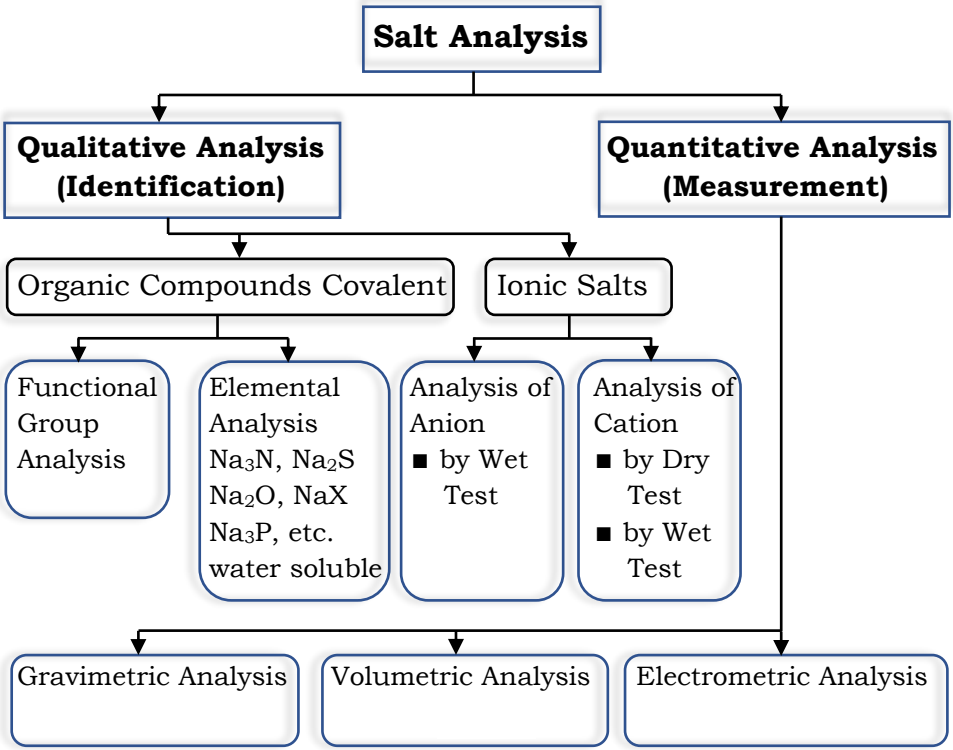
CHAPTER -06
SALT ANALYSIS

Cation: Pb^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+

Anions: CO_3^{2-}, S^{2-}, SO_4^{2-}, NO^{3-}, NO^{2-}, Cl^-, Br^-, I^- (Insoluble salts excluded)

Definition: The identification of a substances usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substance of known composition. The substance which is used to bring about such change is called a reagent.

Qualitative analysis involves the detection of cation(s) and anion(s) of a salt or a mixture of salts.



[Salt/Solids] [Liq./Solution] [Gases]

Analysis of Acidic Radical

Classification of Acidic Radical

Class A (Form volatile product with acid)	**Class B** (Does not form volatile product with acid)
Sub group I [Weak Group]	Sub group I
(Form volatile product with dil. HCl/dil. H_2SO_4) CO_3^{2-}, HCO_3^-, SO_4^{2-}, HSO_3^-, $S_2O_3^{2-}$, S^{2-}, CH_3COO^-, NO_2^-	(Detected by precipitation reaction) SO_4^{2-}, PO_4^{3-}, AsO_3^{3-}, AsO_4^{3-}
Sub group II [Strong group]	Sub group II
(Form volatile product with conc. H_2SO_4) F^-, Cl^-, Br^-, I^-, NO_3^-, BO_3^{3-}, $C_2O_4^{2-}$ + sub group I	(Detected by redox reaction) CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, MnO_4^{2-}

	Observation	Inference
1.	Gas evolved	
	(A) Colourless & odourless gas CO_2 gas – turns lime water milky	CO_3^{2-}
	(B) Colourless gas with odour	
	(i) H_2S gas - Smells like rotten eggs, turns	Hydrated S^{2-} or S^{2-}
	(ii) SO_2 gas - Characteristic suffocating smell of burning sulphur turns acidified potassium dichromate solution or paper green	SO_3^{2-}
	(iii) HCl gas - Pungent smell, white fumes with ammonia, white precipitate with silver nitrate solution	Cl^-

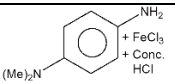
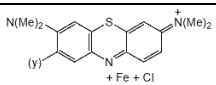
	(iv) Acetic acid vapours-Characteristic vinegar like smell	CH_3COO^-
	(v) NH_3 gas-Characteristic smell, turns Nessler's solution brown	NH_4^+
	(C) Coloured gases-Pungent smell	
	(i) NO_2 gas-Reddish brown, turns ferrous sulphate solution brownish black.	NO_2^- or NO_3^-
	(ii) Cl_2 gas-Greenish yellow, turns starch iodide paper blue	Cl^-
	(iii) Br_2 vapours-Reddish brown, turns starch paper orange red	Br^-
	(iv) I_2 vapours-Dark violet, turns starch paper blue	I^-
2.	Sublimate formed (A) White sublimate	NH_4^+
	(B) Black sublimate accompanied by violet vapours	I^-
3.	Fusion The mixture fuses	Alkali metal salts or salt containing water of crystallisation
4.	Swelling The mixture swells up into voluminous mass	PO_4^{3-}, BO_3^{3-} indicated
5.	Residue (A) Yellow when hot, white when cold	Zn_2^+
	(B) Brown when hot and yellow when cold	Pb_2^+
	(C) Original salt blue becomes white on heating	Hydrated $CuSO_4$ indicated

	(D) Coloured salt becomes brown or black on heating	CO^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+} indicated

Acidic Radical Table

	dil. H_2SO_4	Conc. H_2SO_4	$CaCl_2$	$BaCl_2$	$HgCl_2$	$AgNO_3$	$Pb(OAc)_3$	MnO_4^- / H^+
CO_3^{2-}	$CO_2\uparrow$	$CO_2\uparrow$	$CaCO_3\downarrow$ white	$BaCO_3\downarrow$ white	$HgCO_3 \cdot 3HgO\downarrow$ Reddish brown	$Ag_2CO_3\downarrow$	$PbCO_3 \cdot 2Pb(OH)_2\downarrow$	—
S^{2-}	$H_2S\uparrow$	$S\downarrow + SO_2\uparrow$	—	$BaS\downarrow$ black	$HgS\downarrow$ black	$Ag_2S\downarrow$ black	$PbS\downarrow$ black	$S\downarrow$
SO_4^{2-}	—	—	$CaSO_4\downarrow$ white	$BaSO_4\downarrow$ curdy white ppt	$HgSO_4 \cdot 2HgO\downarrow$ yellow	—	$PbSO_4\downarrow$ white	—
NO_3^-	—	$NO_2\uparrow$	—	—	—	—	—	—
Cl^-	—	$HCl\uparrow$	—	—	—	$AgCl\downarrow$ white	$PbCl_2\downarrow$ white	$Cl_2\uparrow$
Br^-	—	$Br_2\uparrow$ brown	—	—	—	$AgBr\downarrow$ pale yellow	$PbBr_2\downarrow$ white	$Br_2\uparrow$
I^-	—	$I_2\uparrow$ violet	—	—	$HgI_2\downarrow$ scarlet red	$AgI\downarrow$ yellow	$PbCl_2\downarrow$ dark yellow	$I_2\uparrow$
NO_2^-	$NO_2\uparrow$	$NO_2\uparrow$	—	—	—	$AgNO_2\downarrow$	—	NO_3^-

Specific Reaction of Acidic Radical

Anion	Reaction name/with	Reagent	Product	Observation
S^{2-}	Sodium Nitro Prusside	$Na_2[Fe(CN)_5NO]$	$Na_4[Fe(CN)_5NOS]$	Purple Complex
S^{2-}	Methylene Blue Test			Methylene Blue
NO_2^-	Brown Ring Test	$FeSO_4$ + dil. H_2SO_4	$[Fe(H_2SO)_5NO]SO_4$	Brown Ring
NO_3^-	Brown Ring Test	$FeSO_4$ + Conc. H_2SO_4	$[Fe(H_2O)_5NO]SO_4$	Brown Ring
Br^-	Layer Test	Cl_2 Water + CCl_4	Br_2 + CCl_4	Red Layer
I^-	Layer Test	Cl_2 Water + CCl_4	I_2 + CCl_4	Violet Layer
I^-	$HgCl_2$	$HgCl_2$	HgI_2	Red/Yellow

Cl^-	Chromyl Chloride Test	(i) $K_2Cr_2O_7(s)$ + conc. H_2SO_4 (ii) NaOH (iii) $Pb(CH_3COO)_2$ + CH_3COOH	CrO_2Cl_2 $\downarrow CrO_4^{2-}$ $PbCrO_4$	Reddish brown vapour ↓ Yellow solution ↓ Yellow ppt
CrO_4^{2-} / Cr_2O_7	Acidic Solution of H_2O_2 + Pyridine	$H_2O_2 + H^+$ 	CrO_5	Blue Solution

Basic Radical Analysis

Dry Text of Cation

Flame Test: Used for s-block cation (except Be^{+2}, Mg^{+2})

Cation	Li^+	Na^+	K^+	Ca^{+2}	Sr^{+2}	Ba^{+2}	Cu^{+2}
Observation (Naked eye	Carmine red	Golden yellow	Lilac	Brick red	Crimson red	Apple green	Green flame
Cobalt glass		Flame disappear	Crimson red	Green	Purple	Bluish green	Green flame

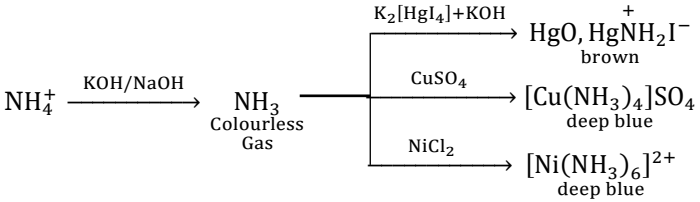
Group	Group Reagent	Basic Radical	Composition & Colour of Precipitate
Zero	NaOH or $Ca(OH)_2$ heat if required	NH_4^+	Ammonia gas is evolved
1.	Dil. HCl	Ag^+ Hg_2^{2+}	AgCl; White Hg_2Cl_2; White
2(A).	H_2S in presence of dil. HCl (Insoluble in YAS)	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+}	HgS; Black PbS; Black Bi_2S_3; Black CuS; Black CdS; Yellow
2(B).	H_2S in presence of dil. HCl (Soluble in YAS)	As^{3+} Sb^{3+} Sn^{2+} Sn^{4+}	As_2S_3; Yellow Sb_2S_3; Orange SnS; Brown SnS_2; Yellow
3.	NH_4OH in presence of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	$Fe(OH)_3$; Reddish brown $Cr(OH)_3$; Green $Al(OH)_3$; Gelatinous white
4.	H_2S in presence of NH_4OH & NH_4Cl	Zn^{2+} Mn^{2+} Co^{2+} Ni^{2+}	ZnS; White MnS; Buff (or Pink) CoS; Black NiS; Black
5.	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	$BaCO_3$; White $SrCO_3$; White $CaCO_3$; White
6.	Na_2HPO_4 in presence of NH_4OH	Mg^{2+}	$Mg(NH_4PO_4$; White

Test of Basic Radical

	Pb^{2+}	Cu^{+2}	Al^{+3}	Fe^{+3}	Zn^{+2}	Ni^{+2}
KI	PbI_2 yellow	$CuI + I_3^-$ white solution	—	$FeI_2 + I_3^-$ yellowish brown sol.	—	—
ex KI	$[PbI_4]^{2-}$ soluble complex	—	—	—	$Zn(CN)_2$ white	—
KCN	$Pb(CN)_2$ white	$CuCN + (CN)_2\uparrow$	—	$Fe(CN)_3$ brown	—	$Ni(CN)_2$ green
ex KCN	—	$K_3[Cu(CN)_4]$ soluble complex	—	$K_3[Fe(CN)_6]$ yellow	—	$K_2[Ni(CN)_4]$ soluble complex
NaOH	$Pb(OH)_2$ white	$Cu(OH)_2$ white	$Al(OH)_3$ gelatinous white	$Fe(OH)_3$ reddish brown ppt	$Zn(OH)_2$ white	$Ni(OH)_2$ green
ex NaOH	$Na_2[Pb(OH)_4]$ soluble complex	—	$Na[Al(OH)_4]$ soluble complex	—	$Na_2[Zn(OH)_4]$	—
NH_4OH	$Pb(OH)_2$ white	$Cu(OH)_2$ white	$Al(OH)_3$ gelatinous white	$Fe(OH)_3$ reddish brown ppt	$Zn(OH)_2$	$Ni(OH)_2$ green
ex NH_4OH	—	$[Cu(NH_3)_4]^{2+}$ deep blue	—	—	$[Zn(NH_3)_4]^{2+}$	$Ni(NH_3)_6]^{2+}$ deep blue
H_2S/ $*(NH_4)_2S$	PbS black	CuS black	$Al(OH)_3$ gelatinous white	FeS + black yellow	ZnS white	NiS black
K_2CrO_4	$PbCrO_4$	—	—	—	—	—
$Na_2S_2O_3$	PbS_2O_3 white	$Cu_2S_2O_3$ white	—	Fe^{+2} green solution	—	—
$K_4[Fe(CN)_6]$	—	$Cu[Fe(CN)_6]$ brown	—	$Fe_4[Fe(CN_6)]_3$ prussian blue	$K_2Zn_3[Fe(CN)_6]$ white	$Ni_2[Fe(CN)_6]$ light green
$K_3[Fe(CN)_6$	—	$Cu_3[Fe(CN)_6]$ green	—	$Fe[Fe(CN_6)]$ brown	—	—

Other Important Reaction of Basic Radical

Basic Radical	Reagent	Product	Observation
Fe^{+3}	$SCN-$	$Fe(SCN)_3$	Blood Red Colouration
Ni^{+2}	dmg/NH^{4+}	$[Ni(dmg)_2]$	Rosy Red Complex


NH_4^+
KOH/NaOH
NH_3
Colourless
Gas
$K_2[HgI_4]+KOH$
$HgO, HgNH_2I^+$
brown
$CuSO_4$
$[Cu(NH_3)_4]SO_4$
deep blue
$NiCl_2$
$[Ni(NH_3)_6]^{2+}$
deep blue