

Chapter **21**Chemical Analysis

Analytical chemistry deals with qualitative and quantitative analysis of substances.

Qualitative analysis: A salt consists of two parts known as radicals. The positively charged part of a salt (cation) which has been derived from a base is termed as basic radical and the negatively charged part of salt (anion) which has been derived from an acid is termed as acidic radical. In qualitative inorganic analysis, the given compound is analysed for the basic and acid radicals (*i.e.*, the cations and the anions), that it contains. For example zinc blende is analysed for the Zn^{2+} and S^{2-} ions that it contains

Test for Different Gases

(1) Colourless gases

(i) **Tests for CO**: It is colourless and odourless gas. It gives white ppt. with lime water which dissolves on passing excess of CO_2 . $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$ The water A

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

White ppt. Excess So luble

- (ii) *Test for CO*: It is colourless and odourless gas. It burns with a blue flame. $2CO+O_2 \rightarrow 2CO_2$
- (iii) *Test for O*: It is colourless and odourless gas. It rekindles a glowing splinter.
- (iv) *Tests for HS*: It is a colourless gas with a smell of rotten eggs. It turns moist lead acetate paper black.

$$(CH_3COO)_2Pb + H_2S \rightarrow 2CH_3COOH + PbS_{Plant}$$

(v) **Tests for SO**: It is a colourless gas with a suffocating odour of burning sulphur. It turns acidified $K_2Cr_2O_7$ solution green. $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(vi) **Tests for NH**: It is a colourless gas with a characteristic ammonical smell. It gives white fumes of NH_4Cl with HCl, $NH_3 + HCl \rightarrow NH_4Cl$. With Nessler's reagents, it gives brown ppt.

$$2K_2[HgI_4] + NH_3 + KOH \rightarrow NH_2HgOHgI + 7KI + 2H_2O$$
Nessler's reagent

India of Milloris base

(Recomposite

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(vii) *Tests for HCl gas*: It is colourless gas with a pungent irritating smell. It turns moist blue litmus paper red i.e., it is acidic in nature. It gives white ppt with $AgNO_3$ solution. This white ppt is soluble in NH_4OH . $HCl + AgNO_3 \rightarrow AgCl + HNO_3$;

$$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2] + 2H_2O$$
.

 $NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-.$

(viii) $\textit{Test for } \text{CH}_3 \text{COOH} \ \textit{vapours}: \text{These vapours are colourless}$ with a vinegar like smell.

(2) Coloured gases

- (i) **Tests for Cl**: It is a greenish yellow gas with a pungent smell. In small quantity it appears almost colourless. It bleaches a moist litmus paper, $Cl_2 + H_2O \rightarrow 2HCl + \big[O\big]; \ Colour + \big[O\big] \rightarrow Colourless \ \ \text{Blue litmus}$ paper first turns red and then becomes colourless.
- (ii) Tests for Br: Brown vapours with a pungent smell. It turns moist starch paper yellow.
- (iii) *Tests for I*: Violet vapours with a pungent smell. It turns moist starch paper blue.
- (iv) *Tests for NO*: Brown coloured pungent smelling gas. It turns moist starch *KI* paper blue

$$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$$
; $I_2 + Starch \rightarrow Blue colour$.

It turns ferrous sulphate solution black,

$$3FeSO_4 + NO_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + FeSO_4.NO + H_2O_4$$

Systematic Procedure for Qualitative Analysis of Inorganic Salts

It involves the following steps : (1) Preliminary tests (2) Wet tests for acid radicals and (3) Wet tests for basic radicals.

(1) Preliminary tests

 $\mbox{(i) $\textit{Physical examination}:$ It involves the study of colour, smell, density etc.}$

Table : 21.1 Colour

Colour	Salt		
Black	Oxides : MnO_2 , FeO , CuO , Co_3O_4 , Ni_2O_3		
	Sulphides : Ag_2S , CuS , Cu_2S , FeS , CoS , NiS ,		
	PbS, HgS , Bi_2S_3 (blackish brown)		
Blue	Hydrated $\ CuSO_4$, anhydrous $\ CoSO_4$		
Orange	KO_2 , some dichromate $(K_2Cr_2O_7), Sb_2S_3$,		
	ferricyanides		
Green	Nickel salts, hydrated ferrous salts, potassium		
	permanganate $(KMnO_4)$, some copper (II) salts		
Brownish yellow	SnS		
Dark brown	$PbO_2, Ag_2O, CdO, Fe_2O_3, CuCrO_4, FeCl_3$		
	(but yellow in aq. solution)		
Pale brown	$MnCO_3$		
Light pink	Hydrated manganese salts		
Reddish pink	Hydrated cobalt (II) salts		
Red	HgI_2, Pb_3O_4		
Yellow	CdS , PbI_2 , $AgBr$, AgI , chromates		

(ii) Dry heating: Substance is heated in a dry test tube.

Table : 21.2

Observation	Result	
(a) A gas or vapour is evolved.	Compounds with water of crystallisation	
Vapour, evolved, test with litmus	Ammonium salts, acid salts, and	
paper.	hydroxides. (usually accompanied	
	by change of colour)	
The vapour is alkaline.	Ammonium salts.	
The vapour is acidic.	Readily decomposable salts of strong acids.	
Oxygen is evolved	Nitrates,chlorates and certain oxides.	
Dinitrogen oxide	Ammonium nitrate or nitrate mixed with an ammonium salt.	
Dark-brown or reddish fumes (oxides of nitrogen), acidic in reaction.	Nitrates and nitrites of heavy metals.	
CO_2 is evolved, lime water becomes turbid.	Carbonates or hydrogen carbonates.	
NH_3 is evolved which turns red	Ammonium salts.	
litmus blue.		
SO_2 is evolved, which turns	Sulphates and thiosulphates.	
-	·	
acidified $K_2Cr_2O_7$ green,		
decolourises fuschin colour.	11.1 . 11:1 . 11:1 .	
H_2S is evolved, turns lead acetate paper black, or cadmium acetate yellow.	Hydrates, sulphides or sulphides in the presence of water.	
Cl_2 is evolved, yellowish green gas, bleaches litmus paper, turns \emph{KI} – starch blue, poisonous.	Unstable chlorides e.g., copper chlorides in the presence of oxidising agents.	
Br_2 is evolved (reddish brown,	Bromides in the presence of	
turns fluorescent paper red).	oxidising agents.	
I_2 is evolved, violet vapours	Free iodine and certain iodides	
condensing to black crystals		
(b) A sublimate is formed	Ammonium and mercury salts.	
White sublimate	As_2O_3,Sb_2O_3	
Grey sublimate	Hg	
Steel grey, garlic odour	As	
Yellow sublimate	S , $As_2S_3HgI_2(\operatorname{Re}d)$	

Action of heat on different compounds: Many inorganic salts decomposes on heating, liberating characteristic gases. A few such reactions are tabulated as follows,

Table : 21.3

$2HgO \xrightarrow{\Delta} 2Hg + O_2$ (Silverydeposit)	$2Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$ (Red) (Yellow)	$ \begin{array}{c} 2PbO_2 \xrightarrow{\Delta} 2PbO + O_2 \\ (Brown) \end{array} $
$CuCO_3 \xrightarrow{\Delta} CuO + CO_2$ (Green)	$ZnO_3 \xrightarrow{\Delta} ZnO + CO_2$ $(White) \xrightarrow{White (cold)} + CO_2$	$CuSO_4.5H_2O \xrightarrow{\Delta} CuSO_4 + 5H_2O$ (White)
$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$	$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$	$2Ag_2O \rightarrow 4Ag + O_2$
$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$ (White) (Brown)	$2AgNO_3 \xrightarrow{450^{\circ}C} 2Ag + 2NO_2 + O_2$	$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$

$2Ag_2CO_3 \rightarrow 4Ag + 2CO_2 + O_2$	$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$		$(NH_4)_2 Cr_2 O_7 \rightarrow N_2 + Cr_2 O_3 + 4H_2 O$ (Green)	
$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$		$CaCO_3 \rightarrow CaO + CO_2$	
$2NaNO_3 \rightarrow 2NaNO_2 + O_2$	$MgCO_3 \rightarrow MgO + CO_2$		$2NH_3 \xrightarrow{\text{Red hot}} N_2 + 3H_2$	
$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$	$2Ca(NO_3)_2 \rightarrow 2CaO + 4$	$NO_2 + O_2$	$Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} Al_2O_3 + 3SO_3$	
$2CaSO_4.2H_2O \rightarrow 2CaSO_4.H_2O + 2H_2O$ (Plaster of Paris)	$2AlCl_3.6H_2O \rightarrow Al_2O_3 + 6$	$HCl + 9H_2O$	$2BeSO_4 \xrightarrow{ \Delta } 2BeO + 2SO_2 + O_2$	
$2AgNO_3 \xrightarrow{350^{o}C} 2AgNO_2 + O_2$	$2MgSO_4 \xrightarrow{\Delta} 2MgO + 1$	$2SO_2 + O_2$	$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$	
$(COO)_2 Sn \xrightarrow{\Delta} SnO + CO_2 + CO$	$CaC_2O_4 \rightarrow CaCO_3 + Co$	9	$NH_4NO_2 \rightarrow N_2 + 2H_2O$	
$NH_4NO_3 \rightarrow N_2O + 2H_2O$	$2KClO_3 \rightarrow 2KCl + 3O_2$		$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$	
$Li_2CO_3 \rightarrow Li_2O + CO_2$	$(COO)_2 Fe \rightarrow FeO + CO$	+ CO ₂	$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$	
$MgCl_2.6H_2O \rightarrow HgCl_2 + Hg$	$NH_4Cl \rightarrow NH_3 + HCl$		$2LiNO_3 \rightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$	
$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$	$2CuCl_2 \xrightarrow{\Delta} Cu_2Cl_2 +$	- Cl ₂	$2Co(NO_3)_2 \xrightarrow{\Delta} 2CoO + 4NO_2 + O_2$	
$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$	$4K_2Cr_2O_7 \to 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$		$2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + H_2O + 2NH_3$	
$2Zn(NH_4)PO_4 \xrightarrow{\Delta} Zn_2P_2O_7 + H_2O + 2NH_3$		$K_4 Fe(CN)_6 \xrightarrow{\Delta} 4KCN + Fe + 2C + N_2$		
$ZnCl_2.2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$		$2(ZnCl_2.H_2O) \xrightarrow{\Delta} Zn_2OCl_2 + 2HCl + H_2O$		
$2[FeCl_3.6H_2O] \xrightarrow{\Delta} Fe_2O_3 + 9H_2O + 6HCl$		$2ZnSO_4 - 800^{\circ}C$	$\rightarrow 2ZnO + 2SO_2 + O_2$	
$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ (Glassy bead)				

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$
 (Glassy bead)

$$H_3BO_3 \xrightarrow{\quad 100^{o}C\quad} HBO_2 \xrightarrow{\quad 160^{o}C\quad} H_2B_4O_7 \xrightarrow{\quad \text{Red hot}\quad} B_2O_3$$

$$ZnSO_{4}.7H_{2}O \xrightarrow{-70^{\circ}C} ZnSO_{4}.6H_{2}O \xrightarrow{-100^{\circ}C} ZnSO_{4}.H_{2}O \xrightarrow{450^{\circ}C} ZnSO_{4}$$

(iii) Flame test

Characteristic flame colour: Certain metals and their salts impart specific colours to Bunsen burner flame.

- (a) Pb imparts pale greenish colour to the flame.
- (b) Cu and Cu salts impart blue or green colour to the flame.
- (c) Borates also impart green colour to the flame.
- (d) Ba and its salts impart apple green colour to the flame.
- (e) Sr imparts crimson red colour to the flame.
- (f) Ca imparts brick red colour to the flame.
- (g) Na imparts yellow colour to the flame.
- (h) K imparts pink-violet (Lilac) colour to the flame.
- (i) Li imparts crimson-red, Rb imparts violet and Cs imparts violet colours to the flame.
 - (j) Livid- blue flame is given by As, Sb and Bi.
- (iv) Borax bead test : The transparent glassy bead $(NaBO_2 + B_2O_3)$ when heated with inorganic salt and the colour produced gives some idea of cation present in it.

Table : 21.4

Colour of bead in	Colour of bead in reducing	Basic radical present
oxidising flame	flame	basic radical present
Greenish when hot, blue in cold.	Red and opaque	Си
Dark green in hot and cold	Same	Cr
Deep – blue	Deep blue	Со
Yellow when hot	Green	Fe
Violet in hot and cold	Colourless	Mn
Brown in cold	Grey or black or opaque	Ni

Microcosmic salt bead Microcosmic test $Na(NH_4)HPO_4.4H_2O$ is also used to identify certain cations just like borax. When microcosmic salt is heated in a loop of platinum wire, a colourless transparent bead of sodium metaphosphate is formed.

$$Na(NH_4)HPO_4.4H_2O \rightarrow Na(NH_4)HPO_4 + 4H_2O$$

$$Na(NH_4)HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

Now NaPO3 reacts with metallic oxides to give coloured orthophosphates.

$$NaPO_3 + CuO \rightarrow NaCuPO_4$$
 (Blue);

$$NaPO_3 + CoO \rightarrow NaCoPO_4$$
 (Blue);

(v) Charcoal cavity test

Table : 21.5

(a) Compound fused in cavity directly			
Nature and colour of bead	Cation		
Yellow, brittle bead	Bi^{3+}		
Yellow, soft bead which marks on paper	Pb^{2+}		
White, brittle	Sb 3+		
White yellow when hot	ZnO		
White garlic odour	As_2O_3		
Brown	CdO		
Grey metallic particles attracted by magnet	Fe, Ni, CO		
Maleable beads	Ag and Sn (White), Cu (Red flakes)		

(b) Compound mixed with Na_2CO_3 Crystalline

Sustance Decrepitates	Salts,NaCl, KCl;
Substance deflagrates	Oxidisingagents like NO ₃ , NO ₂ chlorates

Substance infusible, perform test (a)

(vi) Cobalt Nitrate test

Table : 21.6

Colour	Composition	Result
Blue residue	$CoO.Al_2O_3$	Al
Green residue	CoO.ZnO	ZnO
Pink dirty residue	CoO.MgO	MgO
Blue residue	NaCoPO ₄	PO_4^{3-} in absence of Al.

(2) Wet tests for acid radicals : Salt or mixture is treated with dil. $H_2SO_4\,$ and also with conc. $H_2SO_4\,$ separately and by observing the types of gases evolved. Confirmatory tests of anions are performed.

Table : 21.7 Observations with Dilute $\,H_2SO_4\,$

Observations	Acid Radical	Confirmatory test		
Brisk effervescence with evolution of colourless and odourless gas.	CO_3^{2-} (carbonate)	Gas turns lime water milky but milkyness disappears on passing gas inexcess, $Na_2CO_3 + H_2SO_4 - \longrightarrow Na_2SO_4 + H_2O + CO_2$		
		$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$ lime water milky		
		$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$ soluble		
Brown fumes	NO_2^- (Nitrite)	Add ${\it KI}$ and starch solution blue colour ${\it 2NaNO}_3 + {\it H}_2 {\it SO}_4 - \longrightarrow {\it Na}_2 {\it SO}_4 + 2 {\it HNO}_2;$		
		$HNO_2 \longrightarrow NO \text{ (colourless)}; $ $2NO + O_2(\text{air}) \longrightarrow 2NO_2 \text{ (brown)}$		
		$2KI + H_2SO_4 + 2NHO_2 \longrightarrow K_2SO_4 + 2H_2O + 2NO + I_2$		
		I_2 + starch \longrightarrow blue colour		
Smell of rotten eggs $(H_2S \text{ smell})$ on	S^{2-} (sulphide)	Gas turn lead acetate paper black		
heating		Sodium carbonate extract $\left(SE\right)^*$ + sodium nitroprusside – purple colour,		
		$Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4$		
		$H_2S + (CH_3COO)_2Pb \longrightarrow PbS + 2CH_3COOH$		
		$Na_2S + Na_2[Fe(CN)_5 NO] \longrightarrow Na_4[Fe(CN)_5 NOS]$		
		sodiumnitroprusside (purple)		
Colourless gas with pungent smell of burning sulphur	SO_3^{2-} (sulphite)	Gas turns acidified $K_2Cr_2O_7$ solution green [different from CO_3^{2-}] since gas also turns lime		
		water milky $Na_2SO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_2$		
		$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^2 + H_2O$ (green)		

		$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3$ (milky)
Solution gives smell of vinegar	CH_3COO^- (acetate)	Aq. Solution + neutral $FeCl_3 \rightarrow blood$ red colour $3CH_3COONa + FeCl_3 \longrightarrow Fe(CH_3COO)_3 + 3NaCl$
		neutral (red)
White or yellowish white turbidity on warming	$S_2 O_3^{2-}$ (thiosulphate)	Aq. Solution + $AgNO_3 ightarrow$ white ppt. changing to black (viii) on warming ,
		$Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$ white ppt.
		$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ black ppt.

Table : 21.8 Observation with concentrated H_2SO_4

Observation	Acid Radical	Confiramatory Test
Colourless pungent gas giving	Cl^- (chloride)	Add MnO_2 in the same test tube and heat–pale green Cl_2 gas (i)
white fumes with aq. NH_4OH		$S.E.+\ HNO_3+AgNO_3$ solution –white ppt. soluble in aq. NH_3 (ii)
		Chromyl chloride test (iii)
Reddish brown fumes	Br^- (bromide)	Add Mn_2O and heat –yellowish brown Br_2 gas (iv)
		$\it S.E.+ HNO_3 + AgNO_3$ solution –pale yellow ppt. partially soluble aq. $\it NH_3$ (v)
		Layer test (vi)
Violet pungent vapours turning starch paper blue.	I ⁻ (iodide)	$\textit{S.E.+ HNO}_3 + \textit{AgNO}_3 \rightarrow \textit{yellow ppt. insoluble in aq. } \textit{NH}_3 \; (\textit{vii})$
staren paper blue.		Layer test (vi)
Brown pungent fumes intensified by the addition of <i>Cu</i> - turnigs.	NO_3^- (nitrate)	Ring test (viii)
Colourless gases turning lime water milky and burning with	$C_2O_4^{2-}$ (oxalate)	Acidified KMnO_4 solution is decolorised (ix)
blue flame.		$S.E. + CH_3COOH + CaCl_2$ white ppt. decolorising acidified $KMnO_4$ solution (x)

Reactions

$$\begin{split} \textbf{Chloride} &: (i) \ \textit{KCl} + \text{conc.} \\ \textit{HCl} + \textit{NH}_3 & \longrightarrow \textit{NH}_4 \textit{Cl} \\ & \text{(white fumes)} \\ 4 \textit{HCl} + \textit{MnO}_2 & \xrightarrow{\Delta} \textit{MnCl}_2 + \textit{Cl}_2 + 2\textit{H}_2 \textit{O} \\ \\ (ii) \ \textit{KCl} + \textit{AgNO}_3 & \longrightarrow \textit{AgCl} \downarrow + \textit{KNO}_3 \\ & \text{white ppt.} \end{split}$$

$$AgCl + aq. 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$$

(iii) Chromyl- chloride test :

$$KCl + \operatorname{conc.} H_2SO_4 \stackrel{\Delta}{\longrightarrow} KHSO_4 + HCl \; ;$$

$$K_2Cr_2O_7 + 2H_2SO_4 \stackrel{\Delta}{\longrightarrow} 2KHSO_4 + 2CrO_3 + H_2O$$

$$CrO_3 + 2HCl \stackrel{\longrightarrow}{\longrightarrow} CrO_2Cl_2 + 2H_2O$$

$$CrO_2Cl_2 + 4NaOH \stackrel{\longrightarrow}{\longrightarrow} Na_2CrO_4 + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \stackrel{\longrightarrow}{\longrightarrow} PbCrO_4 \stackrel{\downarrow}{\downarrow} + 2CH_3COONa \text{ yellowppt.}$$

$$\mathbf{Bromide} \; : \; \text{ (iv)} \quad KBr + \operatorname{conc.} H_2SO_4 \stackrel{\Delta}{\longrightarrow} KHSO_4 + H \; ;$$

$$4HBr + MnO_2 \stackrel{\Delta}{\longrightarrow} Br_2 + 2H_2O + MnBr_2$$

$$\text{ (v)} \quad NaBr + AgNO_3 \stackrel{\longrightarrow}{\longrightarrow} AgBr \stackrel{\downarrow}{\downarrow} + NaNO_3 \text{ pale yellowppt.}$$

$$AgBr + \operatorname{aq.} 2NH_3 \stackrel{\longrightarrow}{\longrightarrow} [Ag(NH_3)_2]Br \text{ partially soluble}$$

(vi) Layer Test: $S.E. + Cl_2$ water $+ CHCl_3 \xrightarrow{\text{shake}}$ yellowish orange colour in $CHCl_3$ layer (CS_2 or CCl_4 can be taken instead of $CHCl_3$);

In case of I^- , violet colour of I_2 in $CHCl_3$ layer, $2NaI+Cl_2 \longrightarrow 2NaCl+I_2 \text{ (violet)}$

lodide : (vii)
$$KI + \text{conc.} H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HI$$
;
 $2HI + H_2SO_4 \xrightarrow{} I_2 + 2H_2O + SO_2$

$$\begin{aligned} \text{Nitrate}: & NaNO_3 + H_2SO_4 & \longrightarrow NaHSO_4 + HNO_3 \\ & 4HNO_3 & \longrightarrow 4NO_2 + O_22H_2O \ ; \\ & \text{brown fumes} \end{aligned}$$

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O_3$$

(viii) *Ring test*: To water extract (all NO_3^- are water soluble) add freshly prepared $FeSO_4$ solution and then conc. H_2SO_4 carefully by the side of the test- tube. A dark brown ring of $[Fe(H_2O)_5\,NO]^{2+}\,SO_4^{2-}$ at the interface between the two liquids is formed.

$$2NaNO_3 + H_2SO_4 \longrightarrow 2NaHSO_4 + 2HNO_3;$$

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow$$

$$3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5 NO]^{2+} SO_4^{2-} + H_2O$$

Oxalate : $Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO + CO_2$

 $\it CO$ burns with blue flame and $\it CO_2$ turns lime water milky.

(ix)
$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10 CO_2 + 2Mn^{2+} + 8H_2O$$
 (violet) colourless

(3) Wet tests for basic radicals: Analysis of Basic Radicals

(x)
$$CaCl_2 + NaC_2O_4 \longrightarrow CaC_2O_4 \downarrow + 2NaCl \quad CaC_2O_2$$
white ppt.

decolourises acidified $KMnO_4$.

Specific test in solution

- (i) **Sulphate**: S.E. add dil. (to decompose CO_3^{2-} until reaction ceases). Add $BaCl_2$ solution. White ppt. insoluble in conc. HNO_3 , $BaCl_2 + NaSO_4 \longrightarrow BaSO_4 \downarrow + 2NaCl$ white ppt.
- (ii) $\it Borate:$ Ignite the mixture containing borate, conc. H_2SO_4 . And ethanol in a china-dish with a burning splinter –green edged flame of ethyl borate.

$$\begin{split} 2Na_3BO_3 + 3H_2SO_4 &\rightarrow 2H_3BO_3 + 3Na_2SO_4\,; \\ (\text{conc.}) \\ H_3BO_3 + 3C_2H_5OH &\xrightarrow{\Delta} & (C_2H_5O)_3B + 3H_2O \\ &\xrightarrow{\text{ethanol}} & \text{burns with green flame} \end{split}$$

In presence of Cu^{2+} , perform this test in a test tube since Cu^{2+} salts are not volatile.

(iii) $S.E. + HNO_3 + \text{ammonium molybdate solution}$. Heat, yellow crystalline ppt. confirms

$$Na_3PO_4 + 12(NH_4)_2MoO_4 + 24HNO_3 \xrightarrow{\Delta}$$

 $(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 3NaNO_3 + 12H_2O_3$
yellowppt.

Arsenic also gives this test. Hence presence of phosphate should also be checked after group II.

(iv) **Fluoride**: Sand +salt (F^-) +conc. H_2SO_4 ; heat and bring a water wetted rod in contact with vapours at the mouth of the test tube. A white deposit on the rod shows the presence to F^-

$$NaF + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HF$$

 $SiO_2 + 4HF \xrightarrow{\Delta} SiF_4 + 2H_2O$
 $3SiF_4 4H_2O \xrightarrow{\Delta} 2H_2SiF_6 + H_4SiO_4$
white

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Table : 21.9

Group	Basic radicals	Group reagent	Ppt. as	Explanation
1	$Ag^{+}, Hg_{2}^{2+}(I), Pb^{2+}$	dil <i>HCl</i>	Chloride	$K_{\it SP}$ values of chlorides are low, hence
			$(AgCl, Hg_2Cl_2, PbCl_2)$	precipitated. Others have higher $K_{\it SP}$
				values hence not precipitated.
11	$Cu^{2+}, Cd^{2+}, Pb^{2+},$	H_2S gas in presence	Sulphides (CuS, As_2S_3)	K_{SP} values of sulphides are low hence
	Hg^{2+} (11), Bi^{3+} , As^{3+} ,	of dil. <i>HCl</i>	etc.)	precipitated by low $[S^{2-}]$ ion. HCl (with
	Sb^{3+}, Sn^{2+}			common H^+ ion) decreases ionization of
				H_2S which gives low $[S^{2-}]$. Hence II
				group is precipitated. Others with higher
				K_{SP} values not precipitated.
111	$Al^{3+}, Cr^{3+}, Fe^{3+}$	NH_4OH in presence	Hydroxide, $Al(OH)_3$ etc.	K_{SP} values of $Al(OH)_3$ etc. are low.
		of NH ₄ Cl		NH_4Cl (with common NH_4^+ ion)
				decreases ionization of $N\!H_4O\!H$ giving

				low $[OH^-]$. Hence group III is precipitated.
IV .	Zn^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+}	H_2S in ammonical	Sulphides (ZnS etc.)	K_{SP} values of sulphides of group IV are
		medium		high hence precipitation takes place in
				higher $[S^{2-}]$. Basic medium increases
				ionization of H_2S increasing $[S^{2-}]$ hence
				precipitation of group IV.
V	$Ca^{2+}, Ba^{2+}, Sr^{2+}$	$(NH_4)_2 CO_3 + NH_4 Cl$	Carbonates (CaCO ₃	K_{SP} values of carbonate are less than that
			etc.)	of group VI (Mg^{2+}) hence precipitation
				before Mg^{2+} .
VI	$Mg^{2+},(Na^+,K^+)$ also	$NH_4OH + Na_2HPO_4$	White ppt. (MgHPO ₄)	-
	included)	(only for Mg^{2+})		
0 (Zero)	NH ₄ +	=	=	Tested independently from original solution.

Chemical reactions involved in the tests of basic radicals

Group 1 : When dil. *HCl* is added to original solution, insoluble chlorides of lead, silver mercurous mercury are precipitated.

$$Pb(NH_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$
;

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

$$Hg(NO_3)_2 + 2HCl \longrightarrow HgCl_2 + 2HNO_3$$

Pb (lead)

- (i) $PbCl_2$ is soluble in hot water and on cooling white crystals are again formed.
- (ii) The solution of $PbCl_2$ gives a yellow precipitate with potassium chromate solution which is insoluble in acetic acid but soluble in sodium hydroxide.

$$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KCl$$
; yellowppt.

$$PbCrO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

(iii) The solution of $PbCl_2$ forms a yellow precipitate with potassium iodide solution.

$$PbCl_2 + 2KI \longrightarrow PbI_2 + 2KCl$$
Yellow ppt.

(iv) White precipitate of lead sulphate is formed with dilute H_2SO_4 . The precipitate is soluble in ammonium acetate, $PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HCl$;

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow Pb(CH_3COO)_2 + (NH_4)_2SO_4$$

Ag(silver)

(i) AgCl dissolves in ammonium hydroxide, $AgCl + 2NH_4OH \xrightarrow{\hspace*{1cm}} Ag(NH_3)_2Cl + 2H_2O$ Diaminine silver(I) chloride

(ii) On adding dilute HNO_3 to the above solution, white precipitate is again obtained

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4NO_3$$

Whiteppt.

(iii) On adding KI to the complex solution, yellow precipitate is obtained.

$$Ag(NH_3)_2Cl + KI \longrightarrow AgI + KCl + 2NH_3$$

Hg_2^{2+} (mercurous)

(i)
$$Hg_2Cl_2$$
 turns black with NH_4OH , $Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black}} + NH_4Cl + 2H_2O$

(ii) The black residue dissolves in aqua-regia forming mercuric chloride.

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$

 $2Hg(NH_2)Cl + 6Cl \longrightarrow 2HgCl_2 + 4HCl + N_2$
 $Hg + 2Cl \longrightarrow HgCl_2$

(iii) The solution of $HgCl_2$ forms white or slate-coloured precipitate with stannous chloride.

$$\begin{aligned} 2HgCl_2 + SnCl_2 & \longrightarrow Hg_2Cl_2 + SnCl_4 \\ & \text{white ppt.} \end{aligned}$$

$$Hg_2Cl_2 + SnCl_2 & \longrightarrow 2Hg + SnCl_4 \\ & \text{Grey ppt.} \end{aligned}$$

(iv) The solution of $HgCl_2$ with copper turning forms a grey deposit.

$$HgCl_2 + Cu \longrightarrow Hg + CuCl_2$$
Grey ppt.

Group II: When hydrogen sulphide is passed in acidified solution, the radicals of second group are precipitated as sulphides. The precipitate is treated with yellow ammonium sulphide. The sulphides of IIB are first oxidised to higher sulphides which then dissolve to form thio-compounds.

$$Ag_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + As_2S_5$$

$$Sb_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + Sb_2S_5$$

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2S + SnS_2$$

$$As_2S_5 + 3(NH_4)S \longrightarrow 2(NH_4)_3AsS_4$$
Ammonium

$$Sb_2S_5 + 3(NH_4)_2S {\longrightarrow} 2(NH_4)_2SbS_4 \\ {\stackrel{Ammonium}{Ammonium}} \\ {\stackrel{Ammonium}{thioantimonate}}$$

$$SnS_2 + (NH_4)_2 S \longrightarrow (NH_4)_2 SnS_3$$
Ammonium thiostannate

All the three are soluble.

In case, the precipitate does not dissolve in yellow ammonium sulphide, it may be either HgS or PbS or Bi_2S_3 or CuS or CdS. The precipitate is heated with dilute HNO_3 . Except HgS, all other sulphides of IIA are soluble.

$$3PbS + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 3S + 4H_2O$$

 $Bi_2S_3 + 8HNO_3 \rightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$
 $3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$
 $3CdS + 8HNO_3 \rightarrow 3Cd(NO_3)_2 + 2NO + 3S + 4H_2O$

Hg (mercuric)

HgS is dissolved in aqua-regia,

$$3HgS + 2HNO_3 + 6HCl \rightarrow 3HgCl_2 + 3S + 2NO + 4H_2O$$

The solution is divided into two parts:

Part 1: Stannous chloride solution reduces $HgCl_2$ first into white Hg_2Cl_2 and then to grey metallic mercury.

Part II: Copper displaces Hg from $HgCl_2$ which gets coated on copper turnings as a shining deposit.

Pb (lead)

In case the sulphide dissolves in dilute HNO_3 , a small part of the solution is taken. Dilute H_2SO_4 is added. If lead is present, a white precipitate of lead sulphate appears, $Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2HNO_3$ (White ppt.)

In absence of lead, the remaining solution is made alkaline by the addition of excess of NH_4OH . Bismuth forms a white precipitat of $Bi(OH)_3$, copper forms a deep blue coloured solution while cadmium forms a colourless soluble complex,

$$Bi(NO_3)_3 + 3NH_4OH \longrightarrow Bi(OH)_3 + 3NH_4NO_3$$

Whiteppt.

$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow [Cu(NH_3)_4](NO_3)_2 + 4H_2O;$$

Tetrammin e cupric nitrate
(deep blue solution)

$$Cd(NO_3)_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4](NO_3)_2 + 4H_2O$$
Tetrammin e cadmium nitrate
(colourless solution)

Bi (bismuth) : The precipitate dissolves in dilute *HCl*, $Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$

 $\mbox{\it Part 1}$: Addition of excess of water to $\mbox{\it BiCl}_3$ solution gives a white precipitate due to hydrolysis.

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

Bismuth Oxychloride (Whiteppt.)

Part II: The solution of $BiCl_3$ is treated with sodium stannite when a black precipitate of metallic bismuth is formed, $2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow$

$$3Na_2SnO_3 + 2Bi + 6NaCl + 3H_2O$$

Ctr (copper): Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added a chocolate coloured precipitate is formed

$$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow$$

$$Cu(NO_3)_2 + 4CH_4COONH_4$$

$$2Cu(NO_3)_2 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6 + 4KNO_3]$$

Chocolate ppt.

 $\it Cd$ (cadmium): $\it H_2S$ is passed through colourless solution. The appearance of yellow precipitate confirms the presence of cadmium,

$$Cd\left(NH_{3}\right)_{4}\left(NO_{3}\right)_{2} + H_{2}S \xrightarrow{\hspace*{1cm}} CdS + 2NH_{4}NO_{3} + NH_{3}$$
 Yellow ppt.

Group IIB: In case the precipitate dissolves in yellow ammonium sulphide, the tests of the radicals arsenic, antimony and tin are performed. The sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphide dissolve while arsenic sulphide remains insoluble.

As (arsenic): The insoluble sulphide is treated with concentrated nitric acid which is then heated with ammonium molybdate. Yellow precipitate of ammonium arsenomolybdate is formed.

$$As_2S_5 + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O + 5S$$
Arsenic acid

$$\begin{array}{c} H_3 AsO_4 + 12(NH_4)_2 MoO_4 + 21 HNO_3 \longrightarrow \\ (NH_4)_3 AsO_4 \cdot 12 MoO_3 + 21 NH_4 NO_3 + 12 H_2 O \\ \text{Yellowppt.} \end{array}$$

Srr or **Srr** (tin): Solution of sulphide in concentrated *HCl* is reduced with iron fillings or granulated zinc.

$$SnS_2 + 4HCl \longrightarrow SnCl_4 2H_2S$$
White ppt.

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_4$$
Grey

 $HgCl_2$ solution is added to above solution which gives first a white precipitate that turns to grey.

$$2HgCl_2 + SnCl_2 \longrightarrow HgCl_2 + SnCl_4$$

White ppt.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$
Grey

 \emph{Sb} (antimony) : Filtrate of sulphide in concentrated \emph{HCl} is divided into two parts.

Part 1: On dilution with excess of water, a white precipitate of antimony oxychloride is obtained.

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
White ppt.

Group III: Hydroxides are precipitated on addition of excess of ammonium hydroxide in presence of ammonium chloride.

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$$
Gelatinous ppt.

$$CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3 + 3NH_4Cl$$
Green put

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$$
Brownish red ppt.

Fe (iron): The brownish red precipitate dissolves in dilute HCl. The solution is divided into two parts.

Part 1 $: K_4 [Fe(CN)_6]$ solution is added which forms deep blue solution or precipitate.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$4 \operatorname{\mathit{FeCl}}_3 + 3 K_4 [\operatorname{\mathit{Fe}}(CN)_6] {\longrightarrow} \operatorname{\mathit{Fe}}_4 [\operatorname{\mathit{Fe}}(CN)_6]_3 + 12 \operatorname{\mathit{KCl}}$$
 Prusian blue

 $\ensuremath{\textit{Part II}}$: Addition of potassium thiocyanate solution gives a blood red colouration.

$$FeCl_3 + 3KCNS \longrightarrow Fe(CNS)_3 + 3KCl$$
Blood red colour

Cr(chromium): The green precipitate is fused with fusion mixture $(Na_2CO_3 + KNO_3)$. The fused product is extracted with water or the precipitate is heated with NaOH and bromine water.

$$2Cr(OH)_3 + 3KNO + 2Na_2CO_3 \longrightarrow$$

$$2Na_{2}CrO_{4} + 3KNO_{2} + 2CO_{2} + 3H_{2}O$$

or
$$2NaOH + Br_2 \longrightarrow NaBrO_4 + NaBr + H_2O$$

$$NaBrO \longrightarrow NaBr + [O]$$

$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2NaCrO_4 + 5H_2O$$

The solution thus obtained contains sodium chromate. The solution is acidified with acetic acid and treated with lead acetate solution. A yellow precipitate appears.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 + 2CH_3COONa$$

Yellowppt.

AP (aluminium) : The gelatinous precipitate dissolves in NaOH , $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$ Soluble

The solution is boiled with ammonium chloride when $\ Al(OH)_3$ is again formed.

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 + NaCl + NH_3$$

Group IV : On passing H_2S through the filtrate of the third group, sulphides of fourth group are precipitated. *NiS* and *CoS* are black and insoluble in concentrated *HCI* while *MnS* (buff coloured), *ZnS* (colourless) are soluble in conc. *HCI*.

$$\mbox{\it Zn}$$
 (zinc) : The sulphide dissolves in $\it HCl.$ $\it ZnS+2HCl-\longrightarrow \it ZnCl_2+H_2S$

When the solution is treated with NaOH, first a white precipitate appears which dissolves in excess of NaOH

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$
White ppt.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$
(Soluble)

On passing H_2S , white precipitate of zinc sulphide is formed

$$Na_2ZnO_2 + H_2S \longrightarrow ZnS + 2NaOH$$

Mnr (manganese): Manganese sulphide dissolves in
$$HCI$$
 $MnS + 2HCI \longrightarrow MnCl_2 + H_2S$

On heating the solution with NaOH and Br_2 -water, manganese dissolve gets precipitated.

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl$$

$$Mn(OH)_2 + O \longrightarrow MnO_2H_2O$$

The precipitate is treated with excess of nitric acid and PbO_2 or Pb_3O_4 (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.

$$\begin{split} 2MnO_2 + 4HNO_3 & \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2 \\ 2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 & \longrightarrow \\ & 2HMnO_4 + 15Pb \ (NO_3)_2 + 12H_2O \\ & \text{Permanganic acid(pink)} \end{split}$$

The above test fails in presence of HCl.

$N\dot{r}$ (nickel) and $C\sigma$ (cobalt)

The black precipitate is dissolved in aqua- regia.

$$3NiS + 6HCl + 2HNO_3 \longrightarrow 2NiCl_2 + 2NO + 3S + 2H_2O$$

$$3CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$

The solution is evaporated to dryness and residue $\,$ extracted with dilute $\,$ $\,$ HCI. It is divided into three parts.

 $Part\ I: Add\ NH_4OH\ (excess)$ and dimethyl glyoxime. A rosy red precipitate appears, if nickel is present,

$$CH_{3} - C = NOH$$

$$NiCl_{2} + 2 \qquad | \qquad +2NH_{4}OH \longrightarrow$$

$$CH_{3} - C = NOH$$

$$OH \qquad O$$

$$| \qquad \uparrow$$

$$CH_{3} - C = N$$

$$| \qquad N = C - CH_{3}$$

$$| \qquad +2NH_{4}Cl + 2H_{2}O$$

$$CH_{3} - C = N$$

$$| \qquad N = C - CH_{3}$$

$$| \qquad OH$$

Part II: Add CH_3COOH in excess and KNO_2 . The appearance of yellow precipite confirms the presence of cobalt.

$$KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2$$

 $CoCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + 2KCl$
 $Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2)_3 + NO + H_2O$
 $Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$

 $Part\ III:$ Solution containing either nickel or cobalt is treated with $NaHCO_3$ and bromine water. Appearance of apple green colour is observed, the solution is heated when black precipited is formed, which shows the presence of nickel,

$$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3H_2O + 3CO_2$$

$$Br_2 + H_2O \longrightarrow 2HBr + O$$

$$2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow 2Na_3Co(CO_3)_3 + 2NaOH$$

sod. cobalticarbonate
(Green colouration)

$$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2$$

$$2NiCO_3 + [O] \longrightarrow Ni_2O_3 + 2CO_2$$
(Black)

 $\label{eq:Group V} \textbf{Group V}: Ammonium \ carbonate \ precipitates \ V \ group \ radicals \ in \ the form \ of \ carbonates \ are \ soluble \ in \ acetic \ acid.$

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$$

$$SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Sr + CO_2 + H_2O$$

$$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2OO)_2Ca + CO_2 + H_2OOO$$

 $\emph{\textit{Bar}}$ (barium): Barium chromate is insoluble and precipitated by the addition of potassium chromate solution,

$$Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2CH_3COOK$$

Sr (Strontium): Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution,

$$Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow SrSO_4 + 2CH_3COONH_4$$
White ppt.

Car (calcium): Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.

$$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 + 2CH_3COONH_4$$
White ppt.

Group VI: In the filtrate of V group, some quantity of ammonium oxalate is added as to remove Ba, Ca and Sr completely from the solution. The clear solution is concentrated and made alkaline with NH_4OH . Disodium hydrogen phosphate is now added, a white precipitate is formed.

$$MgCl_2 + Na_2HPO_4 + NH_4OH \longrightarrow$$

$$\begin{array}{c} Mg(NH_4)PO_4 + 2NaCl + H_2O \\ \text{Megnesium ammonium phosphate} \\ \text{(White ppt.)} \end{array}$$

Zero group NH_4^+ (ammonium): The substance (salt or mixture) when heated with NaOH solution evolves ammonia.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

When a rod dipped in HCl is brought on the mouth of the test tube, white fumes of ammonium chloride are formed, $NH_3 + HCl \longrightarrow NH_4Cl$

To the aqueous solution of ammonium salt when Nessler's reagents is added, brown coloured precipitate is formed.

Volumetric analysis

Volumetric analysis is a quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution.

Titration : The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as titration. Thus, a titration involves two solutions:

- (i) *Unknown solution*: The solution consisting the substance to be estimated is termed unknown solution. The substance is termed titrate.
- (ii) Standard solution: The solution in which an accurately known amount of the reagent (titrant) has been dissolved in a known volume of the solution is termed standard solution. There are two types of reagents (titrants):
- (a) Primary standards: These can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid $(H_2C_2O_4.2H_2O)$, potassium dichromate $(K_2Cr_2O_7)$, silver nitrate $(AgNO_3)$, copper sulphate $(CuSO_4.5H_2O)$, ferrous ammonium sulphate $[FeSO_4(NH_4)_2SO_4.6H_2O]$, sodium thiosulphate $(Na_2S_2O_3.5H_2O)$, etc., are the examples of primary standards.
- (b) Secondary standards: The solutions of these reagents are to be standardised before use as these cannot be weighed accurately. The examples are sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrochloric acid (HCl), sulphuric acid (H_2SO_4) , potassium permanganate $(KMnO_4)$, iodine, etc.

Law of equivalence : It is applied in all volumetric estimations. According to it, the chemical substances react in the ratio of their chemical equivalent masses.

 $\frac{\text{Mass of substance } A}{\text{Mass of substance } B} = \frac{\text{Chemical equivalent mass of } A}{\text{Chemical equivalent mass of } B}$

or $\frac{\text{Mass of substance } A}{\text{Chemical equivalent mass of } A}$

Mass of substance B
Chemical equivalent mass of B

or gram equivalent of A = gram equivalent of B

or milli-gram equivalent of A = milli-gram equivalent of B

The point at which the amounts of the two reactants are just equivalent is known as equivalence point or end point. An auxiliary substance which helps in the usual detection of the completion of the titration or equivalence point or end point is termed as indicator, *i.e.*, substances which undergo some easily detectable changes at the equivalence point are used as indicators.

Methods of expressing concentrations of solutions

The concentration of a solution can be expressed in various ways.

- (1) Percent by mass
- (2) Molarity
- (3) molality

- (4) Mole fraction
- (5) Normality

Types of titrations: Titrations can be classified as:

- (1) Acid base titrations or acidimetry and alkalimetry
- (2) Oxidation reduction titrations or redox titrations
- (3) Precipitation titrations
- (4) Complexometric titrations.
- (I) **Acid-base titrations**: When the strength of an acid is determined with the help of a standard solution of base, it is known as **acidimetry**. Similarly, when the strength of a base (alkali) is determined with the help of a standard solution of an acid, it is known as **alkalimetry**. Both these titrations involve neutralisation of an acid with an alkali. In these titrations H^+ ions of the acid combine with OH^- ions of the alkali to form

 $H^{^{+}}$ ions of the acid combine with $\,OH^{^{-}}$ ions of the alkali to form unionised molecules of water.

$$HA + BOH \longrightarrow BA + H_2O$$
Acid Alkali $\longrightarrow BA + H_2O$
or $H^+ + A^- + B^+ + OH^- \longrightarrow B^+ + A^- + H_2O$
or $H^+ + OH^- \longrightarrow H_2O$

The end point in these titrations is determined by the use of organic dyes which are either weak acids or weak bases. These change their colours within a limited range of hydrogen ion concentrations, *i.e.*, pH of the solution. Phenolphthalein is a suitable indicator in the titrations of strong alkalies (free from carbonate) against strong acids or weak acids. Methyl orange is used as an indicator in the titrations of strong acids against strong and weak alkalies. As no indicator gives correct results in the titrations of weak acids against weak bases, such titrations are performed by some other methods (physical methods).

- (2) Oxidation reduction titrations: The titrations based on oxidation-reduction reactions are called redox titrations. The chemical reactions proceed with transfer of electrons (simultaneous loss or gain of electrons) among the reacting ions in aqueous solutions. Sometimes these titrations are named after the reagent used, as:
- (i) **Permanganate titrations:** These are titrations in which potassium permanganate is used as an oxidising agent in acidic medium. The medium is maintained by the use of dilute sulphuric acid. Potassium permanganate acts as a self-indicator. The potential equation, when potassium permanganate acts as an oxidising agent, is:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

or $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

Before the end point, the solution remains colourless (when $KMnO_4$ solution is taken in burette) but after the equivalence point only one extra drop of $KMnO_4$ solution imparts pink colour, *i.e.*, appearance of pink colour indicates the end point. Potassium permanganate is used for the estimation of ferrous salts, oxalic acid, oxalates, hydrogen peroxide, etc. The solution of potassium permanganate is always first standardised before its

(ii) *Dichromate titrations*: These are titrations in which, potassium dichromate is used as an oxidising agent in acidic medium. The medium is maintained acidic by the use of dilute sulphuric acid. The potential equation is

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

or $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

The solution of potassium dichromate can be directly used for titrations. It is mainly used for the estimation of ferrous salts and iodides. In the titration of $K_2Cr_2O_7$ versus ferrous salt either an external indicator (potassium ferricyanide) or an internal indicator (diphenyl amine) can be used.

(iii) lodimetric and iodometric titrations: The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$$I_2 + 2e^- \longrightarrow 2I^-$$
 (reduction)

$$2I^{-} \longrightarrow I_2 + 2e^{-}$$
 (oxidation)

These are divided into two types:

(a) Iodimetric titrations: These are the titrations in which free iodine is used. As it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in potassium iodide solution.

$$KI + I_2 \longrightarrow KI_3$$
Potassium tri-iodide

This solution is first standardised before use. With the standard solution of I_2 . Substances such as sulphite, thiosulphate, arsenite, etc., are estimated

(b) Iodometric titrations: In iodometric titrations, an oxidising agent is allowed to react in neutral medium or in acidic medium, with excess of potassium iodide to liberate free iodine.

$$KI$$
 + oxidising agent $\longrightarrow I_2$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogens, oxyhalogens, dichromates, cupric ion, peroxides, etc., can be estimated by this method.

$$I_2 + Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow$$

$$Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

In iodimetric and iodometric titrations, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point the blue or violet colour disappears when iodine is completely changed to iodide.

(3) Precipitation titrations: The titrations which are based on the formation of insoluble precipitates, when the solutions of two reacting substances are brought in contact with each other, are called precipitation titrations. For example, when a solution of silver nitrate is added to a solution of sodium chloride or a solution of ammonium thiocyanate, a white precipitate of silver chloride or silver thiocyanate is formed.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$AgNO_3 + NH_4CNS \longrightarrow AgCNS + NH_4NO_3$$

Such titrations involving silver nitrate are called argentometric titrations.

(4) **Complexometric titrations :** A titration, in which an undissociated complex is formed at the equivalence point, is called **complexometric titration**. These titrations are superior to precipitation titrations as there is no error due to co-precipitation.

$$Hg^{2+} + 2SCN^{-} \longrightarrow Hg(SCN)_{2}$$

 $Ag^{+} + 2CN^{-} \longrightarrow [Ag(CN)_{2}]^{-}$

EDTA (ethylenediamine tetra-acetic acid) is a useful reagent which forms complexes with metals. In the form of disodium salt, it is used to estimate Ca^{2+} and Mg^{2+} ions in presence of eriochrome black-T as an indicator.

Equivalent masses of acids and bases : Equivalent masses of some acids and bases are given in the following table

Table: 21.10

Acid	Basicity	Mol. Mass	Eq. Mass
HCl	1	36.5	$\frac{36.5}{1}$ =36.5
HNO,	1	63	$\frac{63}{1}$ =63.0
H,SO _.	2	98	$\frac{98}{2}$ =49.0
СӉСООН	1	60	$\frac{60}{1}$ =60.0
H,C,O,2H,O	2	126	$\frac{126}{2}$ =63.0
<i>Н,РО</i> .	3	98	$\frac{98}{3}$ =32.7
<i>Н,РО</i> ,	2	82	$\frac{82}{2}$ =41.0
<i>Н,РО</i> ,	1	66	$\frac{66}{1}$ =66.0

Table : 21.11

Alkali	Acidity	Mol. Mass	Eq. Mass
NaOH	1	40	$\frac{40}{1} = 40$
КОН	1	56	$\frac{56}{1} = 56$
Ca(OH)	2	74	$\frac{74}{2} = 37$
NH _i OH	1	35	$\frac{35}{1} = 35$

Calculations of Volumetric analysis

The following points should be kept in mind while making calculations of volumetric exercises.

(i) 1g equivalent mass of a substance reacts completely with 1g equivalent mass of any other substance. 1g equivalent mass of a substance means equivalent mass of the substance in grams. For example,

1g equivalent mass of NaOH = 40g of NaOH

1g equivalent mass of $H_2SO_4 = 49g$ of H_2SO_4

1g equivalent mass of KMnO_4 in acidic medium

=31.6 g of $KMnO_4$

1g equivalent mass of hydrated oxalic acid

=63g of hydrated oxalic acid

Note : Equivalent mass is a variable quantity and depends on the reaction in which the substance takes part. The nature of the reaction should be known before writing the gram equivalent mass of the substance. For example in the reactions.

$$2NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HCl$$
(i)

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$
(ii)

The value of $\,g\,$ equivalent mass of $\,H_{\,2}SO_{\,4}\,$ in reaction (i) is $\,98\,g\,$ and in reaction (ii) $\,49\,g$.

(ii) Number of g equivalents

Mass of the substance in g

Equivalentmass of the substance

Number of g moles = $\frac{\text{Mass of the substance in } g}{\text{Molecular mass of the substance}}$

 $= \frac{\text{Volume in litres of the substance at N.T.P.}}{\text{(only for gases)}}$

Number of milli-equivalent =
$$\frac{\text{Mass in } g \times 1000}{\text{Equivalent mass}}$$

Number of milli-moles = $\frac{\text{Mass in } g \times 1000}{\text{Molecular mass}}$

(iii) Molarity =
$$\frac{\text{No. of moles of the solute}}{\text{No. of litresof the solution}} = \frac{w}{m \times V}$$

Molarity \times molecular mass = strength of the solution (g/L) No. of moles of the solute = Molarity \times No. of litres of solution Mass of the solute in $g(w) = \text{molarity} \times \text{No.}$ of litres of solution \times mol. mass of solute

Normality =
$$\frac{\text{No. of } g \text{ equivalent of the solute}}{\text{No. of litresof the solution}} = \frac{w}{E \times V}$$

Normality \times equivalent mass = strength of the solution (g/L)

No. of equivalents of the solute = Normality $\,\times\,$ No. of litres of solution

Mass of the solute in $\ g(w) = \ \text{Normality} \ \times \ \text{No.}$ of litres of solution $\times \ \text{Eq.}$ mass of the solute

$$\frac{\text{Molecular mass}}{\text{Equivalent mass}} = n = \frac{\text{Normality}}{\text{Molarity}}$$

Normality = $n \times$ Molarity

(iv) $\ensuremath{\textit{Normality}}$ $\ensuremath{\textit{equation}}$: When solutions A and B react completely.

$$N_{\scriptscriptstyle A} V_{\scriptscriptstyle A} = N_{\scriptscriptstyle B} V_{\scriptscriptstyle B}$$

Normality of $A \times$ volume of A = Normality of $B \times$ volume of B

$$\text{or } \frac{\text{Strength } A}{\text{Eq. mass } A} \times V_A = \frac{\text{Strength } B}{\text{Eq. mass } B} \times V_B$$

 $\frac{\text{Wt.of metal hydroxide}}{\text{wt,of metal oxide}} = \frac{\text{Eq.wt.of metal hydroxide}}{\text{Eq.wt.of metal oxide}}$

$$= \frac{\text{Eq.wt of metal } + \text{Eq.wt of } OH}{2}$$

Eq.wt. of metal + Eq.wt of O^{2-}

 $\left(\nu\right)$ When the solution is diluted, the following formulae can be applied :

$$N_1 V_1 = N_2 V_2$$
 or $M_1 V_1 = M_2 V_2$ or $S_1 V_1 = S_2 V_2$

Before dilution = After dilution

(vi) If a number of acids are mixed, the combined normality of the mixture, $N_{\rm x}$, is given

$$N_{r}V_{r} = N_{1}V_{1} + N_{2}V_{2} + N_{3}V_{3} + \dots$$

Where $\,V_x\,$ is the total volume of the mixture, $\,N_1\,$ and $\,V_1\,$ are the normality and volume respectively of one acid, $\,N_2\,$ and $\,V_2\,$ of the second acid and so on.



- Solars rod should never be used in flame test as it gives a golden yellow colour due to sodium present in it. An asbestos fibre can be safely used in place of platinum wire.
- The transparent bead in borax bead test is made of NaBO + BO.
- Filter ash test is an alternative to cobalt nitrate test and gives better results
- Both CO and SO turn lime water milky.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$
(Milkiness)

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 \downarrow + H_2O$$
(Milkiness)

Eq. wt. of *KMnO* is different in acidic, alkaline and neutral medium *i.e.*, 31.6, 158 and 52.67 respectively.