Purification and Characterization of Organic Compounds

Purification of organic compounds: A large number of methods are available for the purification of substances

(i) ***Simple crystallisation*: ** This is the most common method used to purify organic solids. It is based upon the fact that whenever a crystal is formed, it tends to leave out the impurities.

(ii) ***Fractional crystallisation*: ** The process of separation of different components of a mixture by repeated crystallisations is called fractional crystallisation.

(iii) ***Sublimation*: ** Certain organic solids on heating directly change from solid to vapour state without passing through a liquid state, such substances are called *sublimable* and this process is called *sublimation.*

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapour}$$

(iv) ***Steam distillation*: ** This method is applicable for the separation and purification of those organic compounds (solids or liquids) which (a) are insoluble in water (b) are volatile in steam (c) possess a high vapour pressure (10-15 *mm Hg*) at 373 *K* and (d) contain non-volatile impurities.

(vii) ***Azeotropic distillation*****:** Azeotropic mixture is a mixture having constant boiling point. The most familiar example is a mixture of ethanol and water in the ratio of 95.87 : 4.13 (a ratio present in rectified spirit). It boils at 78.13^oC.

Types of chromatography: Depending upon the nature of the stationary and the mobile phases, the different types of chromatographic techniques commonly used are in a given table,

Type of Chromatography	Mobile/Stationary Phase	Uses
Adsorption or column chromatography	Liquid/Solid	Large scale separations
Thin-layer chromatography	Liquid/Solid	Qualitative analysis (identification and characterization of organic compounds)
High performance liquid	Liquid/Solid	Qualitative and quantitative analysis

chromatography		
Gas-liquid chromatography (GLC)	Gas/Liquid	Qualitative and quantitative analysis
Partition chromatography or ascending paper chromatography	Liquid/Liquid	Qualitative and quantitative analysis of polar organic compounds (sugars, α-amino acids and inorganic compounds)

Qualitative analysis:

Carbon is an essential component of an organic compound. The following method is known as the copper oxide test.

$$C + 2CuO \xrightarrow{\text{Heat}} CO_2 + 2Cu \;;$$

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

$$H_2 + CuO \xrightarrow{\text{Heat}} H_2O + Cu \;;$$

$$\underset{\substack{\text{Colourles s}\\ \text{(Anhydrous)}}}{CuSO_4} + 5H_2O \longrightarrow \underset{\substack{\text{Blue}\\ \text{(Hydrated)}}}{CuSO_4.5H_2O}$$

Lassaigne method

This is used to detect nitrogen, halogen and sulphur.

Lassaigne method (Detection of elements)

Element	**Sodium Extract (S.E.)**	**Confirmed Test**	***Reaction***
Nitrogen	$Na + C + N \xrightarrow{\Delta} \underset{\text{(S.E.)}}{NaCN}$	S.E.+ $FeSO_4$ + NaOH , boil and cool + $FeCl_3$ + conc.HCl Blue or green colour	$2NaCN + FeSO_4 \longrightarrow Fe(CN)_2 + Na_2SO_4$ $Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{Sodium ferrocyanide}}{Na_4[Fe(CN)_6]}$ $3Na_4[Fe(CN)_6] + 4FeCl_3 \xrightarrow{HCl} \underset{\substack{\text{Ferric ferrocyanide} \\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$
Sulphur	$2Na + S \xrightarrow{\Delta} \underset{\text{(S.E.)}}{Na_2S}$	(i) S.E. + sodium nitro prusside (ii) S.E+ $CH_3CO_2H + (CH_3CO_2)_2Pb$ A black ppt.	(i) $Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{(Purple)}}{Na_4[Fe(CN)_5NO.S]}$ or $\underset{\substack{\text{Sodium thionitroprusside} \\ \text{(Violet)}}}{Na_3[Fe(ONSNa)(CN)_5]}$ (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} \underset{\text{black ppt.}}{PbS \downarrow} + 2CH_3COONa$
Halogen	$Na + X \xrightarrow{\Delta} \underset{\text{(S.E.)}}{NaX}$ (*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.*	$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{\text{ppt}}{AgX \downarrow}$ $\underset{\text{White ppt}}{AgCl} + 2NH_3(aq) \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl}$ $\underset{\text{Yellow ppt.}}{AgBr} + 2NH_3(aq) \rightarrow \underset{\text{Partially soluble}}{[Ag(NH_3)_2]Br}$ $AgI + NH_3(aq) \longrightarrow$ Insoluble
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} \underset{\text{(S.E.)}}{NaCNS}$ with excess of *Na* the thiocyanate formed decomposes into cyanide and sulphide. $NaCNS + 2Na \rightarrow NaCN + Na_2S$	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric sulphocyanide} \\ \text{(Blood red colour)}}}{[Fe(SCN)_3 \text{ or } [Fe(SCN)]Cl_2} + 3NaCl$

Calculation of Empirical and Molecular formula

(i) ***Empirical formula***: *Empirical formula of a substance gives the simplest whole number ratio between the atoms of the various elements present in one molecule of the* *substance*. For example, empirical formula of glucose is CH_2O, *i.e.* for each carbon atom, there are two *H*-atoms and one oxygen atom. Its molecular formula is however, $C_6H_{12}O_6$.

(ii) ***Molecular formula***: *Molecular formula of a substance gives the actual number of atoms present in one molecule of the substance.*

Molecular formula = $n \times$ Empirical formula

Where, *n* is a simple integer 1, 2, 3,...... etc. given by the equation,

$$n = \frac{\text{Molecular mass of the compound}}{\text{Empirical formula mass of the compound}}$$