture, one is able to analyse the mixture very quickly and reach some important conclusive results.

Physical Examination of the Mixture

It provides valuable information regarding the identify of some basic and acidic radicals. The inference can be drawn from the table given below :

Observation	*Inference*
1. The substance is coloured	
(i) Blue	Copper salts (Cu)
(ii) Dark green	Salts and oxides of chromium (Cr)
(iii) Green	Salts of Fe, Ni, Cu, Cr
(iv) Light yellow or brown	Salts of Fe
(v) Dark brown	PbO_2, Bi_2S_3
(vi) Reddish brown	Fe_2O_3
(vii) Light pink	Salts of Mn
(viii) Pink	Salts of cobalt
(ix) Orange red	Sb_2S_3
(x) Red	HgO, HgI_2, Pb_3O_4
(xi) Yellow	Hg (Freshly precipitated)
(xii) Black	CdS, As_2S_3, SnS_2, CuS, CuO, MnO_2, Sb_2S_3, FeS, CoO and sulphides of Ag, Hg, Pb, Bi, Ni and Co.
2. The substance is wet	$CaCl_2$, $ZnCl_2$, $MgCl_2$, $MnCl_2$. Nitrates, nitrites of metals.
3. The substance is heavy	Salts of Pb, Hg and Ba.
4. The substance is light	Carbonates of Bi, Mg, Zn etc.
5. The substance turns black to brown on exposure to laboratory atmosphere (H_2S gas).	Pb, Bi salts.

Wet Tests

Acetate (Ch_3COO^-) : Rub a little of the given mixture with a few crystals of oxalic acid and few drops of water on your palm and smell it very carefully → **Vinegar smell** (CH_3COOH).

Sulphite (SO_3^{2-}) : Rub a little of the given mixture with a few drops of dil. HCl on your palm and smell it very carefully → **Burning sulphur smell (SO_2).**

Sulphide (S^{2-}) : Rub a little of the given mixture with a few drops of dil. H_2SO_4 on your palm and smell it very carefully → **Rotten eggs smell (H_2S).**

Ammonia (NH_4^+) : Rub a little of the given mixture with a few drops of NaOH soln. on your palm and smell it very carefully → **Ammonia smell (NH_3).**

Copper (Cu^{2+}): Original solution (O.S.) is **blue**. To it add NH_4OH, deep blue colour will get developed. To it add CH_3COOH (in excess) + $K_4Fe(CN)_6$ → **Chocolate ppt.**

Iron (Fe^{2+}) : O.S. + 1 drop of conc. HNO_3 boil it for few minutes and divide it in two parts.

(*i*) Add $K_4[Fe(CN)_6]$ → **Deep blue colour.**

(*ii*) Add NH_4CNS → **Blood red colour.**

Nickel (Ni^{2+}) : O.S. is **greenish blue**. O.S. + 1 drop of conc. HNO_3 boil it for few minutes and add excess of NH_4OH + Dimethyl glyoxime→**red ppt.**

Cobalt (Co^{2+}) : O.S. is **pink**. O.S. + Excess of CH_3COOH + KNO_2 in excess → **yellow ppt.**

Manganese (Mn^{2+}) : (*i*) Mixture + PbO_2 (Soild) + con. HNO_3. Boil it for five minutes, cool and add water → **Pink coloration.**

(*ii*) Take a dry test tube. In it take equal amounts of conc. HCl (1 c.c.) and conc. HNO_3 (1c.c.). Now add a little amount of mixture. It turns black. Add a little water in it and shake. **The colour gets discharged.**

Chromium (Cr^{3+}) : O.S. is green. O.S. + NaOH + Br_2 water or H_2O_2 and boil it for five minutes. Centrifuge it.

Centrifugate + CH_3COOH + $(CH_3COO)_2Pb$ → **yellow ppt.**

Barium (Ba^{2+}), Strontium (Sr^{2+}), Calcium (Ca^{2+}) : Take sodium carbonate extract residue. Now treat it with 10 ml of acetic acid, boil it and filter. Now with this filtrate, Ba, Sr, Ca can be tested as usual.

Bisaumth, Antimony (Bi^{3+}, Sb^{3+}) : If original solution becomes turbid after dilution, then either bismuth or antimony may be present.

Mercuric (Hg^{2+}) : Rub the given mixture on copper coin→coin gets silver like shine. O.S. + $SnCl_2$ Soln. →white grayish ppt.

NOTE

(i) If mixture is having SO_4^{2-} as the acidic radical then Pb, Ba, Ca cannot be there in that mixture. It is only applicable if insoluble salts are not given.

(ii) If mixture is perfectly white, then Cu, Fe, Ni, Co, Mn, Cr can not be there in that mixture.

(iii) To the mixture and dil. H_2SO_4 add a little lead carbonate it turns black→sulphide is confirmed.

(iv) Manganese can only be tested directly by method (i) if cobalt it absent.

Caution : We should not reach a definite conclusion concerning the identity of basic and acidic radicals unless we confirm them by other confirmatory tests.