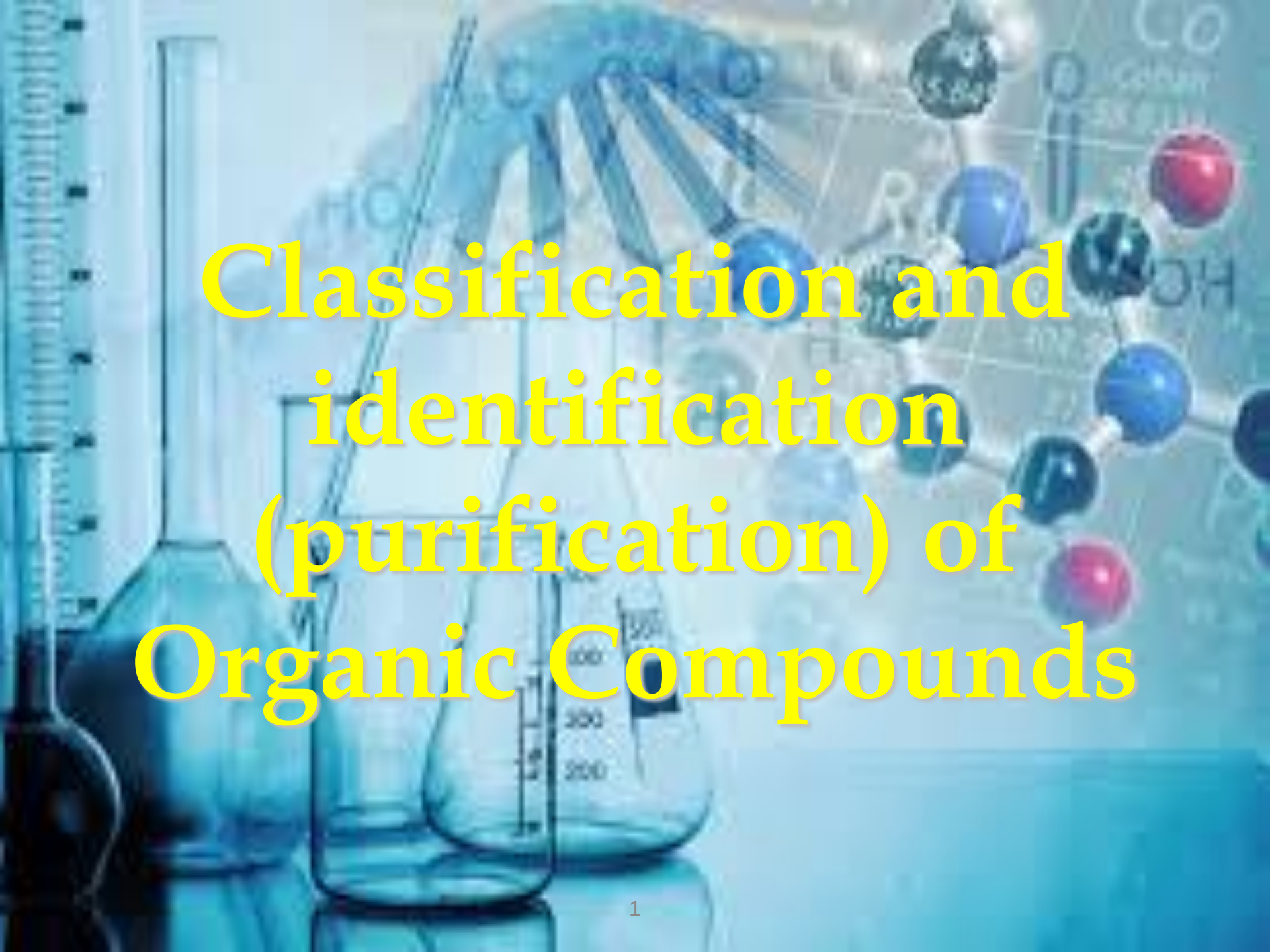
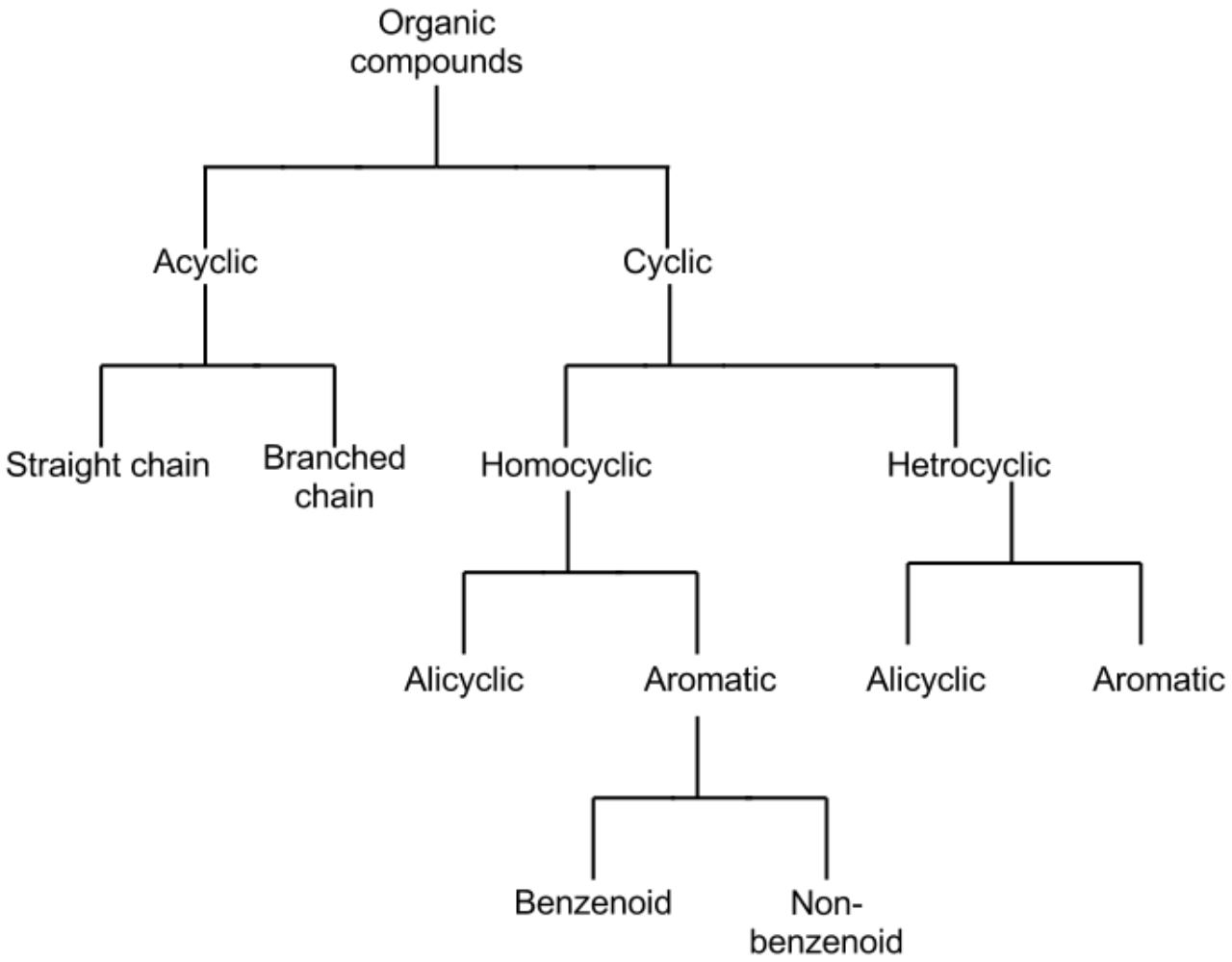


Classification and identification (purification) of Organic Compounds

Classification based on structure of organic compounds

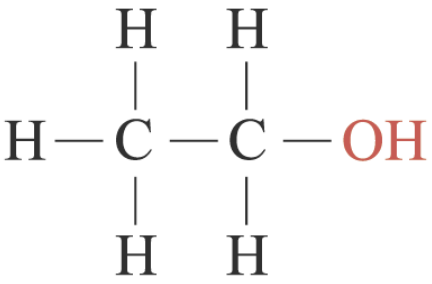


Classification based on Functional Groups

Organic compounds are classified by the the presence of characteristic functional groups.

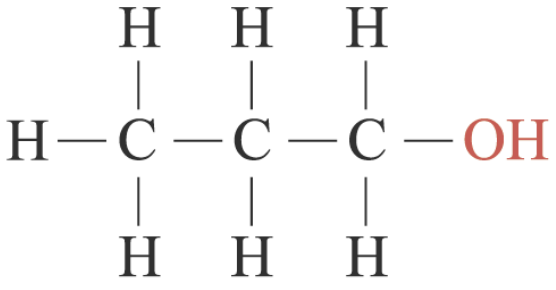
A functional group is defined as an atom or a group of atoms that effectively determines the chemical properties of an organic compound.

Functional Groups



Ethanol

and

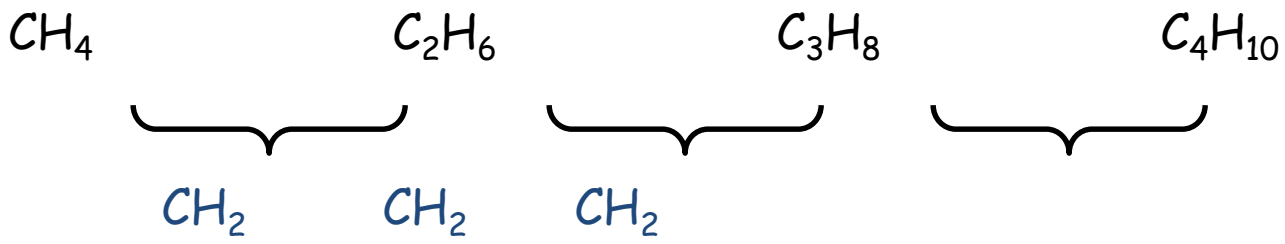


Propan-1-ol

- The above 2 compounds have similar chemical properties
  ➔ they contain the same functional group –OH
  ➔ they are classified into the same homologous series — alcohols

Homologous Series

- A homologous series is a series of compounds that have the same functional group, and each member differs from the next member by a – CH2 – unit in their formulae.



Homologous Series

- Members in the same series can be represented by a general formula.

e.g. alkanols: $C_nH_{2n+1}OH$

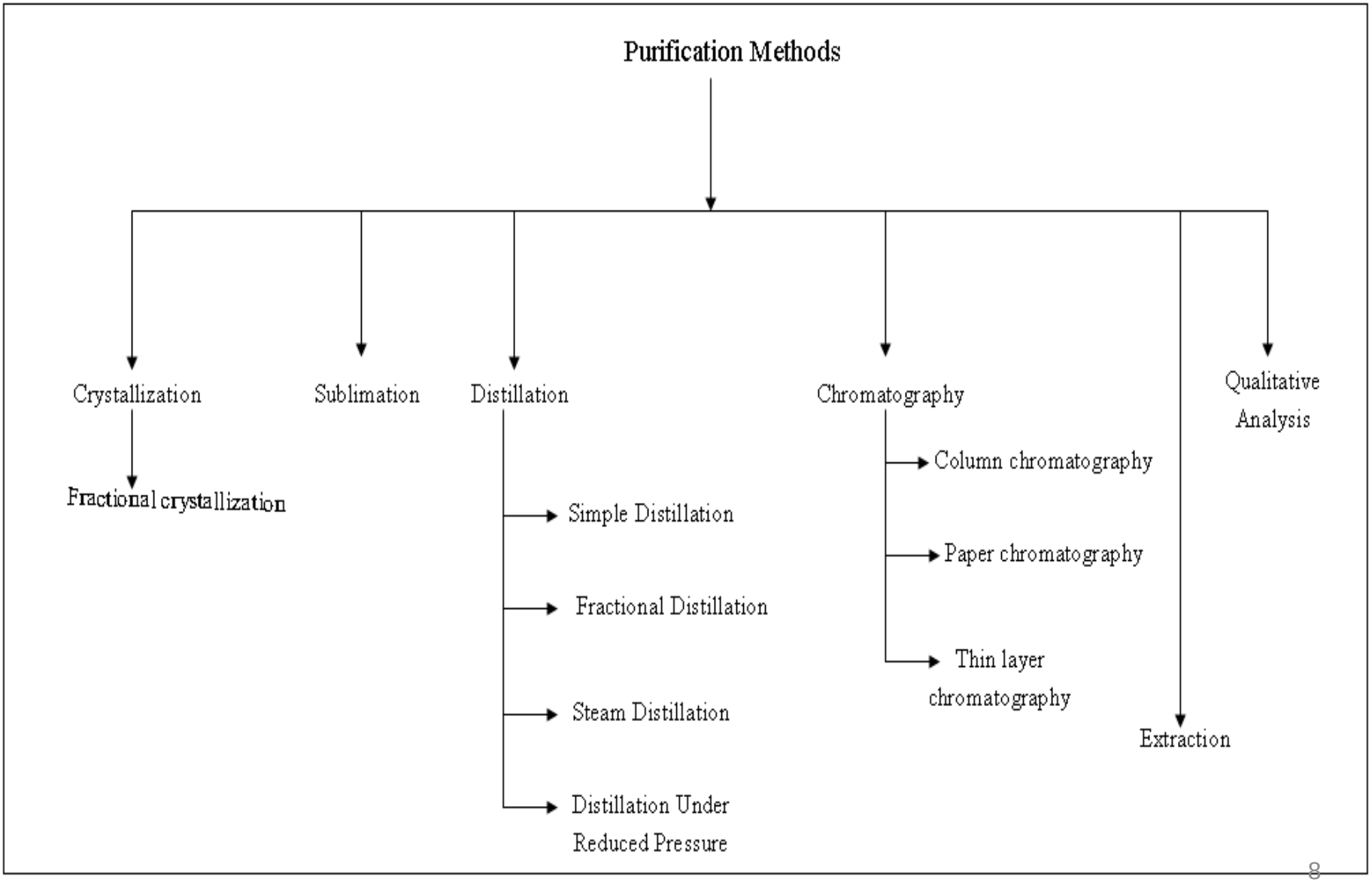
alkanals: $C_nH_{2n+1}CHO$

alkanoic acids: $C_nH_{2n+1}COOH$

INTRODUCTION – Purification of organic compounds

Organic compounds are isolated either from natural sources or from reactions mixtures. These compounds are seldom pure and are usually contaminated with small amounts of other similar compounds, which are found to exist together or formed during the reaction. In order to characterize them, it is important to purify them.

SUMMARY


Purification Methods
Crystallization
Fractional crystallization
Sublimation
Distillation
Simple Distillation
Fractional Distillation
Steam Distillation
Distillation Under Reduced Pressure
Chromatography
Column chromatography
Paper chromatography
Thin layer chromatography
Extraction
Qualitative Analysis

Methods of purification of organic compounds

- **Sublimation:** In this process the solid substance changes from solid to vapour form without going to the liquid state it is used to separate sublimable compound from non-sublimable impurities.

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

- **Distillation:** This important method is used to separate:-

(i) Volatile liquids from nonvolatile impurities

(ii) And the liquids having sufficient difference in their boiling points.

Methods of purification of organic compounds

Distillation is further divided in to :

i) Fractional distillation: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The technique of fractional distillation is used in such cases.

ii) Steam distillation : This technique is applied to separate substances which are steam volatile and are immiscible with water.

- **Differential Extraction:** The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel.

- **Chromatography:** In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase.

PROCESSES FOR PURIFICATION

1. Crystallization
2. Sublimation
3. Distillation
4. Chromatography
5. Differential Extraction
6. Qualitative Analysis

1. CRYSTALLIZATION

Aim

To separate a solid compound in pure and geometrical form.

Principle

A saturated solution of the impure substance in a suitable solvent is made at a temperature higher than the room temperature.

On cooling this solution, the substance reappears in the form of well shaped crystals.

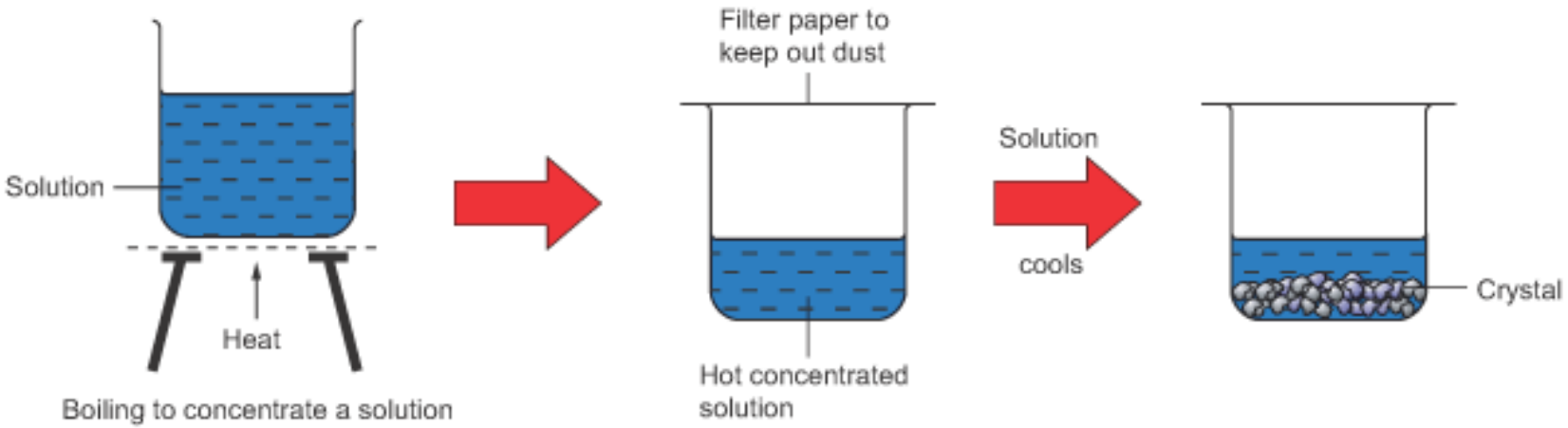
Process

- Purification by crystallization involves the following steps:
- Choice of solvent
- Preparation of solution
- Filtration of the solution
- Separating the crystals
- Drying of crystals

Example

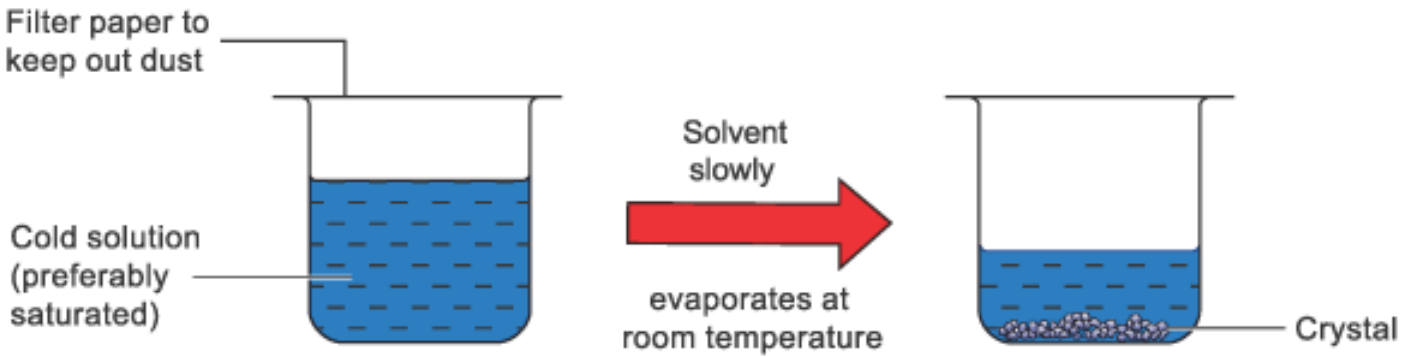
Crystallisation of Phthalic acid

Crystallization by Cooling a Hot Concentrated Solution



Crystallization by cooling a hot concentrated solution

Crystallization by Evaporating a Cold Solution at Room Temperature



Crystallization by slow evaporation of a solution (preferably saturated) at room temperature

2. SUBLIMATION

Aim

To separate volatile solids, which pass directly into vapour state on heating from a non-volatile solid.

Principle

A mixture of solid substances, such as camphor, benzoic acid, ammonium chloride, iodine etc., containing non-volatile substances, when heated, change directly into vapour without passing through the liquid state.

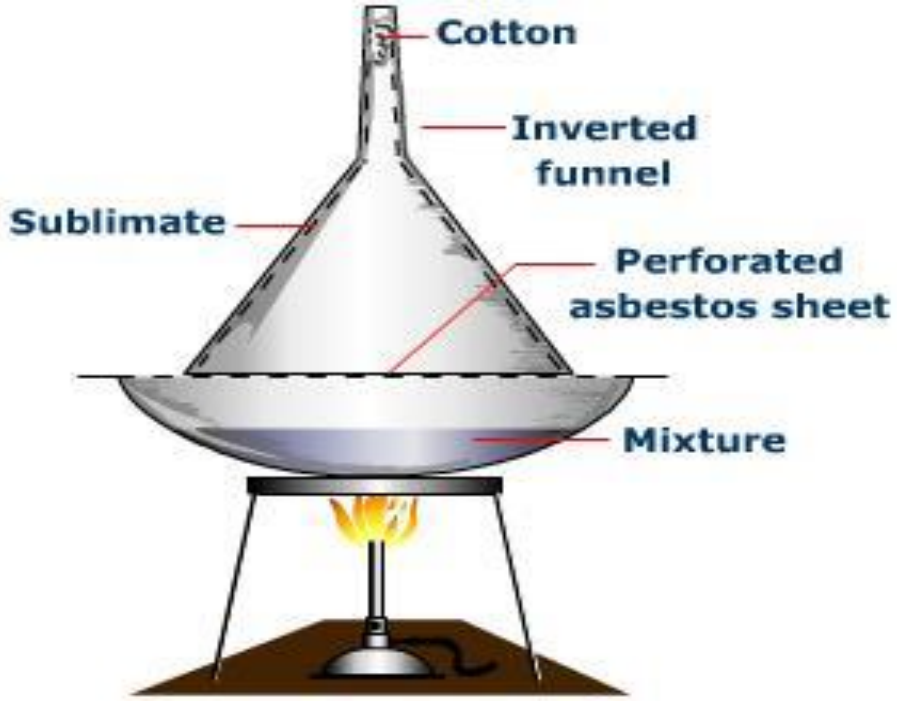


Fig :-Sublimation

Substance	Mp	Substance	Mp
1,4-dichlorobenzene	55	Benzoic acid	122
Naphthalene	82	Salicylic acid	159
1-Naphthol	96	Camphor	177
Acetanilide	114	Caffeine	235

3. DISTILLATION

Aim

To separate a solution of a solid in a liquid and for separating a solution of two liquids whose boiling points are different.

Principle

Distillation involves the conversion of a liquid into its vapors upon heating and then cooling the vapors back into the liquid. Depending on the difference in boiling points of liquids.

Types of distillation

- Simple Distillation
- Fractional Distillation
- Distillation Under Reduced Pressure or Vacuum Distillation
- Steam Distillation

SIMPLE DISTILLATION

Principle

It is used for separating liquids having boiling points differing by 10-20 degrees. The liquid having the lower boiling point distills over first, and the other liquid component is left behind. In this process, vaporization and condensation occur side by side.

Process

Example

Simple distillation of a Cyclohexane- Toluene mixtures

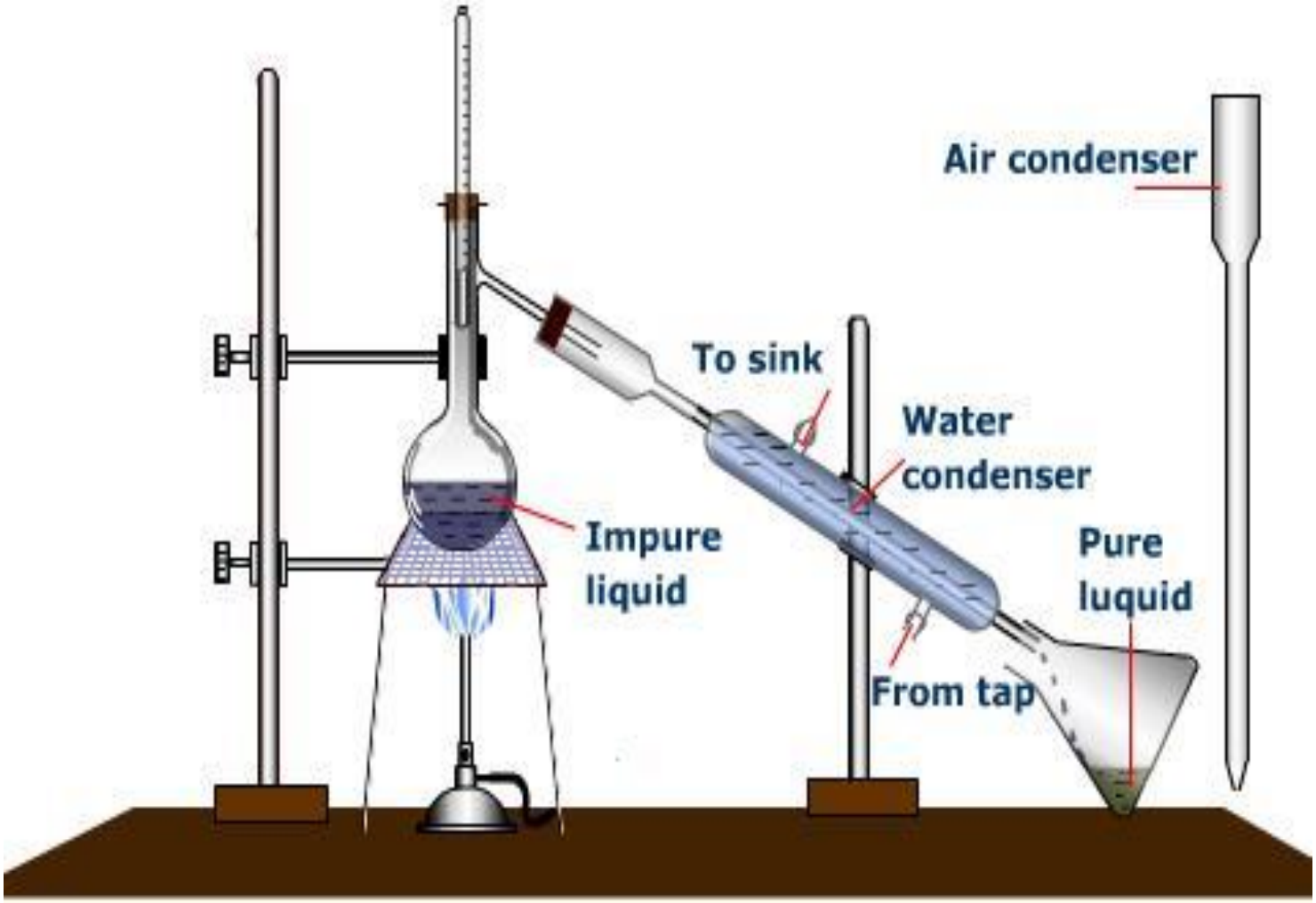


Fig : - Simple distillation

FRACTIONAL DISTILLATION

Principle

It is used for separating two liquids in any mixture, which have boiling points within a narrow range of temperatures. In such cases, simple distillation does not give complete separation and a modified version called fractional distillation is employed.

Process

Example

Fractional Distillation of a Cyclohexane- Toluene mixtures

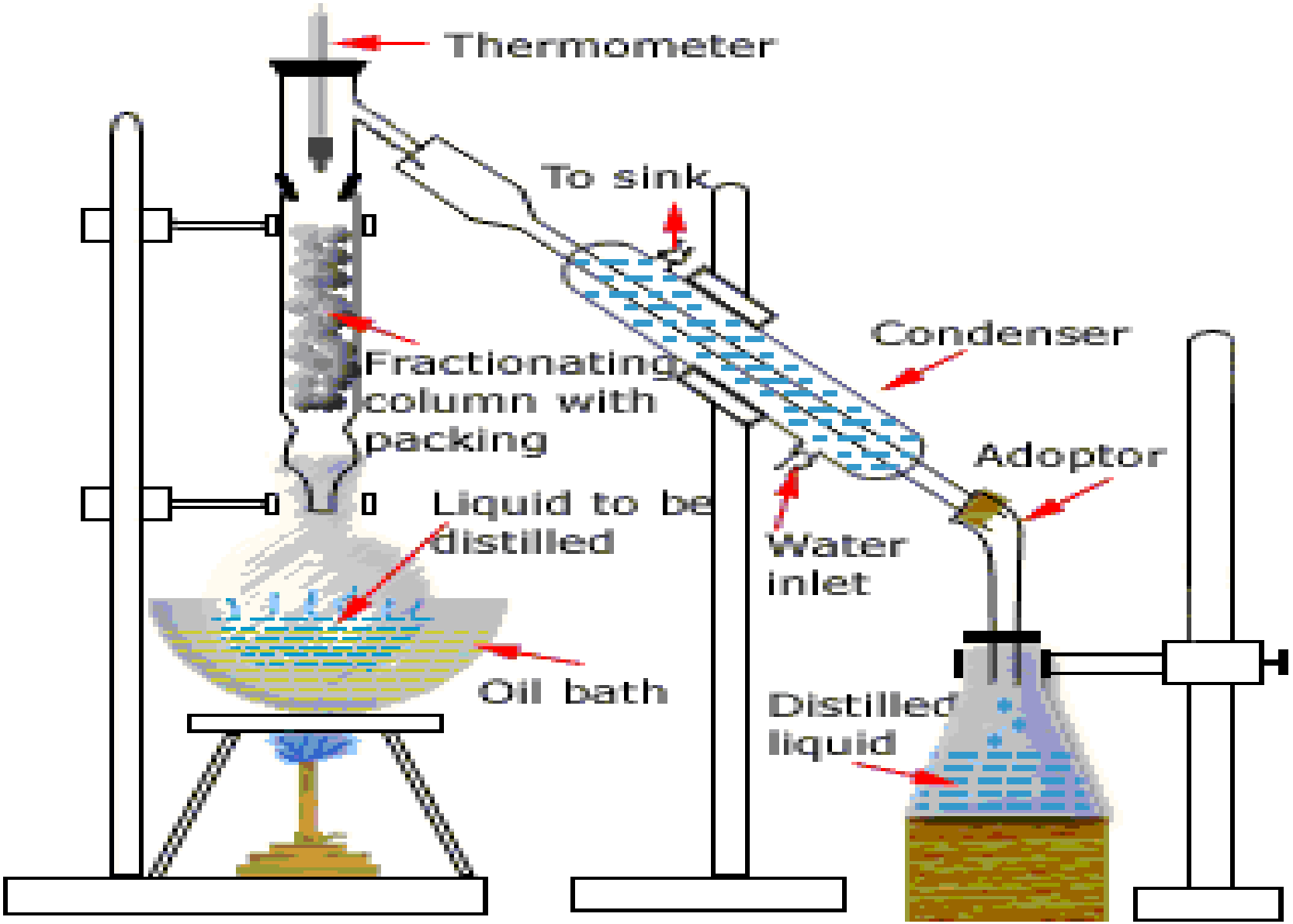


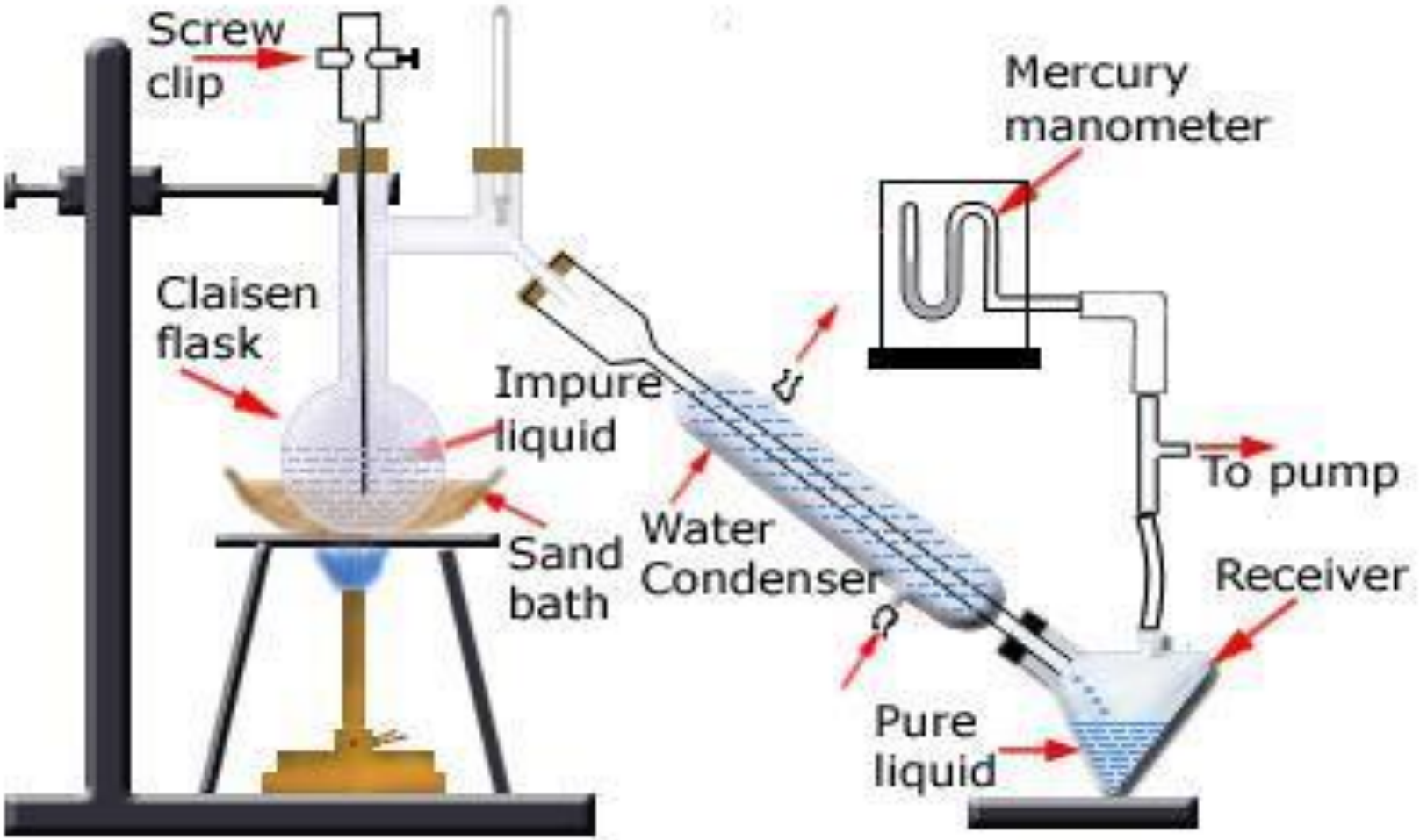
Fig : -Fractional distillation

DISTILLATION UNDER REDUCED PRESSURE OR VACUUM DISTILLATION

Principle

The lowering of pressure on the surface of a liquid lowers its boiling point. As a result of this, a liquid can be boiled and distilled, without any decomposition, at temperature much below its normal boiling point.

DISTILLATION UNDER REDUCED PRESSURE OR VACUUM DISTILLATION



STEAM DISTILLATION

Principle

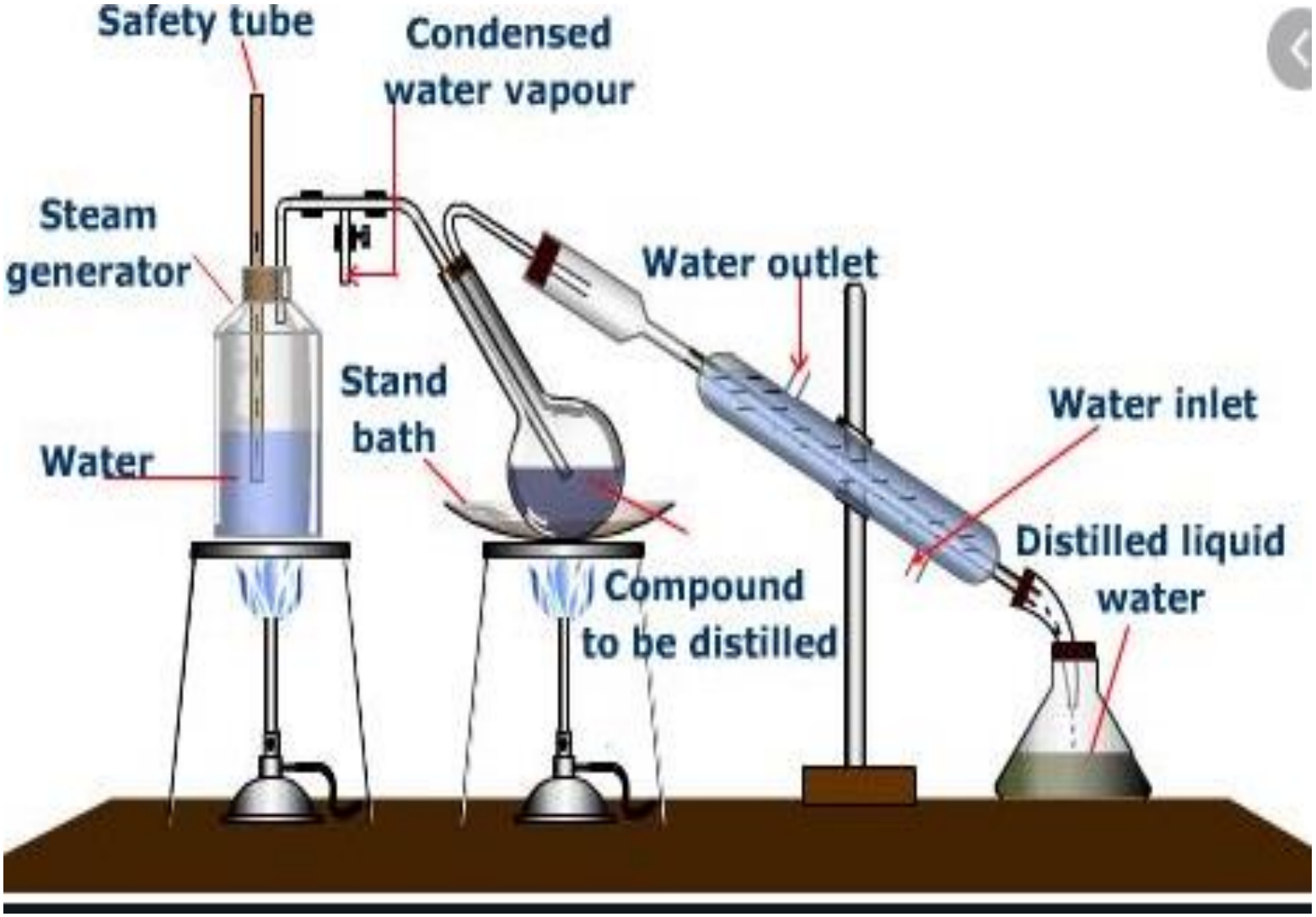
This technique is used for separating/purifying liquids, which are immiscible with water, volatile in steam, & have high vapor pressure at the boiling temperature of water.

Process

Example

Isolation of essential oils

STEAM DISTILLATION



CHROMATOGRAPHY

Aim

To identify, purify and/or separate constituents of a mixture that are present in very small amounts.

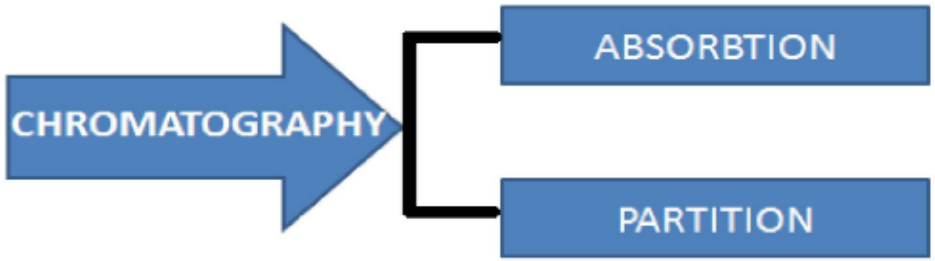
Principle

The principle behind this technique is the differential adsorption of the various components of a mixture between two different phases that are as follows:

- Fixed or stationary phase
- Mobile or Moving phase

Methods of purification of organic compounds

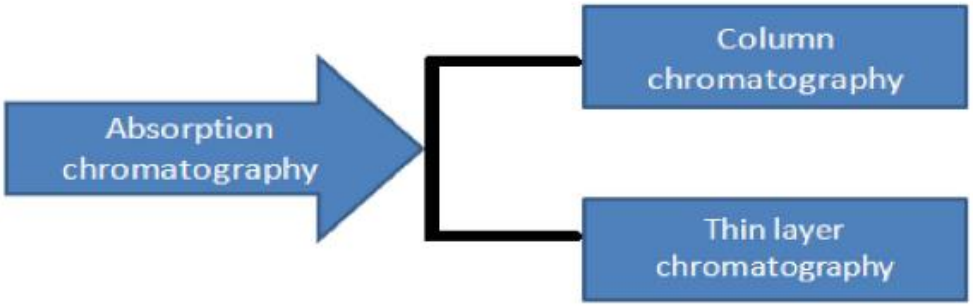
❑ **Chromatography:** In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase.



Adsorption chromatography : Is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.

- Commonly used adsorbents are silica gel and alumina.

Methods of purification of organic compounds



Column chromatography: It involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube.

Thin layer chromatography (TLC): Is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.

Methods of purification of organic compounds

The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor.**

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

Partition chromatography

Continuous differential partitioning of component of a mixture between stationary and mobile phase.

COMMONLY EMPLOYED CHROMATOGRAPHIC TECHNIQUES

- Column Chromatography
- Paper Chromatography
- Ascending and Descending Paper Chromatography
- Radial Paper Chromatography
- Thin Layer Chromatography

COLUMN CHROMATOGRAPHY

This is the simplest chromatography based on the differential adsorption of the constituents of a mixture. A suitable adsorbent like alumina (Al_2O_3), taken in the form of a slurry in petroleum ether, constitutes the stationary phase.

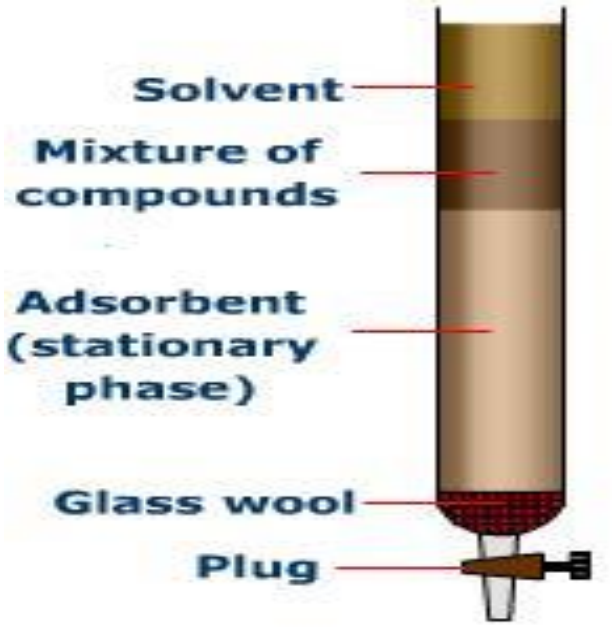


Fig : -Column chromatography

THIN LAYER CHROMATOGRAPHY

Principle

In this chromatography, the stationary phase is a thin layer of an adsorbent (generally alumina) coated on Flat glass strip. The solvent (mobile phase) moves up the layer due to the capillary action and thus causes the separation of constituents of the mixture.

The constituents are identified by measuring their RF values.

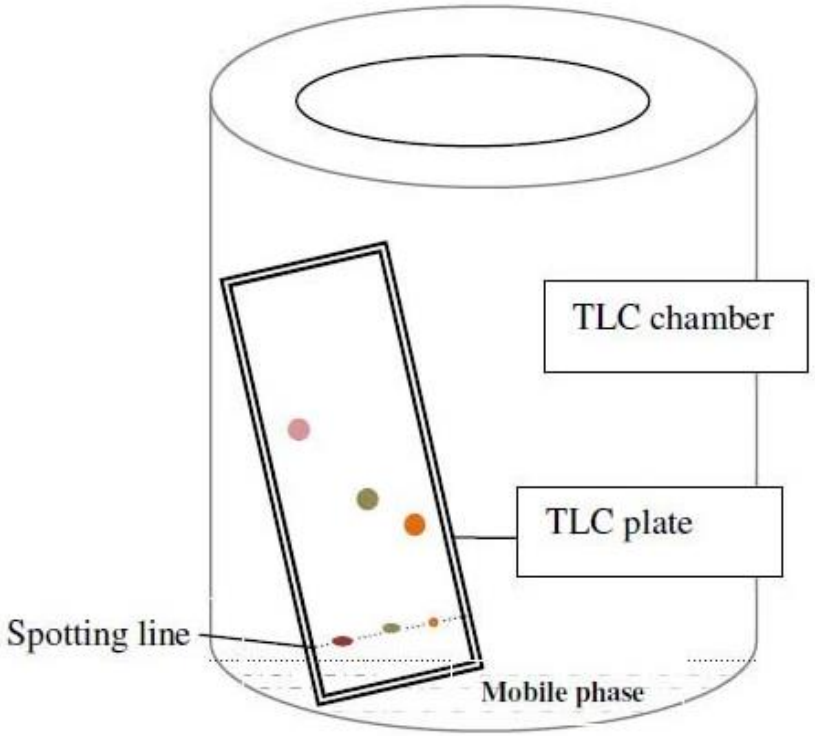
Example

Separation of vitamins by thin layer chromatography

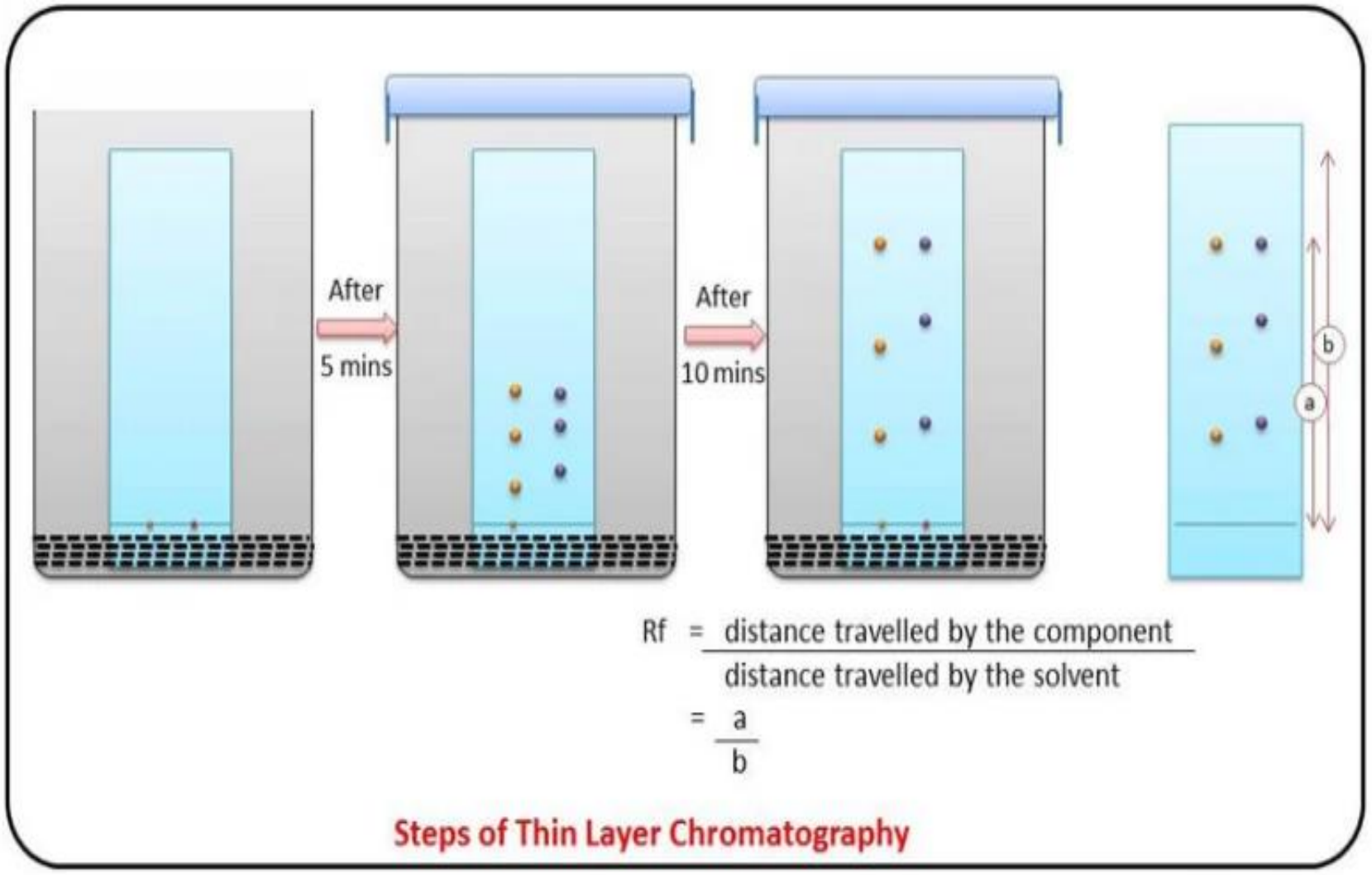
THIN LAYER CHROMATOGRAPHY

- TLC system components consists of:

- **TLC plates,**
- **TLC chamber,**
- **Mobile phase**



THIN LAYER CHROMATOGRAPHY

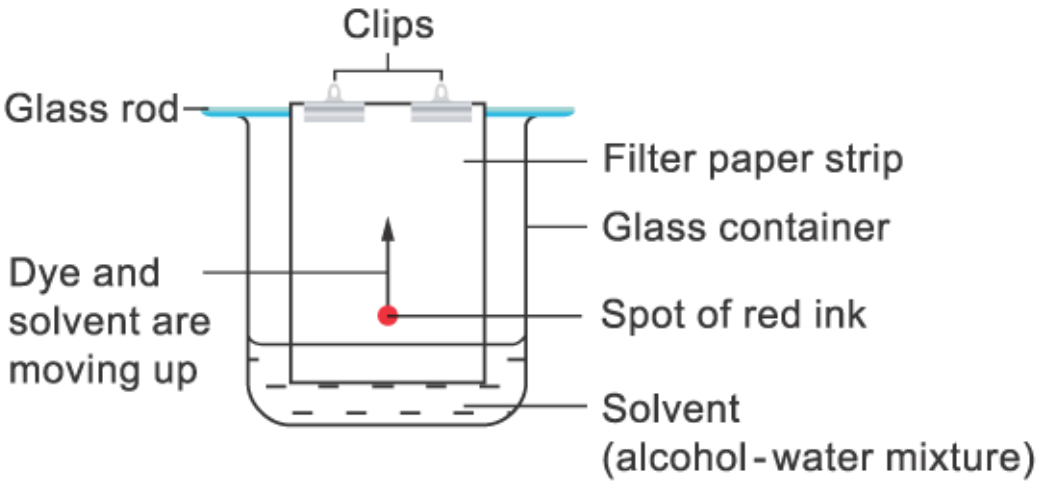


$$Rf = \frac{\text{distance travelled by the component}}{\text{distance travelled by the solvent}} = \frac{a}{b}$$

Steps of Thin Layer Chromatography

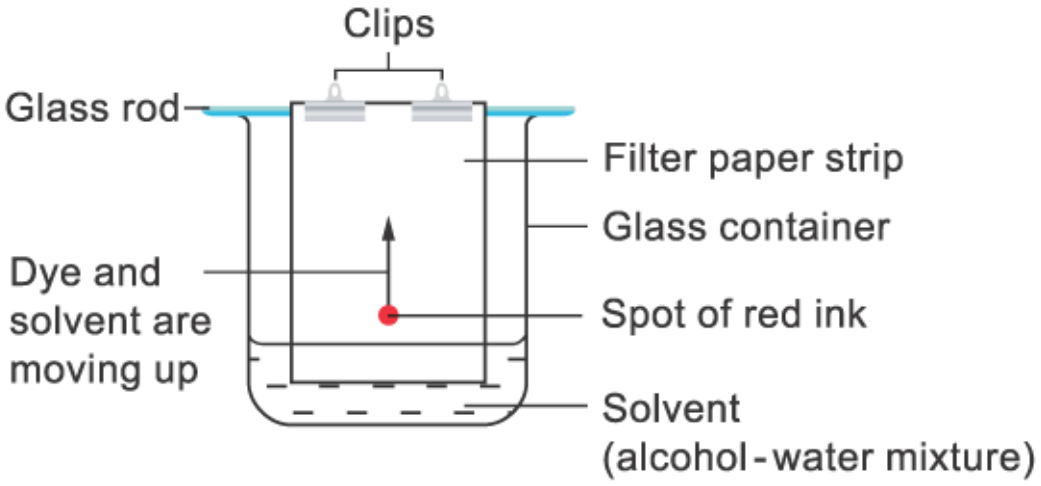
Paper Chromatography

- Paper chromatography is a common type of chromatography
- A solution of the mixture is dropped at one end of the filter paper



Paper Chromatography

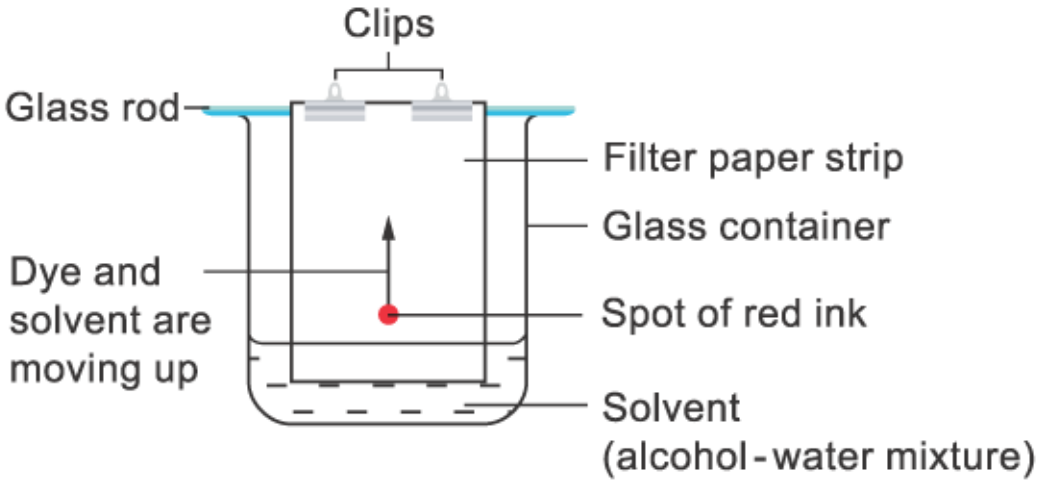
- The thin film of water adhered onto the surface of the filter paper forms the stationary phase
- The solvent is called the mobile phase or eluent



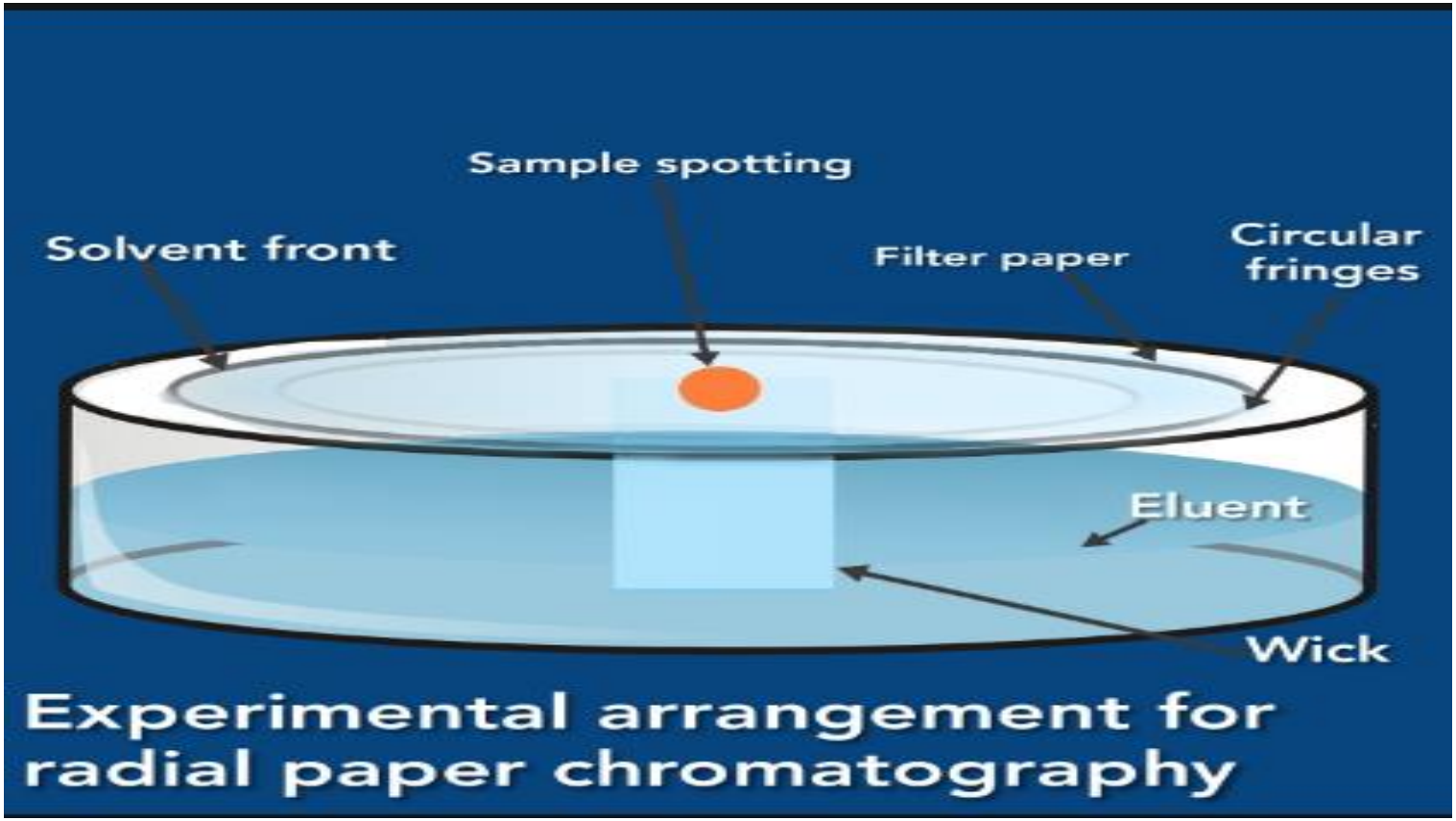
Chromatography

- When the solvent moves across the sample spot of the mixture,

  ➔ partition of the components between the stationary phase and the mobile phase occurs



Radial Paper Chromatography



5. DIFFERENTIAL EXTRACTION

Principle

To extract a compound that is present in very small amounts in an aqueous solution with the help of an organic liquid in which that compound is highly soluble.

Process

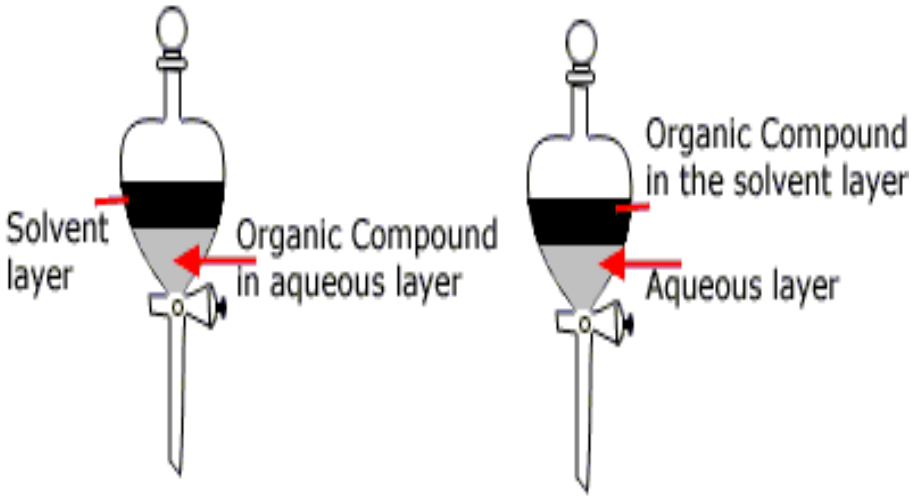


Fig :- Differential extraction

Example :-Extraction of Caffeine from Tea

Solvent Extraction

- Involves extracting a component from a mixture with a suitable solvent
- Water is the solvent used to extract salts from a mixture containing salts and sand
- Non-aqueous solvents (e.g. 1,1,1-trichloroethane and diethyl ether) can be used to extract organic products

Solvent Extraction

- Often involves the use of a separating funnel
- When an aqueous solution containing the organic product is shaken with diethyl ether in a separating funnel,

  ➔ the organic product dissolves into the ether layer

Solvent Extraction

- The ether layer can be run off from the separating funnel and saved
- Another fresh portion of ether is shaken with the aqueous solution to extract any organic products remaining
- Repeated extraction will extract most of the organic product into the several portions of ether

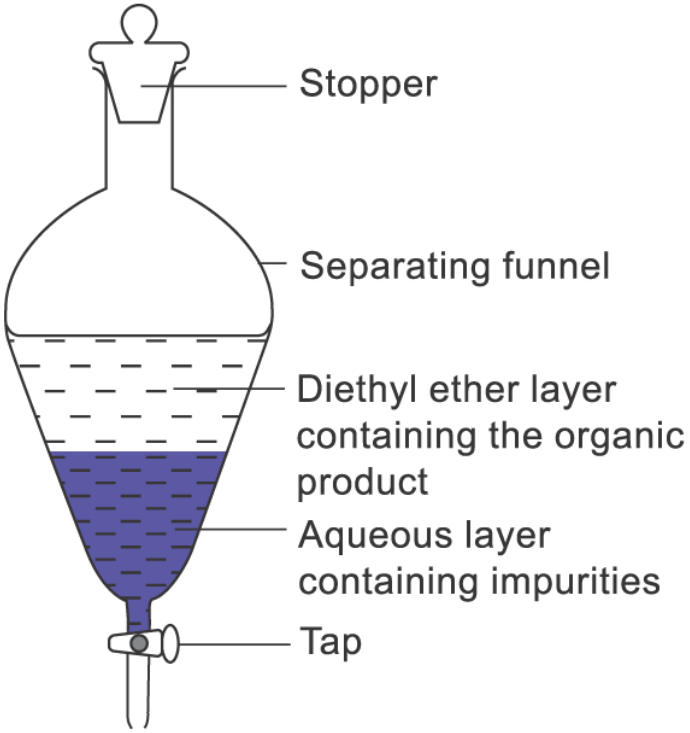
Solvent Extraction

- Conducting the extraction with several small portions of ether is more efficient than extracting in a single batch with the whole volume of ether
- These several ether portions are combined and dried

  ➔ the ether is distilled off

  ➔ leaving behind the organic product

Solvent Extraction



The organic product in an aqueous solution can be extracted by solvent extraction using diethyl ether

6. QUALITATIVE ANALYSIS

The systematic qualitative analysis of organic compounds includes the following different stages:

- Preliminary tests and physical examinations.
- Detection of elements
- Determination of functional group or groups.
- Determination of physical constant.
- Identification of the compound by search of literature with similar physical and chemical properties.
- Confirmation of compounds by preparing suitable derivative and specific chemical tests.

Qualitative Analysis of Organic compounds

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

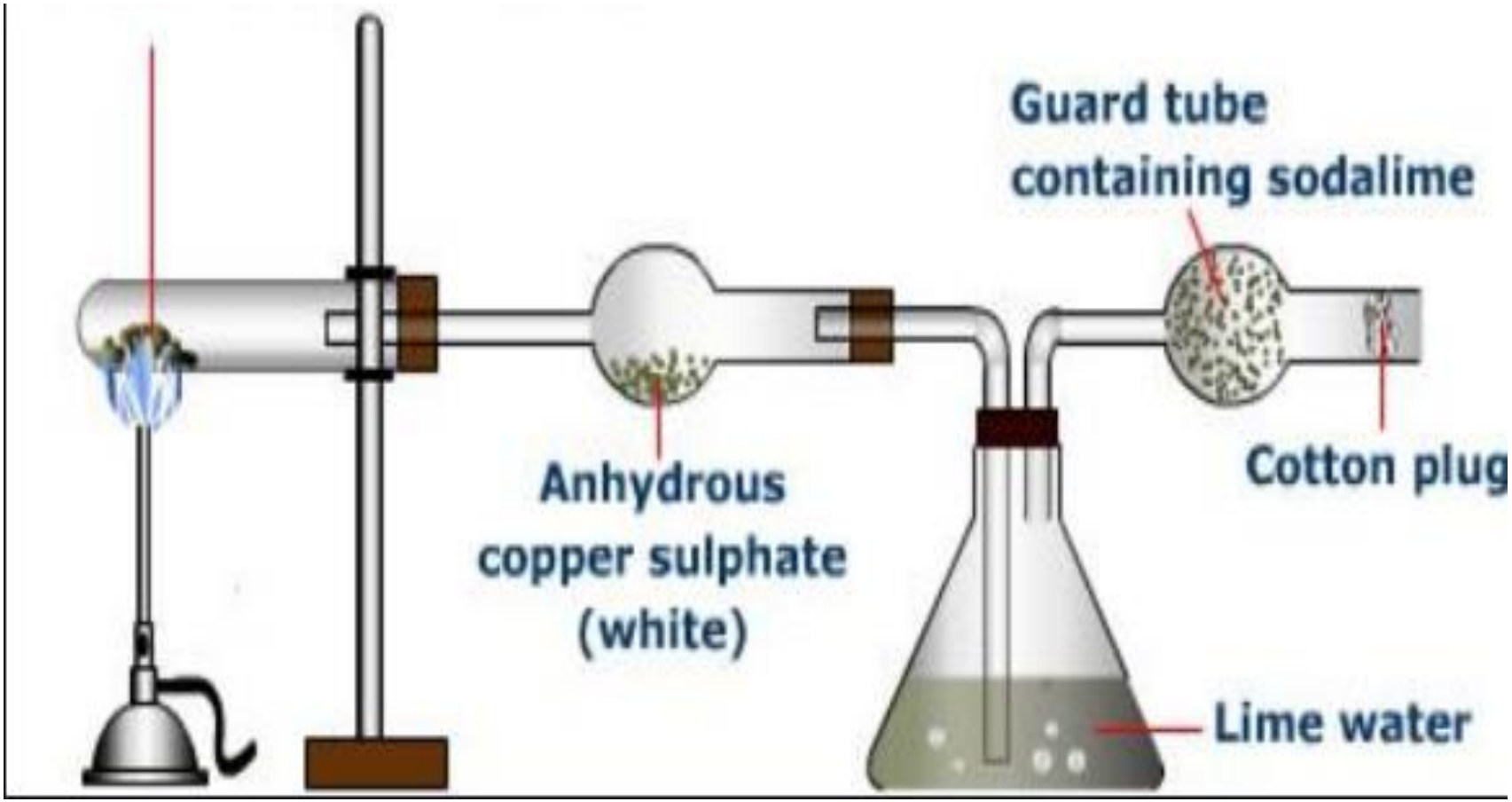
Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide.

Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity)

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

Qualitative Analysis of Organic compounds

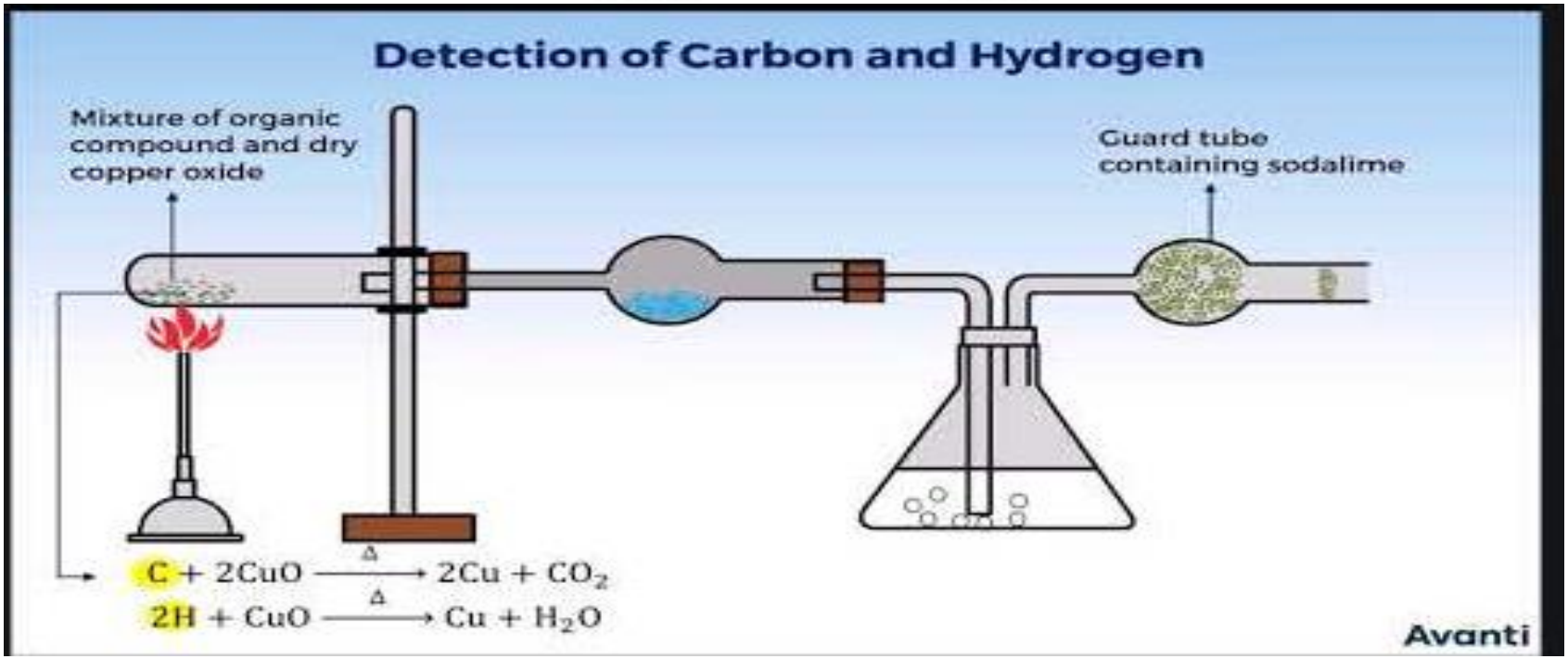


Qualitative Analysis of Organic compounds

Hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$5H_2O + CuSO_4 \longrightarrow CuSO_4.5H_2O$$

White → Blue



Qualitative Analysis of Organic compounds

Detection of Other Elements: Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by **"Lassaigne's test".**

(A) Test for Nitrogen: The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.

$$Na + \underbrace{C + N}_{\text{(From organic compound)}} \xrightarrow{\text{Fuse}} NaCN$$

Qualitative Analysis of Organic compounds

✓ Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II).

✓On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferri-ferrocyanide) which is Prussian blue in colour.

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$$

Prussian blue

Ferrous Sulphate

Test for Nitrogen

Qualitative Analysis of Organic compounds

(B) Test for Sulphur:

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$S^{2-} + Pb^{2+} \longrightarrow \underset{\text{Black}}{PbS}$$

Lead acetate
Test for Sulphur

Qualitative Analysis of Organic compounds

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$$

Sodium nitroprusside Test for Sulphur

Qualitative Analysis of Organic compounds

(C) Test for Halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

Results:

✓ A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine.

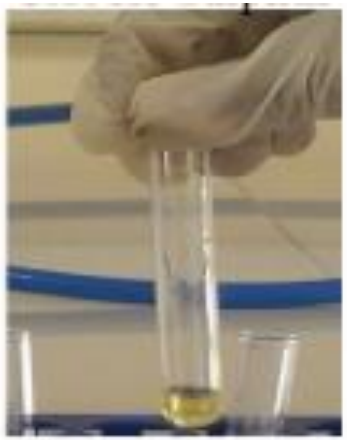
✓ A yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine.

✓ A yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$

X represents a halogen – Cl, Br or I.

$AgNO_3$ Test for Cl^-



$AgNO_3$ Test for Br^-

Qualitative Analysis of Organic compounds

(D) Test for Phosphorus: The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate.

Result: A yellow colouration or precipitate indicates the presence of phosphorus.

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

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$$

Ammonium molybdate

$$(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$$

Ammonium phosphomolybdate

Quantitative Analysis of Organic compounds

Carbon and Hydrogen: A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide.

✓ Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

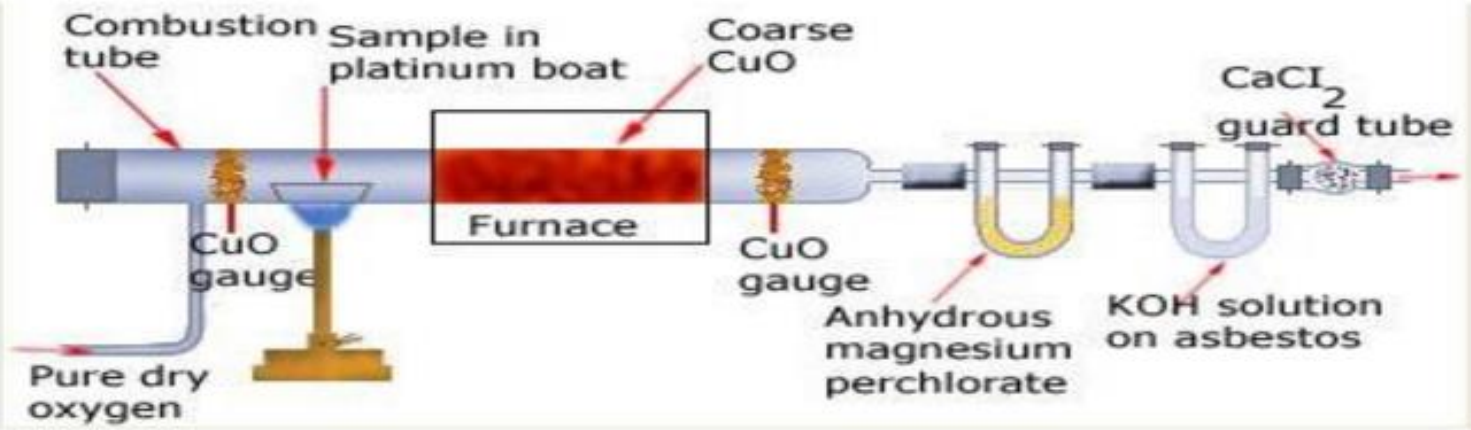
$$C_xH_y + (x + y/4)\, O_2 \longrightarrow x\, CO_2 + (y/2)\, H_2O$$

Observation

✓ The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride.

✓ Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide.

Quantitative Analysis of Organic compounds



The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

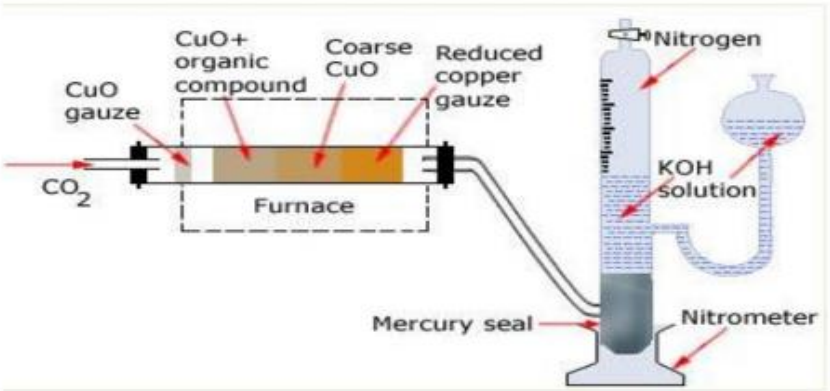
Quantitative Analysis of Organic compounds

❑ **Nitrogen:** There are two methods for estimation of nitrogen: (i) Dumas method
(ii)Kjeldahl's method.

(i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x + y/2)\,CuO \longrightarrow$$

$$x\,CO_2 + y/2\,H_2O + z/2\,N_2 + (2x + y/2)\,Cu$$



Quantitative Analysis of Organic compounds

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate .

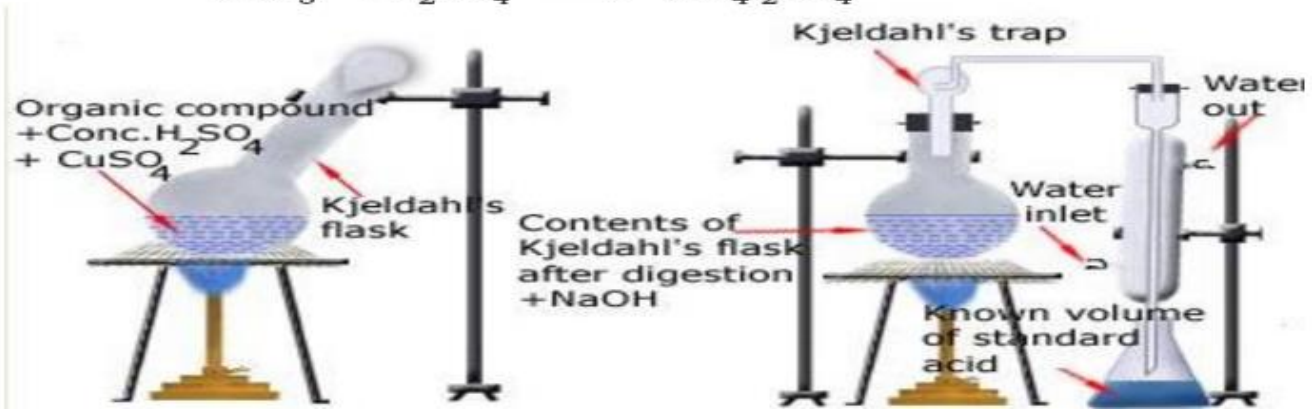
✓ The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid.

✓ The amount of ammonia produced is determined by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution.

$$\text{Organic compound} + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$



Quantitative Analysis of Organic compounds

Drawbacks of this method: It is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

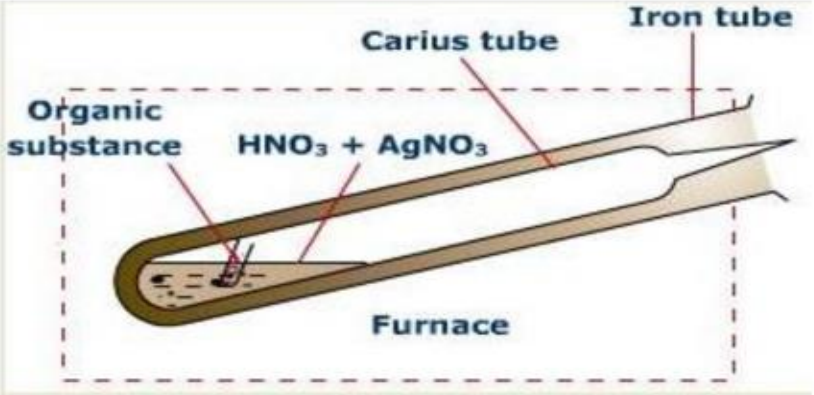
❑ Halogens

Carius method: A known mass 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, in a furnace.

✓ Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water.

✓ The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

Quantitative Analysis of Organic compounds



Sulphur: A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid.

✓It is precipitated as barium sulphate by adding excess of barium chloride solution in water.

✓ The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.

Quantitative Analysis of Organic compounds

Phosphorus: A known mass of an organic compound is heated with fuming nitric acid where upon phosphorus present in the compound is oxidised to phosphoric acid.

✓It is precipitated as ammonium phosphomolybdate, by adding ammonia and ammonium molybdate.

Oxygen: 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 when carbon monoxide is oxidised to carbon dioxide producing iodine.

✓ The percentage of oxygen can be derived from the amount of carbon dioxide or iodine produced.

CONCLUSION

- Purification process is widely used in industry.
- Distillation is among most important and widely used in industrial operation today. About 95% of all separation process today is carried out in industry with more than 40,000 distillation system.
- Sublimation is also use to create freeze- dried substances. e.g. tea, soup, drug.
- Steam distillation is employed in industry for the recovery of various essential oils from plant and flowers.
- Better chemical stability, crystallization process is use due it help to increase physical stability, bioavailability and sustain release.