05 Purification, Quantitative and Qualitative Analysis

Methods of purification of organic compounds :

- Organic compounds obtained either from natural source (or) synthesized in laboratory are contaminated with impurities.
- Various methods are used for removal of impurities from an organic compound depends on the nature of compound and type of impurities present in it.

Note:

Most of the pure compounds contain sharp Melting point and Boiling points.

1. Sublimation

- The process of conversion of sublimable solid to vapour state directly by heating without passing through liquid state is called sublimation.
- This method is used for purification of solids.
- Sublimation process is used for separation of sublimable volatile compounds from non sublimable impurities.
- Sublimation is generally used for purification of camphor, naphthalene, Anthracene, Benzoic acid, phthalic anhydride, Anthraquinone, Indigo, Iodine and solid SO_3.

2. Crystallisation

- Most commonly used technique for purification of solid organic compounds.
- Crystallisation is based on the difference in solubilities of the compound and impurities in a suitable solvent.
- The principle involved in this method is impure compound dissolved in a solvent is sparingly soluble at low temperature, but appreciably soluble at high temperature.
- Insoluble impurities are separated by filtration. The filtrate on cooling saturated solution, pure compound crystallises out.
- If a compound is highly soluble in one solvent and too little soluble in another solvent then crystallisation is carried out by using mixture of these solvents.
- Impurities, which impart colour are removed by adsorbing over activated charcoal.
- Repeated crystallisation is required if organic compound contains impurities of comparable solubilities.

3. Distillation

Distillation is an important method used to separate

(i) Volatile liquids from non-volatile impurities.

(ii) Liquids having sufficient difference in boiling points.

(a) Simple Distillation

- This process is used for purification of liquids which do not undergo decomposition at their boiling points
- The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation.
- Liquid mixture is taken in a round bottom flask and heated carefully, the vapour component with lower boiling point distills first, the vapour formed is condensed by using condenser and the liquid is collected in a receiver. The vapours of component with higher boiling point distills later.
- The liquids that have boiling point difference greater than 40°C can be purified by this method,

Example :

(i) Chloroform (BP. 334 K) and Aniline (B.P. 457 K)
(ii) Ether (B.P. 308 K) and Toluene (B.P. 384 K)
(iii) Benzene (B.P. 353 K) and Aniline (B.P. 457 K)

(b) Fractional Distillation

- Fractional distillation is used if the difference in boiling point of two liquids is less than 40° C.
- Vapours of liquid mixture are passed through fractionating column before condensation, which is fitted over mouth of the round bottom flask.
- Vapours of liquid with higher boiling point condense before the vapours of liquid with lower boiling point.
- The vapours raising up in the fractionating column is richer in more volatile component.
- Each successive condensation and vapourisation unit in the fractionating column is called a theoretical plate.
- Liquids forming a constant boiling mixture (azeotropic mixture) can not be separated by this method.
- Fractional distillation is used to separate different fractions of crude oil in petroleum industry.
- This method is used for separation of mixture of acetone (B.P. 330K) and methyl alcohol (B.P. 338K)

(c) Distillation under reduced pressure (Vacuum Distillation)

- This method is used to purify liquids having very high boiling points, which decompose at or below their boiling points.
- These liquids are made to boil at a temperature lower than their normal boiling point by reducing pressure on their surface with the help of vacuum pump.
- Glycerol can be separated from spent-lye in soap industry by using vacuum distillation.

(d) Steam Distillation

- This method is used for separation and purification of organic compounds (solids or liquids) which are steam volatile and are insoluble in water.
- In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel.

- In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. $p = p_1 + p_2$. Since p_1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point.
- Compounds which can be purified by steam distillation are aniline, nitrobenzene, o-nitrophenol.

4. Solvent Extraction (Differential Extraction)

- If an organic compound in aqueous medium is separated by mixing it in organic solvent in which it is more soluble than in water.
- Organic solvent should be immiscible with water.
- Organic solvent and aqueous solution are immiscible with each other, so they can form two distinct layers (which can be separated by separatory funnel).
- If organic compound is less soluble in organic solvent then large quantity of solvent is required to extract small quantity of compound, which is said to be continuous extraction.
- Benzoic acid can be extracted from its aqueous solution using benzene as solvent.

5. Chromatography

- This method is used for separation of mixtures into their components.
- Chromatography is obtained from the greek word "Chroma" means colour.
- This method was first used for separation of coloured substances found in plants.
- This technique have two phases

(i) Stationary phase: The mixture of substance is applied on this phase.

(ii) Mobile phase: A solvent or gas is allowed to move slowly over the stationary phase

- The component of mixture gets gradually separated from one another.
- Based on the principle involved chromatography is classified in to
  (a) Adsorption Chromatography and (b) Partition Chromatography

(a) Adsorption Chromatography

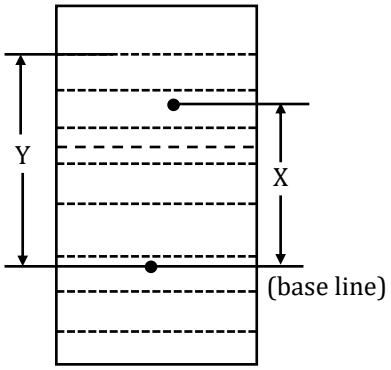
- Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents are silica gel, alumina.
- Adsorption chromatography is of two types
  (i) Column chromatography; (ii) Thin layer chromatography (TLC)

(i) Column Chromatography

- The mixture to be separated is placed at the top of the stationary phase.
- An appropriate eluent (solvent) is allowed to flow down the column slowly.
- The strongly adsorbed substances are retained near the top and others come down to various distances in the column.

(ii) Thin Layer Chromatography (TLC)

- A glass plate is coated with adsorbent (ex: silica gel, alumina) as a thin layer (about 0.2mm thick) is called chromatography plate or chroma plate.
- The solution of mixture to be separated is applied as small spot about 2cm above from one end of the TLC plate.
- The glass plate is placed in a closed jar containing the eluent. As the eluent rises up, the components of the mixture move up along the eluent to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e, Rf value.



$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- The spots of coloured compounds are visible on TLC plate due to their original colour.
- The colourless compound which fluoresce are detected with ultraviolet light.
- Amino acids are detected by spraying the plate with ninhydrin solution.

(b) Partition Chromatography

- Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography.
- A special quality paper known as chromatography paper, is used.
- Chromatography paper contains water (as a stationary phase).
- At the base of jar a suitable solvent act as mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.
- The paper selectively retains different component according to their differing partition in the two phases. The paper strip so developed is called chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.
- The spots of the separated colourless compound may be observed either under ultraviolet or by the use of appropriate spraying agent.

Quantitative Analysis :

Estimation of Carbon and Hydrogen

- CO_2 and H_2O produced are weighed by absorbing in concentrated solution of potassium hydroxide and anhydrous calcium chloride (or) magnesium perchlorate respectively

$$\%C = \frac{12}{44} \times \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of organic compound}} \times 100$$

$$\%H = \frac{2}{18} \times \frac{\text{Weight of } H_2O \text{ formed}}{\text{Weight of organic compound}} \times 100$$

Estimation of Nitrogen

- Nitrogen present in organic compound is estimated by
  (1) Dumas Method, (2) Kjeldahl's Method

(1) Dumas Method

- In this method nitrogen present in the organic compound is converted in to N_2 (molecular nitrogen)
- A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbondioxide.
- Carbon and hydrogen present in the compound are oxidised to CO_2 and H_2O, while N_2 is free.

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

- Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze
- The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs CO_2.
- Nitrogen is collected in the upper part of nitro meter.
- 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

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

- Calculations of % nitrogen

∵ 22400 ml of N_2 at STP weight = 28gm

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

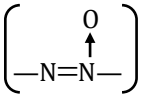
$$\%N_2 = \frac{28}{22400} \times \frac{V}{W} \times 100 \text{ ; W = Weight of organic substance}$$

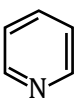
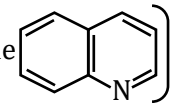
(2) Kjeldahl's Method

- In this method nitrogen in the organic compound is converted into ammonia (NH_3)
- A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of K_2SO_4 and $CuSO_4$ then nitrogen present in the compound is converted into ammonium sulphate. K_2SO_4 increases boiling point of H_2SO_4 and $CuSO_4$ acts as catalyst.
- Organic compound + $H_2SO_4 \longrightarrow (NH_4)_2SO_4$
- The resulting solution is distilled with excess of sodium hydroxide
  $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$
- Ammonia gas is absorbed in excess of standard solution of H_2SO_4.
  $NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
- The amount of ammonia produced is determined by estimating the amount of H_2SO_4 consumed.
  Normality of H_2SO_4 taken = N_1
  Volume of H_2SO_4 taken = V_1
- Estimation of H_2SO_4 is done by titrating the H_2SO_4 left after absorption of ammonia with standard alkali solution.
  Normality of NaOH taken = N_2
  Volume of NaOH taken = V_2
- The difference between the initial amount of acid taken and that left after absorption of ammonia is the amount of H_2SO_4 used.
- ∵ Milli equivalent of H_2SO_4 used for neutralization of Produced NH_3
  = Milli equivalent of NH_3
  = $(N_1V_1 - N_2V_2)$
- ∵ 1000 ml of 1N NH_3 contain 14 gm Nitrogen

  ∵ $(N_1V_1 - N_2V_2)$ ml of 1N NH_3 contain = $\frac{14}{1000} \times (N_1V_1 - N_2V_2)$ gm N_2

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

  Then % of N = $\frac{1.4}{W} \times (N_1V_1 - N_2V_2)$; mass of organic substance is W g.
- This method is not applicable to compounds containing nitro ($-NO_2$), Nitroso (NO), azo group ($-N=N-$), azoxy compounds  and nitrogen present in the ring

  (pyridine  , quinoline )

  because nitrogen present in these compounds is not quantitatively converted into ammonium sulphate.

Estimation of Halogens (Carius Method) :

- A weighed amount of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube.
- Carbon and hydrogen present in the compound is converted into CO_2 and H_2O.
- Halogen present in the organic compound is converted into silver halide.
- The precipitate is washed, dried and weighed

$$\text{Percentage of halogen} = \frac{\text{atomic weight of halogen}}{\text{Mol weight of silver halide}} \times \frac{\text{Weight of silver halide formed}}{\text{weight of organic compound}} \times 100$$

$$\%\,Cl = \frac{35.5}{143.5} \times \frac{\text{Weight of AgCl formed}}{\text{weight of organic compound}} \times 100$$

$$\%\,Br = \frac{80}{188} \times \frac{\text{Weight of AgBr formed}}{\text{weight of organic compound}} \times 100$$

$$\%\,I = \frac{127}{235} \times \frac{\text{Weight of AgI formed}}{\text{weight of organic compound}} \times 100$$

Estimation of Sulphur

- A weighed amount of organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised into sulphuric acid, which is treated with $BaCl_2$ solution and gives precipitate of $BaSO_4$.
- It is filtered, the precipitate is washed, dried and weighed.

$$\%\,S = \frac{\text{Atomic weight of Sulphur}}{\text{Mol. weight of } BaSO_4} \times \frac{\text{Weight of } BaSO_4 \text{ formed}}{\text{weight of organic compound}} \times 100$$

$$\%\,S = \frac{32}{233} \times \frac{\text{Weight of } BaSO_4 \text{ formed}}{\text{weight of organic compound}} \times 100$$

Estimation of Phosphorus

- A weighed amount of organic compound is heated with fuming nitric acid, then phosphorus present in the compound is oxidised to phosphoric acid. Phosphoric acid is precipitated as magnesium ammonium phosphate (NH_4MgPO_4), by addition of magnesia mixture ($MgCl_2 + NH_4OH + NH_4Cl$).
- Magnesium ammonium phosphate is washed, dried and it is heated strongly to get magnesium pyrophosphate ($Mg_2P_2O_7$).

$$H_3PO_4 \xrightarrow{\text{Magnesia mixture}} MgNH_4PO_4$$

(Phosphoric acid) **(Magnisium ammonium phosphate)**

$$2MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$$

(Magnesium pyrophosphate)

$$\%\,P = \frac{62}{222} \times \frac{\text{Weight of } Mg_2P_2O_7 \text{ formed}}{\text{weight of organic compounds}} \times 100$$

Estimation of Oxygen

- The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements.
- However, oxygen can also be estimated directly as follows:

  A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

  Compound $\xrightarrow{\text{heat}}$ O_2 + other gaseous products

  $2C + O_2 \xrightarrow{1373\ K} 2CO \times 5$ (A)

  $I_2O_5 + 5CO \xrightarrow{1373\ K} I_2 + 5CO_2 \times 2$ (B)

  Percentage of oxygen = $\frac{32 \times m_1 \times 100}{88 \times m}\%$ m_1 = mass of carbon dioxide

  m = mass of organic compound
- The percentage of oxygen can be derived from the amount of iodine produced also.

Qualitative Analysis of Organic Compounds (Detection of elements) :

- The qualitative analysis of an organic compound involves detection of all elements present in it.

Detection of Carbon and Hydrogen

- Carbon and hydrogen are detected by heating the compound with cupric oxide (CuO).
- Carbon present in the compound is oxidised to carbondioxide, which turns lime water milky.

  $C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

  $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$
- Hydrogen present in the compound is converted into water, which turns anhydrous copper sulphate into blue.

  $H_2 + CuO \xrightarrow{\Delta} Cu + H_2O$

  $CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$

  Anhydrous (Colourless) **Hydrated (Blue)**

Detection of Nitrogen, Sulphur Halogens and Phosphorus

- Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.
- Organic compounds are fused with dry sodium in fusion tube and Na fusion extract is obtained.
- The following reactions takes place

  $Na + C + N \xrightarrow{\Delta} NaCN$

  $2Na + S \xrightarrow{\Delta} Na_2S$

  $2Na + X_2 \xrightarrow{\Delta} 2NaX$ **(X=Cl, Br or I)**

(1) Test for Nitrogen

- Sodium fusion extract is boiled with freshly prepared ferrous sulphate ($FeSO_4$) solution and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.

$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]_3 + Na_2SO_4$

$FeSO_4 + H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3$

$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN_6)_3 + 6Na_2SO_4$

Ferriferrocyanide

(Prussian Blue)

- This test fails in case of diazo compounds. **(—N≡N—)**

(2) Test for Sulphur

(i) Sodium fusion extract is reacted with lead acetate, a black precipitate of lead sulphide is formed, which indicates presence of sulphur.

$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS\downarrow + 2CH_3COONa$

Black

(ii) Sodium fusion extract is treated with freshly prepared sodium nitroprusside, appearance of violet colour (purple) indicates presence of sulphur.

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

(Sodium Nitro Prusside) **(Violet)**

- In case both nitrogen and sulphur are present in an organic compound sodium thiocyanate is formed, which gives blood red colour with Fe^{+3}.

$Na + C + N + S \longrightarrow NaCNS$ **(Sodium fusion)**

$Fe^{+3} + SCN^- \longrightarrow [Fe(SCN)]^{+2}$ **(No Prussian blue means no free CN^-)**

(Blood red)

- If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide, these ions gives their usual tests.

$NaSCN + 2Na \longrightarrow NaCN + Na_2S$

(3) Test for Halogens

- Sodium fusion extract is acidified with nitric acid and then treated with silver nitrate solution.
- White precipitate, soluble in ammonium hydroxide indicates presence of chlorine.

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

(White ppt)

$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2Cl] + 2H_2O$

(Soluble complex)

$NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$

(Yellow ppt)

(Sparingly Soluble in NH_4–OH)

$NaI + AgNO_3 \longrightarrow AgI\downarrow + NaNO_3$

(Yellow precipitate)

(Insoluble in NH_4OH)

(4) Test for Phosphorus

- The compound is heated with oxidising agent (sodium peroxide) phosphorus present in the compound is oxidised to sodium phosphate.
- The solution is boiled with nitric acid and then treated with ammonium molybdate, a canary yellow (ammonium phospho molybdate) precipitate formation indicates presence of phosphorus.

$2P + 5Na_2O_2 \xrightarrow{\Delta} 2Na_3PO_4 + 2Na_2O$

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

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$

BEGINNER'S BOX-1

1. 0.3960 gm of an organic compound on combustion gives 0.792 gm CO_2 and 0.324 gm of H_2O. Calculate the % of C and H

(1) 54.55% and 9.09% (2) 9.09% and 54.55%

(3) 35% and 65% (4) 65% and 35%

CEC098

2. 0.25 gm of an organic compound at NTP gives 31 ml of N_2 gas by Duma's method. Find out of % of N

(1) 14.5 (2) 15.5 (3) 16.5 (4) 20.5

CEC099

3. 31.7 ml of moist N_2 was obtained from 0.2033 gm of an organic compound in Duma's method at 14°C and 758 mm pressure. If aq. tension at 14°C = 14 mm than calculate % of N

(1) 15% (2) 18% (3) 25% (4) 30%

CEC100

4. 30 ml 0.25 N H_2SO_4 are used in neutralizing NH_3 obtained from 0.75 gm of an organic compound in Kjeldhal's method find out % of N in the compound

(1) 7% (2) 14% (3) 21% (4) 28%

CEC101

5. In Kjeldhal's method, NH_3 evolved from 0.25 gm of an organic compound was passed into 30 ml N/2 H_2SO_4. 50 ml N/10 NaOH were required to neutralize the unreact acid, calculate % of N.

(1) 14% (2) 28% (3) 42% (4) 56%

CEC102

6. 0.35 gm of an organic compound was analysed by Kjeldhal's method. Ammonia evolved was absorbed in 100 mℓ $\frac{N}{10}$ H_2SO_4. Unused acid required 30 mℓ $\frac{N}{10}$ NaOH for neutralisation calculate % of N

(1) 28% (2) 14% (3) 56% (4) 42%

CEC103

7. In Duma's method estimation of nitrogen, 0.3g of an organic compound gave 50 ml of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K = 15 mm)

(1) 10.46% (2) 17.46% (3) 27.46% (4) 35.46%

CEC104

8 During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mℓ of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

(1) 24% (2) 42% (3) 56% (4) 28%

CEC105

9. In carius method of estimation of halogen, 0.15g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

(1) 34% (2) 51% (3) 17% (4) 25%

CEC106

10. In sulphur estimation, 0.157g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound ?

(1) 21.1% (2) 52.1% (3) 42.1% (4) 31.1%

CEC107

BEGINNER'S BOX ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	**1**	**2**	**2**	**2**	**4**	**1**	**2**	**3**	**1**	**3**