METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Organic compounds, whether obtained from nature or made in a lab, are often not pure. They usually have impurities, meaning they contain other substances. There are various ways to make them pure again. The method chosen depends on the type of compound (solid or liquid) and the kind of impurities present.

Here are the usual methods employed for purification:

(i) Sublimation (ii) Crystallisation (iii) Distillation

(iv) Differential extraction (v) Chromatography

After making sure the substances are pure and checking their purity through melting or boiling points, we observe that pure compounds usually have distinct and well-defined temperature ranges for melting and boiling. Modern methods now use various chromatographic and spectroscopic techniques to assess the purity of organic compounds.

Let us briefly learn about different methods for purifying the organic compounds.

(i) Sublimation

Some solid organic substances, when heated, turn directly into vapor without becoming liquid first. These substances are called sublimely, and this transformation is known as sublimation. When the vapors cool down, they return to the solid state.

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

Sublimation is a method used to separate substances that can turn directly from a solid to vapor, like camphor, naphthalene, anthracene, and benzoic acid, from impurities that don't undergo sublimation.

(ii) Crystallization

Crystallization is the most widely used technique for purifying organic solids. It relies on the varying solubility of the organic compound and its impurities in a specific solvent. The process includes the following steps:

(a) **Making the Solution:** First, the organic compound is dissolved in a suitable solvent through heating. It's important to use just enough solvent to dissolve the entire solid when heated. The solvent chosen should not dissolve the impurities and should not react chemically with the compound.

(b) **Filtering the Solution:** After obtaining the hot solution, it is promptly filtered.

(c) **Crystallization:** The heated liquid that passed through the filter is allowed to cool slowly and peacefully in a container. After a while, pure compound crystals start forming. Once the crystallization is finished, these crystals are separated from the remaining liquid by using a filter. The crystals in the filter are rinsed one or two times with a bit of cold solvent to get rid of any impurities that might be sticking to them.

(d) **Drying the Crystals:** The crystals are dried by gently squeezing them between layers of filter paper and then left in a steam or air oven for a while. To ensure thorough drying, the crystals are finally placed over sulfuric acid or calcium chloride inside a container called a desiccator.

(e) **Removal of Colour**: Occasionally, the crystals we get may have a bit of color because of some colored impurities. In such situations, the crystals are dissolved again in the same solvent, and a bit of activated charcoal is added to the mix. The mixture is then heated for about 15-20 minutes. During this process, the charcoal soaks up all the colored impurities. Afterward, the charcoal is filtered out, and the filtered liquid is left to cool, resulting in clear crystals of the pure substance.

(iii) Distillation

"Distillation is a method where a liquid is turned into vapors by heating and then these vapors are cooled down to return to a liquid state."

$$\text{Liquid} \xrightarrow{\Delta} \text{Vapour} \xrightarrow{\text{Cool}} \text{Liquid}$$

Simple distillation is a way to clean up organic liquids that stay pretty stable at their boiling temperatures, and the impurities in them don't evaporate easily. This method works well for liquids like benzene, toluene, ethanol, acetone, chloroform, and carbon tetrachloride.

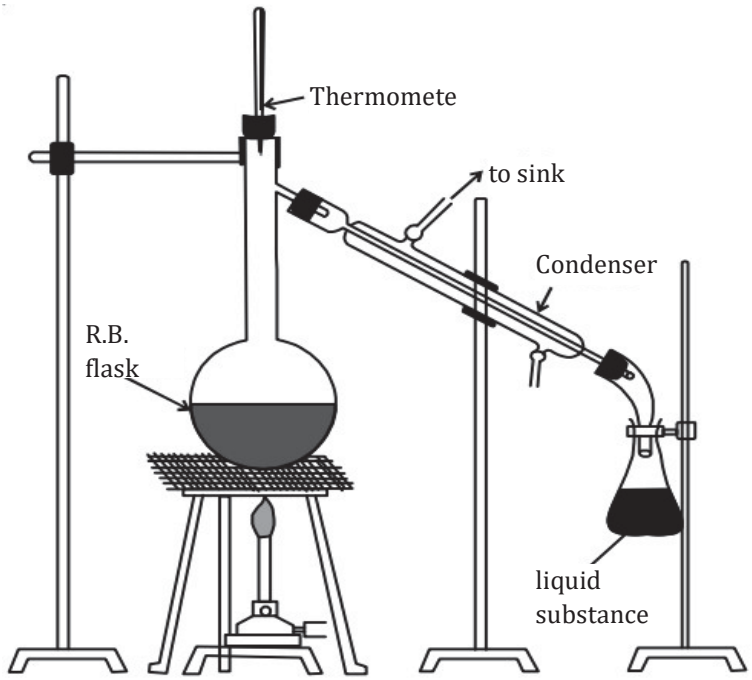


Fig.: Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.

Procedure

To purify the impure liquid, it is put into a distillation flask equipped with a condenser known as Liebig's condenser and a thermometer. The flask is heated using a water bath, sand bath, or direct heat, depending on the liquid's boiling point. Once the liquid reaches its boiling point, it turns into vapors. These vapors move through the condenser, where water circulates, causing them to condense back into liquid form. The pure liquid collects in a receiver, while the impurities that don't evaporate are left in the distillation flask. The temperature stays constant throughout the process until it starts to rise at the end, signaling the completion of distillation. Simple distillation can even make seawater drinkable by leaving non-evaporating impurities like NaCl behind and distilling the pure water.

Fractional Distillation

We use this method when we need to separate two liquids with really close boiling points (like a difference of 10 K to 30 K) that simple distillation can't handle. To make this separation possible, we use a fractionating column.

This column is usually a long tube with a series of bulbs or packing material like glass beads inside. Some examples of fractionating columns are shown in the picture below:

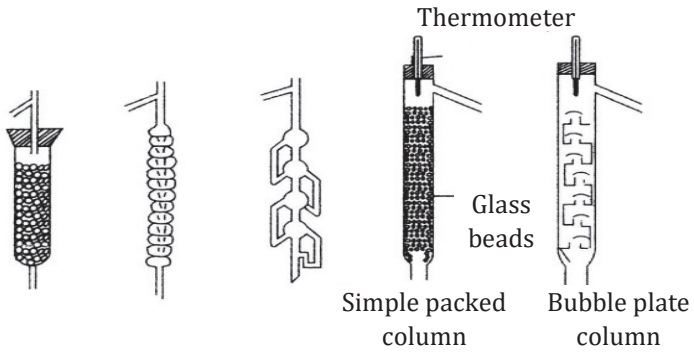


Fig.: Common types of fractionating column

Using a column in the distillation flask, we carry out the distillation process. Let's say our mixture has two parts, A and B. If A is more likely to turn into vapor when heated, then as the vapors rise, they are mostly A. When these vapors reach the first bulb, the B vapors (which are less likely to turn into vapor) cool down and condense, releasing heat that helps the rising A vapors. With this extra heat, A keeps going up to the next bulbs, while B continues to condense in the lower bulbs. By the time the vapors reach the top of the column, it's mostly pure A, as B has already condensed and fallen back into the flask. The vapors of pure A are then cooled and collected in the receiver using a water condenser. How well we separate A and B depends on how long the fractionating column is – the longer, the better. This process works well for certain mixtures.

(i) Fractional distillation of crude oil (Petroleum)

(ii) Methyl alcohol (CH_3OH) and acetone (CH_3COCH_3)

(iii) A mixture of C_2H (Benzene) and CH_3CH, (Toluene)

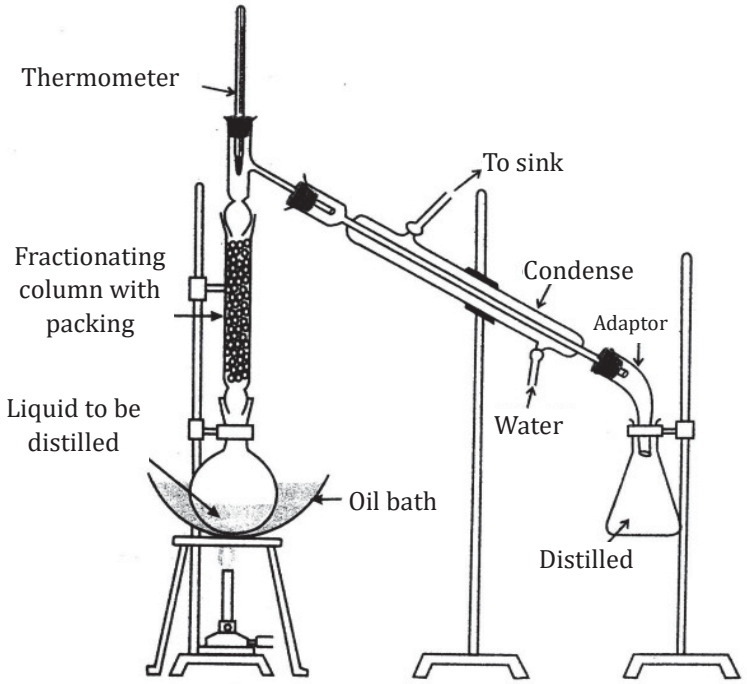


Fig.: Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

Distillation Under Reduced Pressure or Vacuum Distillation

This technique is employed to purify liquids that have high boiling points or tend to break down at or below their boiling points.

When a liquid boils, it happens when its vapor pressure matches the external pressure. If we decrease the pressure on the liquid, it will boil at a lower temperature. This is beneficial because when the liquid boils at a lower temperature, it doesn't break down.

In the lab, water section pumps can reduce pressure up to 10-20 mm of Hg, but vacuum pumps can easily achieve pressures as low as 0.1 mm of Hg.

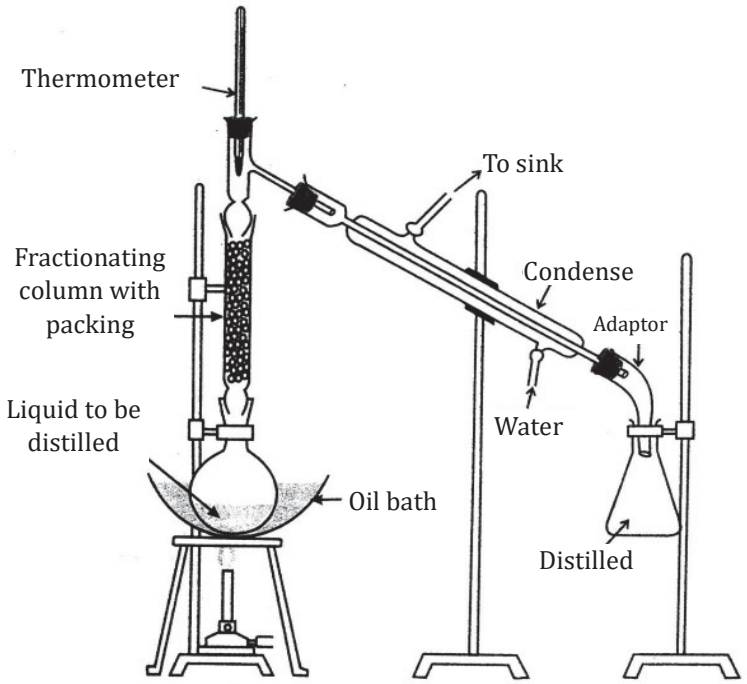


Fig.: Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

Here are a few examples where vacuum distillation has been employed to clean liquids:

a) Glycerol, which breaks down at its boiling point of 563 K, can be distilled without breaking down at a lower temperature of 453 K under a pressure of 12 mm Hg.

b) Making sugarcane more concentrated in the sugar industry.

c) Glycerol can be removed from spent-lye in the soap industry.

Steam Distillation

This method is used to distill substances, whether solid or liquid, that:

(i) don't dissolve in water,

(ii) have a high molecular mass,

(iii) (Have a relatively high vapor pressure at around 373 K, and

(iv) easily evaporate in steam, while their impurities don't evaporate.

In steam distillation, steam is sent through a heated flask with the liquid to be distilled. The steam and the volatile organic compound mix, condense, and are collected. Later, the compound is separated from water using a separating funnel.

This process involves heating a mixture of two liquids that don't mix well—water and an organic liquid. Each liquid has its own vapor pressure, and they start boiling together when the sum of the vapor pressure of the organic liquid (p_2) and water (p_1) equals the atmospheric pressure (P).

$$P = P_1 + P_2$$

the boiling temperature of the mixture must be lower than the usual boiling points of both substances. This means the organic liquid boils at a temperature below its usual boiling point, preventing decomposition.

The quantity of the substance that distills over is determined by the relationship:

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$$

Where,

w_1 = Weight of water which distills over

W_2 = Weight of organic compound which is being distilled.

P_2 = Vapour pressure of the organic compound.

P_1 = Vapour pressure of water vapour

18 = Molecular mass of water

M = Molecular mass of the organic compound

The method of steam distillation can be used to separate a mixture of o-nitrophenol and p-nitrophenol. In this process, water vapors carry along vapors of o-nitrophenol, which is more volatile. These vapors condense in the receiver, while p-nitrophenol, with a higher boiling point, stays in the distillation flask.

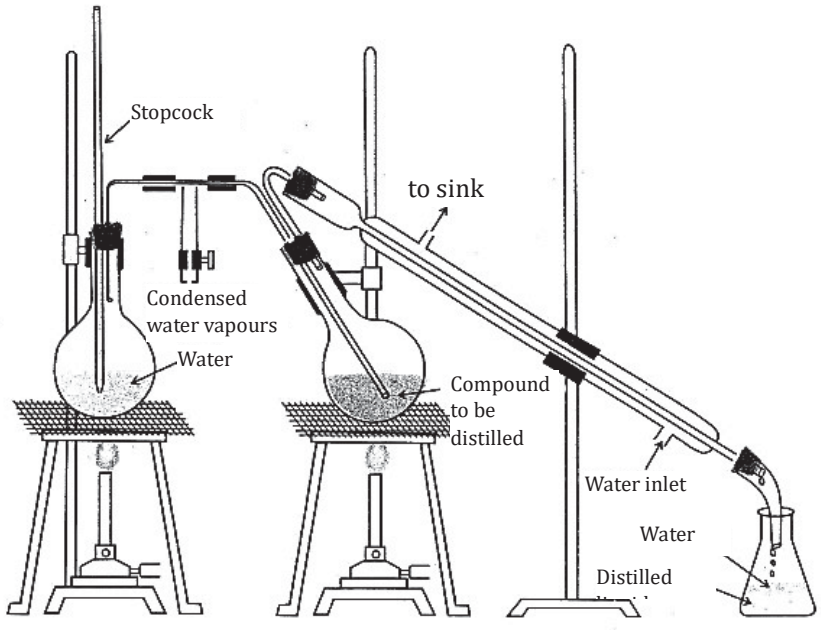


Fig.: Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask

This technique is also applicable to purify an impure sample of aniline.

Differential Extraction

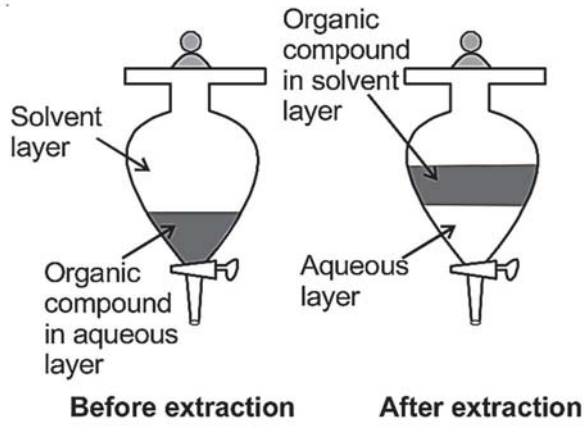
This method is typically used to separate specific organic solids dissolved in water by shaking them with the right organic solvent. This extraction process takes place in a separating funnel. The chosen organic solvent should be such that

(a) The solid should dissolve more in the organic solvent than in water.

(b) Water and the organic solvent shouldn't mix together.

The usual organic solvent is ether, and benzene or acetone can also work. However, alcohol is not suitable because it mixes too well with water.

Process: Take the water solution of the organic solid in a separating funnel, as depicted in the figure. Mix it with the chosen organic solvent. Close the funnel with a stopper and shake the contents vigorously.



After that, let it sit quietly for a while. Water and the organic solvent will separate into different layers, and the solid will move from the watery layer to the organic layer because it dissolves more in the organic solvent. It's important to know that the solvent makes the upper layer, and water forms the lower layer. To get them back, open the stopcock and collect each layer in different beakers. By evaporating the organic solvent, you can recover the solid. The effectiveness of the extraction process depends on how many times you repeat the extraction.

Chromatography

Chromatography is a modern and sensitive method used for quickly and effectively separating or analyzing components in a mixture and purifying compounds.

The term "chromatography" comes from the Greek words "Chroma," meaning color, and "Graphy," meaning writing, because it was initially used to separate colored substances in plants. Chromatography is essentially a way to physically separate components. Here's the definition:

"The technique of separating the components of a mixture, where separation occurs by the individual components moving differently through a stationary phase under the influence of a mobile phase."

Chromatography is categorized based on the principle involved.

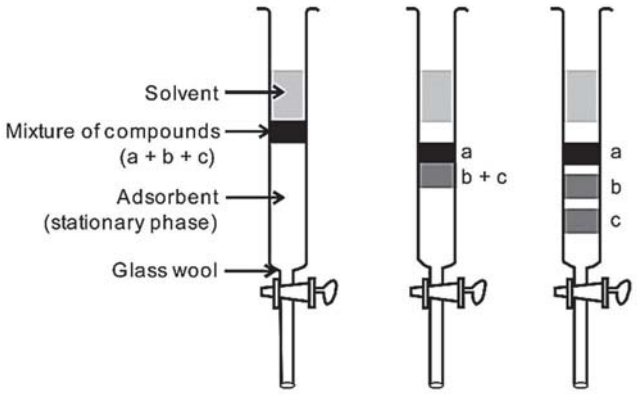
a) Adsorption chromatography → Column chromatography
a) Adsorption chromatography → Thin layer chromatography (TLC)

b) Partition chromatography - Paper chromatography

(a) Adsorption Chromatography

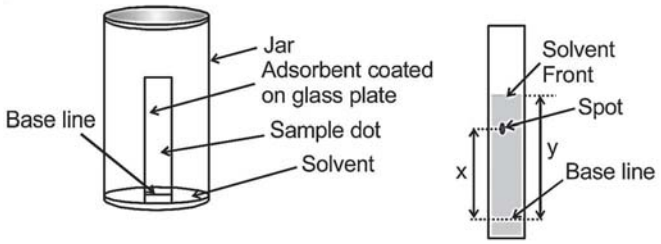
Principle: This method works by having the different parts of a mixture stick to a suitable adsorbent like silica gel or alumina. Since some substances stick more strongly than others, they will move through the column at different speeds and become separated.

Column Chromatography: Involving the separation of a mixture over a column of absorbent (stationary phase) packed into a glass tube, column chromatography is equipped with a stopcock at its lower end. The mixture, adsorbed on the adsorbent, is placed on top of the column in the glass tube.



A suitable liquid or a mix of liquids is made to move down the column slowly. Depending on how much the compounds stick, they get completely separated. The substances that stick the most are kept near the top, while others move down to different distances in the column, as illustrated in the figure above.

Thin Layer Chromatography (TLC): This is another form of adsorption chromatography. Here, the separation of components in a mixture happens over a thin layer of an adsorbent. A thin layer of adsorbent, like silica gel or alumina, is spread on a glass sheet, creating what's called a Thin Layer Chromatography plate (TLC-plate). The mixture's solution is applied as a small spot at one end of the plate. The plate is then placed in a solvent. As the solvent moves up, it carries the mixture's components along with it. Depending on how much they stick, the components move up different distances, leading to separation. The relative stickiness of components is measured in terms of retention factor, represented as (Rf) value or retardation factor.



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

Colored compounds create visible spots on the TLC plate because of their natural color. However, colorless compounds, which can't be seen with the naked eye, can be detected if they fluoresce when the plate is placed under UV light. Another way to detect compounds is by putting the plate in

a covered jar with a few iodine crystals. Compounds that absorb iodine will appear as brown spots. Occasionally, a suitable reagent may be sprayed on the plate. For instance, amino acids can be identified by spraying the plate with a ninhydrin solution.

(b) Partition Chromatography - Paper Chromatography

This is a unique kind of chromatography where both the stationary and mobile phases are liquids. A common example is paper chromatography, where chromatographic paper is used, similar to a TLC plate in thin layer chromatography. The water trapped in the paper acts as the stationary phase. In paper chromatography, the chromatography paper is dotted with a mixture containing various components. It is then placed in a solvent, which acts as the mobile phase and moves up through capillary action. The paper selectively holds onto different components, creating what's called a chromatogram. These chromatograms can be observed under ultraviolet light or by spraying with suitable reagents.