Principles Related to Practical Chemistry

Qualitative Analysis of Organic Compounds:

This is used to detect nitrogen, halogen and sulphur present in organic compound.

a) Sodium Extract: Aqueous solution containing soluble sodium salt of the elements *i.e* NaCl, Na_2S and NaCNS formed by fusion of compound with sodium metal.

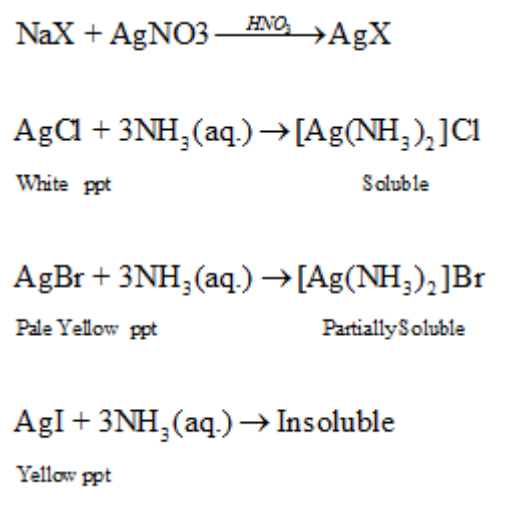
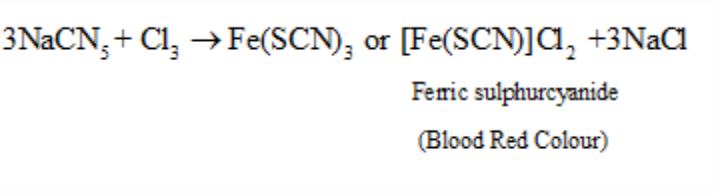
b) Formation of Sodium Extract: It is a two step process

Step 1: Organic compounds are fused with dry sodium in a fusion-tube

Step 2: Fused mass after extraction with water is boiled and filtered.

c) Use of Sodium Extract: Sodium extract (S.E.) is used to detect elements (other than C and H) and the tests are given in the table.

Element	Sodium Extract (S.E.)	Confirmed Test
Nitrogen	$Na + C + N + \Delta \rightarrow NaCl$	S.E.+ $FeSO_4$ +NaOH, boil and cool + $FeCl_3$ + conc. HCl → Blue/ green colour **Reactions Involved**: $2NaCN + FeSO_4 \rightarrow Fe(CN)_2 + Na_2SO_4$ $Fe(CN)_2 + 4NaCN \rightarrow Na_4[Fe(CN)_6]$ Sodium Ferrocyanide $3Na_4[Fe(CN)_6] + 4FeCl_3 \xrightarrow{HCl} Fe_4[Fe(CN)_6]_3 + 12NaCl$ Ferric Ferrocyanide Prussian Blue
Sulphur	$2Na + S \rightarrow Na_2S$	(i) S.E. + sodium nitroprusside → Violet Colour (ii) S.E + CH_3CO_2H + $(CH_3CO_2)_2Pb$ → black ppt. **Reactions Involved:** (i) $Na_2S + Na_2[Fe(CN)_3NO] \rightarrow Na_4[Fe(CN)_5NOS]$ (Sodium Nitroprusside) (Violet Coloure) (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} PbS\downarrow + 2CH_3COONa$ (Black ppt)
Halogen	$Na + X + \Delta \rightarrow NaX$ (X = Cl, Br, I)	S.E. + HNO_3+$AgNO_3$→ (i) White ppt soluble in aq NH_3 confirms Cl.

		(ii) Pale yellow ppt partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt insoluble in aq. NH_3 confirms I. **Reactions Involved:** 
Nitrogen and sulphur together	Na+ C + N + S+ Δ→ NaCNS with excess of Na the thiocyanate formed decomposes into cyanide and sulphide. NaCNS + 2Na → NaCN +Na_2S	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both. **Reactions Involved:** 

Qualitative Analysis of Inorganic Salts:

1. Physical Examination of Salts/Mixture

Observation	Inference
1. Substance is coloured	
i) Blue	Copper salt

ii) Dark green	Chromium salt
iii) Green	Salts of Fe(II), Ni, Cu or Cr
iv) Light yellow or brown	Salts of Fe(III)
v) Dark brown	PbO_2,Bi_2S_3
vi) Light pink	Salts of Mn
vii) Pink	Salts of Co
viii) Red	HgO, HgI_2,Pb_3O_4
ix) Orange red	Sb_2S_3
2. Substance is deliquescent	$CaCl_2$,$ZnCl_2$,$MgCl_2$, $MnCl_2$, nitrites, nitrates
3. Substance is heavy	Salts of Pb, Hg and Ba
4. Substance is light	Carbonates of Bi, Mg, Al, Zn, Ca, Sr

2. Effect of Heating:

Observation	Inference
1. Substance melts	Salts of alkali metals and salts having water of crystallisation.
2. Substance decripitates (crackling noise)	NaCl, KI, $Pb(NO_3)_2$ and $Ba(NO_3)_2$
3. Substance swells (due to loss of water of crystallisation)	Alums, borates and phosphates
4. The substance sublimes and the colour of sublimate is	
i) White	$HgCl_2$, Hg_2Cl_2,NH_4X, $AlCl_3$, As_2O_3, Sb_2O_3
ii) Yellow	As_2S_3 and HgI_2 (turns red when rubbed with glass rod).
iii) Blue black and violet vapours	Iodides
5. A residue (generally oxide) is left and its colour is	
i) Yellow (hot) and white (cold)	ZnO

ii) Reddish brown (hot); yellow (cold)	PbO
iii) Black (hot); Red (cold)	HgO, Pb_3O_4
iv) Black (hot); Red brown (cold)	Fe_2O_3
6. Gas is evolved	
(A) Colourless and odourless	
i) O_2 - rekindles a glowing splinter	Alkali nitrates ($2KNO_3 \rightarrow 2KNO_2 + O_2$)
ii) CO_2 - turns lime water milky	Carbonates and oxalates ($CaCO_3 \rightarrow CaO + CO_2$)
iii) N_2	Ammonium nitrite ($NH_4NO_2 \rightarrow N_2 + 2H_2O$)
(B) Colourless gas with odour	
i) NH_3 - Turns red litmus blue and mercurous nitrate paper black	Ammonium salts $(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3$
ii) SO_2 - Smell of burning sulphur, turns acidified $K_2Cr_2O_7$ paper green	Sulphites and thiosulphates $CaSO_3 \rightarrow CaO + SO_2$
iii) HCl - Pungent smell, white fumes with ammonia	Hydrated chlorides $CaCl_2.6H_2O \rightarrow Ca(OH)_2 + 4H_2O + 2HCl$
iv) H_2S - smell of rotten eggs, turns lead acetate paper black	Sulphides $Na_2S + 2H_2O \rightarrow 2NaOH + H_2S$
(C) Coloured gas	
i) NO_2 - Brown, turns starch iodide paper blue	Nitrites and nitrates of heavy metals $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$
ii) Br_2 - Reddish brown	Bromides $2CdBr_2 + O_2 \rightarrow 2CdO + 2Br_2$
(A) Turns starch paper yellow	
(B) turns starch iodide paper blue	
iii) I_2 - Violet, turns starch paper blue	Iodides $2CdI_2 + O_2 \rightarrow 2CdO + 2I_2$

iv) Cl_2 - Greenish yellow	Chlorides
(A) bleaches moist litmus paper	$CuCl_2 + H_2O \rightarrow CuO + 2HCl$ $CuO + 2HCl \rightarrow Cu + H_2O + Cl_2$
(B) bleaches indigo solution	
(C) turns starch iodide paper blue	

3. Flame test:

Metals	Colour
Li	crimson red
Na	golden yellow
K	Violet
Ca	Brick red
Sr	Crimson
Ba	apple green

- **Test for Anions:**

1. Carbonate (CO_3^{2-})

i) ***Dilute HCl :*** gives effervescence, due to the evolution of carbon dioxide.

$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

The gas gives turbidity with lime water and baryta water.

$CO_2 + Ca^{2+} + 2OH^- \rightarrow CaCO_3 \downarrow + H_2O$

$CO_2 + Ba^{2+} + 2OH^- \rightarrow BaCO_3 \downarrow + H_2O$

On prolonged passage of carbon dioxide in lime water, the turbidity slowly disappears due to the formation of soluble hydrogen carbonate.

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

ii) ***Barium chloride or Calcium chloride solution:*** White ppt of barium or calcium carbonate is obtained, which is soluble in mineral acid.

$CO_3^{2-} + Ba^{2+} \rightarrow BaCO_3 \downarrow$

$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 \downarrow$

iii) ***Silver nitrate solution:*** White ppt of silver carbonate is obtained.

$CO_3^{2-} + 2Ag^{+} \rightarrow Ag_2CO_3 \downarrow$

The ppt so obtained is soluble in nitric acid and in ammonia. The ppt becomes yellow or brown on addition of excess reagent and same may also happen if the mix is boiled, due to the formation of silver oxide

$Ag_2CO_3 \downarrow \rightarrow Ag_2O \downarrow + CO_2$

2. Sulphites (SO_3^{2-})

i) ***Dilute HCl or Dilute H_2SO_4 :*** decomposes with the evolution of sulphur dioxide

$SO_3^{2-} + 2H^{+} \rightarrow SO_2 + H_2O$

The gas has a suffocating odour of burning sulphur.

ii) ***Acidified potassium dichromate solution:*** Turns filter paper moistened with acidified potassium dichromate solution, green due to the formation of Cr^{3+}ions.

iii) ***Lime water :*** On passing the gas through lime water, a milky ppt is formed.

Precipitate dissolves on prolonged passage of the gas, due to the formation of hydrogen sulphite ions.

iv) ***Barium chloride or Strontium chloride solution:*** Gives white ppt. of barium or strontium sulphite.

3. Sulphide (S^{-2})

i) ***Dil. HCl or Dil. H_2SO_4:*** A colourless gas smelling of rotten eggs (H_2S) is evolved.

$S^{2-} + 2H^{+} \rightarrow H_2S$

ii) The gas turns lead acetate paper black

iii) Gives yellow ppt. with $CdCO_3$

$Na_2S + CdCO_3 \rightarrow CdS \downarrow + Na_2CO_3$

iv) ***Silver nitrate solution:*** black ppt. of silver sulphide insoluble in cold but soluble in hot dil nitric acid.

$S^{2-} + 2Ag^{+} \rightarrow Ag_2S \downarrow$

v) ***Sodium nitroprusside solution :*** Turns sodium nitroprusside solution purple

$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$

4. Nitrites (NO_2^-)

i) ***Dil HCl and Dil. H_2SO_4 :*** Adding to solid nitrite in cold yields pale blue liquid (due to the presence of free nitrous acid HNO_2 or its anhydride N_2O_3) & the evolution of brown fumes of nitrogen dioxide, the latter being largely produced by combination of nitric oxide with the oxygen of the air

ii) Silver nitrate solution : White crystalline ppt. is obtained

$NO_2^- + Ag^+ \rightarrow AgNO_2$

iii) Turns acidified KI - starch paper blue

$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$

Starch + I_2 → Blue colour

iv) ***Brown ring test:*** When the nitrite solution is added carefully to a conc. solution of Iron(II) sulphate acidified with dil acetic acid or with dilute sulphuric acid, a brown ring is formed, due to the formation of $[FeNO]SO_4$ at the junction of the two liquids.

5. Acetate (CH_3COO^-)

i) ***Dilute Sulphuric Acid :*** Smell of vinegar is observed.

$CH_3COO^- + H^+ \rightarrow CH_3COOH$

The following test is performed with the aqueous salt solution.

ii) ***Iron (III) Chloride Solution:*** Gives deep - red colouration

$CH_3COONa + FeCl_3 \rightarrow (CH_3COO)_3Fe + 3NaCl$

Brown colour

6. Thiosulphates

i) ***Dil Hydrochloric acid:*** Gives sulphur & sulphur di oxide

ii) ***Silver nitrate solution:*** Gives white ppt. of silver thiosulphate.

$S_2O_3^{2-} + 2Ag^+ \rightarrow Ag_2S_2O_3$

The ppt. is unstable, turning dark on standing, when silver sulphide is formed.

$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$

iii) ***Lead acetate or Lead nitrate solution:*** Gives white ppt.

$S_2O_3^{2-} + Pb^{2+} \rightarrow PbS_2O_3$

On boiling it turns black due to the formation of PbS.

$PbS_2O_3 + H_2O \rightarrow PbS + 2H^+ + SO_4^{2}$

7. Chloride (Cl^-)

i) ***Conc. H_2SO_4 :*** decomposes with the evolution of HCl.

$Cl^- + H_2SO_4 \rightarrow HCl + HSO$

Gas so produced

(1) Turns blue litmus paper red

(2) Gives white fumes of NH_4Cl when a glass rod moistened with ammonia solution is brought near the mouth of test tube.

ii) ***Silver nitrate solution:*** White, curdy ppt. of AgCl insoluble in water & in dil .nitric acid, but soluble in dilute ammonia solution.

v) ***Chromyl chloride test:*** When a salt containing chloride ion is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 orange red fumes of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

orange – red fumes

Chlorides of mercury, owing to their slight ionization, do not respond to this test and only partial conversion to CrO_2Cl_2 occurs with the chlorides of lead, silver, antimony and tin.

When chromyl chloride vapours are passed into sodium hydroxide a yellow solution of sodium chromate is formed which when treated with lead acetate gives yellow ppt. of lead chromate.

$$CrO_2Cl_2 + 2NaOH \rightarrow Na_2CrO_4 + 2HCl$$

Yellow solution

$$Na_2CrO_4 + (CH_3COO)_2 Pb \rightarrow 2CH_3COONa + PbCrO_4 \downarrow \quad \text{(yellow ppt.)}$$

8. Bromide (Br^-)

i) ***Conc. H_2SO_4 :*** Gives reddish brown vapours of bromine accompanying the hydrogen bromide.

ii) ***Manganese dioxide and conc. sulphuric acid :*** When a mix of solid bromide, MnO_2 and conc. H_2SO_4 is heated reddish brown vapours of bromine are evolved.

$$2KBr + MnO_2 + 2H_2SO_4 \rightarrow Br_2 + K_2SO_4 + MnSO_4 + 2H_2O$$

The following tests are performed with the aqueous salt solution.

iii) ***Silver nitrate solution:*** Pale yellow ppt. of silver bromide is obtained. This ppt. is sparingly soluble in dil but readily soluble in conc. ammonia solution and insoluble in dil. HNO_3.

iv) ***Lead acetate solution:*** White crystalline ppt. of lead bromide which is soluble in boiling water.

9. Iodide (I^-)

i) ***Conc. H_2SO_4 :*** Gives violet vapours of iodine

ii) ***Silver nitrate solution:*** Yellow ppt. of silver iodide AgI, very slightly soluble in conc. ammonia solution and insoluble in dil nitric acid.

10. Nitrate (NO_3^-)

i) ***Conc H_2SO_4 :*** Gives reddish - brown vapours of nitrogen dioxide

$4NO_3^- + 2H_2SO_4 \rightarrow 4NO_2 + 2SO_4^{2-} + 2H_2O + O_2$

ii) ***Brown ring test:*** When freshly saturated solution of iron (II) sulphate is added to nitrate solution and conc. H_2SO_4 is poured slowly down the side of the test - tube, a brown ring is obtained.

$2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2NO + 4SO_4^{-2} + 4H_2O$

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

On shaking and warming the mix, the brown colour disappears, nitric oxide is evolved and a yellow solution of Iron(III) ions remains.

11. Sulphate (SO_4^{2-})

i) ***Barium chloride solution:*** White ppt. of barium sulphate $BaSO_4$ insoluble in warm dil. hydrochloric acid and in dilute nitric acid, but moderately soluble in boiling, conc. hydrochloric acid.

ii) ***Mercury (II) nitrate solution:*** Gives yellow ppt. of basic mercury (II) sulphate

12. Chromate CrO_4^{2-} and Dichromate (Cr_2O)

i) ***Barium chloride solution:*** Pale - yellow ppt. of barium chromate soluble in dilute mineral acids but insoluble in water and acetic acid.

$CrO + Ba^{2+} \rightarrow BaCrO_4^{-}$

Dichromate ion also gives the same ppt. but due to the formation of strong acid precipitation is partial.

$Cr_2O + 2Ba^{2+} + H_2O \quad 2\ BaCrO_4^{-} + 2H^+$

If sodium hydroxide or sodium acetate is added, precipitation becomes quantitative.

ii) ***Silver Nitrate Solution:*** Brownish - red ppt. of silver chromate Ag_2CrO_4 which is soluble in dil. nitric acid & in ammonia solution, but insoluble in acetic acid.

A reddish brown ppt. of silver dichromate $Ag_2Cr_2O_7$ is formed with a conc. solution of a dichromate.

13. Permanganate MnO

i) Hydrogen peroxide : It decolourises acidified potassium permanganate solution

$2MnO_4^- + 5H_2O_2 + 6H^+$ ¾¾® $5O_2 + 2Mn^{2+} + 8H_2O$.

ii) Iron (II) sulphate, in the presence of sulphuric acid, reduces permanganate to manganese (II). The solution becomes yellow because of the formation of iron (III) ions

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Test For Cations:

Group	Group reagent	Ions	Colour & ppt.
Group I	dil HCl	Pb^{2+}, Hg^+, Ag^+	$PbCl_2$, Hg_2Cl_2, AgCl - white

Group II Group II A Group II B	H_2S in dil HCl	Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+} As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}	Yellow-CdS,As_2S_3, As_2S_5 , SnS_2 Black - HgS, CuS, PbS Orange - Sb_2S_3, Sb_2S_5 Brown - Bi_2S_3 ,SnS
Group III A	NH_4OH in presence of NH_4Cl	Fe^{3+}, Al^{3+}, Cr^{3+}	$Fe(OH)_3$, $Al(OH)_3$,$Cr(OH)_3$ Brown White Green
GroupIII B	H_2S in presence of NH_3 & NH_4Cl or $(NH_4)_2S$.	Ni^{2+}, Co^{+2}, Mn^{+2}, Zn^{2+}	ZnS - white or grey, Black - CoS, NiS MnS - Buff (light pink)
Group IV	$(NH_4)_2CO_3$ in presence of NH_4Cl & NH_4OH.	Ba^{+2}, Sr^{2+}, Ca^{+2}	$BaCO_3$, $SrCO_3$, $CaCO_3$ - white
Group V	No common group reagent.	Mg^{+2}, Na^+, K^+, NH_4^+	¾

Group I (Pb^{2+}, Ag^+, Hg^+)

(A) $PbCl_2$ gives a yellow ppt. with K_2CrO_4. The ppt. is insoluble in acetic acid but soluble in NaO

(B) $PbCl_2 + 2KI \rightarrow PbI_2 + 2KCl$