QUALITATIVE & QUANTITATIVE ANALYSIS

PURIFICATION METHODS

Distillation Techniques :

Type	Conditions	Examples
(A) Simple distillation	(i) When liquid sample has non volatile impurities (ii) When boiling point difference is 80° K or more.	(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K) (ii) Mixture of Ether (BP = 308K) & Toluene (BP = 384K)
(B) Fractional distillation	When BP difference is 10°	(iii) Hexane (342K) and Toulene(384K) (i) Crude oil in petroleum industry (ii) Acetone (329) and Methyl alcohol(338K)
(C) Distillation under reduced pressure (Vacuum distillation)	When liquid boils at higher temperature and it may decompose before BP is attained.	(i) Concentration of sugar juice (ii) Recovery of glycerol from spent lye. (iii) Glycerol
(D) Steam distillation	When the substance is immiscible with water and steam volatile. $\underset{\text{Vapour pressure}}{P} = \underset{\text{Vapour pressure of Organic liquid}}{P_1} + \underset{\text{Vapour pressure of water}}{P_2}$	(i) Aniline is separated from water (ii) Turpentine oil (iii) Nitro Benzene (iv) Bromo Benzene (v) Naphthalene (vi) o-Nitrophenol

CHROMATOGRAPHY

This technique initially used to separate mixture of colour pigment found in plants so named given chromatography (greek word **chroma** = colour). Now a days this technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds.

In this technique, mixture of substances are applied on stationary phase which may be solid or liquid. A pure solvent, mixture of solvent or a gas is allowed to move slowly over stationary phase. The moving phase is called mobile phase. The component of the mixture get gradually separated from one another.

According to principle involved, chromatography is classified into category.

(i) Adsorption chromatography

Principle – adsorption

Adsorbate – Substances which are being purified

Adsorbent – Silica gel and alumina

(ii) Partition chromatography

Principle – Continuous differential partioning of components of a mixture between stationary and mobile phase.

	Adsorption chromatography		**Partition chromatography**
	a) Column chromatography	**b) Thin layer chromatography**	**Paper chromatography**
Stationary phase	Silica gel and alumina	Silica gel and alumina	Chromatography paper contain water trapped in it
Mobile phase	Eluant which is a liquid or a mixture of liquid	Liquid or a mixture of liquid	Liquid or a mixture of liquid
Process	Mobile phase flow from top to bottom in a column having stationary phase	Mobile phase flow from bottom to top over a thin layer of an adsorbent coated on glass plate	Mobile phase flow from bottom to top over chromatography paper

QUALITATIVE AND QUANTITATIVE ANALYSIS OF ORGANIC COMPOUND

Qualitative analysis : Detection of element present in compound :-

(i) Detection of C and H : Compound heated with cupric oxide and produced vapour is passes through lime water or anhydrous $CuSO_4$. If lime water turn milky, it shows presence of CO_2 or carbon.

If anhydrous $CuSO_4$ turn blue than it shows presence of H_2O or hydrogen.

$$\text{Compound} + CuO \xrightarrow{\Delta} CO_2 + H_2O + Cu$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milky}}{CaCO_3\downarrow} + H_2O$$

$$H_2O + \underset{\text{Colourless}}{CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4 . 5H_2O}$$

(ii) Detection of Nitrogen, Sulphur and halogen :- [Lassaigne's Test]

Preparation of lassaigne's solution or sodium extract.

Compound is heated with sodium in combustion tube and poured in cold water and heated for some time it gives lassaigne's solution or sodium extract.

In lassaigne solution elements present in compound get converted from covalent to ionic.

e.g $Na + C + N \longrightarrow NaCN$

$Na + S \longrightarrow Na_2S$

$Na + X \longrightarrow NaX$ (Ionic)

(i) Test of Nitrogen : Sodium extract is boiled with $FeSO_4$ which gives sodium hexacyano ferrate (II). Now few amount of $FeCl_3$ is added which gives prussian blue coloured ferro ferri cyanide that shows presence of Nitrogen.

$$6\ NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

$$Na_4[Fe(CN)_6] + FeCl_3 \longrightarrow \underset{\text{Prussian blue colour}}{Fe_4[Fe(CN)_6]_3} + NaCl$$

(ii) **Test of sulphur :** Sulphur is present in form of Na_2S

(a) Sodium Extract is acidified with acetic acid and lead acetate is added to it which gives black ppt of PbS and shows the presence of Sulphur

$$Na_2S + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + PbS(\text{Black})\downarrow$$

(b) **Nitroprusside test**

$$\text{Sodium extract} + \text{Sodium Nitroprusside} \longrightarrow \text{Violet colour.}$$

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS] \text{ (Violet colour)}$$

Note : If Nitrogen and sulphur both are present in compound then they form sodium thiocyanate in sodium extract.

$$Na + C + N + S \longrightarrow NaCNS$$

during test of Nitrogen in place of prussian blue, we get blood red colour of $Fe(CNS)_3$

$$3NaCNS + FeCl_3 \longrightarrow \underset{\text{(Blood Red)}}{Fe(CNS)_3} + 3HCl$$

Therefore sodium extract is prepared in presence of excess of sodium which decomposes sodium thiocyanate.

$$NaCNS + Na(\text{Excess}) \longrightarrow Na_2S + NaCN$$

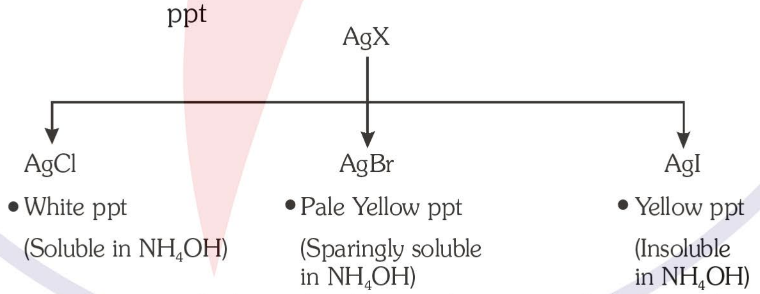
(iii) **Test of halogen :** Before the test of halogen sodium extract is boiled with conc. HNO_3 to decompose the Na_2S and NaCN in form of H_2S and HCN

$$Na_2S + \text{Conc. } HNO_3 \longrightarrow H_2S\uparrow$$

$$NaCN + \text{Conc. } HNO_3 \longrightarrow HCN$$

Now sodium extract is treated with silver nitrate which gives precipitate of AgX.

$$NaX + AgNO_3 \longrightarrow \underset{\text{ppt}}{AgX} + NaNO_3$$



(iv) **Test of phosphorous :** Compound is heated with an oxidising agent $[Na_2O_2]$ so the phosphorus in compound is converted in to phosphate which on further reaction with ammonium molybdate in presence of HNO_3 gives canary yellow ppt of ammonium phospho molybdate and shows the presence of phosphorus.

$$\text{Compound} + Na_2O_2 \longrightarrow Na_3PO_4$$

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\,HNO_3 \longrightarrow \underset{\text{(canary yellow)}}{(NH_4)_3PO_4 \cdot 12\,MoO_3} + 21\,NH_4NO_3 + 12\,H_2O$$

Quantitative analysis : Calculation of precentage of element in compound.

(i) Estimation of carbon and hydrogen : [Leibigs method]

A known mass of organic compound is burnt in presence of excess of CuO so carbon and hydrogen oxidise to CO_2 and H_2O respectively.

Now above vapour is passed through weighed u-tube having anhyd. $CaCl_2$ followed by KOH solution. anhyd. $CaCl_2$ absorbs H_2O while KOH absorbs CO_2.

Now we can calculate the amount of H_2O and CO_2 produced in combustion.

Calculation of % of C and H :-

If mass of organic compound is W gm.

mass of H_2O or CO_2 produced is m gm

For H $H_2O \equiv 2H$

18 2

$\therefore$ 18 gm of H_2O contains 2 gm of hydrogen

$\because$ 1 gm of H_2O contains $\frac{2}{18}$ gm of hydrogen

$\because$ m gm of H_2O contains $\frac{2}{18} \times$m gm of hydrogen

Precentage of hydrogen in W gm organic substance = $\boxed{\%\text{ of H} = \frac{2}{18} \times \frac{m}{W} \times 100}$

For C $CO_2 \equiv C$

44 gm 12 gm

$\because$ 44 gm CO_2 contain 12 gm carbon

1 gm CO_2 contain $\frac{12}{44}$ gm carbon

m gm CO_2 contain $\frac{12}{44} \times$m gm carbon

% of C in W gm organic substance = $\boxed{\%\text{ of C} = \frac{12}{44} \times \frac{m}{W} \times 100}$

Estimation of Nitrogen :

These are two method for the estimation of nitrogen

(i) Duma's method [in form of N_2]

(ii) Kjeldahl's method [in form of NH_3]

(1) Duma's method :

Organic compound is heated with CuO to give free Nitrogen, CO_2 and H_2O.

$$C_x H_y N_z + CuO \longrightarrow x\, CO_2 + \frac{y}{2} H_2O + \frac{z}{2} N_2 + Cu$$

Now the above mixture is collected over Aq. KOH in nitrometer tube which absorb all the gases except N_2. Now volume of nitrogen is calculated at STP.

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ V_1 = Volume of N_2 gas.

P_1 = Pressure of N_2 – Aqueous tension

T_1 = Room temperature

$$\boxed{V_2 = \frac{P_1V_1 \times 273}{T_1 \times 760}}$$

Calculation of % of Nitrogen

$\therefore$ 22400 ml of N_2 at STP weight = 28 gm

$\because$ V ml of N_2 at STP weight = $\frac{28}{22400} \times V$ gm

% of Nitrogen in W gm organic substance = $\boxed{\% \text{ of N} = \frac{28}{22400} \times \frac{V}{W} \times 100}$

(2) Kjeldahl's method : Compound containing nitrogen is heated with H_2SO_4 so compound gets converted in to ammonium sulphate.

Now above mixture is heated with excess of NaOH which liberates Ammonia gas.

Ammonia gas is absorbed in excess of standard solution of H_2SO_4.

The amount of ammonia produced is determined by estimating the amount of H_2SO_4 consumed.

Estimation of H_2SO_4 is done by titrating the H_2SO_4 left after absorption of ammonia with standard alkali solution.

The difference between the initial amount of acid taken and that left after absorption of ammonia is the amount of H_2SO_4 used.

Organic substance + $H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$$(NH_4)_2SO_4 + NaOH \longrightarrow Na_2SO_4 + 2NH_3\uparrow + H_2O$$

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

If Normality of H_2SO_4 taken = N_1

Volume of H_2SO_4 taken = V_1

If Normality of NaOH used = N_2

Volume of NaOH used = V_2

$\because$ Milli equivalent of H_2SO_4 used for neutralisation of produced NH_3 = $(N_1V_1 - N_2V_2)$

Which is equal to the milli equivalent of NH_3

$\because$ 1000 ml of 1N NH_3 contain 14 gm Nitrogen.

$\because$ $(N_1V_1 - N_2V_2)$ ml of 1N NH_3 contain $\frac{14}{1000} \times (N_1V_1 - N_2V_2)$ gm Nitrogen.

If mass of organic substance is W g.

Then % of N = $\frac{14}{1000} \times \frac{(N_1V_1 - N_2V_2)}{W} \times 100$

$\boxed{\% \text{ of } N = \frac{1.4}{W} \times (N_1V_1 - N_2V_2)}$ or $\boxed{\% \text{ of N} = \frac{1.4}{W} \times NV}$

N = Normality of H_2SO_4 V = Volume of H_2SO_4 used in neutralisation.

(3) Estimation of halogen : (by carius method)

A known mass of organic compound is heated with fuming HNO_3 in presence of $AgNO_3$. The halogen gets ppt in the form of AgX which can be filtered, washed and dried and weighed.

If mass of organic substance = W gm

mass of ppt = m gm

AgX	$\equiv$	X
[108 + atomic mass of X]		[Atomic mass of X]

mass of halogen in m gm AgX is $= \dfrac{\text{Atomic mass of X}}{\text{Molar mass of AgX}} \times m\ \text{gm}$

$$\boxed{\%\ \text{of halogen} = \frac{\text{Atomic mass of X}}{\text{Molar mass of AgX}} \times \frac{m}{W} \times 100}$$

(4) Estimation of sulphur : (by Carius method)

Sulphur is estimated in the form of $BaSO_4$.

Now ppt is filtered, washed, dried and weighed.

$BaSO_4$	$\equiv$	S
233 gm		32 gm

mass of sulphur in m gm ppt of $BaSO_4 = \dfrac{32}{233} \times m\ \text{gm}$

% of sulphur in W gm organic sub.

$$\boxed{\%\ \text{of S} = \frac{32}{233} \times \frac{m}{W} \times 100}$$

(5) Estimation of phosphorus : (by Carius method)

Phosphorus is estimated in the form of magnesium pyrophosphate ($Mg_2P_2O_7$)

$Mg_2P_2O_7$	$\equiv$	P_2
222 gm		31×2 gm

mass of sulphur in m gm $Mg_2P_2O_7$ is

$$\frac{62}{222} \times m\ \text{gm}$$

% of P in W gm organic sub.

$$\boxed{\%\ \text{of P} = \frac{62}{222} \times \frac{m}{W} \times 100}$$