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CHAPTER

purification & analysis

- Purification means the removal of undesirable impurities associated with a particular organic compound, *i.e.*, to obtain the organic compound in pure state.
- The method applied to purify a definite compound depends on the nature of the organic compound and the impurities present in it.
- Some important methods of purification are as follows:

(i) Crystallisation
  (a) Simple crystallisation
  (b) Fractional crystallisation

(ii) Sublimation
(iii) Distillation
  (a) Simple distillation
  (b) Fractional distillation
  (c) Vacuum distillation
  (d) Steam distillation
(iv) Solvent extraction
(v) Chromatography
  (a) Column or Adsorption chromatography
  (b) Thin layer chromatography
  (c) Paper chromatography
  (d) Gas chromatography
  (e) Ion-exchange chromatography.

	Type of chromatogaphy	**Mobile/ Stationary Phase**	**Uses**
1.	Adsorption or column chromatography	Liquid/Solid	Large scale separations
2.	Thin-layer chromatography	Liquid/Solid	Qualitative analysis (identi-fication and characterisation of organic compounds)
3.	High performance liquid chromatography	Liquid/Solid	Qualitative and quantitative analysis
4.	Gas-liquid chromatography (GLC)	Gas/Liquid	Qualitative and quantitative analysis
5.	Paper or Partition chromatography	Liquid/Liquid	Qualitative and quantitative analysis of polar organic compounds (a-amino acids, sugars and inorganic compounds)

- Simple crystallisation involves selection of a solvent in which the given substance is more soluble at higher temperature than at room temperature. In addition to water various other solvents like alcohol, ether, benzene, CCl_4 etc. are used for crystallisation.
- Fractional crystallisation is the process of separation of different components of a mixture by repeated crystallizations.
- Fractional crystallisation is carried out to separate organic solids having small difference in their solubilities in suitable solvent.
- Sublimation involves separation of volatile substance from non-volatile solids by heating.
- Simple distillation is used when the boiling point of the components differ widely (30°-50°C).
- If the boiling points of the two liquids of a mixture are very close *i.e.* differ by (10°-15°C) fractional distillation is done to separate the mixture.
- Petroleum and its components are separated by fractional distillation.
- Fractionating column is used to increase the cooling surface area and obstruct the path of ascending vapours and descending liquid in fractional distillation.
- Azeotropes are constant boiling mixtures so they are separated by azeotropic distillation.
- Normal boiling point of a liquid is that temperature at which its vapour pressure is equal to atmospheric pressure. If atmospheric pressure is reduced the liquid will boil earlier than its normal boiling point. This principle is used in the purification of those compounds which decompose at their normal boiling points, i.e., by carrying out distillation under reduced pressure.
- The process of separation of an organic compound from its aqueous solution by shaking with a suitable organic solvent is termed solvent extraction. The solvent should be immiscible with water and the organic compound to be separated should be highly soluble in it.
- A mixture of *o*-hydroxyacetophenone and *p*-hydroxy-acetophenone can be separated by steam distillation as *o*-hydroxyacetophenone due to chelation is steam volatile but due to intermolecular H-bonding *p*-hydroxyacetophenone is not.
- Tswett discovered chromatography in which the separation and purification is brought about by the differential movement of the individual components of a mixture through a stationary phase under the influence of a mobile phase.
- Column chromatography is based upon differential adsorption - desorption of different components of mixture.
- The technique of gas chromatography is suitable for compounds which vapourize without decomposition.
- In Lassaigne's test, the organic compound is fused with a piece of sodium metal to convert covalent compounds into ionic compounds (NaCN, Na_2S, NaX).
- In the Lassaigne's test for detection of nitrogen in an organic compound the blue colour is due to the formation of ferricferrocyanide, $Fe_4[Fe(CN)_6]_3$.
- A violet colour with sodium nitroprusside is the test for sulphur, is due to the formation of $Na_4[Fe(CN)_5NOS]$.

- Copper wire test for halogens is known as Beilstein test.
- Beilstein's test is not given by fluorine since cupric fluoride is not volatile.
- A freshly prepared $FeSO_4$ solution is used in Lassaigne's test for nitrogen as on keeping $FeSO_4$ solution oxidises to basic ferric sulphate and cannot be used for detection.
- Siwolowoff's method for determining the boiling point of liquid is used when the amount of liquid available is small.
- Sometimes crystallisation can be induced by adding a few crystals of the pure substance to the concentrated solution. This is called as seeding.
- Lithium is not used in Lassaigne's test since it reacts slowly and its compounds are generally covalent. Potassium can also not be used since it reacts evidently and cannot be handled.

Qualitative analysis of organic compounds

- ***Detection of carbon and hydrogen*** **:**

  A small amount of dry organic compound containing carbon and hydrogen are oxidised by cupric oxide to carbon dioxide and water respectively.

  $C + 2CuO \longrightarrow 2Cu + CO_2$ (turns lime water milky)

  $H_2 + CuO \longrightarrow Cu + H_2O$ (turns anhydrous $CuSO_4$ blue)

- ***Lassaigne's test :*** In Lassaigne's test, the organic compound (containing N, S, halogen) is fused with sodium metal as to convert these elements into ionisable inorganic substances.

Elements	**Sodium salt of ions in Lassaigne's extract**
N	NaCN
S	Na_2S
Both N and S	NaCNS
Halogen (X)	NaX

- ***Detection of nitrogen*** **:**

  $2NaCN + FeSO_4 \longrightarrow Fe(CN)_2 + Na_2SO_4$

  $Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$

  $4Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

- ***Detection of sulphur*** **:**

  (i) $Na_2S + \underset{\text{sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet}}{Na_4[Fe(CN)_5NOS]}$

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

- ***Detection of nitrogen and sulphur together*** **:**

  $3NaCNS + FeCl_3 \longrightarrow \underset{\text{blood red colour}}{Fe(CNS)_3} + 3NaCl$

  Note : This test fails in case of diazo compounds.

- ***Detection of halogen*** **:** $AgNO_3$ test :

$$NaX + \text{conc. } HNO_3 + AgNO_3$$

white ppt. soluble in aq. $NH_3 \rightarrow$ chlorine	yellow ppt. partially soluble in aq. $NH_3 \rightarrow$ bromine	yellow ppt. insoluble in aq. $NH_3 \rightarrow$ iodine

Note: From colour of AgBr and AgI, it is difficult to judge whether one organic compound contains bromine or iodine. To confirm their presence, the filtrate is supplemented by chlorine water test (layer test). To acidified filtrate 1 ml of $CHCl_3$ or CCl_4 is added followed by addition of excess of chlorine water with constant shaking. If chloroform layer becomes yellow or brown, bromine is present and if violet, iodine is present. *Beilstein test* or copper wire test is also used to detect halogens.

Quantitative analysis of organic compounds

- ***Estimation of carbon and hydrogen - Leibig's method***

$$C_xH_y + \underset{\text{excess}}{O_2} \longrightarrow xCO_2 + y/2\ O_2$$

$$\% \text{ of carbon} = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of organic compound}} \times 100$$

$$\% \text{ of hydrogen} = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of organic compound}} \times 100$$

- ***Estimation of nitrogen:***

(i) *Duma's method* : In this method a nitrogen containing compound is strongly heated with cupric oxide in the atmosphere of CO_2 to get free nitrogen along with CO_2 and water.

$$C_xH_yN_z + CuO \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + Cu$$

$$\% \text{ of nitrogen} = \frac{28}{22400} \times \frac{\text{vol. of } N_2 \text{ collected at N.T.P. in c.c}}{\text{wt. of organic compound}} \times 100$$

(ii) *Kjeldahl's method* : In this method nitrogen containing compound is heated with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is estimated volumetrically. The percentage of nitrogen is then calculated from the amount of ammonia evolved.

$$\% \text{ of nitrogen} = \frac{1.4 \times \text{vol. of acid used in ml} \times \text{normality of acid}}{\text{wt. of organic compound}}$$

- ***Estimation of halogens - Carius method:*** A weighed amount of the organic compound is heated with fuming HNO_3 in Carius tube containing few crystals of $AgNO_3$. Halogen present in the compound is converted into insoluble AgX which is separated and weighed.

$$X + AgNO_3 + \text{conc. } HNO_3 \longrightarrow AgX$$

$$\% \text{ of } X = \frac{\text{At. mass of } X}{108 + \text{At. mass of } X} \times \frac{\text{wt. of } AgX}{\text{wt. of org. compound}} \times 100$$

Determination of molecular mass

- **Physical methods:**

(A) ***For volatile compound*** **:**

(i) *Victor Meyer's method*

$$\text{Molecular mass of substance} = \frac{\text{wt. of organic compound} \times 22400}{\text{volume of vapours obtained}}$$

(ii) *Duma's method*

$$\text{Molecular mass of substance} = \frac{\text{mass of vapours} \times 22400}{\text{volume of vapours at N.T.P.}}$$

(B) ***For non-volatile compounds*** **:**

(i) *Depression of freezing point*

$$\text{Molecular mass of substance} = \frac{\begin{array}{c}1000 \times \text{molar depression constant of} \\ \text{pure solvent} \times \text{wt. of solute}\end{array}}{\text{wt. of solvent} \times \text{depression in freezing point}}$$

(ii) *Elevation in boiling point*

$$\text{Molecular mass of substance} = \frac{\begin{array}{c}1000 \times \text{molal elevation constant of} \\ \text{pure solvent} \times \text{wt. of solute}\end{array}}{\text{wt. of solvent} \times \text{elevation in boiling point}}$$

- **Chemical methods:**

(i) *Silver salt method for organic acids* :

$$R - COOH \longrightarrow R - COOAg \xrightarrow{\Delta} Ag$$

$$\text{Molecular wt. of acids} = \left(\frac{\text{wt. of silver salt} \times 108}{\text{wt. of metallic silver}} - 107\right) \times \text{basicity of acid}$$

(ii) *Platinum chloride method for organic bases*

$$B + HCl \longrightarrow B \cdot HCl$$

$$2B \cdot HCl + PtCl_4 \longrightarrow B_2H_2PtCl_6 \xrightarrow{\Delta} Pt$$

$$\text{Molecular weight of base} = \frac{1}{2}\left(\frac{\text{wt. of platinum salt} \times 195}{\text{wt. of platinum}} - 410\right) \times \begin{array}{c}\text{acidity of} \\ \text{the base}\end{array}$$

(iii) *Titration method for organic acids and organic bases*

$$\text{Equivalent weight of acid} = \frac{\text{wt.of acid} \times 1000}{\text{normality of alkali} \times \text{vol. of alkali used for end point}}$$

Molecular weight of acid = Eq. wt. of acid × basicity

Similarly,

$$\text{Equivalent weight of base} = \frac{\text{weight of base} \times 1000}{\text{normality of acid} \times \text{vol. of acid used for end point}}$$

Molecular wt. of base = Eq. wt. of base × acidity

- *Empirical formula* : The formula of a compound which gives the simplest whole number ratio of the atoms of various elements present in one molecule of the compound is called empirical formula of the compound.
- *Molecular formula* : The formula of a compound which gives the actual ratio of the atoms of various elements present in one molecule of the compound is called the molecular formula of the compound.

- Molecular formula = n × empirical formula, where $n = 1, 2, 3, ...$
- Molecular weight = 2 × vapour density.
- All compounds containing an odd number of nitrogen atoms (*i.e.* 1, 3, 5, ...) have odd masses and those with even number of nitrogen atoms (*i.e.* 2, 4, 6, ...) have even masses. This is called **nitrogen rule**.
- Empirical formula of a compound represents simplest ratio of atoms.
- Molecular formula of a compound represents actual number of atoms of the various atoms present in one molecule.
  Molecular formula = n × empirical formula
- Eudiometry is a direct method for determination of molecular formula of gaseous hydrocarbons without determining the percentage composition of various elements in it and without knowing the molecular weight of the hydrocarbon.
- A mixture of benzene (b.p. 80°C) and chloroform (b.p. 61.5°C) is separated by distillation (fractional distillation) as their boiling points are close.
- Since alcohol and water form a constant boiling mixture (azeotrope) therefore absolute alcohol is prepared by azeotropic distillation.
- Human hair on heating strongly with soda-lime smells of ammonia as they contain amino acids.
- Sugar can be separated by using paper chromatography.
- On adding $FeCl_3$ solution to acidified Lassaigne's extract a blood red colouration is produced due to the formation of ferric thiocyanate or sulphocyanide, $Fe(CNS)_3$ indicates the presence of N and S.
- Aniline is purified by steam distillation as it is steam volatile.
- Equivalent weight of an acid is equal to molecular weight/basicity.
- Molecular mass of a volatile substance can be obtained by Victor-Meyer's method.
- Anhydrous copper sulphate is used to test the presence of water in a liquid as anhydrous $CuSO_4$ turns blue in presence of water.

$$\underset{\text{white}}{CuSO_4} + 5H_2O \rightarrow \underset{\text{blue}}{CuSO_4 \cdot 5H_2O}$$

- Thiophene can be removed from commercial benzene by shaking it with concentrated H_2SO_4.
- In Kjeldahl's method, during digestion, the nitrogen of the organic compound is converted into $(NH_4)_2SO_4$.
- Fusion of organic compound with fusion mixture ($Na_2CO_3 + K_2CO_3$) converts phosphorus into Na_3PO_4.
- For the detection of phosphorus, the organic compound after fusion with Na_2O_2 is extracted with water, boiled with HNO_3 and then ammonium molybdate is added to it we get the yellow precipitate of ammonium phosphomolybdate.
- In organic compounds phosphorus is estimated as magnesium pyrophosphate, $Mg_2P_2O_7$.
- The Lassaigne's extract is boiled with dilute HNO_3 before testing for halogen because Na_2S and NaCN are decomposed by HNO_3 otherwise Na_2S will give black ppt. of Ag_2S and NaCN will give white ppt. of AgCN which would interfere with the test of halogens.

- In Kjeldahl's method for estimation of nitrogen, K_2SO_4 is added to raise the boiling point of H_2SO_4 to ensure complete conversion of nitrogen into $(NH_4)_2SO_4$ while $CuSO_4$ or mercury is added to catalyse the above conversion.
- Steam distillation can be regarded as analogous to distillation under reduced pressure.
- Messenger's method is used for estimation of sulphur. In this method, the organic compound is heated with alkaline $KMnO_4$ solution when sulphur of the organic compound is oxidised to K_2SO_4 which is estimated as $BaSO_4$.
- Alkaline solution of pyragallol *i.e.* 1,2,3-trihydroxy benzene is used to absorb oxygen.
- Soxhlet extractor is used for continuous extraction of organic compounds with a minimum amount of organic solvent.
- Lassaigne's test for the detection of nitrogen will fail in case of $\mathbf{H_2N \cdot NH_2 \cdot 2HCl}$ because for Lassiagne's test of N, compound must contain N in addition to carbon, so that NaCN can be formed in sodium extract.
- Azo compounds does not give a positive Lassaigne's test for N as azo compounds on moderate heating lose N_2, before the sodium melts in preparation of sodium extract.
- **Organic compounds** are studied separately from others, because of the special characteristics of carbon compounds like catenation, formation of compounds both with electropositive and electronegative elements and their tendency to show isomerism.
- The most suitable method of separation of 1 : 1 mixture of ortho and para nitrophenols is **distillation** as para nitrophenol has higher boiling point due to H-bonding.
- Phenol is soluble in **NaOH solution** because of their weakly acidic behaviour.
- Carbon shows maximum capacity of catenation because **C–C bond strength is very high.**
- A mixture of camphor and benzoic acid can be separated by **chemical methods** as both possess the sublimation nature; benzoic acid reacts with alkalies, whereas camphor does not.
- The function of boiling the sodium extract with conc. HNO_3 before testing for halogens is **to destroy CN^- and S^{2-} ions which will otherwise give ppt.**
- **Simple distillation** can be used to separate a mixture of ether (b. pt. 35ºC) and toluene (b.pt. 110ºC) as simple distillation is used when the boiling point of two components differ widely (30°-50°C).
- When petroleum is heated gradually, first batch of vapours evolved will be rich in **petroleum ether.**
- For detection of sulphur in an organic compound, sodium nitroprusside is added to the sodium extract. A violet colour is obtained due to the formation of $\mathbf{Na_4[Fe(CN)_5NOS]}$, (sodium thionitroprusside).
- Raw juice in sugar factories is generally concentrated by **vacuum distillation** as at low pressure boiling point is lowered and evaporation of water becomes more fast.
- Turpentine oil can be purified by **steam distillation** as it is steam volatile.
- To determine the weight of halogen in the organic compound, the compound is heated with fuming HNO_3 in presence of $\mathbf{AgNO_3}$ which gives precipitation of silver halides.

- Salts can be obtained from a concentrated sea water by **crystallisation** as crystallisation of conc. solution separates out salts.
- Silica gel is used for keeping away the moisture because it **adsorbs H_2O.**
- Anhydrous $CaCl_2$ is used as drying agent because it **absorbs water molecules.**
- **Lavoisier** is called the father of Chemistry.
- If an organic compound contains C, H and S. When C and H are to be estimated the combustion tube at the exit should contain a **lead chromte.**
- If the compound contains C, H and halogen. When C and H are to be estimated the combustion tube at the exit should contain a **silver spiral.**
- The technique of gas chromatography is suitable for compounds which are **vaporised without decomposition.**
- Generally it is more difficult to purify organic compounds than inorganic compounds because **physical constants of organic compounds and the impurities associated with them are very close to each other.**
- **Sublimation** cannot be used for purification of liquids because sublimation is the process involving direct conversion of a solid species to gaseous phase.
- When sodium extract is prepared, generally the substance ignites **H_2** as hydrogen of organic compound ignites.
- First systematic classification of naturally occurring compounds was given by **Lemery.**
- **Na metal** is most commonly used to dry organic liquids.
- An Azeotropic mixture of ethanol and water is first treated with **anhydrous lime and C_6H_6** before subjecting for fractional distillation to separate them as anhydrous lime or C_6H_6 disturbs the nature of azeotropic mixture of alcohol and water.
- There is no test (Direct) for the detection of **O** in an organic compound.
- The latest technique used for the purification of organic compounds containing minute quantities is **chromatography.**
- Boiling point of a liquid can be increased by **increasing the pressure** because liquids boil above boiling point if atmospheric pressure is higher than 1 atm.
- The substance used as an adsorbent in the column chromatography is **Al_2O_3.**
- The sodium extract of organic compound containing sulphur on acidification with acetic acid and them adding lead acetate solution gives a black precipitate.
- Organic compound + CaO + Na_2CO_3 $\xrightarrow[\text{a Pt. crucible}]{\text{heat in}}$ Cool the solution and add dil. HNO_3

  and then $AgNO_3$. A precipitate of AgX is dried and weighed and the percentage of halogen is obtained as usual. This is Schiffs and Piria method used for the estimaion of **halogens.**

End