Qualitative Inorganic Analysis

Qualitative inorganic analysis is a method of analytical chemistry which seeks to establish elemental composition of inorganic compounds through various reagents. It involves the identification of the constituents of a substance, or mixture of substances. It may be macro (0.5-1 g, 10 ml), semi-micro (50 mg, 1 ml), or micro (5 mg, 0.1 ml). The concentration of the solutions used for analysis is retained in each of these techniques.

Systematic Macro Qualitative Analysis

Inorganic salts ionize into cations and anions in solution. Cations are called basic radicals and anions are called acid radicals. Detection of these radicals is done by carrying out the following tests systematically

a) Dry tests for acid radicals
b) Wet test for acid radicals
c) Test for interfering radicals
d) Dry test for basic radicals
e) Wet test for basic radicals

Bunsen burner: A luminous flame is obtained by keeping the air hole closed and a non-luminous flame is obtained on keeping the air hole opened.

1. Common ion effect:

The decrease in ionization of weak electrolyte by the addition of a strong electrolyte having ion common with the weak electrolyte, is termed as **common ion effect**.

Let us consider a weak electrolyte AB in presence of a strong electrolyte AC having a common A^- ion. To keep the equilibrium constant same, we will have less ionization of AB electrolyte.

In Group II analysis, the ionization of weak acid H_2S is depressed by the presence of strong acid HCl having a common ion H^+. Because of this, the concentration of S^{2-} ion is low. Hence ionic concentration product of the sulphides of only Group II ions, i.e. $[M^{2+}][S^{2-}]$, can exceed their solubility product values. This results in the precipitation of sulphides of Group II cations only.

Similarly, in Group III the ionization of weak base NH_4OH is depressed by the prior addition of NH_4Cl which gives high concentration of NH_4^+ ion. Because of this the conc. of OH^- ion is low which is sufficient enough to precipitate as hydroxide of Group III cations.

2. Solubility Product:

Solubility product of an electrolyte may be defined as the product of the molar concentrations of its constituent ions in the solution, when each ionic concentration term being raised to the number of times the ion occurs in the equation representing the solution of 1 mol of the electrolyte. For the electrolyte, A_xB_y solubility product, K_{sp} is given by

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$$

Ionic product is simply the product of molar concentrations of the constituent ions of an electrolyte.

For, precipitation to occur the ionic product should be greater than its solubility product.

The precipitation of the metal ions into different groups is discussed below:

Group I (Pb^{2+}, Hg_2^{2+}, Ag^+): Addition of dilute HCl precipitates as their chlorides. The chlorides are precipitated because the values of their solubility products are very low. The chlorides of other metal ions are soluble and hence remain in solution.

Group II (Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Sn^{2+}, As^{2+}, Bi^{3+}, Sb^{3+}): The sulphides of these radicals get precipitated from HCl acid medium by the passage of H_2S through their solution. Other metal ions are not precipitated because H^+ ion from HCl suppress the ionization of weak electrolyte H_2S (common ion effect). Under such condition the solubility products of only Group II metal sulphides are exceeded.

Group III (Al^{3+}, Fe^{3+}, Cr^{3+}): The hydroxides of these radicals are precipitated by NH_4OH in presence of NH_4Cl. NH_4OH alone precipitates not only the cations of this group but also the hydroxide of the metals of the latter groups. The ionization of weak base NH_4OH is depressed by the prior addition of NH_4Cl which gives high conc. of NH_4^+ ion. Because of this, the conc. of OH^- ion is low which is sufficient enough to exceed the K_{sp} values Gr III cations only and hence the other metal ions remain in the solution.

Group IV (Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}): These ions are precipitated as sulphides by passage of H_2S through ammonical solution of their ions. NH_4OH added to the solution enhances the ionization of H_2S. In the solution the OH^- ion from NH_4OH remove H^+ ions from H_2S as unionized H_2O molecule as a consequence the concentration of S^{2-} increases and the solubility product is thus get exceeded to give the precipitate.

Group V (Ba^{2+}, Sr^{2+}, Ca^{2+}): The carbonates of these radicals are precipitated by addition of $(NH_4)_2CO_3$ in presence of NH_4OH and NH_4Cl. The presence of excess of NH_4^+ ion retards the ionization of $(NH_4)_2CO_3$ causing considerable decrease in the concentration of CO_3^{2-} ion so that solubility products of carbonates of these exceed.

If NH_4Cl is not added, Mg^{2+} will be precipitated in Gr V as hydroxide. Addition of NH_4Cl increases the concentration of NH_4^+ ion which subsequently removes OH^- ion produced from $Mg(OH)_2$ as weakly ionizable NH_4OH. In order to maintain the equilibrium, more of $Mg(OH)_2$ will undergo into solution producing Mg^{2+} and OH^- ion. The OH^- ion thus produced is again removed as NH_4OH.

3. Physical observations: Color of the supplied salt mixture

Blue or bluish green – Cu(II) salts, anhydrous Co(II) salts
Green – Ni(II) salts, Fe(II) salts, Cr(III) salts, MnO
Pink-red – Hydrated Co(II) salts, Mn(II) salts
Brown – Fe(III) salts, CdO, PbO_2, $MnCO_3$
Red – Fe_2O_3, Cu_2O, HgO, Pb_3O_4, HgI_2, Sb_2S_3
Yellow – Bi_2O_3, PbO, CdS, AgI, PbI_2
White or colorless – Cu, Ni, Fe, Cr, Mn, Co etc. is absent. Information obtained by observing the color is not always reliable.
Ammonium salts give the characteristic smell of ammonia

4. Solubility

All nitrates and nitrites are water soluble. Salts of Zero group viz. NH_4^+, K^+, Na^+ are also soluble in water. They are generally analyzed before/after proceeding for separation of cations in terms of groups with the water extract.

Qualitative Analysis of the Anions (Acid Radicals)

1. Dry test for acid radicals

Experiment	Observation	Inference
1. 0.2g Sample + 1 ml dil. H_2SO_4/HCl, warm	a) colorless gas, turning lime water milky b) brown fumes, turning starch-KI paper bluish-black c) colorless gas with a smell of rotten eggs, turning lead acetate paper black d) colorless gas with smell of burning sulphur, turning acidified $K_2Cr_2O_7$ paper green e) same as d, reacting solution changes to yellow due to deposition of sulphur f) colorless vapors with smell of vinegar	CO_3^{2-} NO_2^- S^{2-} SO_3^{2-} $S_2O_3^{2-}$ CH_3COO^-
2. 0.2g Sample + 1 ml conc. H_2SO_4, warm if required (do not boil)	a) white fumes, becomes dense when in contact with glass rod moistened with NH_4OH. b) reddish brown vapors, intensity increases on addition of MnO_2 and turns blue litmus red. c) violet vapors, turning moist starch paper blue. d) light brown fumes, color intensify on addition of Cu-turnings. e) oily drops inside the test tube, leaves a white deposit on the moistened glass rod. f) colorless gas turning lime water milky and burns with blue flame	Cl^- Br^- I^- NO_3^- F^- $C_2O_4^{2-}$
3. Chromyl chloride test (if 2a responds) – sample + $K_2Cr_2O_7$ + conc. H_2SO_4, heat	Brown red vapors of CrO_2Cl_2, pass through NaOH solution (yellow solution), acidify with CH_3COOH and add lead acetate solution - yellow ppt $PbCrO_4$ soluble in NaOH	Cl^-

Reactions Involved:

With dilute HCl/H_2SO_4:

For CO_3^{2-}, $CO_3^{2-} + H_2SO_4 \rightarrow SO_4^{2-} + H_2O + CO_2$, $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
For SO_3^{2-}, $SO_3^{2-} + H_2SO_4 \rightarrow SO_4^{2-} + SO_2 + H_2O$, $K_2Cr_2O_7 + H_2SO_4 + SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
For S^{2-}, $S^{2-} + H_2SO_4 \rightarrow SO_4^{2-} + H_2S$, $Pb(CH_3COO)_2 + H_2S \rightarrow 2CH_3COOH + PbS$
For $S_2O_3^{2-}$, $S_2O_3^{2-} + H_2SO_4 \rightarrow SO_4^{2-} + SO_2 + S + H_2O$, $K_2Cr_2O_7 + H_2SO_4 + SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
For NO_2^-, $NO_2^- + H_2SO_4 \rightarrow SO_4^{2-} + 2HNO_2$, $3 HNO_2 \rightarrow H_2O + HNO_3 + 2NO$, $2NO + O_2 \rightarrow 2NO_2$

With conc. H_2SO_4:

For Cl^-, $Cl^- + H^+ \rightarrow HCl$, $HCl + NH_3 \rightarrow NH_4Cl$
For Br^-, $2Br^- + 6H^+ + 3SO_4^{2-} \rightarrow 2HSO_4^- + SO_2 + Br_2 + 2H_2O$
For I^-, $2I^- + 6H^+ + 3SO_4^{2-} \rightarrow 2HSO_4^- + SO_2 + I_2 + 2H_2O$
For NO_3^-, $NO_3^- + H^+ \rightarrow HNO_3$, $4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O$
$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Chromyl chloride test:

$4Cl^- + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2KHSO_4 + 4HSO_4^- + 3H_2O$
$2CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$
$Pb(CH_3COO)_2 + Na_2CrO_4 \rightarrow 2CH_3COONa + PbCrO_4$

2. Wet test for acid radicals

If the sample is colorless and soluble in water perform the wet test with the sample solution made in water. If the sample is neither of the above nor any one of them then prepare soda extract (SE) to perform the wet tests.

Preparation of solution: The solid sample may be soluble or insoluble in water.

1. **Soluble** (nitrates, nitrites, thiosulphates): 1g of the sample dissolved in 20 ml cold water if not soluble then boil. Residues, if any, then filter. The filtrate is called **water extract (WE).**

2. **Insoluble and/or colored sample**: To 1g of the sample add 4g of Na_2CO_3 followed by addition of 30 ml water. Boil the mixture for 15 min, cool the content and filter. The filtrate is called **Soda (sodium carbonate) extract (SE)**

With sample solution-

Experiment	Observation	Inference
1.Test for SO_4^{2-} To 1 ml of WE/SE add dilute HCl (to acidify), boil off CO_2 and add $BaCl_2$/$Ba(NO_3)_2$ solution	White ppt insoluble in conc. HCl and conc. HNO_3	SO_4^{2-}
2. Test for halides To 1 ml of WE/SE add dilute HNO_3 (to acidify), boil off CO_2 and add $AgNO_3$ solution	a) Curdy white ppt, soluble in NH_4OH solution. b) Pale yellow ppt, partially soluble in NH_4OH solution (soluble in strong, excess of NH_4OH). c) Pale yellow ppt, insoluble in NH_4OH solution.	Cl^- Br^- I^-
3. Test for S^{2-} (a) To 1 ml of WE/SE add freshly prepared sodium nitroprusside solution. a) Drop few drops of WE/SE to $Pb(CH_3COO)_2$ paper	Purple/pink/violet coloration (CdS, PbS, ZnS etc. do not respond) The paper turns black	S^{2-} S^{2-}
4. Test for $S_2O_3^{2-}$ To 1 ml of WE/SE add acetic acid (to acidify) and add $AgNO_3$ solution	White ppt turning to yellow, orange-brown and finally black	$S_2O_3^{2-}$
5. Test for SO_3^{2-} To 1 ml of WE/SE add dilute H_2SO_4 (to acidify) in excess and add 2-3 drops of $KMnO_4$ solution	Decolorizations of pink color	SO_3^{2-}
6. Test for NO_2^- To 1 ml of WE/SE add 5 drops of KI, and 1ml starch solution followed by dilute 1 ml H_2SO_4	Appearance of deep blue color	NO_2^-
7. Test for CH_3COO^- To 0.5 g of the sample add 1 ml conc H_2SO_4 and 2 ml ethanol. Warm the mixture gently for few minutes	Fruity smell	CH_3COO^-
8. Test for $C_2O_4^{2-}$: To 1ml WE/SE add CH_3COOH (to acidify) and add NH_3 (smell of NH_3). Heat to remove excess NH_3 and add 1 ml $CaCl_2$ soln	White ppt	$C_2O_4^{2-}$
9. Test for F- To 1ml WE/SE add CH_3COOH (to acidify) and boil off CO_2, add 1ml $CaCl_2$ soln	White ppt	F^-
10. Test for borate 0.2g sample + 2-3 drops conc. H_2SO_4, add 1 ml methanol/ethanol, heat gently and ignite the vapors in flame.	Green edge flame	BO_3^{3-} conf.
11. Test for phosphate 0.2g sample + 2 ml conc. HNO_3, add ammonium molybdate solution, warm (if required)	Canary yellow ppt (soluble in NH_4OH and NaOH)	PO_4^{3-} conf

Reactions involved:

For SO_4^{2-}, $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + Cl^-$

For X^-, $X^- + AgNO_3 \rightarrow AgX + NO_3^-$ ($X^- = Cl^-, Br^-, I^-$) $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$ (soluble)

For S^{2-}, $S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$

For $S_2O_3^{2-}$, $S_2O_3^{2-} + 2\ AgNO_3 \rightarrow Ag_2S_2O_3 + NO_3^-$, $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$

For SO_3^{2-}, $5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

Test for nitrites and nitrates (always perform with WE) – if the sample is water insoluble then treat the mixture with water and filter. Perform the test for these ions with the filtrate.

Experiment	Observation	Inference
1. Test for NO_2^- To 1ml WE add acetic acid solution (to just acidify), cool and add 1 ml freshly prepared $FeSO_4$ soln	A brown ring or coloration	NO_2^- conf

2. Test for NO_3^- To 1ml WE add 2 ml of conc. H_2SO_4, shake and cool, add 2 ml freshly prepared $FeSO_4$ soln by the side of the test tube	A brown ring at the juncture of two liquids	NO_3^- conf

Reactions involved:

For NO_2^-, $NO_2^- + H^+ \rightarrow HNO_2$, $HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]2^+ + H_2O$

For NO_3^-, $NO_3^- + 4H^+ + 3Fe^{2+} \rightarrow 3Fe^{3+} + NO + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$

For BO_3^{3-}, $BO_3^{3-} + 3H^+ + 3CH_3OH \xrightarrow{\textbf{conc. } H_2SO_4} B(OCH_3)_3 + 3H_2O$

$2\,B(OCH_3)_3 + 9O_2 \longrightarrow B_2O_3 + 6\,CO_2 + 9H_2O$

- HCl can't be used instead of H_2SO_4 as CH_3Cl formed in this reaction burns with green flame
- Generally, Cu^{2+} and Ba^{2+} do not interfere here as they form non-volatile sulphates, but sometimes they may interfere giving same green flame. Perform this test in a test tube. Vapors of only alkyl borate are able to reach mouth of the test tube and Cu and Ba are left behind.
- Ethyl alcohol can be used but ethyl borate has higher boiling point. Moreover, if halides are present, halogen acids formed can react with alcohol to give ethyl halide that burns with green flame.

For PO_4^{3-}, $PO_4^{3-} + NH_4^+ + 12\,MoO_4^{2-} + 24H^+ \longrightarrow (NH_4)_3[P(Mo_3O_{10})_4] + 12H_2O$

- All phosphates and arsenates are soluble in conc. HNO_3. Both arsenate and phosphate correspond to this test, the yellow ppt for both dissolve on boiling with ammonium acetate solution but the yellow ppt of ammonium arsenomolybdate gives white ppt on cooling. The presence of phosphate ion is further confirmed by performing the same test with Group II filtrate after removing H_2S. In presence of tartaric acid, only phosphates correspond to the test whereas arsenate does not. So to the nitric acid solution of the sample, add 1 ml tartaric acid solution followed by ammonium molybdate solution (warm if requires).

4. Special tests for mixture of anions

(i). Nitrite and nitrate:

Acidify WE/SE with dil. H_2SO_4/acetic acid and heat gently. Add KI soln – blue color –NO_2^- conf.

To 5 ml WE add 2g NH_4Cl and boil till effervescence ceases (NO_2^- is removed as N_2 - ensure complete removal). Divide the solution into two parts.

a. To first part, add dil H_2SO_4 (to acidify), add small amount of KI and 1 ml starch solution - absence of blue color indicates complete removal of NO_2^- (if blue color appears boil until blue color disappears) - Add metallic Zn - appearance of blue color confirms the presence of NO_3^-

b. With second part, perform the ring test for NO_3^-

~~**Reactions involved:**~~

In presence of nitrite, nitrate can't be detected because both liberate NO_2 either with conc H_2SO_4 or in ring test.

(ii). Nitrate with bromide and/or iodide:

Acidify a portion of SE with dil. H_2SO_4 and add few drops of $CHCl_3$ or CCl_4. Add freshly prepared Cl_2 water (with constant shaking)/conc HNO_3 (slight warming). Violet color appears at the organic layers - I^- is conf.

Go on adding Cl_2 water/conc HNO_3 and repeat the above. The violet color disappears and the organic layer becomes brown confirming the presence of Br^- (for detecting NO_3^- use Cl_2 water)

Acidify another portion of SE/above solution with dil. H_2SO_4, add Zn dust and heat gently. Add KI solution and starch solution - blue color - NO_3^- conf.

~~**Reactions involved:**~~

Bromide and iodide interfere in the ring test of nitrate because of the color of the liberated bromine and iodine. So, the halide ion should be removed for confirming NO_3^-

(iii). Chloride, bromide and iodide in presence of each other

Acidify a portion of SE with dil. H_2SO_4 and add few drops of $CHCl_3$ or CCl_4. Add freshly prepared Cl_2 water (with constant shaking)/conc HNO_3 (slight warming). Violet color appears at the organic layers - I^- is conf.

Go on adding Cl_2 water/conc HNO_3 and repeat the above. The violet color disappears and the organic layer becomes orange brown confirming the presence of Br^-. The mixture is boiled thoroughly to remove Br^- ion.

To the mixture add $AgNO_3$, formation of curdy white ppt soluble in dil. NH_4Cl confirms the presence of Cl^- ion

~~**Reactions involved:**~~

Chloride, bromide, and iodide ions react with $AgNO_3$soln to form a ppt, special tests are required to identify if more than one of them are present in the mixture.

(iv). Sulphide, sulphite, thiosulphate and sulphate ion in presence of each other

To 5ml of SE add solid $CdCO_3$ (in excess) or $PbCO_3$ – yellow ppt ($CdCO_3$) or black ppt ($PbCO_3$) – S^{2-} is conf. Filter the ppt and use the filtrate for detection of sulphite, thiosulphate and sulphate.

To the filtrate add $Sr(NO_3)_2/BaCl_2$ soln. Filter if ppt appears	
White residue ($Sr/BaSO_3$, 24 hrs- and/or $Sr/BaSO_4$): add dilute HCl and filter.	

White residue: insoluble in conc. HCl – SO_4^{2-}conf	Filtrate: Divide into two parts a) add conc. HNO_3 and heat – white ppt – SO_3^{2-}conf b) add 2 drops of I_2 solution – the solution decolorizes - SO_3^{2-}conf	Filtrate (Sr/BaS_2O_3): add few drops $AgNO_3$ solution, white ppt turning yellow, orange, brown and finally black – $S_2O_3^{2-}$ conf

Reactions involved:

Removal of interfering radicals

Theory: Borates, phosphates, oxalates, fluoride etc. are generally soluble in dilute acids and insoluble in alkaline medium. When NH_4OH is added after Group II analysis, not only the hydroxides but the borates and phosphates of cations of Group III onwards also gets precipitated from the soln. Such precipitation may occur in absence of the metal ions of the concerned group. Thus, these interfering anions interfere in the analysis of Group III to Group V cations.

1. Removal of Borate (before Group I analysis)

Take 0.5 g of sample in a porcelain basin, add 1 ml of conc. HCl. Evaporate the mixture to dryness. Repeat the process for three more times. Take small amount and perform the test for borate. If present, repeat the process till borate is completely removed. Finally extract the residue with water or dilute HCl and use the solution for group separation.

2. Removal of Phosphate (before Group III analysis)

Boil the filtrate of Group II to remove H_2S completely ***(****test with lead acetate paper*). Add few drops of conc. HNO_3. Boil and add NH_4Cl and NH_4OH till alkaline – white ppt – add 5 ml of glacial acetic acid followed by lead acetate until complete precipitation. Filter.

Residue: $Pb_3(PO_4)_2$ – reject (ensure complete precipitation)

Filtrate: Add 1ml dilute HCl warm and pass H_2S. Filter

Residue: Black-PbS – reject (ensure complete precipitation)

Remove H_2S from the filtrate and use for analysis of cations of Group III onwards.

3. Removal of Oxalate (before Group III analysis)

Oxalate ion can be removed by repeatedly evaporating the solid mixture or the filtrate of Gr II (boil off H_2S first) with conc. HNO_3 to near dryness. (heating to complete dryness may result in the formation of insoluble M(III) oxides of Fe, Cr and Al). The process is to be repeated several times until the residue gives a negative test for the oxalate ions (conc. HNO_3 oxidizes the oxalate ions to CO_2 and water). Extract the oxalate removed part with dil. HCl and use the solution for further analysis.

4. Removal of fluoride (before Group III analysis)

Fluoride ions can be removed by repeatedly evaporating the dry mixture or the filtrate of Gr II (H_2S removed part) with conc. HCl in a porcelain basin. Fluoride ions are volatilized off as hydrofluoric acid. The process should be repeated several times until fluoride is eliminated. Extract the residue in dil. HCl and use the solution for the analysis.

<u>Qualitative Analysis of the Cations (Basic Radicals)</u>

1. Dry tests for basic radicals

(a) Heating in a dry test tube:

Not very useful for mixtures!

Color of the residue (due to the formation of colored oxides)

In hot: yellow (Zn), Brown (Pb, Bi, Sn), Reddish brown (Fe), Dark & or red (Cd)

Color of the residue (due to loss of water of crystallization)

Blue → white ($CuSO_4$) Crimson → blue ($CoCl_2$) Dark red → Green ($CoBr_2$)

Dark red → violet (CoI_2) Red → pink ($CoSO_4$,$Co(NO_3)_2$) Green → yellow (Ni salts)

Violet → green (Cr salts)

Sublimate formation

White – Al, Hg, NH_4^+ chlorides

Grey - Hg, As salts

(b) Charcoal Cavity test: The mixture is heated with fusion mixture (Na_2CO_3 + KNO_3), corresponding carbonates are produced and then decomposed to their respective oxides as residues.

Cd, Pb, Cu, Ag etc. give colored residue

Fe, Co, Ni, Mn, Al, Mg, Ca, Ba, Sr, Zn etc. give white residue

(c) Cobalt Nitrate test:

This test is performed if white infusible residue is left in charcoal cavity test. The white residue is heated with $Co(NO_3)_2$ in reducing flame(luminous), CoO formed combines with the white metal oxide residue to form colored compounds.

Green (Zn), Blue (Al), Pink (Mg) etc.

(d) Borax bead test:

This test is performed for colored salts only. Borax loses its water of crystallization giving colorless bead of $NaBO_2$& B_2O_3. The B_2O_3 reacts with metal salts to give metal metaborate (oxidizing flame)

Deep blue (Co), Light brown (Ni), Violet (Mn), Green (Cr), Yellow (Fe), Light blue or green (Cu)

(e) Flame test:

Not very useful for mixtures!

Halides of certain metals when heated, gets thermally ionized and gives characteristic color to the flame.

Make a paste of the mixture in conc. HCl on a watch glass. Take a small quantity in Pt-loop and put it in non-luminous flame.

Golden yellow – Na
Pale-violet – K
Bluish green – Cu
Crimson red – Sr
Brick red – Ca
Green – Ba
Bright Green – borate

***Borate in presence of Cu and Ba: The mixture of sample, conc. H_2SO_4 and ethanol is placed in Round Bottom flask and fitted with a glass jet and the vapor is ignited – green flame – borate confirmed.

2. Wet tests for basic radicals

The following solvents are used one by one viz. water, dil. HCl, conc. HCl, dil. HNO_3, conc. HNO_3, aqua regia (3:1 mixture of conc. HCl and conc. HNO_3). *Heating may be required before trying a new solvent.*

The use of HNO_3 and aqua-regia should be avoided as a solvent as far as practicable. Being strong oxidizing, they give colloidal sulphur with H_2S.

If the sample is dil. HCl soluble and no white ppt occurs on standing, Group I is absent.

Separation of basic radicals or cations into groups:

Experiment	Observation	Inference
1. Sample solution + 2ml dil. HCl	ppt as halides; White - Pb, Hg, Ag	Gr. I present
2. Above solution (*No ppt*) or filtrate (*if ppt appears*) from Group I, warm and pass H_2S gas	ppt as sulphides; Black - Hg, Pb, Bi, Cu Yellow - Cd, As, Sn (ic) Orange - Sb Brown – Sn (ous)	Gr. II present
3. Above solution (*No ppt*) or filtrate (*if ppt appears*) from Group II, boil to remove H_2S, **divide into two parts** **Part 1**: To a small portion add few drops of conc. HNO_3, warm and add $K_4[Fe(CN)_6]$ soln – blue ppt - Fe present If Fe is present *(blue ppt)*, add conc HNO_3 to the remaining portion and perform the test (Part 2). If Fe is absent then the addition of HNO_3 is not required and perform the test (Part 2). **Part 2**: NH_4Cl + NH_4OH soln till ammonical (smell of NH_3)	Ppt as hydroxide; Brown - Fe Gel. White - Al Dirty green - Cr	Gr. III present
4. Above soln *(No ppt)* or filtrate *(if ppt appears)* from Part 2 of Group III, pass H_2S gas	ppt as sulphides; Black - Ni, Co Dirty white - Zn Grey - Mn	Gr. IV present
5. Above soln *(No ppt)* or filtrate *(if ppt appears)* from Group IV, boil to remove H_2S (test with lead acetate paper) add NH_4OH until ammonical and then add $(NH_4)_2CO_3$	ppt as carbonate; White - Ba, Sr, Ca	Gr. V present
6. Above soln *(No ppt)* or filtrate *(if ppt appears)* from Group V add Na_2HPO_4 soln	ppt as hydrogen phosphate; White - Mg	Gr VI present

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

Filter and boil the ppt with water and filter again when hot

<table>
<tr><td colspan="2">Residue (may be Hg_2^{2+}, Ag^+) - Wash the ppt with hot water, add NH_4OH soln and filter</td><td>Filtrate (may be Pb^{2+}) - divide into two parts</td></tr>
<tr><td>Residue (grey or black - may be Hg_2^{2+})
Dissolve the ppt in aqua regia, evaporate to dryness and extract with water and add KI soln. an orange red ppt dissolves in excess of KI - Hg_2^{2+}confirmed.</td><td>Filtrate (may be Ag^+)
Add dil. HNO_3 (to acidify) - white ppt –Ag^+ confirmed</td><td>Part I: add K_2CrO_4soln - yellow ppt soluble in NaOH soln - Pb^{2+}conf
Part II: add KI soln - yellow ppt - Pb^{2+} confirmed.</td></tr>
</table>

- If the soln is prepared in conc HCl, dilute the soln. If ppt appears perform the test for Group I
- $PbCl_2$ is partially soluble in water so Pb may be obtained as PbS in Group II
- If a yellow white ppt is obtained on addition of dil. HCl, thiosulphate may be present. In such case boil it with small amount of $NaNO_3$

Analysis of Group II cations: Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Sn^{2+}, As^{2+}, Bi^{3+}, Sb^{3+}

Separation into Group II(A) and Group II(B) cations

Filter and transfer the ppt to a porcelain basin and add 5ml of yellow ammonium sulphide, warm the mixture for 2 minutes and filter.

Residues: Gr II(A)	**Filtrate: Gr II(B)**
Ppt constitutes Group IIA cations viz. **Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}**. Use this ppt for the analysis of Group IIA cations.	Acidify the filtrate with conc. HCl (warm gently if needed)- Yellow/orange ppt - **Gr II(B) conf ($As^{3+/5+}$, Sb^{3+}, $Sn^{2+/4+}$).** Use this ppt for the analysis of Gr IIB cations.

Analysis of Group IIA cations

Wash the ppt with hot water and add dil. HNO_3 soln and boil for 2 min, filter.

<table>
<tr><td>Residue (black-may be Hg^{2+})</td><td colspan="3">Filtrate (may be Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+})
Add conc H_2SO_4 soln, if ppt appears filter the soln</td></tr>
<tr><td rowspan="3">Dissolve the residue in aqua regia, evaporate to dryness and extract with water add KI soln. an orange red ppt dissolves in excess of KI- Hg^{2+}confirmed.</td><td rowspan="3">White ppt (Pb^{2+})- dissolve it in ammonium acetate soln and add K_2CrO_4 soln - yellow ppt- Pb^{2+} confirmed.</td><td colspan="2">Filtrate – add excess of NH_3soln, if ppt appears filter</td></tr>
<tr><td rowspan="2">White ppt (Bi^{3+})- dissolve it in minimum volume of dil. HCl and add KI solution-black ppt –Bi^{3+} confirmed</td><td>Filtrate
Divide into two parts
Blue - (Cu^{2+})-add acetic acid followed by $K_4[Fe(CN)_6]$ soln- reddish brown ppt - Cu^{2+} confirmed.</td></tr>
<tr><td>colorless-(Cd^{2+})- add dil HCl followed by H_2S gas - a yellow ppt - Cd^{2+} confirmed.</td></tr>
</table>

Analysis of Group IIB cations: Boil the colored ppt with conc. HCl for 5 mins, dilute it by adding H_2O & filter

Residue (As^{3+}/As^{5+})	**Filtrate**: Divided into two parts
Dissolve in conc. HNO_3 & evaporate to dryness, extract with water. Divide into two parts **Part I** + ammonium molybdate solution - yellow ppt/coloration – may be As^{3+}/As^{5+} **Part II** + $AgNO_3$ solution - yellow ppt soluble in HNO_3 and NH_4OH - As^{3+} conf.	**Part I** + NH_4OH solution + solid oxalic acid (until saturated) + H_2S gas - Orange ppt - Sb^{3+} conf. **Part II** + Zn metal, heat (to reduce Sn^{4+} to Sn^{2+}) + $HgCl_2$ - white or grey ppt - Sn^{2+} conf.

- Pass H_2S sufficiently to ensure complete precipitation
- If the solution is too acidic, Pb, Cd, Sn may not be precipitated. Further dilution of dil. HCl may be required

Analysis of Group III cations: Al^{3+}, Fe^{3+}, Cr^{3+}

Wash the ppt with hot water, add NaOH solution and H_2O_2 and boil the mixture till the evolution of O_2 ceases and filter

Residue (may be Fe^{3+} or Mn^{2+})	**Filtrate** (may be colorless - Al^{3+} or yellow - Cr^{3+})
Divide into two portions **Part I:** Dissolve in dil. HCl and again divide into two parts (i) Add $K_4[Fe(CN)_6]$ sol - a Prussian blue ppt - Fe^{3+} confirmed (ii) Add NH_4SCN soln - blood red coloration - Fe^{3+} confirmed	Divide into two portions **Part I:** add acetic acid followed by lead acetate soln- yellow ppt soluble in dil. NaOH - Cr^{3+} confirmed
Part II: Dissolve in dil. HNO_3, add sodium bismuthate solution, shake and allow to settle - violet/pink coloration- Mn^{2+} confirmed	**Part II:** Add NH_4Cl and boil-white gelatinous ppt - Al^{3+} confirmed

Before proceeding to Group III analysis remove interfering radicals if present.

- Solid NH_4Cl should be added in excess otherwise Zn, Mn, Mg may get precipitated
- Too much addition of NH_4Cl also to be avoided otherwise Al may form colloidal soln and Cr will not form ppt
- Fe(II) ions if present should be converted to Fe(III) ions by boiling with conc. HNO_3

Analysis of Group IV cations: Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}

Treat the ppt (obtained after passing H_2S) with dil. HCl and filter

<table>
<tr><td>Residue (may be Ni^{2+} or Co^{2+})
Dissolve the residue in aqua regia, heat to dryness (residue blue - Co^{2+}, yellow - Ni^{2+}, green - both) and extract with water. Divide into three parts</td><td colspan="2">Filtrate (Zn^{2+} or Mn^{2+})
Boil to expel H_2S gas. Cool and add NaOH solution and filter</td></tr>
<tr><td>Part I: Add NH_4OH till alkaline a few drops of DMG soln – pink ppt – Ni^{2+} confirmed</td><td>Residue black (Mn^{2+})- dissolve the ppt in conc HNO_3 and add a pinch of sodium bismuthate or</td><td>Filtrate (Zn^{2+}) - acidify with acetic acid and add H_2S gas</td></tr>
</table>

Part II: Add NH_4OH till alkaline followed by acetic acid and crystals of KNO_2or $NaNO_2$ yellow color or ppt (after evolution of a gas) - Co^{2+} confirmed **Part III:** Add NH_4SCN followed by acetone– blue color – Co^{2+} confirmed	PbO_2 – violet coloration – Mn^{2+} confirmed.	– a dirty white ppt – Zn^{2+} confirmed.

Analysis of Group V cations: Ba^{2+}, Sr^{2+}, Ca^{2+}

Dissolve the ppt in acetic acid and divide the solution into three parts.

Part I (divide into three parts)	**Part II** (divide into two parts)	**Part III**
(i) Add K_2CrO_4 solution, shake - yellow ppt - Ba^{2+} present. Filter and use the filtrate for the test of Sr^{2+} and Ca^{2+} (If Ba^{2+} is absent, then perform the test for Ca^{2+} and Sr^{2+} with part II) (ii) Above filtrate+$(NH_4)_2SO_4$ solution - white ppt - Sr^{2+} present Filter and use the filtrate for the test of Ca^{2+} (iii) Above filtrate +$(NH_4)_2C_2O_4$ solution - white ppt - Ca^{2+} confirmed	(i) Add $(NH_4)_2SO_4$ solution - white ppt - Sr^{2+} present. Filter and use the filtrate for the test of Ca^{2+} (If Sr^{2+} is absent, then perform the test for Ca^{2+} with part III) (ii) Above filtrate + $(NH_4)_2C_2O_4$ solution - white ppt - Ca^{2+} confirmed	Add $(NH_4)_2C_2O_4$ solution - white ppt -Ca^{2+} confirmed

Analysis of Group VI cations: Mg^{2+}

Dissolve the ppt in dil. HCl and add small amount of NaOH soln – white ppt – Mg^{2+} confirmed.

Analysis of Group 0 (soluble group) cations: Na^+, K^+, NH_4^+

Take water extract (if the sample is water insoluble, add small amount of sample to water, shake well and filter, use the filtrate) and divide into four parts

Part I	**Part II**	**Part III and Part IV**
Add zinc uranyl acetate solution and shake vigorously - yellow ppt - Na^+ conf.	Add Nessler's reagent followed by NaOH solution - brown ppt - NH_4^+ conf.	**Part III** + sodium cobaltinitrite soln- yellow ppt – K^+ conf. **Part IV** + tartaric acid solution followed by few drops of alcohol - white ppt - K^+ conf.

- Some ammonium salts liberate NH_3 on heating with NaOH
- Nessler' reagent: alkaline solution of Pot. Mercuriodide, $K_2[HgI_4]$
- Like K^+, NH_4^+ also gives yellow ppt with sodium cobaltinitrite soln hence complete removal of NH_4^+ is essential. If both are present, treat the sample with conc. HNO_3 and evaporate to dryness and use sodium cobaltinitrite for testing K^+.