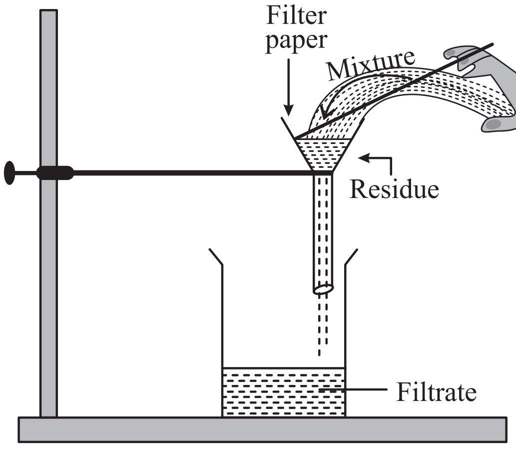
CHAPTER

17 Purification, Quantitative and Qualitative Analysis of Organic Compounds

Filtration: Only one of the compounds is soluble in the given solvent e.g.

(*i*) Urea and Naphthalene

(*ii*) Benzoic acid and anthracene



Filtration

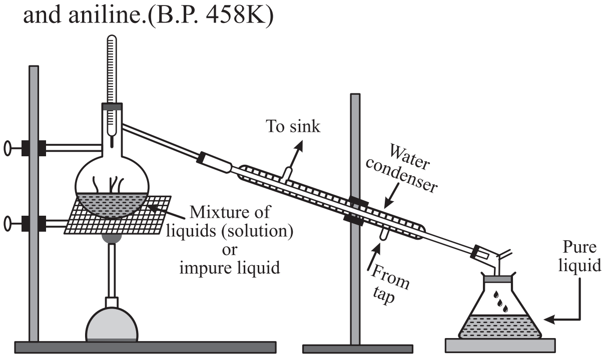
Crystallisation: It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.

Fractional Crystallization: Difference in solubilities of organic compounds and impurities are very less.

eg. urea and copper sulphate.

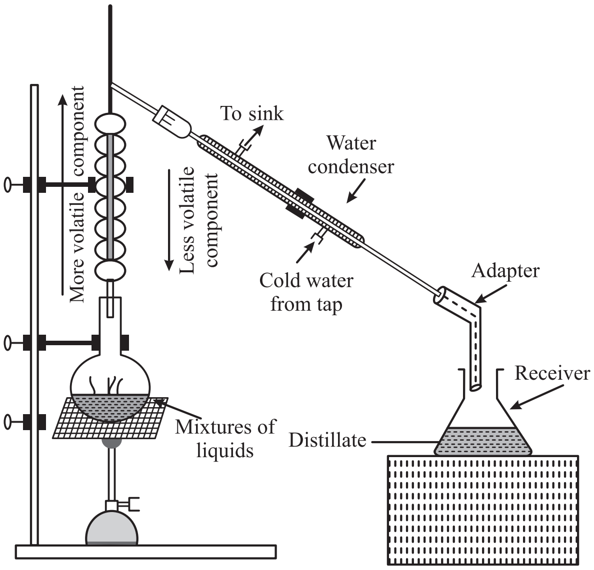
Distillation

(*i*) **Simple distillation:** Difference in boiling points of compounds is more than 40°C. e.g. chloroform (b. p. 334K) and aniline.(B.P. 458K)



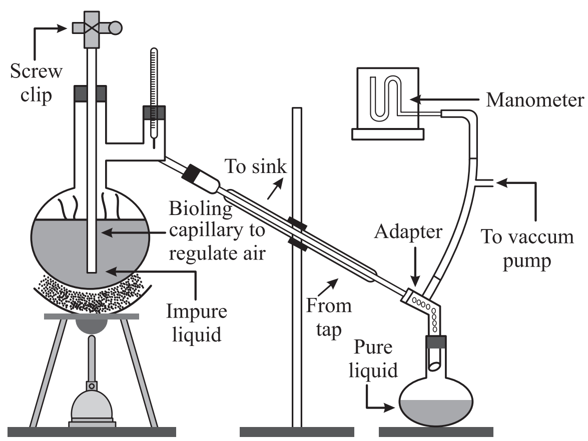
Simple distillation

(*ii*) **Fractional distillation:** Difference in boiling points of compounds is very less (5°C to 10°C). e.g. - acetone (b. p. 329K) and methyl alcohol (b. p. 338K).



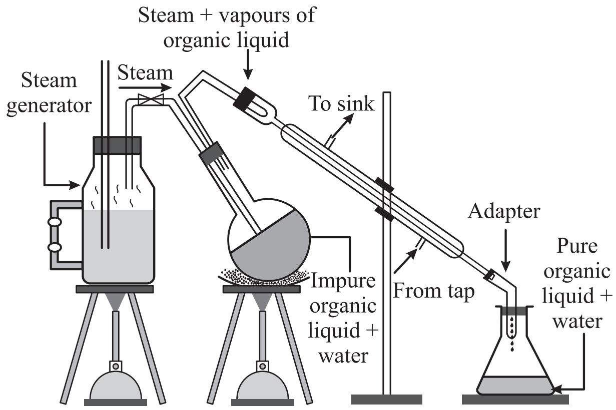
Fractional distillation

(*iii*) **Vacuum distillation:** Used for organic compounds which decompose at or below their boiling points. e.g. Glycerol.



Distillation under reduced pressure

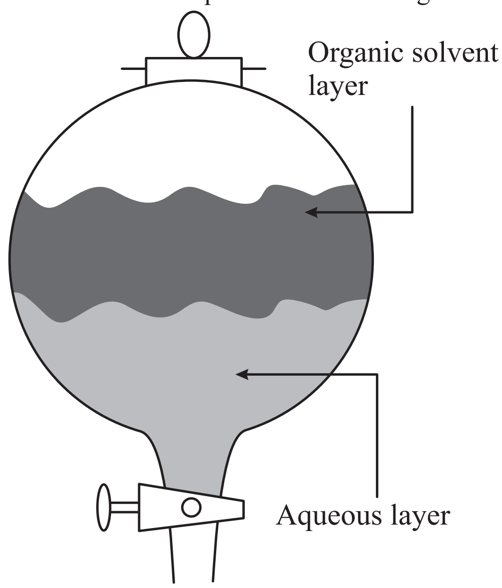
(*iv*) **Steam distillation**: Used for organic compounds which are immiscible with water and are steam volatile. e.g. Aniline.



Apparatus for steam distillation

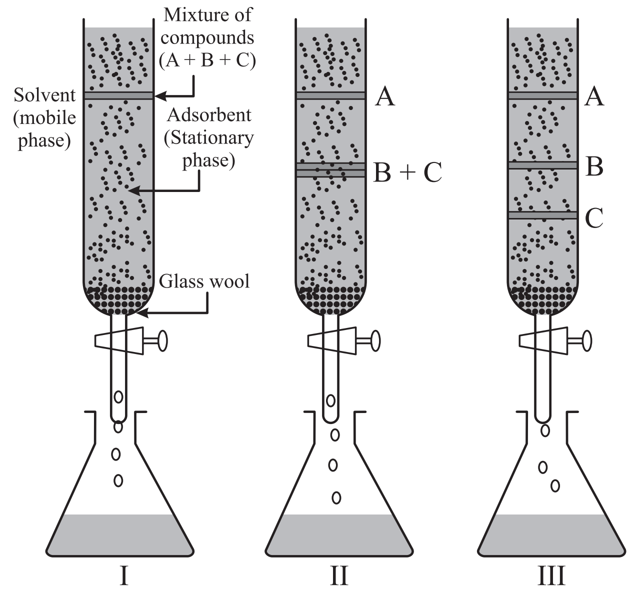
Differential extraction: Used to extract pure organic compounds from their aqueous solution by shaking with organic solvent in which they are highly soluble.

e.g. Benzoic acid from its aqueous solution using benzene.



Chromatography

- Used to purify small samples.
- Based on selective adsorption or partition between stationary and mobile phase.
- Column Chromatography based on adsorption, used for bulk quantities.
- Thin layer Chromatography based on adsorption, used for quantitative analysis.



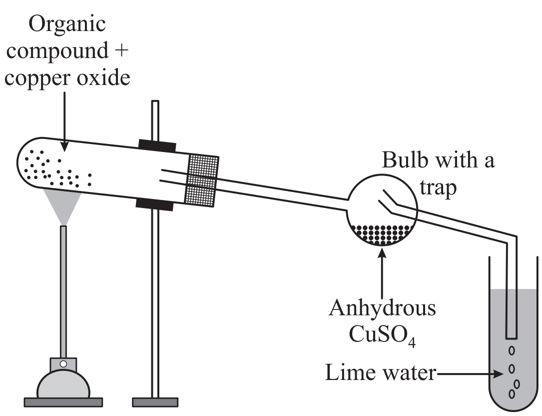
Column chromatography-stage I, II and III represent the progressive separation of the mixture into three bands

- Paper Chromatography- based on partition and used for quantitative and qualitative analysis.

QUALITATIVE ANALYSIS

Detection of C, H, N, halogens P, S, and oxygen.

Detection of Carbon and Hydrogen



Detection of carbon and hydrogen

$$\text{Organic Compound} + CuO \xrightarrow{\Delta} \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{H_2O} + \underset{\text{Copper}}{Cu}$$

CO_2 → Passed into lime water $Ca(OH)_2$ → Lime water turns milky → Carbon (C) present In organic compound

H_2O → Passed into anhydrous $CuSO_4$ → Copper Sulphate turns blue → Hydrogen (H) present in Organic Compound

Detection of Nitrogen

$$\text{Organic Compound} + \underbrace{NaOH + CaO}_{\text{Sodalime}} \xrightarrow{\Delta} \text{Smell of } NH_3 \rightarrow \text{Confirms the presence of nitrogen in organic compound}$$

Lassaigne's Extract

Lassaigne's extract is prepared to convert covalency of organic compound into electrovalency by fusing with Na.

$$\underset{\text{Fused with sodium [Na]}}{\text{Organic Compound}} \xrightarrow{\Delta} \underset{\text{(has NaCN) sodium cyanide}}{\text{Lassaigne's Extract}} \xrightarrow[\text{and freshly prepared } FeSO_4]{\text{Few drops of NaOH}} \underset{\text{Sodium ferrocyanide}}{Na_4[Fe(CN)_6]}$$

$Na_4[Fe(CN)_6]$ → Excess of HCl and $FeCl_3$ (ferric chloride) → $Fe_4[Fe(CN)_6]_3$

Ferric ferrocyanide (prussian blue colouration confirms presence of nitrogen in organic compounds)

Detection of Halogen

Beilstein's test

Organic compound $\xrightarrow[\text{Copper wire}]{\text{Heated over}}$ Green flame confirms the presence of halogen's in the organic compound

$$\underset{\text{Fused with sodium (has covalent bonds with carbon and halogens)}}{\text{Organic Compound}} \xrightarrow{\Delta} \text{Lassaignes extract} \xrightarrow[\text{and } AgNO_3]{\text{dil. } HNO_3}$$

- White ppt of silver chloride (AgCl) soluble in ammonia confirms the presence of chlorine in organic compound
- Pale yellow ppt. of silver bromide (AgBr) sparingly soluble in ammonia confirms the persence of bromine in organic compound
- Yellow ppt. of silver iodide (Agl) insoluble in ammonia confirms the presence of iodine in organic compound

Detection of Phosphorus

$$\text{Organic Compound} \xrightarrow[\text{with } Na_2O \text{ (sodium peroxide)}]{\Delta} \text{Phosphorus present in organic compound change to phosphate } (Na_3PO_4)$$

→ boiled with nitric acid (HNO_3) and added ammonium molybdate $[(NH_4)_2MoO_4]$ →

Yellow ppt. of ammonium phosphomolybdate $[(NH_4)_3PO_4.12MoO_3]$ confirms the presence of phosphorus in organic compound

Detection of Sulphur

$$\text{Organic Compound} \xrightarrow[\text{Potassium nitrite } (KNO_2) \text{ and sodium carbonate}]{\text{Fused with mixture of}} \text{Sulphur present in organic compound changes into sulphate}$$

→ Extracted with water, filtered and added dil. HCl $BaCl_2$ →

White ppt. of barium sulphare ($BaSO_4$) confirms the presence of sulphur inorganic compound

Organic Compound (Fused with sodium) $\xrightarrow{\Delta}$ Lassaignes's extract (has Na_2S (sodium shulphide)) ⟶ Divide the extract in two parts

- To one portion add acetic acid (CH_3COOH) and lead acetate [$Pb(CH_3COO)_2$] ⟶ Black ppt. of lead sulphide (PbS) confirms the presence of sulphur in organic compound
- To other portion add freshly prepared sodium nitroprusside $Na_2[Fe(CN)_5(NO)]$ ⟶ Violet colouration of $Na_2[Fe(CN)_5(NOS)]$ confirms the presence of sulphur in organic compound

Detection of Oxygen

Presence of oxygen in organic compound is detected by testing for functional group containing oxygen e.g. alcohol (–OH), aldehyde (–CHO), ketone (RCOR), carboxylic acid (–COOH), ester (–COOR) and nitro (–NO_2).

Quantitative Analysis

$$\%C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{Wt. of org. compound}}$$

$$\%H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{Wt. of org. compound}} \times 100$$

$$\%N = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at STP}}{\text{Wt. of org. comp.}} \times 100$$

or

$$\%N = \frac{\text{Volume of } N_2 \text{ at STP}}{8 \times \text{Wt. of org. compound}} \quad \text{(Duma's method)}$$

$$(\%N) = \frac{1.4 \times N \times V}{\text{wt. of org. compound}} \quad \text{(Kjeldhal's method)}$$

$$\%X = \frac{\text{At. wt. of X}}{\text{Mol. wt. AgX}} \times \frac{\text{Wt. of AgX}}{\text{wt. of org. compound}}$$

$$\%S = \frac{32}{233} \times \frac{\text{Wt. } BaSO_4}{\text{wt. of org. compound}} \times 100$$

$$\%P = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7}{\text{Wt. of org. compound}} \times 100$$