Unit - 28 - CHEMESTRY PRACTICAL

Important Points

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.

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) Peliminary Test

(i) Physical examination : It involves the study of colour, smell, density etc.

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) 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) Ba and its salts impart apple green colour to the flame.
(d) Ca imparts brick red colour to the flame.

(iii) 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.

Colour of bead in oxidising flame	Colour of bead in reducing flame	Basic radical present
Greenish when hot, blue in cold.	Red and opaque	*Cu*
Yellow when hot	Green	*Fe*
Brown in cold	Grey or black or opaque	*Ni*

(iv) Charcoal cavity test

(a) *Compound fused in cavity directly*	
Nature and colour of bead	Cation
Yellow, soft bead which marks on paper	Pb^{2+}
White yellow when hot	ZnO
Grey metallic particles attracted by magnet	Fe, Ni, CO

(2) Wet tests for acid radicals :

Salt or mixture is treated with dil. H_2SO_4 and also with conc. separately and by observing the types of gases evolved. Confirmatory tests of anions are performed.

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 KI and starch solution blue colour $2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$; $HNO_2 \longrightarrow NO$ (colourless); $2NO + O_2(air) \longrightarrow 2NO_2$ (brown) $2KI + H_2SO_4 + 2NHO_2 \longrightarrow K_2SO_4 + 2H_2O + 2NO + I_2$ I_2 + starch ?? ? → blue colour
Smell of rotten eggs (H_2S smell) on heating	S^{2-} (sulphide)	Gas turn lead acetate paper black Sodium carbonate extract $(SE)^*$ + sodium nitroprusside – purple colour, $Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4$ $H_2S + (CH_3COO)_2Pb \longrightarrow PbS + 2CH_3COOH$ (black) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5\ NOS]$ sodium nitroprusside (purple)

Observations with concentrated H_2SO_4

Observation	Acid Radical	Confiramatory Test
Colourless pungent gas giving white fumes with aq. NH_4OH	Cl^- (chloride)	(i) Add MnO_2 in the same test tube and heat-pale green Cl_2 gas (ii) $S.E.+ HNO_3 + AgNO_3$ solution –white ppt. soluble in aq. NH_3 (iii) Chromyl chloride test
Reddish brown fumes	Br^- (bromide)	(iv) Add Mn_2O and heat –yellowish brown Br_2 gas (v) $S.E.+ HNO_3 + AgNO_3$ solution –pale yellow ppt. partially soluble aq. NH_3 (vi) Layer test
Violet pungent vapours turning starch paper blue.	I^- (iodide)	(vii) $S.E.+ HNO_3 + AgNO_3$ → yellow ppt. insoluble in aq. NH_3 (viii) Layer test
Brown pungent fum es intensified by the addition of Cu - turnigs.	NO_3^- (nitrate)	(ix) Ring test

Reactions

Chloride :

(i) $KCl + \text{conc.}H_2SO_4 \longrightarrow KHSO_4 + HCl$

$HCl + NH_3 \longrightarrow \underset{\text{(white fumes)}}{NH_4Cl}$

$4HCl + MnO_2 \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$

(ii) $KCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + KNO_3$

$AgCl + aq.\,2NH_3 \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl}$

(iii) Chromyl- chloride test :

Chloride + $K_2Cr_2O_7(\text{solid}) + \text{conc.}\,H_2SO_4 \xrightarrow{\text{heat}}$ reddish brown vapours of chromyl-chloride (CrO_2Cl_2). Pass these vapours into $NaOH$, when yellow Na_2CrO_4 solution is formed. On adding CH_3COOH and $(CH_3COO)_2$ Pb, yellow ppt. of lead chromate $(PbCrO_4)$ is formed.

Bromide :

(iv) $KBr + \text{conc.}H_2SO_4 \xrightarrow{\Delta} KHSO_4 + H$; $4HBr + MnO_2 \xrightarrow{\Delta} Br_2 + 2H_2O + MnBr_2$

(v) $NaBr + AgNO_3 \longrightarrow \underset{\text{pale yellow ppt.}}{AgBr\downarrow} + NaNO_3$

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

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

$2NaBr + Cl_2 \longrightarrow 2NaCl + \underset{\substack{\text{orange yellow}\\(\text{soluble in } CHCl_3)}}{Br_2}$

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

Iodide :

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

Nitrate :

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$4HNO_3 \longrightarrow \underset{\text{brown fumes}}{4NO_2} + O_2\,2H_2O$,

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(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 $[Fe(H_2O)_5NO]^{2+}SO_4^{2-}$ at the interface between the two liquids is formed.

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

$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5NO]^{2+}\,SO_4^{2-} + H_2O$

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, $BaCl_2 + NaSO_4 \longrightarrow \underset{\text{white ppt.}}{BaSO_4}\downarrow + 2NaCl$

(ii) ***Borate*** **:** lgnite the mixture containing borate, conc. H_2SO_4. And ethanol in a china-dish with a burning splinter –green edged flame of ethyl borate.

$$\underset{\text{(conc.)}}{2Na_3BO_3} + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3Na_2SO_4 ,$$

$$H_3BO_3 + 3\underset{ethanol}{C_2H_5OH} \xrightarrow{\Delta} \underset{\substack{\text{burns with green flame}\\\text{(volatile)}}}{(C_2H_5O)_3B} + 3H_2O$$

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

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

$$Na_3PO_4 + 12(NH_4)_2MoO_4 + 24HNO_3 \xrightarrow{\Delta} \underset{\text{yellow ppt.}}{(NH_4)_3PO_4 . 12MoO_3} + 21NH_4NO_3 + 3NaNO_3 + 12H_2O$$

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^-.

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

$$SiO_2 + 4HF \xrightarrow{\Delta} SiF_4 + 2H_2O$$

$$3SiF_4 4H_2O \longrightarrow 2H_2SiF_6 + \underset{\text{white}}{H_4SiO_4}$$

(3) Wet tests for basic radicals :

Analysis of Basic Radicals

Group	Basic radicals	Group reagent	Ppt. as	Explanation
I	Ag^+, Hg_2^{2+} (I), Pb^{2+}	dil HCl	Chloride ($AgCl, Hg_2Cl_2, PbCl_2$)	K_{SP} values of chlorides are low, hence precipitated. Others have higher K_{SP} values hence not precipitated.
II	$Cu^{2+}, Cd^{2+}, Pb^{2+}$, Hg^{2+} (II), Bi^{3+}, As^{3+}; Sb^{3+}, Sn^{2+}	H_2S gas in presence of dil. HCl	Sulphides (CuS, As_2S_3 etc.)	K_{SP} values of sulphides are low hence precipitated by low $[S^{2-}]$ ion. HCl (with 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.
III	$Al^{3+}, Cr^{3+}, Fe^{3+}$	NH_4OH in presence of NH_4Cl	Hydroxide, $Al(OH)_3$ etc.	K_{SP} values of $Al(OH)_3$ etc. are low. NH_4Cl (with common NH_4^+ ion) decreases ionization of NH_4OH giving low $[OH^-]$. Hence group III is precipitated.
IV	$Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}$	H_2S in ammonical medium	Sulphides (ZnS etc.)	K_{SP} values of sulphides of group IV are high hence precipitation takes place in higher $[S^{2-}]$. Basic medium increases ionization of H_2S increasing $[S^{2-}]$ hence precipitation of group IV.

Group	Basic radicals	Group reagent	Ppt. as	Explanation
V	$Ca^{2+}, Ba^{2+}, Sr^{2+}$	$(NH_4)_2CO_3 + NH_4Cl$	Carbonates ($CaCO_3$ etc.)	K_{SP} values of carbonate are les s than that of group VI (Mg^{2+}) hence precipitation before Mg^{2+}.
VI	Mg^{2+}, (Na^+, K^+ also included)	$NH_4OH + Na_2HPO_4$ (only for Mg^{2+})	White ppt. ($MgHPO_4$)	–
0 (Zero)	NH_4^+	–	–	Tested independently from original solution.

Chemical reactions involved in the tests of basic radicals

Group I : 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^{2+}* (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.

$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{yellow ppt.}}{PbCrO_4} + 2KCl$;

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

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

$PbCl_2 + 2KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2} + 2KCl$

(iv) White precipitate of lead sulphate is formed with dilute H_2SO_4.

The precipitate is soluble in ammonium acetate, $PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HCl$;

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

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.

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

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

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

$$As_2S_5 + 3(NH_4)S \longrightarrow \underset{\text{Ammonium thioarsenate}}{2(NH_4)_3AsS_4}$$

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

$$SnS_2 + (NH_4)_2S \longrightarrow \underset{\text{Ammonium thiostannate}}{(NH_4)_2SnS_3}$$

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 , all other sulphides of are soluble.

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

$$Bi_2S_3 + 8HNO_3 \rightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$$

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

***Pb^{2+}* (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, $Pb(NO_3)_2 + H_2SO_4 \rightarrow \underset{\text{(White ppt.)}}{PbSO_4} + 2HNO_3$

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,

$$Bi(NO_3)_3 + 3NH_4OH \longrightarrow \underset{\text{White ppt.}}{Bi(OH)_3} + 3NH_4NO_3$$

$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\substack{\text{Tetrammine cupric nitrate}\\ \text{(deep blue solution)}}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O;$$

$$Cd(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\substack{\text{Tetrammine cadmium nitrate}\\ \text{(colourless solution)}}}{[Cd(NH_3)_4](NO_3)_2} + 4H_2O$$

***Cu^{2+}* (copper) :**

Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added a chocolate coloured precipitate is formed,

$$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_4COONH_4$$

$$2Cu(NO_3)_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate ppt.}}{Cu_2[Fe(CN)_6} + 4KNO_3$$

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

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

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{Green ppt.}}{Cr(OH)_3} + 3NH_4Cl$$

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

***Fe^{3+}* (iron) :** The brownish red precipitate dissolves in dilute *HCl*. The solution is divided into two parts.

Part I :

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

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

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

Part II :

Addition of potassium thiocyanate solution gives a blood red colouration.

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

***Al^{3+}*(aluminium) :**

The gelatinous precipitate dissolves in $NaOH$, $Al(OH)_3 + NaOH \longrightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$

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 *HCl* while *MnS* (buff coloured), *ZnS* (colourless) are soluble in conc. *HCl*.

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

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

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2} + 2NaCl \qquad Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{(Soluble)}}{Na_2ZnO_2} + 2H_2O$$

On passing H_2S, white precipitate of zinc sulphide is formed $Na_2ZnO_2 + H_2S \longrightarrow \underset{\text{White ppt.}}{ZnS} + 2NaOH$

***Mn^{2+}* (manganese) :** Manganese sulphide dissolves in *HCl* $MnS + 2HCl \longrightarrow MnCl_2 + H_2S$

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

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl \qquad Mn(OH)_2 + O \longrightarrow MnO_2H_2O$$

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.

$$2MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$$

$$2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 \longrightarrow \underset{\text{Permanganic acid (pink)}}{2HMnO_4} + 15Pb(NO_3)_2 + 12H_2O$$

The above test fails in presence of *HCl*.

Ni^{2+} (nickel) and Co^{2+} (cobalt)

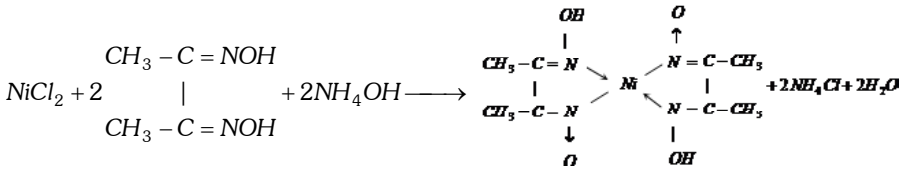
The black precipitate is dissolved in aqua- regia.

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

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

The solution is evaporated to dryness and residue extracted with dilute HCl. It is divided into three parts.

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



$$NiCl_2 + 2\begin{array}{l} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{array} + 2NH_4OH \longrightarrow \begin{array}{l} OH \quad\quad\quad O \\ | \quad\quad\quad\ \uparrow \\ CH_3 - C = N \quad\quad N = C - CH_3 \\ | \quad\quad Ni \quad\quad | \\ CH_3 - C = N \quad\quad N = C - CH_3 \\ \downarrow \quad\quad\quad\ | \\ O \quad\quad\quad OH \end{array} + 2NH_4Cl + 2H_2O$$

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

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

$$Br_2 + H_2O \longrightarrow 2HBr + O \qquad 2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow \underset{\substack{\text{sod. cobalti carbonate} \\ \text{(Green colouration)}}}{2Na_3Co(CO_3)_3} + 2NaOH$$

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

$$2NiCO_3 + [O] \longrightarrow \underset{\text{(Black)}}{Ni_2O_3} + 2CO_2$$

Group V : Ammonium carbonate precipitates V group radicals in the form of carbonates are soluble in acetic acid.

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

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

$$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$$

***Ba^{2+}* (barium) :** Barium chromate is insoluble and precipitated by the addition of potassium chromate solution, $Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2CH_3COOK$

***Ca^{2+}* (calcium) :** Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.

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

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.

$$MgCl_2 + Na_2HPO_4 + NH_4OH \longrightarrow \underset{\substack{\text{Megnesium ammonium phosphate}\\ \text{(White ppt.)}}}{Mg(NH_4)PO_4} + 2NaCl + H_2O$$

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, $NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl}$

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

$$2K_2HgI_4 + NH_4Cl + 4KOH \longrightarrow \underset{\substack{\text{Iodide of Millon's base}\\ \text{(Brown ppt.)}}}{\begin{matrix} & & NH_2 \\ & Hg & \diagup \\ & & O \\ & Hg & \diagdown \\ & & I \end{matrix}} + 7KI + KCl + 3H_2O$$

M.C.Q.

1. In borax bead test, which of the following compound is formed [CBSE PMT 2002]

   (a) Meta borate (b) Tetra borate (c) Double oxide (d) Ortho borate

2. The metal that does not give the borax-bead test is [MP PMT 1999]

   (a) Chromium (b) Nickel (c) Lead (d) Manganese

3. Which of the following is coloured compound? [BCECE 2005]

   (a) CuF_2 (b) CuI (c) NaCl (d) $MgCl_2$

4. The alkaline earth metal that imparts apple green colour to the bunsen flame when introduced in it in the form of its chloride is [EAMCET 1979]

   (a) Barium (b) Strontium (c) Calcium (d) Magnesium

5. Which gives violet coloured bead in borax bead test [BHU 1988; MP PET 1997]

   (a) Fe^{2+} (b) Ni^{2+} (c) Co^{2+} (d) Mn^{2+}

6. When concentrated H_2SO_4 is added to dry KNO_3, brown fumes evolve. These fumes are [CPMT 1988; IIT 1987]

   (a) SO_2 (b) SO_3 (c) NO (d) NO_2

7. Which one of the following salt give green coloured flame when the salt is tested by Pt wire

   (a) Barium salt (b) Calcium salt (c) Borate (d) Lead salt

8. Sodium sulphite on heating with dilute HCl liberates a gas which [NCERT 1972]

   (a) Turns lead acetate paper black

   (b) Turns acidified potassium dichromate paper green

   (c) Burns with a blue flame

   (d) Smells like vinegar

9. Starch-iodide paper is used for the test of

   (a) Iodine (b) Iodide ion (c) Oxidising agent (d) Reducing agent

10. Which of the following salt gives white precipitate with solution and dil. solution and gives green flame test

    (a) $CuCl_2$ (b) $BaCl_2$ (c) $pbCl_2$ (d) $Cu(NO_3)_2$

11. Two gases when mixed give white dense fumes, the gases are

    (a) NH_3 and SO_2 (b) SO_2 and steam (c) NH_3 and HCl (d) NH_3 and N_2O

12. Blue borax bead is obtained with [MADT Bihar 1982; MP PET 1995]

    (a) Zn (b) Cobalt (c) Chromium (d) Fe

13. Which of the following imparts green colour to the burner flame [DCE 2004]

    (a) $B(OMe)_3$ (b) Na(OMe) (c) $Al(OPr)_3$ (d) $Sn(OH)_2$

14. A colourless gas with the smell of rotten fish is [AFMC 2005]

(a) H_2S (b) PH_3 (c) SO_2 (d) None of these

15. MnO_2 and H_2SO_4 added to NaCl, the greenish yellow gas liberated is [Orissa JEE 2005]

(a) Cl_2 (b) NH_3 (c) N_2 (d) H_2

16. Which of the following statement(s) is(are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc H_2SO_4. [IIT 1998; CPMT 1988; AMU 1984; MP PMT 2002]

(a) A deep red vapour is evolved

(b) The vapour when passed into NaOH solution gives a yellow solution of $Na_2Cr_2O_7$

(c) Chlorine gas is evolved

(d) Chromyl chloride is formed

17. Which of the following combines with Fe (II) ions to form a brown complex [AIIMS 1982, 87; AFMC 1988; CBSE PMT 2000; Pb. PMT 2000; MP PET 2000, 01]

(a) N_2O (b) NO (c) N_2O_3 (d) N_2O_5

18. Which of the following will not produce a precipitate with $AgNO_3$ solution [MP PMT 1990]

(a) F^- (b) Br^- (c) CO_3^{2-} (d) PO_4^{3-}

19. Which of the following gives black precipitate when H_2S gas is passed through its solution [CPMT 1974]

(a) Acidic $AgNO_3$ (b) $Mg(NO_3)_2$ (c) Ammonical $BaCl_2$ (d) Copper nitrate

20. A salt gives violet vapours when treated with conc. H_2SO_4. It contains [DPMT 1981; CPMT 1971]

(a) Cl^- (b) I^- (c) Br^- (d) NO_3^-

21. When water is added to a salt solution containing chloroform, chloroform layer turns violet. Salt contains [CPMT 1982]

(a) Cl^- (b) I^- (c) NO_3^- (d) S^{2-}

22. Phosphate radical with ammonium molybdate gives precipitate of which colour

(a) Violet (b) Pink (c) Canary yellow (d) Green

23. Which compound is soluble in NH_4OH [AFMC 1987]

(a) $PbCl_2$ (b) $PbSO_4$ (c) AgCl (d) $CaCO_3$

24. Nitrates of all the metals are [DPMT 1983, 89]

(a) Coloured (b) Unstable (c) Soluble in water (d) Insoluble in water

25. Nitrate is confirmed by ring test. The brown colour of the ring is due to the formation of [EAMCET 1979; AFMC 1981, 88, 90; RPET 1999; MP PMT 2000; MP PET 2002; CPMT 2004]

(a) Ferrous nitrite (b) $FeSO_4NO$ (c) $FeSO_2NO_2$ (d) Ferrous nitrate

26. Aqueous solution of a salt when treated with $AgNO_3$ solution gives a white precipitate, which dissolves in NH_4OH. Radical present in the salt is

(a) Cl^- (b) Br^- (c) I^- (d) NO_3^-

27. When CO_2 is passed into lime water it turns milky. When excess of CO_2 is passed, milkyness disappears because

(a) Reaction is reversed (b) Water soluble $Ca(HCO_3)_2$ is formed

(c) Vaporisable calcium derivative is formed (d) None of these

28. A mixture when heated with conc. H_2SO_4 with MnO_2 brown fumes are formed due to
(a) Br^- (b) NO_3^- (c) Cl^- (d) I^-

29. In the test of sulphate radical, the white precipitate of sulphate is soluble in
(a) Conc. HCl (b) Conc. H_2SO_4 (c) Conc. HNO_3 (d) None of these

30. Which reagent is used to remove SO_4^{2-} and Cl^- [Pb. PMT 2002]
(a) $BaSO_4$ (b) NaOH (c) $Pb(NO_3)_2$ (d) KOH

31. ..... is formed when potassium iodide is heated with conc. H_2SO_4 [CPMT 1971]
(a) HI (b) I_2 (c) HIO_3 (d) KIO_3

32. Chromyl chloride test is performed for the confirmation of the presence of the following in a mixture [CPMT 1990; KCET 1992; RPET 1999]
(a) Sulphate (b) Chromium (c) Chloride (d) Chromium and chloride

33. A solution of a salt in dilute sulphuric acid imparts deep blue colour with starch iodine solution it confirms the presence of which of the following [MP PET 2003; NCERT 1974; CPMT 1977]
(a) NO_2^- (b) I^- (c) NO_3^- (d) $CH_3\ COO^-$

34. Ammonia reacts with excess of chlorine to form [DPMT 2000]
(a) N_2 and HCl (b) NH_4Cl and NCl_3 (c) NCl_3 and HCl (d) N_2 and NH_4Cl

35. Which of the following anions would decolourise acidified $KMnO_4$ solution
(a) SO_4^{2-} (b) S_2^- (c) NO_3^- (d) $CH_3\ COO^-$

36. The gas which is absorbed by ferrous sulphate solution giving blackish brown colour is [AMU 1999]
(a) NO (b) CO (c) N_2 (d) NH_2

37. Which one of the following anions is not easily removed from aqueous solutions by precipitation [IIT 1995]
(a) Cl^- (b) NO_3^- (c) CO_3^{2-} (d) SO_4^{2-}

38. Na_2CO_3 cannot be used to identify [BVP 2004]
(a) CO_3^{2-} (b) SO_3^{2-} (c) S^{2-} (d) SO_4^{2-}

39. The number of hydroxide ions, produced by one molecule of sodium carbonate (Na_2CO_3) on hydrolysis is [Pb. CET 2002]
(a) 2 (b) 1 (c) 3 (d) 4

40. By passing $KMnO_4$ gas in acidified H_2S solution, we get [MP PET 1997]
(a) K_2S (b) S (c) K_2SO_3 (d) MnO_2

41. Which of the following doesn't give a ppt. with silver nitrate solution. [J & K 2005]
(a) Ethyl bromide (b) Sodium bromide (c)Calcium chloride (d) Sodium chloride

42. Which sulphide is soluble in $(NH_4)_2\ CO_3$
(a) SnS (b) AS_2S_3 (c) Sb_2S_3 (d) CdS

43. When acetic acid and $K_4[Fe(CN)_6]$ is added to a copper salt, a chocolate precipitate is obtained of the compound
(a) Copper cyanide (b) Copper ferrocyanide
(c) Basic copper sulphate (d) Basic copper cyanide

44. A precipitate of the following would be obtained when HCl is added to a solution of stannous sulphide (SnS) in yellow ammonium sulphide [CPMT 1977; NCERT 1974]

(a) SnS (b) SnS_2 (c) Sn_2S_3 (d) $(NH_4)_2\ SnS_3$

45. The compound insoluble in acetic acid is [CPMT 1989]

(a) Calcium oxide (b) Calcium carbonate (c) Calcium oxalate (d) Calcium hydroxide

46. Which of the following give white precipitate when HCl is added to its aqueous solution

(a) Hg^+ (b) Mg^{++} (c) Zn^{++} (d) Cd^{++}

47. Reagent used in the qualitative analysis of IVth group is

(a) HCl (b) H_2S (alkaline) (c) $(NH_4)_2S$ (d) None of these

48. Which of the following pairs would be expected to form precipitate when solution are mixed [NCERT 1984]

(a) $K^+,\ SO_4^{2-}$ (b) $Na^+,\ S^{-2}$ (c) $Ag^+,\ NO_3^-$ (d) $Al^{3+},\ OH^-$

49. Addition of solution of oxalate to an aqueous solution of mixture of Ba^{2+}, Sr^{2+} અને Ca^{2+} and will precipitate [MP PMT 1985]

(a) Ca^{2+} (b) $Ca^{2+},\ Sr^{+2}$ (c) $Ba^{2+},\ Sr^{+2}$ (d) All the three

50. Distinguishing reagent between silver and lead salts is [MADT Bihar 1984]

(a) H_2S gas (b) Hot dilute HCl solution

(c) $NH_4Cl_{(S)} + NH_4OH_{(aq)}$ (solid) + solution (d) $NH_4Cl_{(S)}$ (solid) + $(NH_4)_2\ CO_{3(aq)}$ solution

51. The ion that cannot be precipitated by both HCl and H_2S is [IIT 1982; CPMT 1989]

(a) Pb^{2+} (b) Cu^{2+} (c) Ag^+ (d) Sn^{2+}

52. $Pb(CH_3COO)_2$ gives….colour with H_2S [DPMT 2000]

(a) Orange (b) Red (c) Black (d) White

53. Fe^{2+} ion can be distinguished by Fe^{3+} ion by [DPMT 2000]

(a) NH_4SCN (b) $AgNO_3$ (c) $BaCl_2$ (d) None of these

54. Which of the following change the colour of the aqueous solution of $FeCl_3$ [Roorkee Qualifying 1998]

(a) $K_4[Fe(CN)_6]$ (b) H_2S (c) NH_4CNS (d) KCNS

55. Which of the following mixture is chromic acid [Pb. PMT 2000]

(a) $K_2Cr_2O_7$ and HCl (b) K_2SO_4 conc. H_2SO_4

(c) $K_2Cr_2O_7$ and conc. H_2SO_4 (d) H_2SO_4 and HCl

56. If Na^+ ion and S^{2-} ion is larger than Cl^- ion, which of the following will be least soluble in water [AMU (Engg.) 1999]

(a) MgS (b) NaCl (c) Na_2S (d) $MgCl_2$

57. Lead sulphate is soluble [MP PET 1999]

(a) In conc. nitric acid (b) In conc. hydrochloric acid

(c) In a solution of ammonium acetate (d) In water

58. When H_2S gas is passed through the HCl containing aqueous solutions of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$, which does not precipitate out [MP PMT 2002]

(a) CuS (b) HgS (c) Bi_2S_{3-} (d) CoS

59. Group reagent for analytic group IV is [Kurukshetra CET 2002]
(a) $NH_4Cl + NH_4OH$ (b) $NH_4Cl + NH_4OH + H_2S$
(c) $NH_4OH + (NH_4)_2CO_3$ (d) $HCl + H_2S$

60. When H_2S is passed through Hg_2S we get [AIEEE 2002]
(a) HgS (b) $HgS + Hg_2S$ (c) $Hg_2S + Hg$ (d) Hg_2S

61. [X] + $H_2SO_4 \rightarrow$ [Y] a colourless gas with irritating smell
[Y] + $K_2Cr_2O_7 + H_2SO_4 \rightarrow$ green solution
[X] and [Y] is [IIT-JEE (Screening) 2003]
(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl (c) S^{-2}, H_2S (d) CO_3^{2-}, CO_2

62. Concentrated sodium hydroxide can separate a mixture of [MP PMT 2000]
(a) Zn^{2+} and Pb^{2+} (b) Al^{3+} and Zn^{3+} (c) Cr^{3+} and Fe^{3+} (d) Al^{3+} and Cr^{3+}

63. What product is formed by mixing the solution of $K_4[Fe(CN)_6]$ with the solution of $FeCl_3$ [Roorkee 1989]
(a) Ferro-ferricyanide (b) Ferric-ferrocyanide (c) Ferri-ferricyanide (d) None of these

64. When H_2S is passed through a mixture containing Cu^{+2}, Ni^{+2}, Zn^{+2} in acidic solution then ion will precipitate [RPMT 2002]
(a) Cu^{+2}, Ni^{+2} (b) Ni^{+2} (c) Cu^{+2}, Zn^{+2} (d) Cu^{+2}

65. Ferric ion forms a prussian blue coloured ppt. due to [CPMT 1980; BHU 1980; MP PET 1995; Kurukshetra CEE 1998; RPET 1999; MP PMT 2001]
(a) $K_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]$ (c) $KMnO_4$ (d) $Fe(OH)_3$

66. A 0.3 M HCl solution contains the following ions Hg^{2+}, Cd^{2+}, Sr^{2+}, Fe^{2+} અને Cu^{2+}. The addition of H_2S to above solution will precipitate [CPMT 1973]
(a) Cd, Cu and Hg (b) Cd, Fe and Sr (c) Hg, Cu and Fe (d) Cu, Sr and Fe

67. Which of the following gives a ppt. with $Pb(NO_3)_2$ but not with $Ba(NO_3)_2$ [CPMT 1979; MP PET 1997]
(a) NaCl (b) Sodium acetate
(c) Sodium nitrate (d) Sodium hydrogen phosphate

68. In the group III radicals, in place of NH_4Cl which of the following can be used [AIIMS 1980, 82; MP PMT 1985]
(a) NH_4NO_3 (b) $(NH_4)_2\ SO_4$ (c) $(NH_4)_2$ (d) NaCl

69. Which compound does not dissolve in hot dilute HNO_3 [IIT 1996]
(a) HgS (b) PbS (c) CuS (d) CdS

70. Which of the following sulphate is insoluble in water [MNR 1995]
(a) $CuSO_4$ (b) $CdSO_4$ (c) $PbSO_4$ (d) $BaSO_4$

71. Mark the compound which turns black with NH_4OH [AFMC 1981; MP PMT 1995]
(a) Lead chloride (b) Mercurous chloride (c) Mercuric chloride (d) Silver chloride

72. Colour of cobalt chloride solution is [AFMC 1981]
(a) Pink (b) Black (c) Colourless (d) Green

73. Nessler's reagent is used to detect [CPMT 1989; AIIMS 1997; MP PET 1999]
(a) CrO_4^{2-} (b) PO_4^{3-} (c) MnO_4^- (d) NH_4^+

74. $Fe(OH)_3$ can be separated from $Al(OH)_3$ by addition of [BHU 1981]
(a) Dil. HCl (b) NaCl solution
(c) NaOH solution (d) NH_4Cl and NH_4OH

75. The reagents NH_4Cl and aqueous NH_3 will precipitate [IIT 1991]
(a) Ca^{2+} (b) Al^{3+} (c) Mg^{2+} (d) Zn^{2+}

76. Addition of $SnCl_2$ to $HgCl_2$ gives ppt [BVP 2003]
(a) White turning to red (b) White turning to gray
(c) Black turning to white (d) None of these

77. Heamoglobin is a complex of [CPMT 2003]
(a) Fe^{3+} (b) Fe^{2+} (c) Fe^{4+} (d) Cu^{2+}

78. In Nessler's reagent for the detection of ammonia the active species is [Kerala (Med.) 2003]
(a) Hg_2Cl_2 (b) Hg^{2+} (c) Hg_2I_2 (d) HgI_4^{2-}

79. Which one of the following sulphides is only completely precipitated when the acidic solution is made dilute [MP PET 2000]
(a) HgS (b) PbS (c) CdS (d) CuS

80. A reagent used to test the presence of ion is [KCET 1998]
(a) H_2S (b) NH_4CNS (c) $K_4[Fe(CN)_6]$ (d) $K_3[Fe(CN)_6]$

81. The following four solutions are kept in separate beakers and copper metal is put in each of them. Which solution will become blue after some time [MP PMT 2003]
(a) $AgNO_3$ solution (b) $Zn(NO_3)_2$ solution (c) $Ba(NO_3)_2$ solution (d) $NaNO_3$ solution

82. In qualitative analysis, in order to detect second group basic radical, H_2S gas is passed in the presence of dilute HCl to [KCET 2004]
(a) Increase in dissociation of H_2S (b) Decrease the dissociation of salt solution
(c) Decrease the dissociation of H_2S (d) Increase the dissociation of salt solution

83. Sodium nitroprusside when added to an alkaline solution of sulphide ions produce a [AFMC 2005]
(a) Red colouration (b) Blue colouration (c) Purple colouration (d) Brown colouration

84. If 20 ml of 0.25 N strong acid and 30 ml of 0.2 N of strong base are mixed, then the resulting solution is [KCET 2002]
(a) 0.25 N basic (b) 0.2 N acidic (c) 0.25 N acidic (d) 0.2 N basic

85. 10 ml of 10 M H_2SO_4 is mixed to 100 ml 1M NaOH solution. The resultant solution will be [NCERT 1971]
(a) Acidic (b) Neutral (c) Weakly alkaline (d) Strongly alkaline

86. The equivalent weight of $KMnO_4$ in alkaline medium will be [MP PMT 2001]
(a) 31.60 (b) 52.66 (c) 79.00 (d) 158.00

87. Phenolphthalein is most suitable indicator for the titration of [MP PMT 2000]
(a) CH_3COOH and NH_4OH (b) CH_3COOH and NaOH
(c) HCl and NH_4OH (d) H_2CO_3 and NH_4OH

88. 20 ml of a N solution of $KMnO_4$ just reacts with 20 ml of a solution of oxalic acid. The weight of oxalic acid crystals in 1N of the solution is [JIPMER 1999]
(a) 31.5 g (b) 126 g (c) 63 g (d) 6.3 g

ANSWERS KEY

1	a	16	a,b,d	31	b	46	a	61	c	76	b
2	c	17	b	32	c	47	b	62	c	77	b
3	a	18	d	33	a	48	d	63	b	78	d
4	d	19	a	34	c	49	d	64	d	79	c
5	d	20	b	35	b	50	b	65	b	80	d
6	d	21	b	36	a	51	b	66	a	81	a
7	a	22	c	37	b	52	c	67	a	82	c
8	b	23	c	38	a	53	a	68	a	83	c
9	a	24	c	39	a	54	a	69	a	84	d
10	b	25	b	40	b	55	c	70	d	85	a
11	c	26	a	41	a	56	a	71	b	86	d
12	b	27	b	42	b	57	a	72	a	87	d
13	a	28	a	43	b	58	d	73	d	88	c
14	b	29	d	44	b	59	b	74	c		
15	a	30	c	45	c	60	c	75	b