

# **Purification of Organic Compounds & Practical Organic Chemistry**

---

The determination of structure of an organic compound involves the following steps

- (i) Purification of the compounds
- (ii) Qualitative analysis for determining the elements present
- (iii) Quantitative analysis of elements detected under (ii)
- (iv) Determination of molecular mass and
- (v) Determination of structural formula by physicochemical and spectroscopic methods.

## **1. Purification**

In order to obtain the compound in its purest form, the followings techniques can be used

- (i) Filtration
- (ii) Crystallization
- (iii) Sublimation
- (iv) Distillation
- (v) Differential extraction
- (vi) Chromatography

Once the compound has been purified, its purity is checked by determining its melting or boiling point. Most of the pure compounds have sharp melting and boiling points.

### **1.1 Filtration**

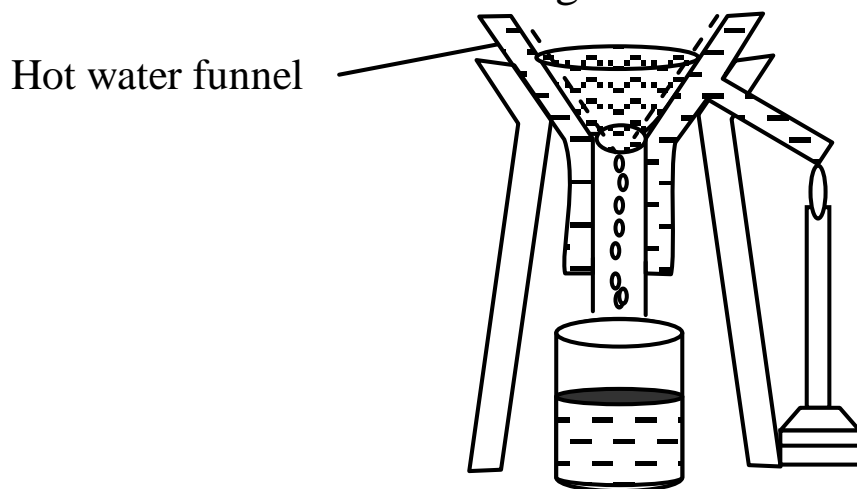
The process of filtration is used to separate insoluble solid component of a mixture from the soluble component of a mixture in a given solvent. For example, a mixture of naphthalene and urea can be separated using water as solvent. Urea dissolves in water while naphthalene remains insoluble. Upon filtration, naphthalene remains on the filter paper while urea is recovered from the filtrate by evaporating water. If the water soluble component of a mixture is appreciably soluble in hot water but only sparingly soluble in cold water, then to separate the mixture, filtration of a

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

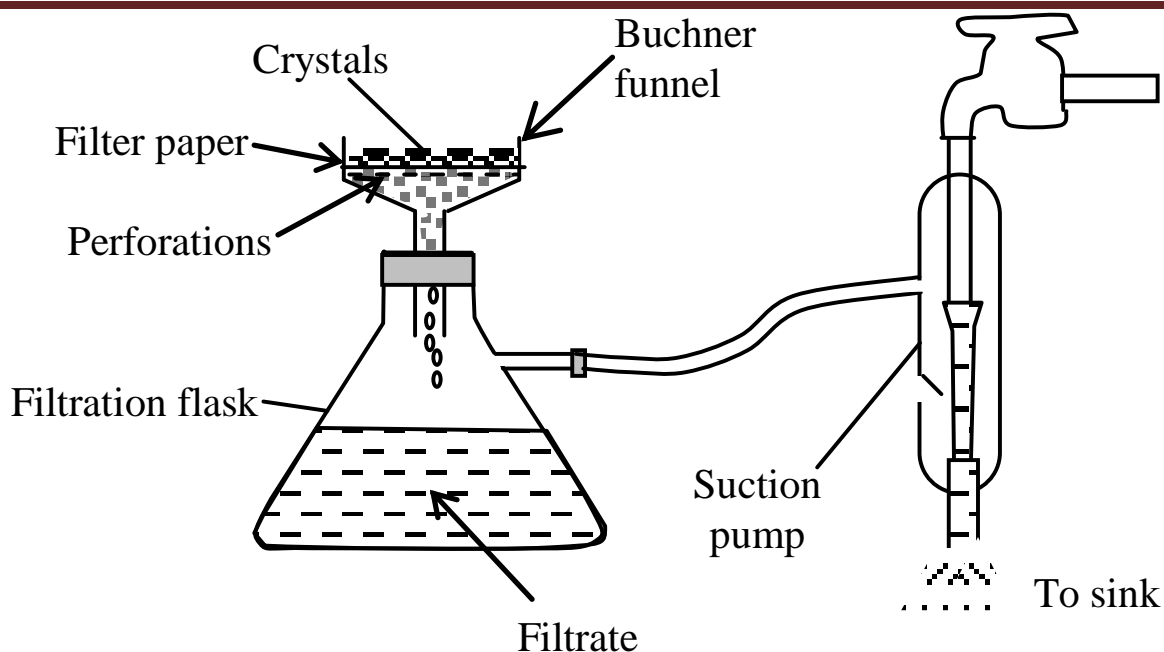
hot solution is required. If the solution to be filtered is sufficiently large, then filtration is done through a 'hot water funnel' to avoid formation of crystals in the funnel and its stem. The jacket of the hot water funnel keeps the solution hot in the glass funnel placed in it.

For example, a mixture of anthracene and benzoic acid is separated by dissolving the mixture in hot water and filtering the hot solution. Benzoic acid dissolves in hot water but anthracene does not. Upon filtration, anthracene remains as a residue on the filter paper while benzoic acid crystallizes from the filtrate on cooling.



Filtering the solution of the substance using hot water funnel to prevent crystallization during filtration

Sometimes, the filtration is very slow and takes a long time. In such cases, filtration is carried out under reduced pressure using a Buchner funnel and water suction pump are shown in figure.



Quick filtration process using a Buchner funnel and a suction pump

### 1.2 Crystallisation

The process by which an impure compound is converted into its crystals is known as crystallisation. This is one of the most commonly used techniques for purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a suitable solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get nearly a saturated solution. When this saturated solution is cooled, crystals of pure substance will separate out which are removed by filtration. The filtrate, i.e., mother liquor contains the impurities alongwith small quantity of the compound. If the compound is highly soluble in one solvent and too little soluble in another solvent, then crystallization can be carried out in a mixture of these solvents taken in a suitable ratio.

A suitable solvent which fulfills the following conditions is selected for crystallisation:

- (a) It should not react chemically with the impure substance.

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

- (b) It should dissolve more of the substance upon heating than at room temperature so that the excess of the substance is thrown out upon cooling.
- (c) Either the impurities should not dissolve at all in the solvent, or if they dissolve, they should be soluble to such an extent that they remain in the solution, i.e., in the mother liquor upon crystallisation.

The various solvents which are commonly employed for crystallisation are water, alcohol, ether, chloroform, carbon tetrachloride, benzene, acetone, ethyl acetate, petroleum ether etc.

Coloured impurities if present are removed first by boiling the solution of the impure substance with activated charcoal for about 15-20 minutes. The charcoal is filtered out and the filtrate is allowed to cool when crystals of pure substance will separate out.

If the compound and the impurities have comparable solubilities, then repeated crystallizations may be necessary to purify the substance. For example,

### **(i) Crystallisation of sugar**

Suppose we have a sample of sugar containing an impurity of common salt (sodium chloride). This can be purified by shaking the impure solid with hot ethanol at 348 K. The sugar will dissolve whereas the common salt remains insoluble. The hot solution is filtered, concentrated and then allowed to cool when crystals of sugar will separate out. In this case, had water been used as a solvent, the purification of sugar would not have been possible since both sugar and common salt are readily soluble in water.

### **(ii) Crystallisation of benzoic acid**

Suppose we have a mixture of benzoic acid and naphthalene. This mixture can be purified by treating the impure solid with hot water. Benzoic acid will dissolve while naphthalene remains insoluble. The hot solution is filtered and then allowed to cool when crystals of benzoic acid separate out. The crystals are separated by filtration and dried. Had benzene been used as a solvent, instead of water in this case, the purification of benzoic

## Purification of Organic Compounds & Practical Organic Chemistry

acid would not have been possible since both benzoic acid and naphthalene are quite soluble in benzene.

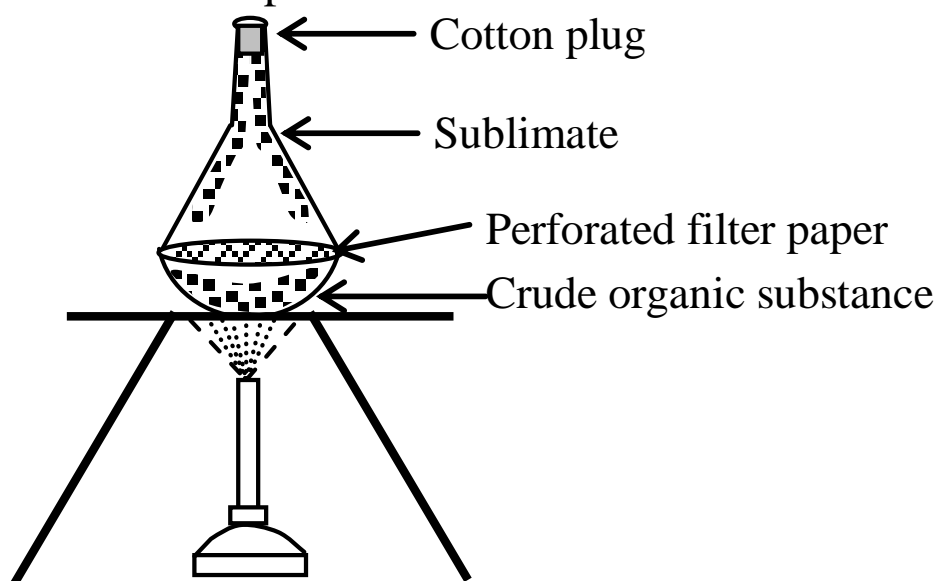
### 1.3 Sublimation

It involves the direct conversion of a solid into the gaseous state on heating without passing through the intervening liquid state and vice versa on cooling.

Only those substances whose vapour pressures become equal to the atmospheric pressure much before their respective melting points are capable of undergoing sublimation. Such substances are called sublimable. Since the number of such compounds is expected to be small, therefore, the process of sublimation is not of general application.

The process of sublimation is very useful in the purification of such solids which sublime on heating and are associated with non-volatile impurities.

The impure substance is taken in a china dish covered with a perforated filter paper over which an inverted funnel is placed. The stem of the funnel is plugged with a little cotton as shown in the figure. On heating the dish on a sand bath, vapours of the volatile solid rise up, pass through the holes in the filter paper and condense on the cooler walls of the funnel leaving behind the non-volatile impurities in the dish.



## Purification of Organic Compounds & Practical Organic Chemistry

Camphor, naphthalene, anthracene, benzoic acid, iodine etc. are purified by this process.

In case of organic compounds which are decomposed by heat, sublimation is done under reduced pressure.

### 1.4 Distillation

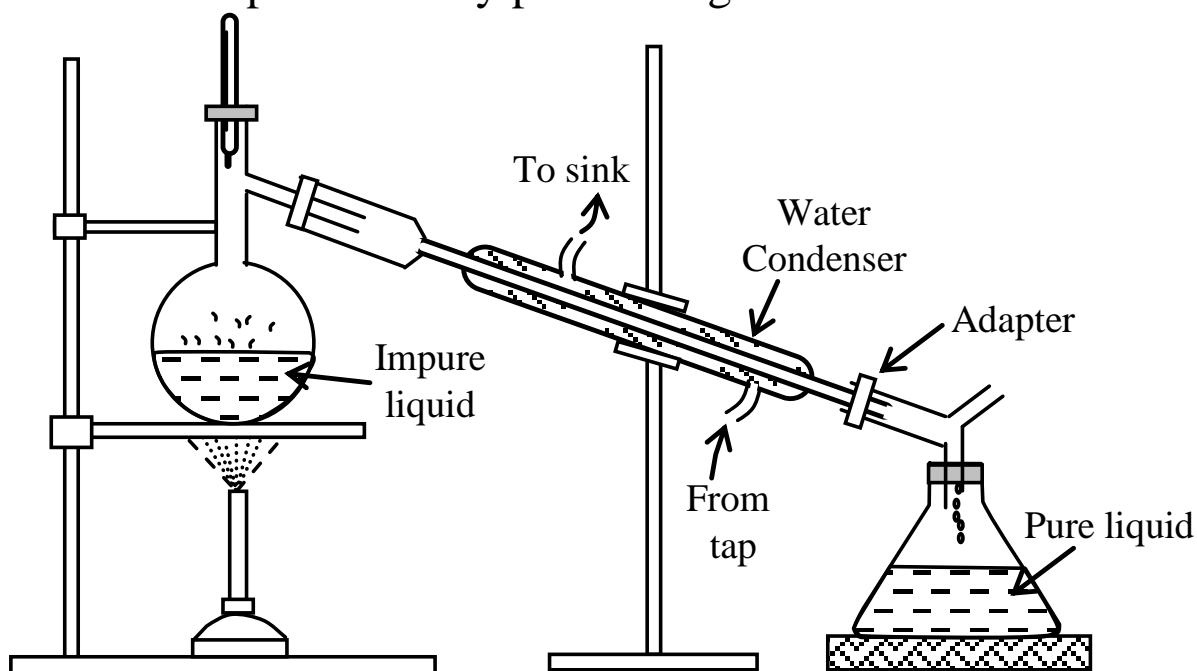
#### 1.4.1 Simple Distillation

Liquids are generally purified by simple distillation.

Distillation involves conversion of a liquid into vapours by heating followed by condensation of the vapours thus produced by cooling.

The method is commonly used for those liquids which are sufficiently stable at their boiling points and which contain non-volatile impurities. For example, simple organic liquids such as benzene, ethanol, acetone, chloroform, carbon tetrachloride, toluene, xylenes, etc. can be purified by simple distillation.

**Procedure:** The apparatus used for simple distillation is shown in figure. When the flask is heated, the temperature rises gradually and the liquid starts boiling when its vapour pressure becomes equal to the atmospheric pressure. These vapours as they pass through the condenser are condensed.



Apparatus for Simple Distillation

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

Only the liquid which distills at a constant temperature is collected in a receiver. This gives us the pure liquid.

### **Purification of a mixture of liquids:**

Simple distillation can also be used for the separation and purification of a mixture of two or more miscible organic liquids provided their boiling points differ by 30–50 K. The separation is based upon the fact that at the b.p. of the more volatile liquid (low boiling) of the mixture, the vapours almost exclusively consist of the more volatile liquid. Likewise, at the b.p. of the less volatile liquid (high boiling), vapours almost entirely consist of the less volatile liquid since the more volatile liquid has already distilled over. Thus, the separation of the liquid mixture into individual components can be achieved at their respective boiling points; the more volatile component distills over first while the less volatile component distills over afterwards. The non volatile impurities and impurities of liquids having boiling points much higher than those of the two liquids separated above are, however, left in the distillation flask. This method can be used to separate :

- (a) a mixture of ether (b.p. 308 K) and toluene (b.p. 384 K),
- (b) a mixture of hexane (b.p. 342 K) and toluene (b.p. 384 K),
- (c) a mixture of benzene (b.p. 353 K) or chloroform (b.p. 334 K) and aniline (b.p. 457 K) and so on.

### **1.4.2 Fractional Distillation**

If the boiling points of the two liquids of the mixture are very close to one another i.e. differ by 10 K or so, the separation cannot be achieved by the simple distillation method as described above. This is due to the reason that at the b.p. of the more volatile liquid of the mixture there will be sufficient vapours of the less volatile liquid as well. As a result, both the liquids of the mixture will distill together and the separation is denied.

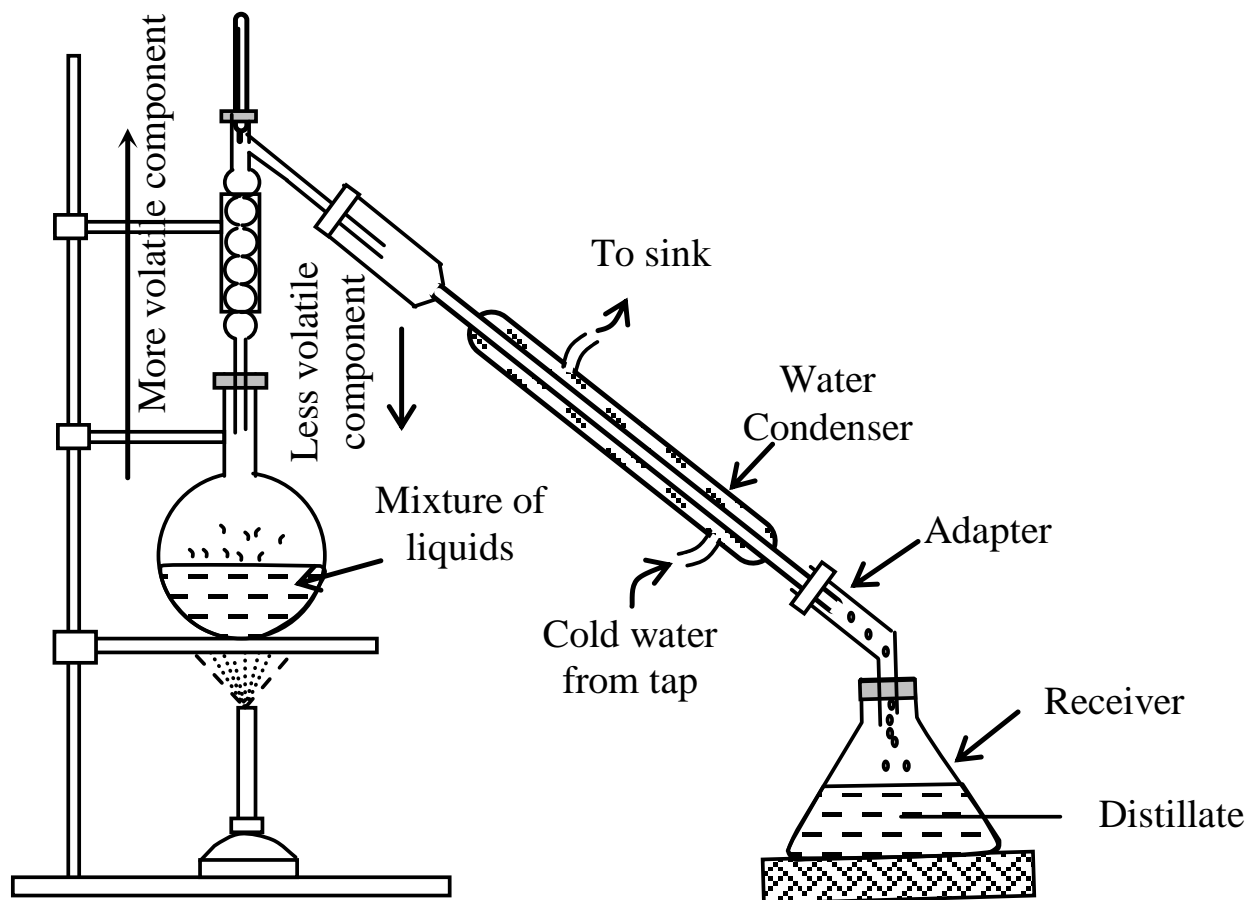
The separation of such a liquid mixture into individual components can, however, be achieved by fractional distillation, which involves repeated distillations and condensations. Fractional distillation is carried out using a fractionating column. It usually consists of a long glass tube with a wide



## Purification of Organic Compounds & Practical Organic Chemistry

bore either packed with glass beads, small stones, porcelain rings or coke, or blown into a number of spherical or pear-shaped bulbs. The actual purpose of the fractionating column is to increase the cooling surface area and to provide hurdles or obstructions to the ascending vapours and descending liquid.

**Procedure:** The apparatus used for fractional distillation is shown in figure.



Apparatus for Fractional Distillation using a Fractional column

Suppose we have a mixture of two liquids 'A' and 'B' of which 'A' is more volatile than 'B'. When such a liquid mixture is heated, the temperature rises slowly and mixture starts boiling. The vapours formed mainly consist of the more volatile liquid 'A' with little of the less volatile liquid 'B'. As these vapours travel up the fractionating column, the vapours of the less volatile liquid 'B' condense more readily than those of the more volatile liquid 'A'. Therefore, the vapours rising up become richer in 'A' and the liquid flowing down becomes richer in 'B'. This



## Purification of Organic Compounds & Practical Organic Chemistry

---

process of distillations and condensations is repeated at every point in the fractionating column. As a result of series of successive distillations, by the time the vapours reach the top of the column and escape into the condenser, they consist mainly of the more volatile component 'A'.

Similarly, after a series of successive distillations, the remaining liquid in the distillation flask gets enriched in higher boiling component. Each successive condensation and vaporization is called **theoretical plate**. Commercially, columns with hundreds of theoretical plates are available.

### Application

- (a) One of the technological applications of fractional distillation is to separate crude oil in petroleum industry into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil etc.
- (b) Fractional distillation has also been used to separate acetone (b.p. 329 K) and methyl alcohol (b.p. 338 K) from pyroligneous acid obtained by destructive distillation of wood.

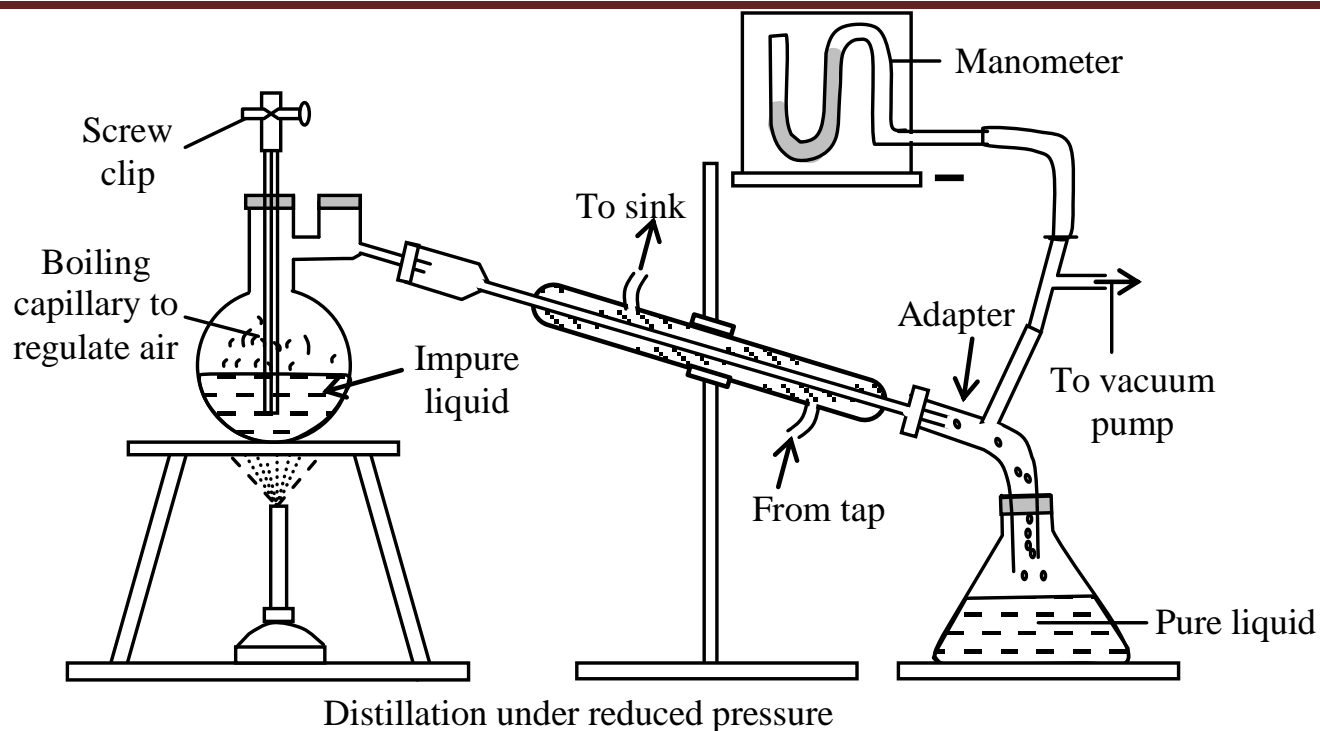
### 1.4.3 Distillation Under Reduced Pressure Or Vacuum Distillation

This method is used for the purification of high boiling liquids and liquids which decompose at or below their boiling points.

**Principle:** A liquid boils when its vapour pressure becomes equal to the external pressure. Obviously, the same liquid would boil at a lower temperature if the pressure acting on it is reduced. Since the liquid now boils at a lower temperature, its decomposition does not occur.

With the commonly used water pumps in the laboratory, a pressure of 10–20 mm Hg can be obtained. Under these conditions, the boiling points are reduced by about 100 degrees. However, with vacuum pumps, pressure of the order of 0.1 mm Hg can be easily obtained.

**Apparatus:** The apparatus used for vacuum distillation is shown in figure.



Given below are some of the examples where vacuum distillation has been used to purify liquids:

- (i) Glycerol which decomposes at its boiling point (563 K) can be distilled without decomposition at 453 K under 12 mm Hg pressure.
- (ii) Concentration of sugarcane in sugar industry.

### 1.4.4 Steam Distillation

This is a convenient method for the separation and purification of organic compounds (solid or liquids) from non-volatile organic or inorganic impurities. This method is applicable to only those compounds which are volatile in steam, insoluble in water, possess a high vapour pressure (10–15 mm Hg) at 373 K and contain non-volatile impurities.

Steam distillation is particularly valuable when the substance to be purified boils above 373 K at 760 mm and decomposes at or below its boiling point. This is due to the fact that steam distillation makes the high-boiling substances to distil at low temperature and hence avoids their decomposition. In this respect, steam distillation is comparable to vacuum distillation even though there is no reduction in the total pressure acting on the solution during the process of distillation.

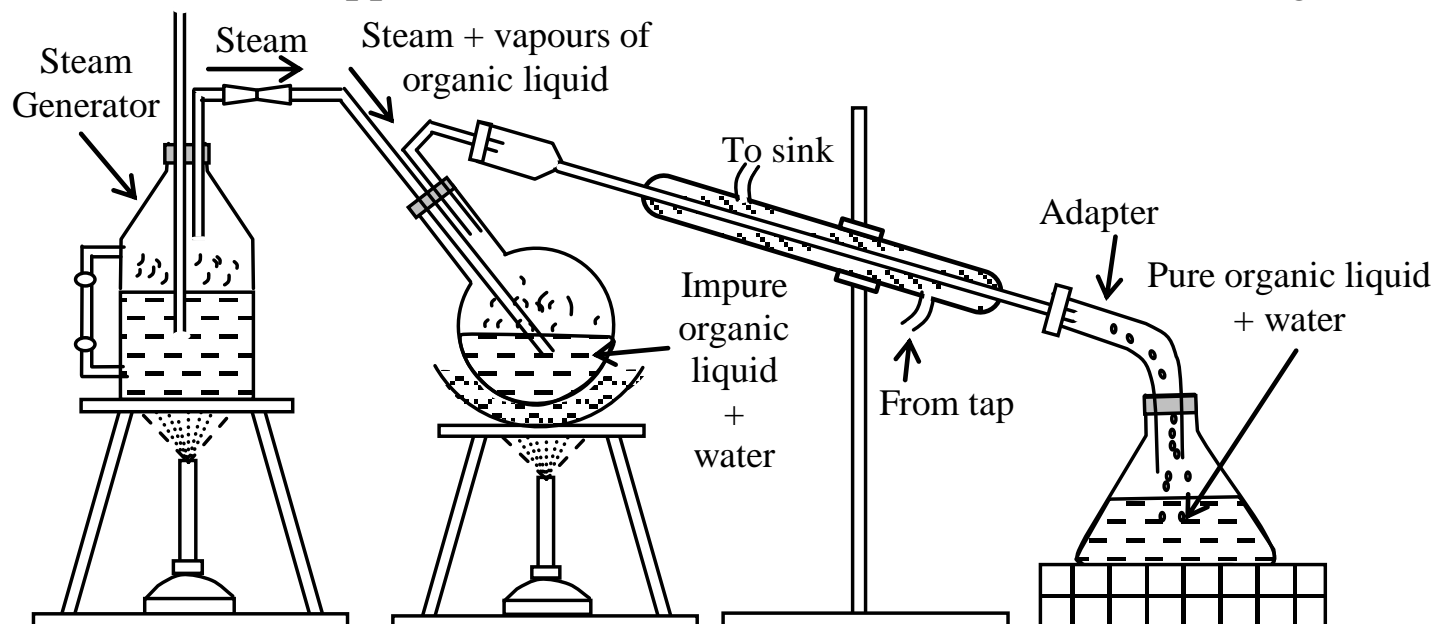
## Purification of Organic Compounds & Practical Organic Chemistry

**Principle:** In this method, a mixture of two immiscible liquids, i.e., water and an organic liquid is heated. Each would exert its own vapour pressure independently of the other and the mixture will begin to boil at a temperature when the sum of the vapour pressures of the organic liquid ( $p_1$ ) and that of water ( $p_2$ ) becomes equal to the atmospheric pressure ( $p$ ).

$$p = p_1 + p_2$$

Unless the vapor pressure of water or that of the organic liquid is zero, the temperature at which the mixture boils must be lower than the normal boiling point of both the organic liquids and the water. In other words, the organic liquids boils at a temperature lower than its normal boiling point and hence the decomposition is avoided.

**Procedure:** The apparatus used for steam distillation is shown in figure.



Apparatus for Steam Distillation

The impure organic compound mixed with water is taken in a round bottomed flask and steam is passed. The mixture starts boiling when the combined vapour pressure becomes equal to the atmospheric pressure. At this temperature, steam mixed with vapours of the compound passes over to the condenser where they are condensed and collected in the receiver. The distillate contains the desired substance and water which can easily be separated with the help of a separating funnel.

## Purification of Organic Compounds & Practical Organic Chemistry

---

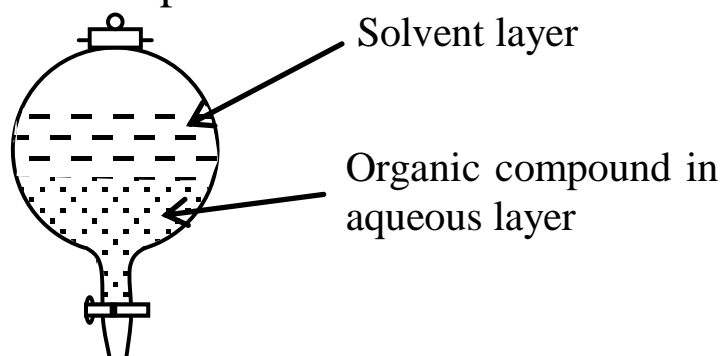
Some of the compounds which can be purified by this process are o-nitrophenol, bromo-benzene, aniline, nitrobenzene, essential oils, turpentine oil etc.

### 1.5 Differential Extraction

This method is used to recover organic compounds (solids or liquids) from their aqueous solutions.

The process essentially involves the shaking of the aqueous solution of the organic compound in a separating funnel with a suitable solvent which is immiscible with water but in which the organic compound is very highly soluble. Ether, benzene, chloroform, carbon tetrachloride are some of the solvents which are generally employed for extraction.

**Procedure:** The aqueous solution is mixed with a small quantity of the organic solvent in a separating funnel. The funnel is stoppered and the contents are shaken thoroughly for sometimes when the organic solvent dissolves the organic compound present in the aqueous solution. The separating funnel is now allowed to stand for some time when the organic solvent and water form two separate layers. The lower aqueous layer (when the organic solvent used is benzene or ether) is run out by opening the tap of the funnel and the organic layer separated. The aqueous solution is again poured into the funnel, mixed again with a small quantity of the organic solvent and the process is repeated several times till the entire amount of the organic compound is extracted.



The organic layers from all the steps are taken in a distillation flask. The organic solvent is distilled off leaving the organic compound in the distillation flask.

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

The efficiency of the process of extraction depends upon the number of times the extraction is repeated. It has been found that with a given amount of the solvent, larger the number of extractions, greater is the amount of the material extracted.

This method is normally applicable to non-volatile compounds. For example, benzoic acid can be extracted from its water solution using benzene.

If the organic compound is less soluble in the organic solvent, a very large quantity of the solvent would be required to extract even a very small quantity of the compound. In such cases, the technique of continuous extraction is employed. In this process, the same solvent is repeatedly used for extraction of the compound. The most commonly used apparatus for this process is called soxhlet extractor.

### **1.6 Chromatography**

Chromatography is the most modern and versatile method used for the separation, purification and testing the purity of organic compounds. This method was first discovered by Tswett, a Russian botanist, in 1906 for the separation of coloured substances (plant pigments) into individual components. Now this method is widely used for separation, purification, identification and characterisation of the components of a mixture, whether coloured or colourless.

Chromatography is essentially a physical method of separation. It is defined as follows:

The technique of separating the components of a mixture in which separation is achieved by the differential movement of individual components through a stationary phase under the influence of a mobile phase.

#### **1.6.1 Types of Chromatography**

The stationary phase can be either a solid or tightly bound liquid on a solid support while the mobile phase can be either a liquid or a gas. Depending

## Purification of Organic Compounds & Practical Organic Chemistry

upon the nature of the stationary and the mobile phases, the different types of chromatographic techniques commonly used are given in table below.

**Table: Some common types of chromatography**

S. No.	Type of Chromatography	Mobile/ Stationary Phase	Uses
1.	Adsorption or Column chromatography	Liquid / Solid	Large scale separations
2.	Thin layer chromatography (TLC)	Liquid / Solid	Qualitative analysis (identification and characterisation of organic compounds).
3.	High performance liquid chromatography (HPLC)	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 (sugars, $\alpha$ -amino acids) and inorganic compounds.

Depending upon the principle involved, chromatography can be divided into the following two categories:

(a) Adsorption chromatography      (b) Partition chromatography

### (a) Adsorption chromatography

**Principle:** This method is based upon the differential adsorption of the various components of a mixture on a suitable adsorbent such as silica gel or alumina. Since some compounds are more strongly adsorbed than the other, they will travel through the column at different rates and thus get separated.



## Types of adsorption chromatography

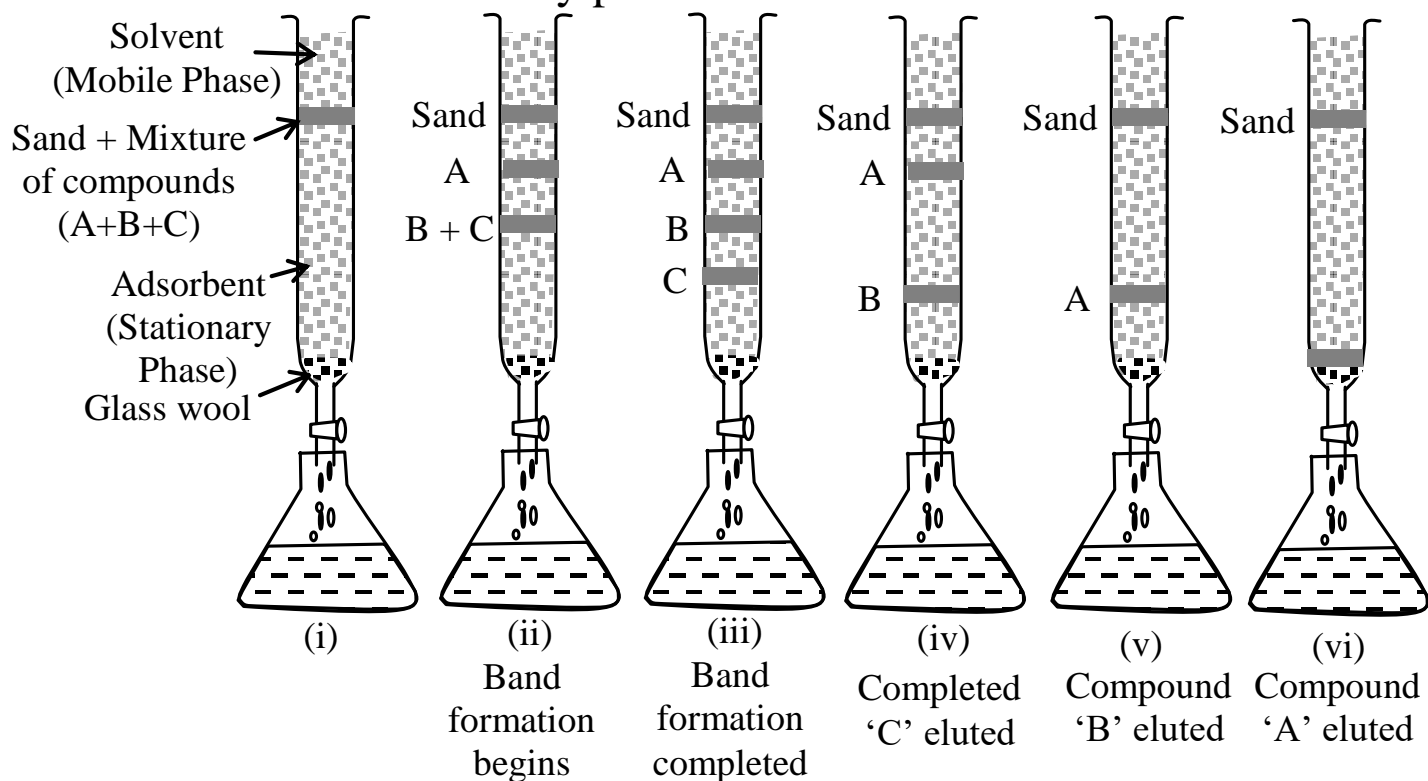
Adsorption chromatography is of the following two types:

(I) Column Chromatography (II) Thin layer chromatography

### Column chromatography:

Column chromatography is the simplest of all the chromatographic techniques and is widely used. The whole process is carried out in a long glass column provided with a stop-cock at the bottom. The various steps involved in this process are:

**(i) Preparation of the Column:** A plug of cotton or glass wool is placed at the bottom of a clean and dry glass column. Above this, a thin layer of acid-washed sand is placed to support the adsorbent. A suitable adsorbent such as alumina ( $\text{Al}_2\text{O}_3$ ), silica gel, magnesium oxide, starch, charcoal etc. is made into slurry with a suitable solvent (preferably non-polar) such as hexane or petroleum ether. The slurry is then carefully packed in the column by gentle tapping so that no air bubble is entrapped in the column. This constitutes the stationary phase.



Column Chromatography – stages (i), (ii), (iii), (iv), (v) and (vi) represents the progressive separation of the mixture into three individual components.



## **Purification of Organic Compounds & Practical Organic Chemistry**

---

**(ii) Adsorption:** The mixture to be separated (or the impure compound to be purified) is dissolved in a minimum volume of a suitable highly polar solvent and applied on the top of the column of the adsorbent with the help of a dropper or a microsyringe. As the solution travels down, the mixture is adsorbed in a narrow band. A thin layer of acid-washed sand is again placed at the top of the column followed by a loose plug of cotton or wool. The sand layer prevents the column from being disturbed during the addition of solvent from time to time.

After the application of the sample, a little amount of the solvent is placed over the sand layer and the column is allowed to stand for about 15–20 minutes as shown in stage I. During this period, the various components of the mixture (say A, B and C) are adsorbed to different extents depending upon their polarity (say  $A > B > C$ ) within a narrow band. Thus, within the narrow band, component A is strongly adsorbed, component B is moderately adsorbed while component C is weakly adsorbed.

**(iii) Elution:** It is the process of extraction of the adsorbed components from the adsorbent with the help of solvents of increasing polarity. The solvents usually employed in the increasing order of polarity are petroleum ether, carbontetrachloride, benzene, chloroform, diethyl ether, ethyl acetate, acetone, alcohol etc.

A solvent or a mixture of solvents which is used to extract the column constitutes the mobile phase and is usually called an eluent. As the eluent passes down the column, it dissolves the different compounds. The least strongly adsorbed component of the mixture i.e. component C is eluted first by the least polar solvent followed by moderately strongly adsorbed component B by solvent of intermediate polarity, while the most strongly adsorbed component A is eluted last of all by the solvents of higher polarity.

In this way, the various components of the mixture can be separated into different fractions. Distillation or evaporation of the solvent from different fractions gives the various components of the mixture in pure form.

## Purification of Organic Compounds & Practical Organic Chemistry

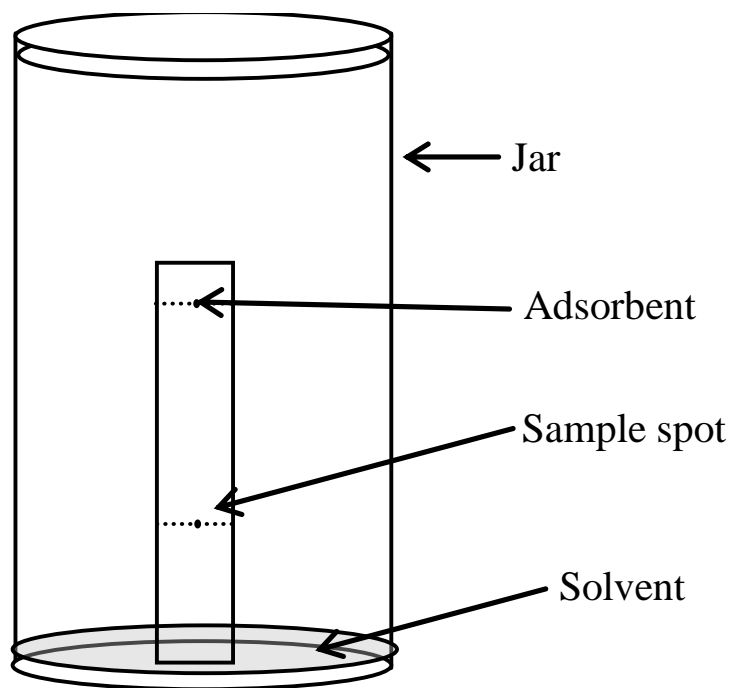
This technique is being widely used throughout the world for the purification of different substances and the separation of mixtures. For example, a mixture of naphthalene (hydrocarbon) and benzophenone (ketone) can be separated over a column of alumina and by using petroleum ether containing benzene as eluent. Naphthalene being less polar is weakly adsorbed while benzophenone being more polar is strongly adsorbed over the column. Elution of the column will first elute naphthalene and then benzophenone.

### Thin layer chromatography (TLC):

It is another type of adsorption chromatography in which separation of the components of a mixture is achieved over a thin layer of an adsorbent. A thin layer (0.2 mm thick) of an adsorbent such as silica gel (or alumina) is spread over a plastic or glass plate of suitable size.

A suitable TLC plate is taken and two pencil lines are drawn across the width of the plate about 1 cm from each end. The lower pencil line is called the starting line while the upper line is called the finish line or solvent front.

A solution of the mixture to be separated is applied as a small spot with the help of a capillary on the starting line. The plate is then placed in a closed jar containing a suitable solvent.



TLC Chromatogram being developed

As the solvent moves up, the components of the mixture also move up along the plate to different distances depending upon their degree or extent

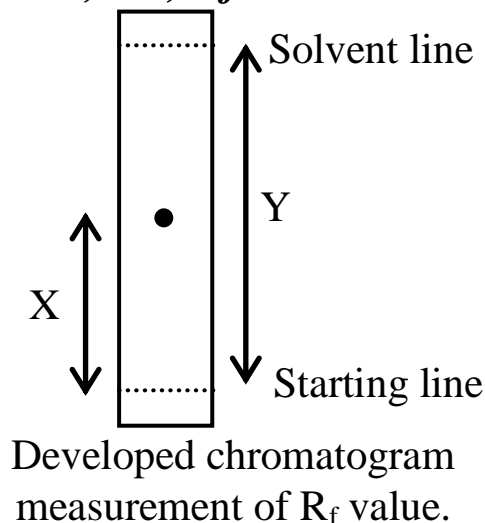
## Purification of Organic Compounds & Practical Organic Chemistry

of adsorption. When the solvent front reaches the finish line, the plate is removed and then dried in air.

The spots of coloured components are visible on TLC plate due to their original colour. The spots of the colourless components which are invisible to the eye can be observed using the following visualization methods.

- (i) Ultraviolet light: Organic compounds which fluoresce can be detected by placing the plate under UV lamp having light of 254 nm. Since all organic compounds do not produce fluorescence under UV light, this method is not of general applicability.
- (ii) Iodine vapours: This is the most commonly used detection reagent. The developed TLC plate is placed in a covered jar containing a few crystals of iodine. Spots of compounds which adsorb iodine will show up as brown spots.
- (iii) Chemical methods: Sometimes a suitable chemical reagent may be sprayed on the plate. For example, amino acids can be detected by spraying the plate with ninhydrin solution. Similarly, aldehydes/ketones can be detected by spraying the plate with the solution of 2,4-dinitrophenylhydrazine.

The various components on the developed TLC plate are identified through their *retention factor, i.e.,  $R_f$  values*. It is defined as



## Purification of Organic Compounds & Practical Organic Chemistry

---

$$R_f = \frac{\text{Distance travelled by the compound (X)}}{\text{Distance travelled by the solvent front (Y)}}.$$

Since the solvent front always moves faster on the TLC plate than the compounds,  $R_f$  values are usually expressed as a decimal fraction.

### (b) Partition chromatography:

We have discussed above the column chromatography or TLC is a liquid/solid chromatography i.e., the mobile phase is a liquid while the stationary phase is a solid. In contrast, partition chromatography is a liquid/liquid chromatography in which both the mobile phase and the stationary phase are liquids.

Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper called chromatographic paper is used. Although paper consists mainly of cellulose, the stationary phase in paper chromatography is not the cellulose but the water which is adsorbed or chemically bound to it. The mobile phase is another liquid which is usually a mixture of two or three solvents with water as one of the components.

**Principle:** Paper chromatography works on the principle of partition i.e., it is based upon continuous differential partitioning (or distribution) of the various components of the mixture between the stationary and the mobile phases.

**Process:** A suitable chromatographic paper is selected and a starting line is drawn across the width of the paper at about 1 or 2 cm from the bottom. A spot of the mixture of components to be separated is applied on the starting line with the help of a fine capillary or syringe. The chromatographic paper is then suspended in a suitable solvent mixture.

The solvent rises up the paper by capillary action and flows over the spot. The different components of the mixture travel through different distances depending upon their solubility in or partitioning between the stationary and the mobile phases. When the solvent reaches the top end of the paper, the paper is taken out and allowed to dry. The paper strip so developed is called the chromatogram. The spots of the separated coloured compounds

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

are visible at different heights from the starting line and are identified by their  $R_f$  values as discussed under TLC. The spots of the colourless compounds may, however, be observed either under ultraviolet light or by the use of an appropriate spray reagent.

The type of chromatography discussed above is called ascending paper chromatography. Alternatively, the paper can be folded into a cylinder and the two ends dipped together. This is also sometimes called circular chromatography.

### **Illustration 1.**

Name the methods by which we can separate the following:

- (i) o-nitrophenol and p-nitrophenol
- (ii) Benzoic acid and NaCl

### **Solution:**

- (i) Steam distillation can be used to separate the o-nitrophenol from p-nitrophenol since the former has got intramolecular hydrogen bonding and is steam distillable.
- (ii) Benzoic acid can be sublimed while NaCl cannot be. Hence, sublimation can be used to separate the two.

### **Illustration 2.**

If a liquid 'X' has a vapour pressure of 0.02 atm and steam has a vapour pressure of  $p$  atm. What is the external pressure at which 'X' is steam distilled.

### **Solution:**

External pressure =  $0.02 + p$  atm.

## 2. Qualitative Analysis

Qualitative analysis of an organic compound involves following operations.

(i) Preliminary examination:

(a) Physical state (b) Colour (c) Odour (d) Ignition test (e) Solubility test

(ii) Detection of elements

(iii) Detection of functional groups

(iv) Determination of melting or boiling point and

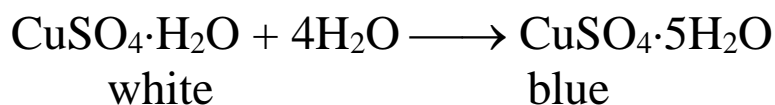
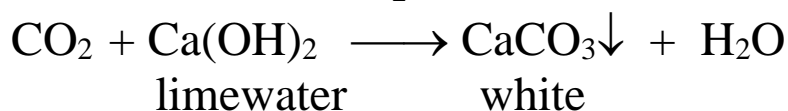
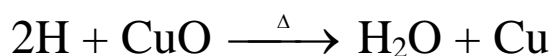
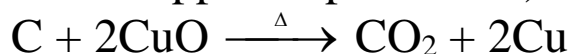
(v) Preparation of derivatives.

### 2.1 Detection of Elements

The elements generally present in organic compounds are carbon, hydrogen and oxygen. The detection of these elements in the organic compounds is not essential. Organic compounds also contain nitrogen, halogens, phosphorus and sulphur, in addition to these elements. Thus, detection of elements basically refers to nitrogen, halogens, phosphorous & sulphur.

#### 2.1.1 Detection of Carbon And Hydrogen

The organic compound is mixed with an equal amount of dry copper oxide and strongly heated. The carbon present in the compound is oxidised to carbon dioxide (turns limewater milky) and hydrogen to water (turns anhydrous copper sulphate blue).



#### 2.1.2 Lassaigine's Test

Nitrogen, sulphur and halogens in an organic compound are detected by **Lassaigine's test** through Lassaigine's extract. Organic compounds contain

## **Purification of Organic Compounds & Practical Organic Chemistry**

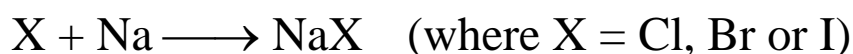
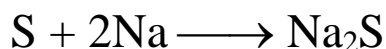
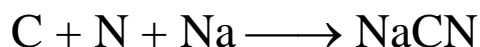
---

these elements mostly linked through covalent bonds. In order to make them free, we convert them into ionic form by treating the compound with sodium. The ionic compound formed are water-soluble and releases the element in ionic form, which is easy to detect.

### **(a) Preparation of Lassaigue's Extract**

A small piece of dry sodium metal is heated gently in a fusion tube till it melts to a shining globule. Then, a small amount of organic substance is added and the tube is heated strongly till it becomes red hot. The red hot tube is plunged into distilled water contained in a china dish. The fusion tube should break into pieces on adding to water. If it is not broken, it is broken using a glass rod. Then the solution is boiled for some time. It is then cooled and filtered. The filtrate is known as sodium extract or Lassaigue's extract.

Sodium reacts with elements of the organic compound to give following reactions.



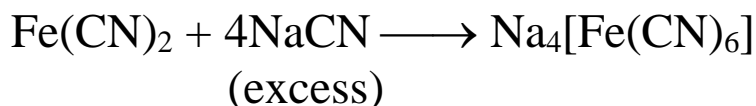
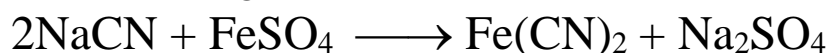
When nitrogen and sulphur both are present in the organic compound, then sodium thiocyanate is formed.



All the sodium salts being soluble in water, can be easily detected.

### **2.1.3 Detection of Nitrogen**

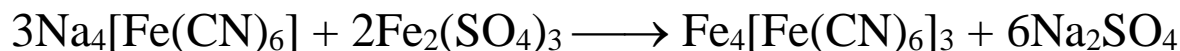
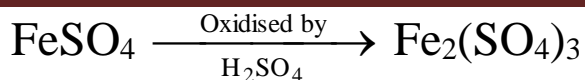
If the organic compound contains nitrogen, the sodium fusion extract will contain sodium cyanide (NaCN). A small portion of the extract is boiled with ferrous sulphate solution and acidified with dilute sulphuric acid. A blue precipitate of Prussian blue (ferric ferrocyanide) confirms the presence of nitrogen.





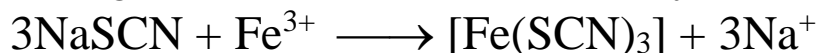
## Purification of Organic Compounds & Practical Organic Chemistry

---



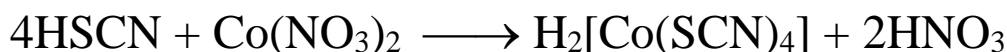
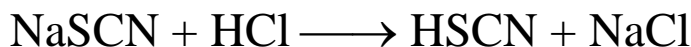
Prussian blue

If the organic compound contains sulphur along with nitrogen and the sodium, present is in insufficient amount then sodium thiocyanate is formed, which gives blood red colouration by reaction with ferric ions.



Blood red colour

However, the absence of blood red colouration does not necessarily mean that sulphur is absent in the organic compound because NaCNS combines with Na to give NaCN and Na<sub>2</sub>S.



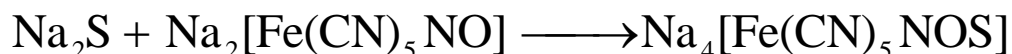
Blue colour

### 2.1.4 Detection of Sulphur

If the organic compound contains sulphur, the sodium fusion extract will contain sodium sulphide. It is divided into two portions and following tests are performed.

#### Sodium Nitroprusside Test:

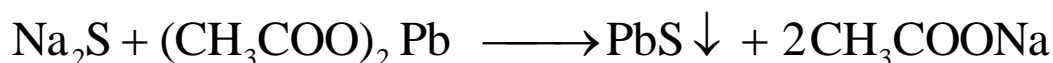
Add freshly prepared sodium nitroprusside solution to one portion. A deep violet colour confirms the presence of sulphur.



Violet colour

#### Lead Acetate Test:

Acidify the second portion with acetic acid and then add lead acetate solution. A black precipitate of lead sulphide confirms the presence of sulphur.

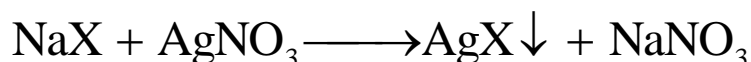


lead acetate

black ppt.

### 2.1.5 Detection of Halogens

If the organic compound contains halogen, the sodium fusion extract will contain sodium halide. The sodium fusion extract is boiled with dilute nitric acid to decompose sodium cyanide or sodium sulphide, (if present) otherwise a white precipitate of silver cyanide or silver sulphide will be formed even in the absence of halogen. The solution is then cooled and silver nitrate solution is added. The characteristic precipitate confirms the presence of a halide.



(a) White precipitate, soluble in aqueous ammonia indicates chlorine. Light yellow precipitate, sparingly soluble in aqueous ammonia indicates bromine. Pale yellow precipitate, insoluble in aqueous ammonia indicates iodine.

### 2.1.6 Detection of Phosphorus

The organic compound containing phosphorus is fused with sodium peroxide and extracted with water. The aqueous solution is boiled with concentrated nitric acid and ammonium molybdate is added. A canary yellow precipitate indicates the presence of phosphorus.

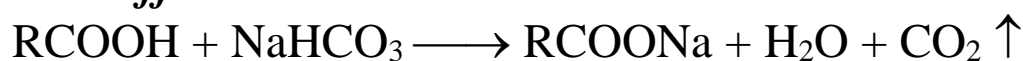
## 2.2 Detection of Functional Groups

Detection of functional groups is an important step in the analysis of organic compounds. It entirely depends on the correct determination of the constituent elements.

### 2.2.1 Tests For Carboxylic Acid Group

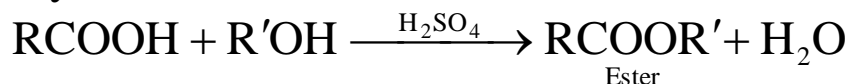
(i) **Litmus test:** Place a small quantity of the organic compound or its aqueous solution on a piece of moist blue litmus paper. If the litmus paper turns *red*, carboxylic acid group may be present.

(ii) **Sodium bicarbonate test:** Add a small quantity of the organic compound to sodium bicarbonate solution taken in a test-tube. Compound dissolves with *brisk effervescences*.



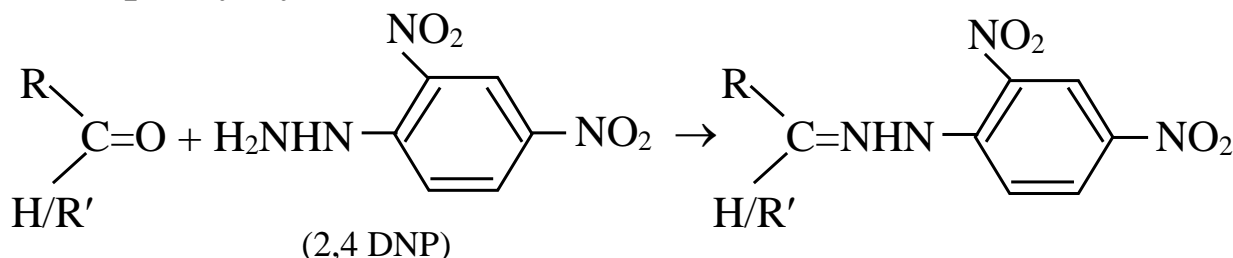
## Purification of Organic Compounds & Practical Organic Chemistry

(iii) Take a small quantity of the organic compound and add some alcohol in a test-tube. Add a few drops of conc. sulphuric acid and warm on a water bath, a fruity smell indicates the formation of an ester.



### 2.2.2 Tests For Carbonyl Group (>C = O)

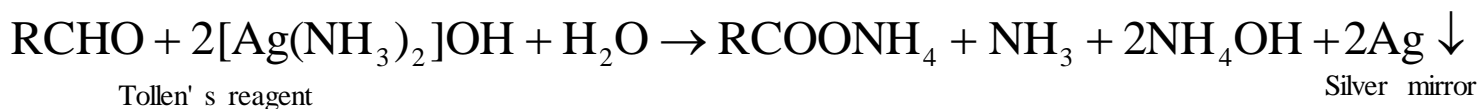
Ketones and aldehydes form *orange or red crystalline precipitate* with 2,4-dinitrophenylhydrazine.



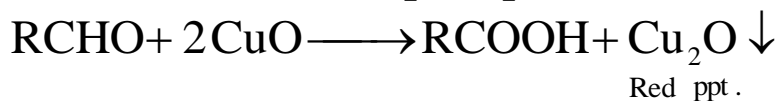
2,4-dinitrophenylhydrazine is called Brady's Reagent. Formation of *orange or red crystalline precipitate* indicate the presence of aldehyde or ketone group. However, some highly sterically hindered ketones do not respond to this test.

### 2.2.3 Tests For Aldehyde Group

(i) **Tollen's test:** Add few drops of Tollen's reagent ppt. to a small quantity of the organic compound and heat on a water bath. A *shining silver mirror* is formed on the inner walls of test-tube.



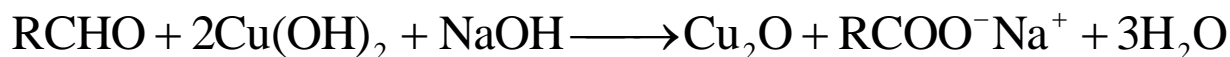
(ii) **Fehling's test:** Mix equal volumes of Fehling's (A) and Fehling's (B) solution in a test-tube. Add a small amount of the organic compound and boil for some time. A *red precipitate* of  $\text{Cu}_2\text{O}$  is obtained.



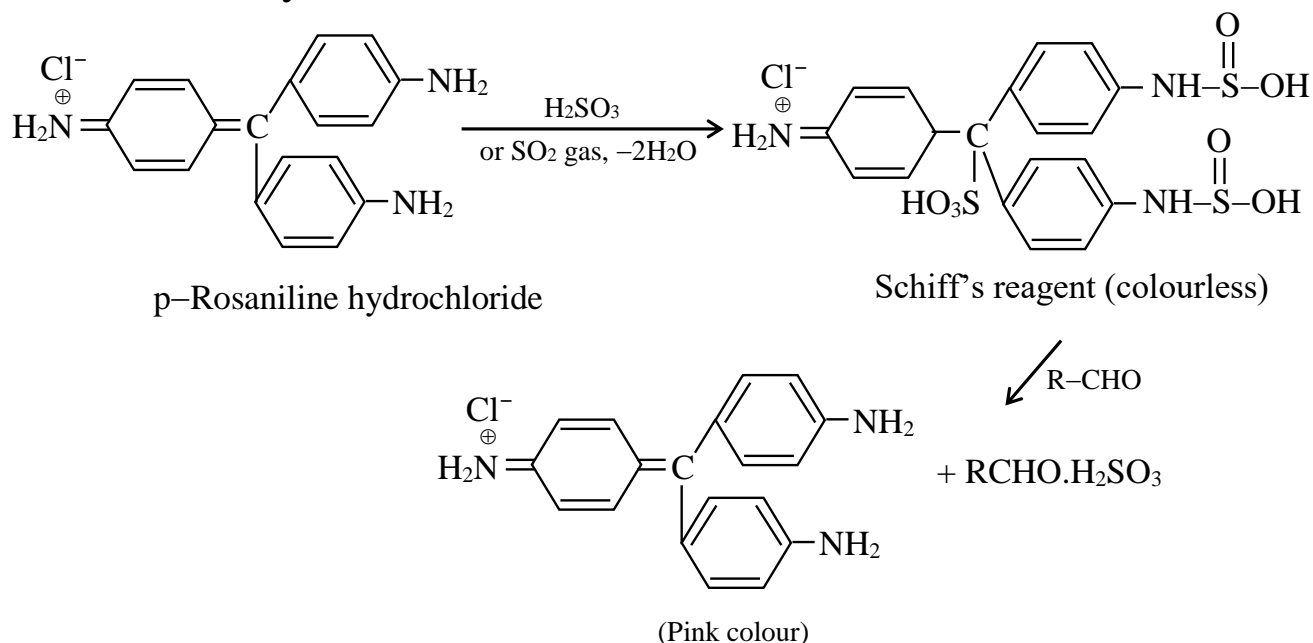
(iii) **Benedict's test:** Take small amount of Benedict's reagent in a test-tube. Add a few ml of the organic compound (or a solution prepared

## Purification of Organic Compounds & Practical Organic Chemistry

in alcohol or water). Heat the mixture to boiling. Formation of **red precipitate** indicates the presence of aldehydic group.



(iv) **Schiff's test:** Take small amount of Schiff's reagent in a test-tube and shake with organic compound (do not heat). A **pink colour** appears instantaneously.



### 2.2.4 Tests For Ketone Group

(i) **Brady's test:** If a compound gives positive test with Brady's reagent but negative tests for aldehydes, it is ketone.

(ii) **Sodium nitroprusside test:** Treat some organic compound with few drops of freshly prepared solution of sodium nitroprusside followed by excess of  $\text{NaOH}$  solution. A **wine-red colour** is obtained.

Ketones also form precipitates with sodium bisulphite reagent.

### 2.2.5 Tests For Phenol Group

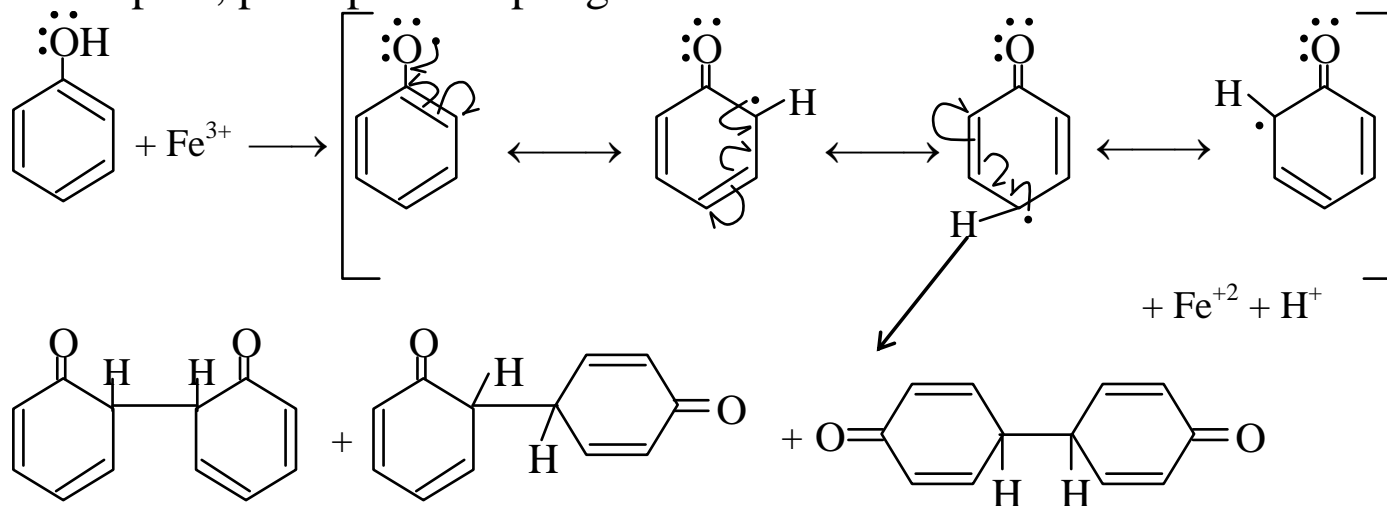
(i) **Litmus test:** Place a trace of the organic compound on the moist blue litmus paper. It turns **red**.

(ii) **Neutral  $\text{FeCl}_3$  test:** When phenols are treated with neutral ferric chloride solution, they form coloured complexes. The colour of the complex may be **violet, red, blue or green**. This is a characteristic reaction

## Purification of Organic Compounds & Practical Organic Chemistry

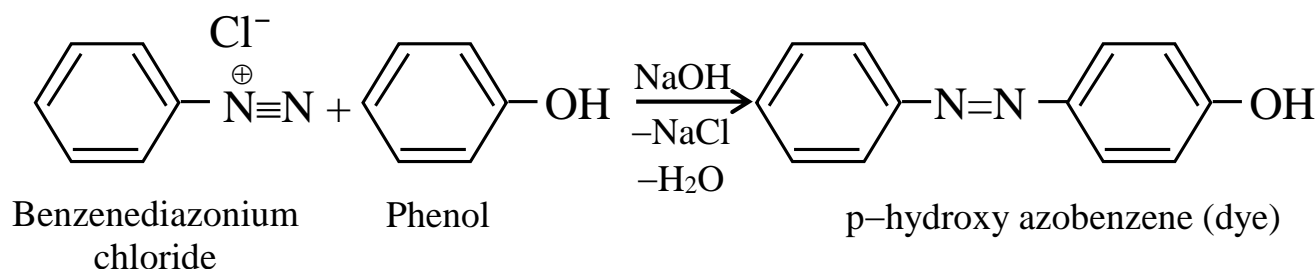
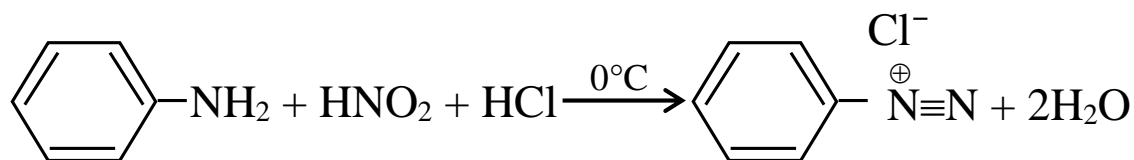
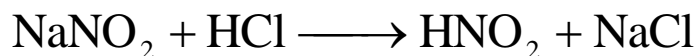
of compounds having enolic group ( $=C-OH$ ). All stable enols respond to this test.

With relatively milder oxidizing agents such as ferric chloride ( $Fe^{3+}$ ), a resonance stabilized phenoxyl radical is formed. This radical soon undergoes dimerization, which may take place by ortho-ortho, ortho-para, para-para coupling.



The phenoxyl radicals are highly coloured and therefore, products are also coloured.

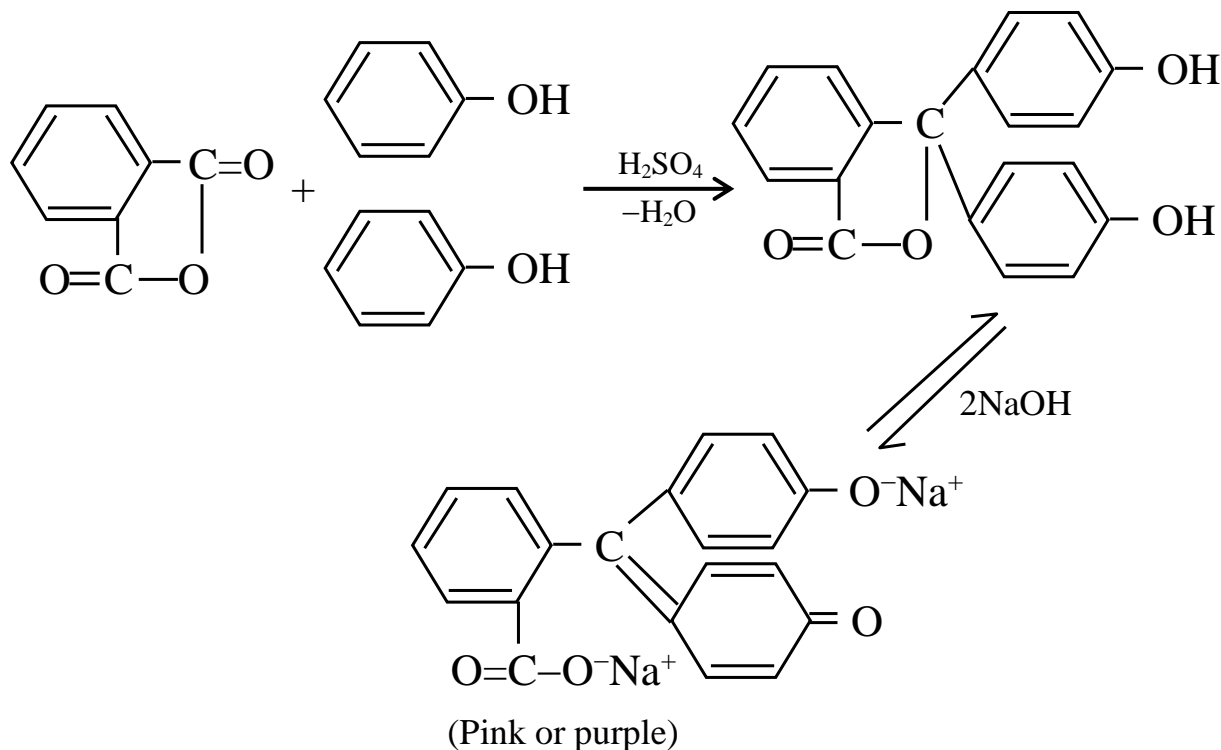
**(iii) Aniline Dye test:** Dissolve a little aniline in dilute hydrochloric acid, cool in ice-cold water and add aqueous solution of sodium nitrite dropwise. To this cold solution, add organic compound already dissolved in sodium hydroxide solution. A **red or orange precipitate** is obtained.



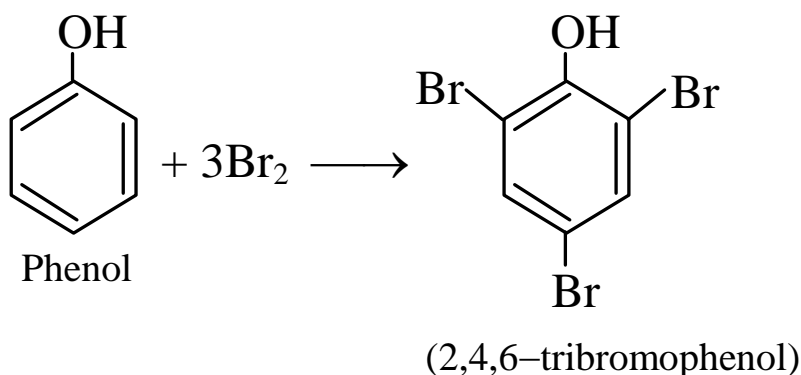
## Purification of Organic Compounds & Practical Organic Chemistry

This test is applicable for the detection of small quantities of phenols with the para position free.

**(iv) Phthalein test (Fluorescein test):** Heat some organic compound and phthalic anhydride with a few drops of concentrated sulphuric acid in a test-tube. Pour the heated mixture into water taken in a beaker and then add sodium hydroxide solution, till it became alkaline. A *beautiful pink or purple colour* appears.

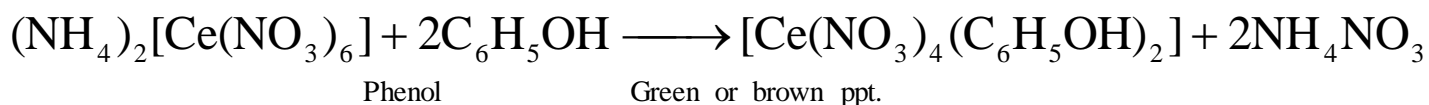


**(v) Bromine water test:** Take aqueous or alcoholic solution of the organic compound in a test-tube. Add excess of bromine water. A *yellowish white precipitate* is obtained.

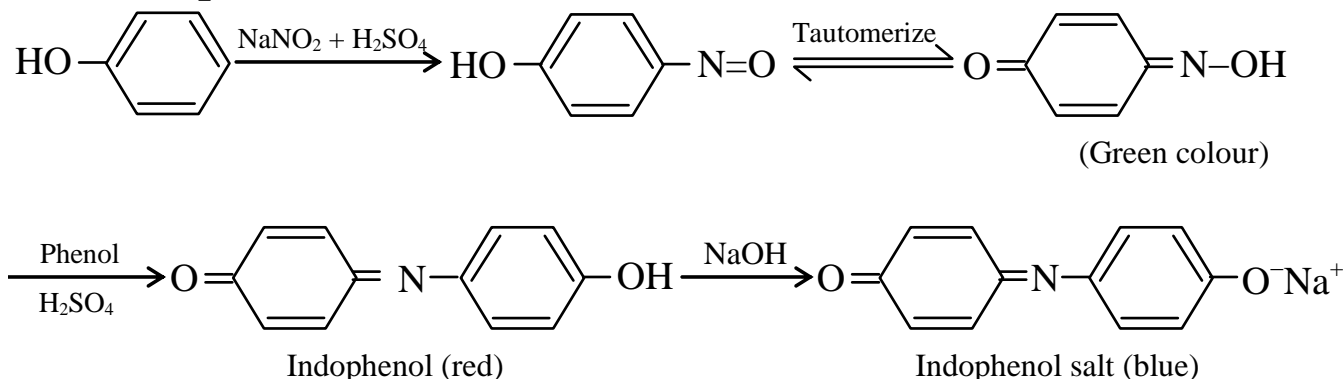


## Purification of Organic Compounds & Practical Organic Chemistry

(vi) **Ceric ammonium nitrate test:** Add few drops of the ceric ammonium nitrate to hot aqueous solution of the organic compound. A **green or brown precipitate** is obtained.



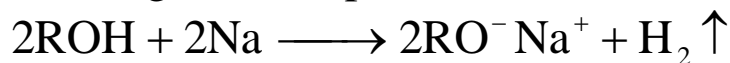
(vii) **Liebermann's Nitroso test:** Take a small amount of the compound and fuse with a few crystals of  $\text{NaNO}_2$  in a test-tube. Cool the test-tube and add some concentrated  $\text{H}_2\text{SO}_4$ . A **deep green colour** is obtained and when poured into large excess of water, **green colour changes to red**. When a little  $\text{NaOH}$  solution is added to the aqueous solution, the solution becomes **deep blue coloured**.



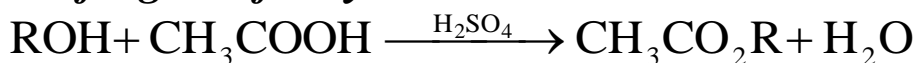
### 2.2.6 Tests For Alcohol Group

Alcohols may be considered as neutral compounds. They are soluble in water or dioxane.

(i) **Sodium test:** Take some organic compound in a test-tube. Add a thin slice of sodium metal to it. A **brisk effervescence** due to the evolution of hydrogen takes place. (Organic compound should be free from water).

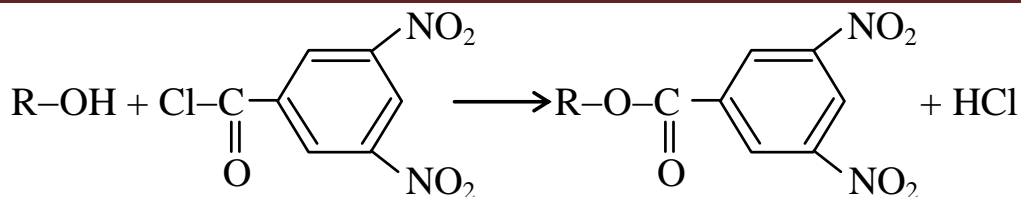


(ii) **Ester test:** Warm the given liquid with acetic acid in presence of sulphuric acid. A **fragrant fruity smell** indicates the formation of ester.

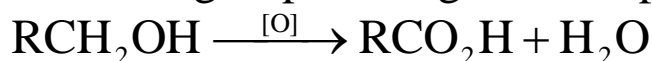


Alcohols give crystalline esters with 3,5-dinitrobenzoyl chloride. These esters have sharp melting points and can be used for testing a given alcohol.

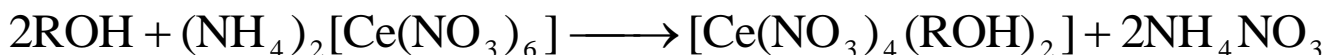




(iii) **Oxidation test:** Take some organic compound in a test tube, add to it  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and concentrated  $\text{H}_2\text{SO}_4$ . Heat the test-tube after fitting a delivery tube. The distillate is passed into another test-tube containing water. The solution becomes green coloured. Test the aqueous solution of the distillate for carboxylic acid group. A positive test indicates the presence of primary alcoholic group in the given compound.

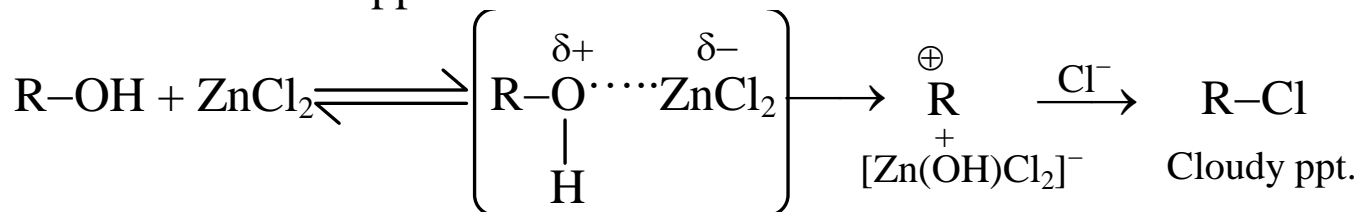


(iv) **Ceric ammonium nitrate test:** Shake a few drops of ceric ammonium nitrate with the organic compound. A **red colour** is produced. This test is useful only when the compound contains less than 10 carbon atoms per molecule.



### Distinction between primary, secondary and tertiary alcohols:

**Lucas test:** Add some amount of alcohol to 2 ml of Lucas reagent (anhydrous  $\text{ZnCl}_2$  + concentrated  $\text{HCl}$ ) in a test-tube. Shake the mixture and allow it to stand at room temperature. If a **cloudy precipitate** of alkyl chloride is obtained **immediately** then it is a tertiary alcohol, if obtained within **5 minutes** then it is a secondary alcohol, while **no cloudy precipitate even after long standing** means it is a primary alcohol. This test is applicable for alcohols with less than 6 carbon atoms.



### 2.2.7 Tests For Primary Amines ( $-\text{NH}_2$ )

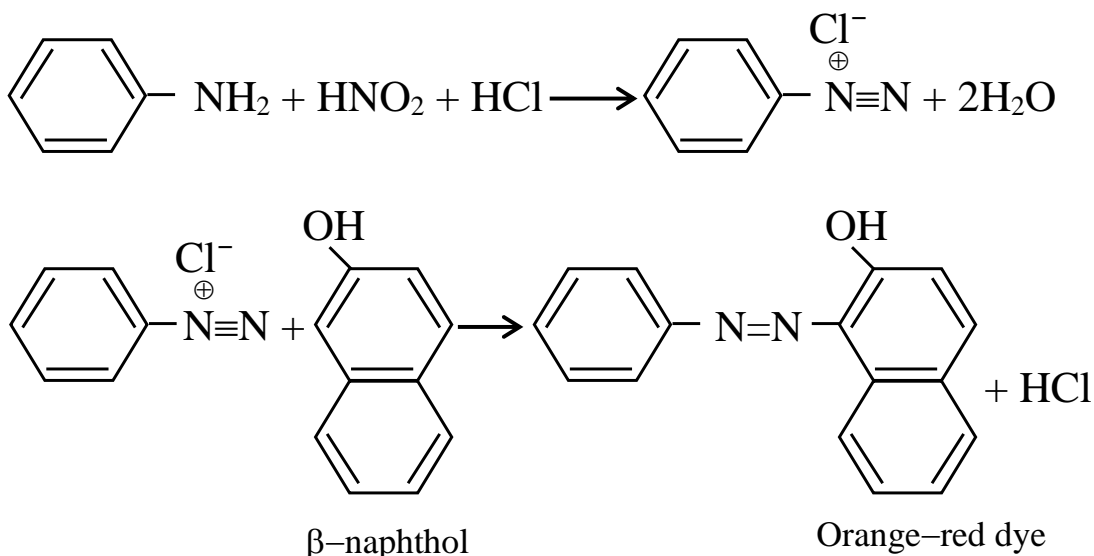
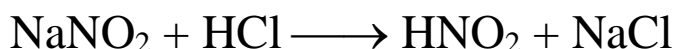
(i) **Carbylamine test:** Heat the organic compound with alcoholic  $\text{KOH}$  and chloroform in a test-tube. A **highly offensive smell** is evolved due to the formation of isocyanides.

# Purification of Organic Compounds & Practical Organic Chemistry



This test is applicable for aliphatic and aromatic primary amines but not for 2° and 3° amines.

**(ii) Dye test:** This test is applicable only for aromatic primary amines. Dissolve a small amount of the organic compound in dilute HCl. Cool it in ice–cold water bath. Add cold solution of sodium nitrite with constant stirring and then alkaline  $\beta$ -naphthol solution. An *orange–red dye* is obtained.



### 2.2.8 Tests For Secondary Amines (–NH–)

### Liebermann's nitroso test:

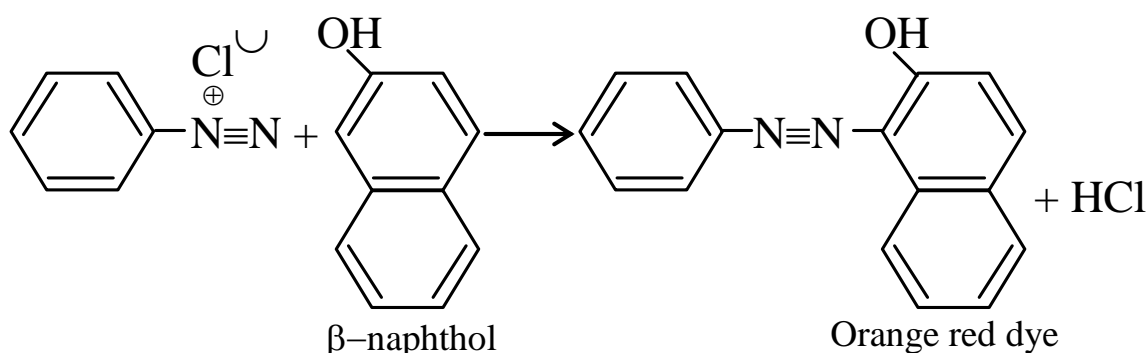
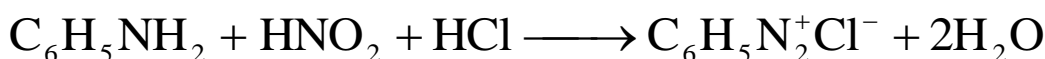
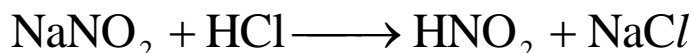
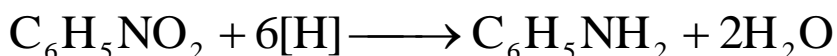
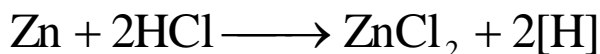
Dissolve some organic compound in concentrated HCl and then add small amount of water. Cool the solution in ice–cold water bath and then add cold dilute  $\text{NaNO}_2$  solution. A *yellow oily emulsion* is produced. Take above emulsion in a test tube and add phenol and concentrated  $\text{H}_2\text{SO}_4$  to it. A *green colour* appears. Addition of water changes *green colour to red*, which changes to *deep blue* on adding NaOH solution.

### 2.2.9 Tests For Nitro Group

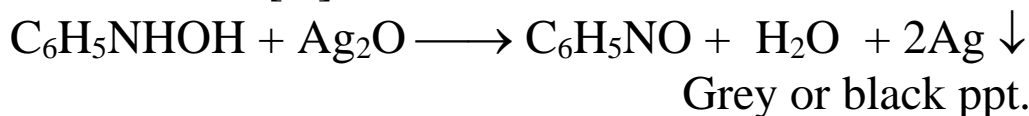
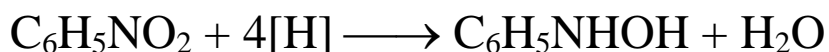
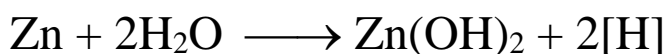
**(i) Reduction test:** Take a small amount of the organic compound in a test-tube. Add a few ml of concentrated hydrochloric acid and one or two pieces of granulated zinc or tin. Heat the mixture gently for few minutes.

## Purification of Organic Compounds & Practical Organic Chemistry

Decant the clear liquid into a test-tube. Cool it in ice-cold water bath and then add cold dilute solution of sodium nitrite. Pour this cold solution into an alkaline solution of  $\beta$ -naphthol. An **orange-red dye** is obtained. This test is applicable only to aromatic nitro compounds.



**(ii) Mulliken's test:** Take a small amount of the organic compound in a test-tube. Add a few ml of water or alcohol, 1 ml of calcium chloride or ammonium chloride solution and then a pinch of zinc dust. Boil the mixture for few minutes. Cool and then filter. Treat this filtrate with ammoniacal silver nitrate solution. A **grey or black precipitate** is obtained.



This test is applicable for aliphatic as well as aromatic nitro compounds.

### 3. Quantitative Analysis

After determining the elements present in the organic compound, the subsequent step is to find out the percentages of elements in the compound. The methods used for determining the percentage of elements involve combustion, oxidation and precipitation etc. of an organic

## Purification of Organic Compounds & Practical Organic Chemistry

compound such that they are converted into inorganic compounds, which can be easily estimated by gravimetric or volumetric techniques.

### 3.1 Estimation of Carbon And Hydrogen

#### 3.1.1 Liebig's Combustion Method

A known mass of the organic compound is heated in a current of dry oxygen (free from  $\text{CO}_2$ ) in the presence of cupric oxide till all the carbon is oxidised to carbon dioxide and all the oxygen is oxidised to water.

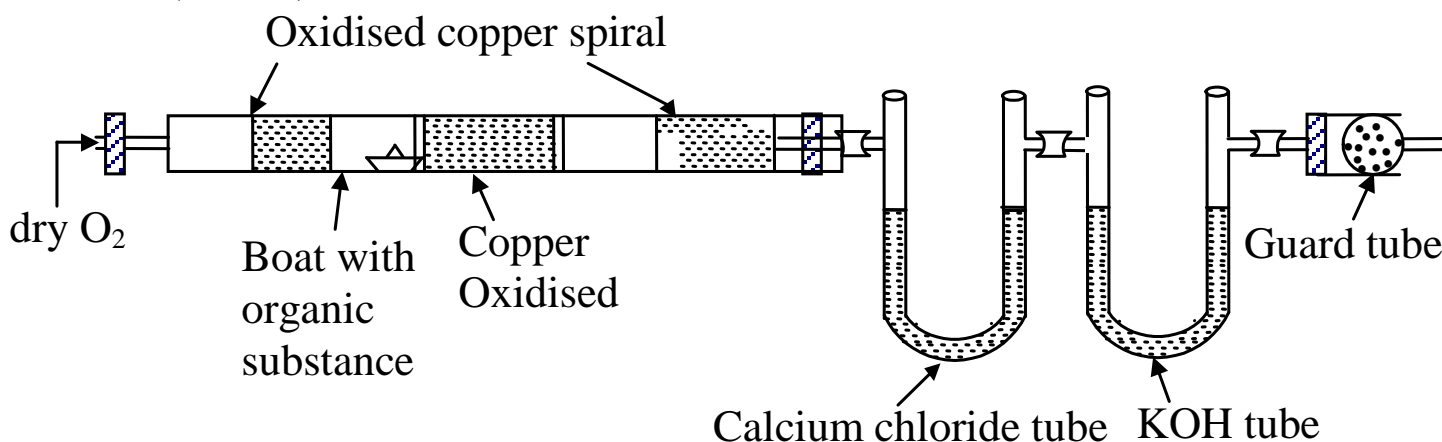
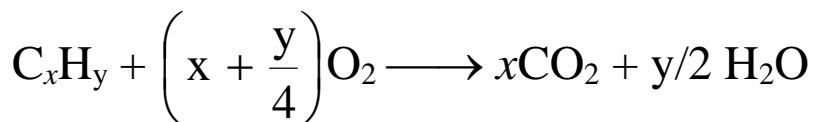


Figure 1

Water is absorbed in a previously weighed U-tube containing anhydrous calcium chloride or anhydrous magnesium perchlorate. Carbon dioxide is absorbed in a previously weighed U-tube containing a strong solution of potassium hydroxide or ascarite ( $\text{NaOH} + \text{CaO}$ ). The weights of carbon dioxide and water thus formed are determined and the amounts of carbon and hydrogen in the organic compound can be calculated as

$$\begin{aligned}\text{Moles of CO}_2 \text{ formed} &= \frac{\text{Mass of CO}_2 \text{ formed}}{44} = \text{Moles of C in CO}_2 \\ &= \text{Moles of C in organic compound} \\ \therefore \text{Mass of carbon in organic compound} &= \frac{\text{Moles of CO}_2 \text{ formed}}{44} \times 12\end{aligned}$$

## Purification of Organic Compounds & Practical Organic Chemistry

---

∴ Percentage of carbon in organic compound

$$= \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Moles of H}_2\text{O formed} = \frac{\text{Mass of H}_2\text{O formed}}{18}$$

$$\text{Moles of H in H}_2\text{O} = \frac{\text{Mass of H}_2\text{O formed}}{18} \times 2 = \text{Moles of H in compound.}$$

$$\text{Mass of hydrogen in the organic compound} = \frac{\text{Mass of H}_2\text{O formed} \times 2 \times 1}{18}$$

∴ Percentage of hydrogen in organic compound

$$= \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of organic compound}} \times 100$$

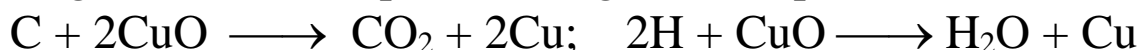
### 3.2 Estimation of Nitrogen

Nitrogen can be estimated either by Dumas' method or Kjeldahl's method.

#### 3.2.1 Duma's Method

Known mass of an organic compound is heated with cupric oxide in an atmosphere of carbon dioxide. The carbon and the hydrogen get oxidised to carbon dioxide and water while the nitrogen is set free. Traces of oxides of nitrogen, which may be formed in some cases are reduced to elemental nitrogen by passing over heated copper spiral. The gaseous mixture is collected over an aqueous solution of potassium hydroxide. CO<sub>2</sub> is absorbed by the caustic potash solution while H<sub>2</sub>O condenses and nitrogen is collected by downward displacement of KOH solution. The volume of nitrogen is measured and this is equivalent to the nitrogen present in the compound. The volume of nitrogen is reduced to STP, its weight calculated and from this the percentage of nitrogen present in the organic compound is estimated.

The following reactions take place during Duma's process.



## Purification of Organic Compounds & Practical Organic Chemistry

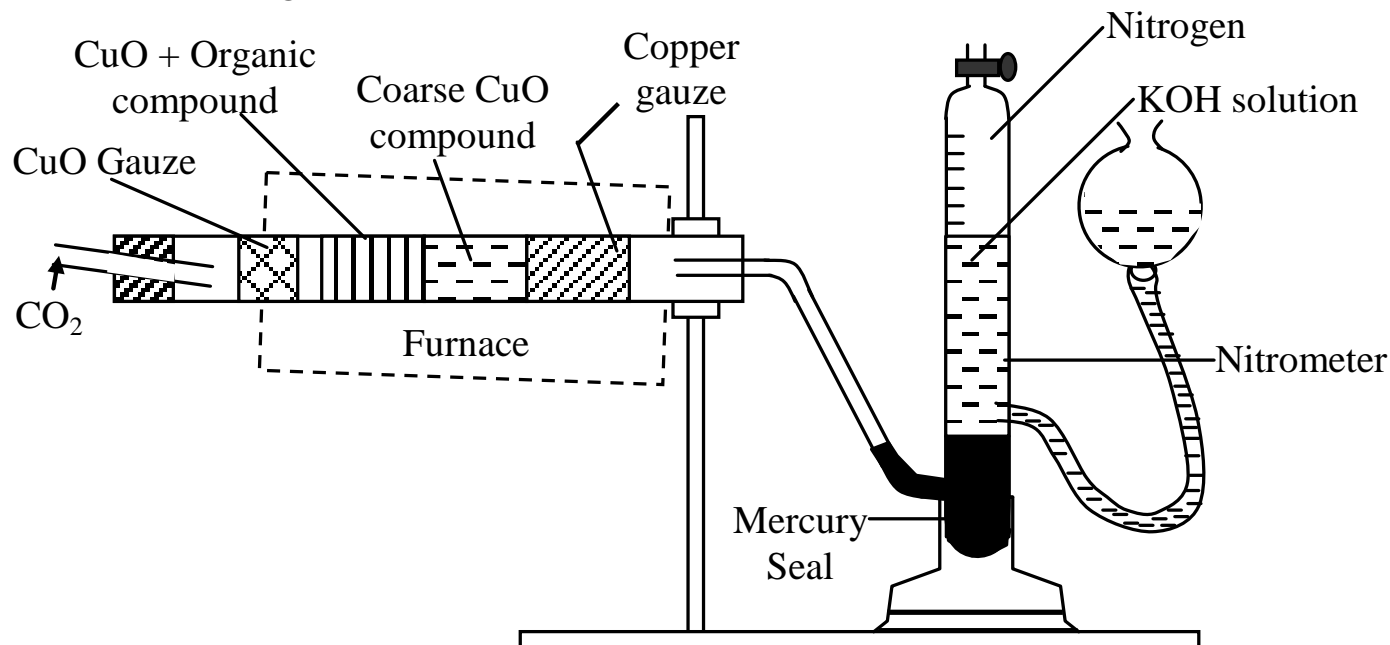
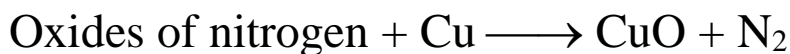
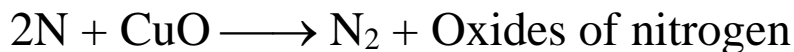


Figure 2. Estimation of nitrogen by Duma's method

Let the mass of organic compound =  $w$  g,

Volume of nitrogen collected =  $V$  cm<sup>3</sup>,

Pressure of moist N<sub>2</sub> =  $P$  mm of Hg,

Room temperature =  $t^\circ\text{C}$ ,

Aqueous tension at  $t^\circ\text{C}$  =  $a$  mm of Hg,

$\therefore$  Pressure of dry nitrogen =  $(P - a)$  mm of Hg,

Let us first convert the volume of nitrogen at given temperature & pressure to the volume of N<sub>2</sub> at STP.

$$P_{\text{N}_2} \times V_{\text{N}_2} = n_{\text{N}_2} \times RT$$

$$n_{\text{N}_2} = \frac{(P - a) \times V \times 10^{-3}}{760 \times 0.0821 \times (273 + t)}$$

$$\therefore \text{Volume of N}_2 \text{ at STP} = \frac{(P - a) \times V \times 10^{-3} \times 22.4}{760 \times 0.0821 \times (273 + t)} = x \text{ L (say)}$$

Now, 22.4 L of N<sub>2</sub> at STP weigh = 28 g

$$\therefore x \text{ L of N}_2 \text{ at STP will weigh} = \left( \frac{28}{22.4} \times x \right) \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100 = \frac{28x \times 100}{22.4 \times w}$$

where x is the volume of N<sub>2</sub> (in litre) at STP.

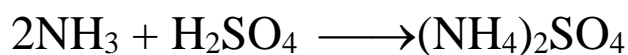
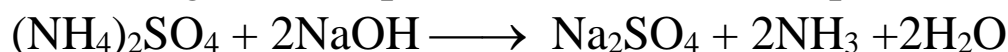
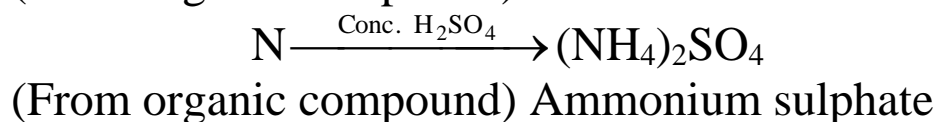
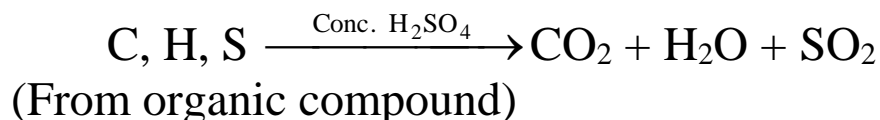
### 3.2.2 Kjeldahl's Method

This method is simpler and more convenient than Duma's method. This method is largely used for the estimation of nitrogen in food stuffs, drugs, fertilizers and many other organic compounds. However, this method cannot be used for

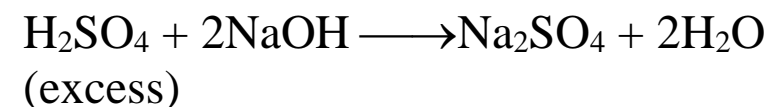
(i) organic compounds containing nitrogen in the ring such as pyridine, quinoline etc.

(ii) organic compounds containing nitro (–NO<sub>2</sub>) & diazo (–N=N–) groups.

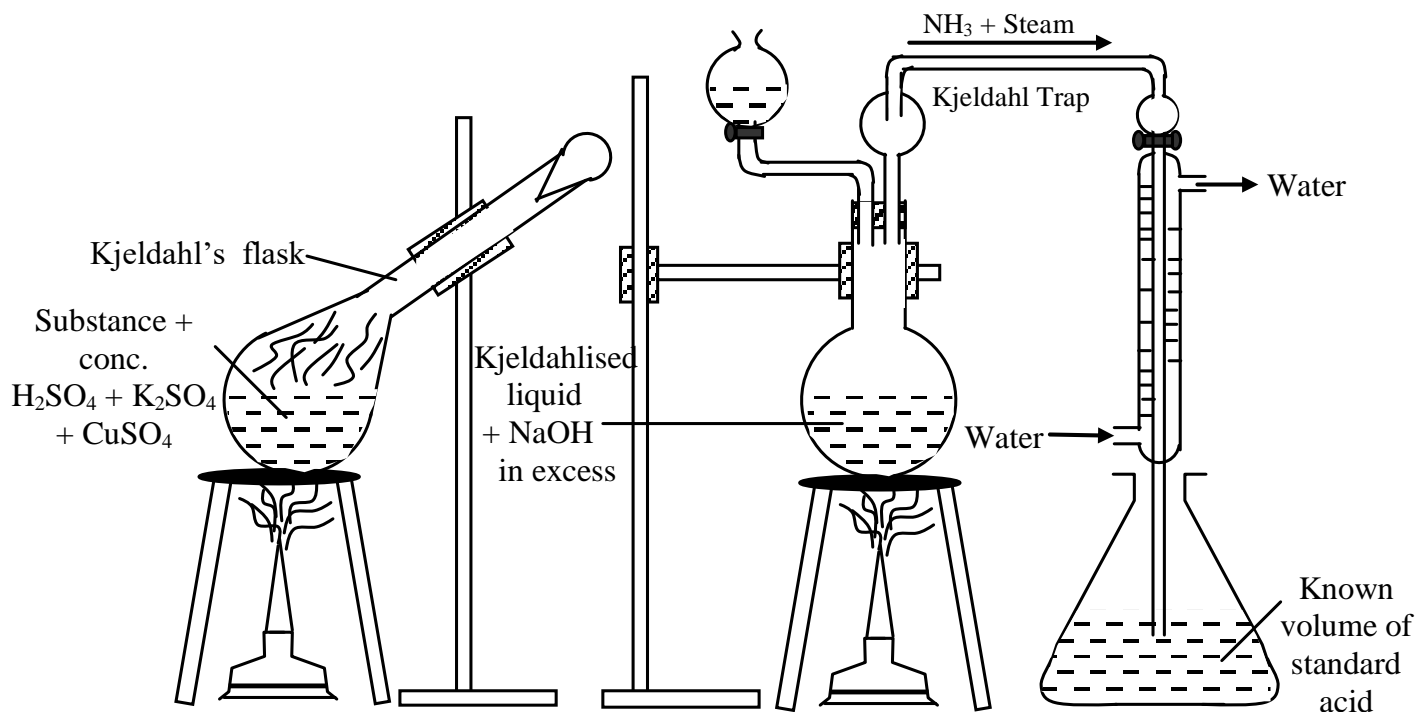
**Principle:** A known weight of the organic compound is heated with concentrated H<sub>2</sub>SO<sub>4</sub> so that nitrogen is quantitatively converted into ammonium sulphate. The solution is then heated with excess of sodium hydroxide. The ammonia gas evolved is passed into a known but excess volume of standard acid (HCl or H<sub>2</sub>SO<sub>4</sub>). The acid left unused is estimated by titrating the solution with standard alkali. From the amount of acid left unused, the amount of acid used for neutralization of ammonia can be calculated. From this, percentage of nitrogen can be calculated. The chemical reactions involved are



(n = 1)







**Figure 3. Estimation of nitrogen by Kjeldahl's method.**

Let the mass of organic compound =  $w$  g,

Total volume of standard acid taken =  $V_1$  cm<sup>3</sup>,

Normality of acid =  $N_1$

Now, the excess acid after dilution is titrated against standard alkali.

Volume of standard alkali used for neutralization of unused acid =  $V_2$  cm<sup>3</sup>,

Normality of standard alkali =  $N_2$ ,

Equivalents of unused acid = Equivalents of alkali =  $N_2 V_2 \times 10^{-3}$

Initial equivalents of acid =  $N_1 V_1 \times 10^{-3}$

Equivalents of acid consumed by  $\text{NH}_3$  =  $(N_1 V_1 - N_2 V_2) 10^{-3}$  = Equivalents of  $\text{NH}_3$  reacted.

Moles of  $\text{NH}_3$  reacted =  $(N_1 V_1 - N_2 V_2) \times 10^{-3}$

Moles of  $\text{NH}_3$  liberated =  $(N_1 V_1 - N_2 V_2) \times 10^{-3}$  = Moles of nitrogen in  $\text{NH}_3$   
= Moles of nitrogen in organic compound.

Mass of nitrogen in the organic compound =  $(N_1 V_1 - N_2 V_2) \times 10^{-3} \times 14$

Percentage of nitrogen =  $\frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100$

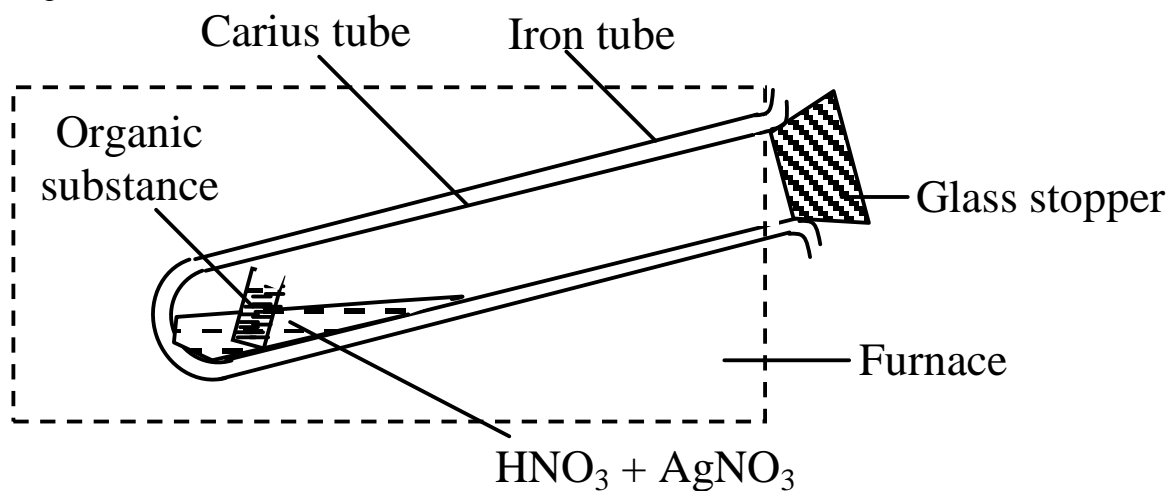
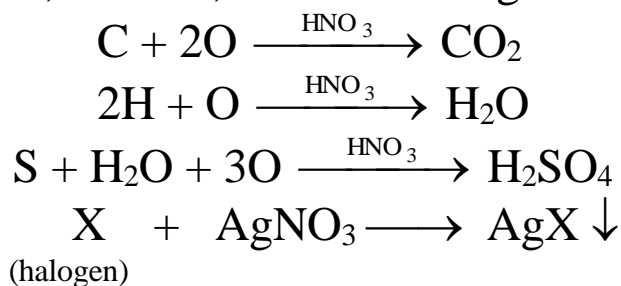
$$= \frac{(N_1 V_1 - N_2 V_2) \times 10^{-3} \times 14}{w} \times 100 = \frac{1.4 (N_1 V_1 - N_2 V_2)}{w}$$

where  $V_1$  and  $V_2$  are the volume of standard acid and alkali respectively, in  $\text{cm}^3$ .

### 3.3 Estimation of Halogens

#### 3.3.1 Carius Method

In this method, a known mass of the organic substance is heated with fuming nitric acid in the presence of silver nitrate in a special sealed tube known as Carius tube. Carbon, hydrogen or sulphur present in the compound will be oxidised to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  respectively. The halogen forms a precipitate of silver halide ( $\text{AgX}$ ). The precipitate is filtered, washed, dried and weighed.



**Figure 4. Carius method for the estimation of halogens**

The Carius tube is a long narrow tube closed at one end and (during the experiment) sealed at the other end. A weighed quantity of the organic substance is taken in the tube with fuming nitric acid and silver nitrate, then

## Purification of Organic Compounds & Practical Organic Chemistry

the open end is sealed and the tube is heated in a furnace. The organic compound decomposes and silver halide is formed. At the end of the experiment, the tube is cooled, the sealed end broken and the contents are transferred to a filter. The precipitated silver halide is filtered, washed, dried and weighed.

$$\begin{aligned}\text{Moles of AgX} &= \frac{\text{Weight of AgX}}{\text{Molar mass of AgX}} = \text{Moles of halogen in AgX} \\ &= \text{Moles of halogen in organic compound}\end{aligned}$$

$$\begin{aligned}\text{Mass of halogen in organic compound} &= \\ \frac{\text{Weight of AgX} \times \text{atomic mass of halogen}}{\text{Molar mass of AgX}}\end{aligned}$$

$$\begin{aligned}\therefore \text{Percentage of halogen} &= \\ \frac{\text{Atomic mass of halogen} \times \text{wt. of AgX}}{(\text{108} + \text{atomic mass of halogen}) \times \text{wt. of organic compound}} \times 100\end{aligned}$$

### 3.4 Estimation of Sulphur

Sulphur is estimated by Carius method. The organic compound containing sulphur is heated with fuming nitric acid. The sulphur in the compound is oxidised to sulphuric acid, which is then precipitated as barium sulphate by adding excess of barium chloride solution. The precipitate is filtered, washed and dried. From the weight of barium sulphate formed, the percentage of sulphur in the organic compound can be estimated.

$$\begin{aligned}\text{Moles of BaSO}_4 &= \frac{\text{Weight of BaSO}_4}{\text{Molar mass of BaSO}_4} = \text{Moles of S in BaSO}_4 \\ &= \text{Moles of S in organic compound.}\end{aligned}$$

$$\text{Mass of sulphur in organic compound} = \frac{\text{Weight of BaSO}_4}{\text{Molar mass of BaSO}_4} \times 32$$

$$\begin{aligned}\therefore \text{Percentage of sulphur} &= \frac{32 \times \text{weight of BaSO}_4}{\text{Molar mass of BaSO}_4 \times \text{weight of organic compound}} \times 100 \\ &= \frac{32 \times \text{weight of BaSO}_4}{233 \times \text{weight of organic compound}} \times 100\end{aligned}$$

### 3.5 Estimation of Phosphorus

A known mass of the organic compound is heated with fuming nitric acid, when the phosphorus present in the organic compound is oxidised to phosphoric acid. The phosphoric acid obtained is treated with magnesia mixture (a mixture of  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ ) to give a precipitate of  $\text{Mg}(\text{NH}_4)\text{PO}_4$ , which on ignition gives  $\text{Mg}_2\text{P}_2\text{O}_7$ .

$$\text{Moles of } \text{Mg}_2\text{P}_2\text{O}_7 = \frac{\text{Weight of } \text{Mg}_2\text{P}_2\text{O}_7}{\text{Molar mass of } \text{Mg}_2\text{P}_2\text{O}_7}$$

$$\text{Moles P in } \text{Mg}_2\text{P}_2\text{O}_7 = \frac{2 \times \text{weight of } \text{Mg}_2\text{P}_2\text{O}_7}{\text{Molar mass of } \text{Mg}_2\text{P}_2\text{O}_7} = \text{Moles of P in compd.}$$

$$\begin{aligned} \therefore \text{Mass of phosphorous in organic compound} \\ = \frac{2 \times \text{weight of } \text{Mg}_2\text{P}_2\text{O}_7}{\text{Molar mass of } \text{Mg}_2\text{P}_2\text{O}_7} \times 31 \end{aligned}$$

Percentage of phosphorus

$$\begin{aligned} &= \frac{2 \times 31 \times \text{weight of } \text{Mg}_2\text{P}_2\text{O}_7}{\text{Molar mass of } \text{Mg}_2\text{P}_2\text{O}_7 \times \text{weight of organic compound}} \times 100 \\ &= \frac{62 \times \text{weight of } \text{Mg}_2\text{P}_2\text{O}_7}{222 \times \text{weight of organic compound}} \times 100 \end{aligned}$$

### 3.6 Estimation of Oxygen

There is no direct method for the estimation of oxygen in a given organic compound. It is estimated by subtracting the sum of the percentages of all other elements in the compound from 100.

Percentage of oxygen = 100 – (combined % of all other elements)

## 4. Determination of Molecular Mass

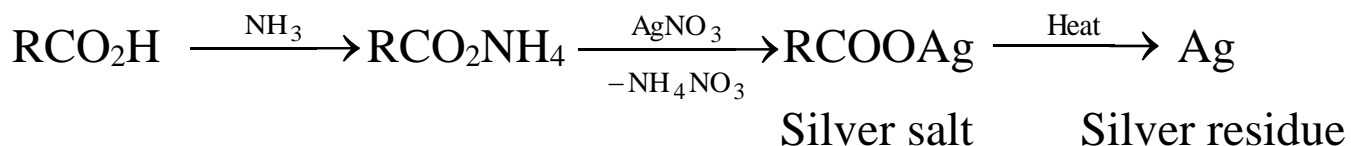
From the percentage composition of the elements present in an organic compound, we can calculate the empirical formula. To know the

## Purification of Organic Compounds & Practical Organic Chemistry

molecular formula, it is necessary to fix the molecular weight. The following are some of the methods for determining the molecular weights of organic compounds.

### 4.1 Silver Salt Method

This method is used for determining the molecular mass of organic acids. Most of the organic acids form insoluble silver salts, which upon ignition decompose to give residue of metallic silver.



A small amount of organic acid is dissolved in water, then a slight excess of  $\text{NH}_3$  solution is added. The solution is then boiled to expel excess  $\text{NH}_3$  and then excess of  $\text{AgNO}_3$  is added, whereby white precipitate of insoluble silver salt is obtained. The precipitate is filtered, washed, dried and weighed.

This weighed silver salt is taken in a crucible and ignited till decomposition is complete. The crucible is cooled and then weighed. Heating, cooling and weighing the crucible is continued till we get constant weight.

Let the weight of silver salt =  $w$  g and the weight of silver residue obtained =  $x$  g.

Since, one atom of hydrogen (H) is equivalent to one atom of silver (Ag), therefore, one equivalent of silver salt will contain one atom of silver in place of hydrogen. Thus, if  $E$  be the equivalent mass of acid, then equivalent mass of silver salt will be

$$(E - H + \text{Ag}) \text{ or } (E - 1 + 108) \text{ or } (E + 107).$$

Equivalent of silver salt = Equivalent of silver

$$\frac{\text{Weight of silver salt}}{\text{Equivalent mass of silver salt}} = \frac{\text{Weight of silver}}{\text{Equivalent weight of silver}}$$

$$\frac{w}{E + 107} = \frac{x}{108}$$

$$\text{Equivalent mass of Acid} = E = \left( \frac{w}{x} \times 108 \right) - 107$$

Molecular mass of the acid = Equivalent mass  $\times$  Basicity

$$\text{Molecular mass of the acid} = \left[ \left( \frac{w}{x} \times 108 \right) - 107 \right] \times n \text{ (where } n \text{ is the basicity of acid)}$$

### 4.2 Platinichloride Method

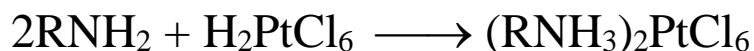
This method is used for determining the molecular masses of the bases. This method is based on the fact that organic bases i.e. amines combine with chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$  to form insoluble double salts known as chloroplatinates or platinichlorides. These salts when ignited leave a residue of metallic platinum.

The base is dissolved in  $\text{HCl}$  and a solution of platinic chloride,  $\text{PtCl}_4$  is added, when a yellow crystalline salt is precipitated. The salt is then filtered, washed, dried and weighed. This weighed amount of salt is ignited in a crucible, which on decomposition gives metallic platinum that is weighed. Heating, cooling and weighing the crucible is continued till we get constant weight.

Let the weight of chloroplatinate =  $w$  g and the weight of platinum obtained =  $x$  g.

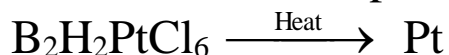
Let  $E$  be the equivalent mass of the monoacidic base, then the molecular formula of the chloroplatinate will be  $\text{B}_2\text{H}_2\text{PtCl}_6$ .

$$\therefore \text{Molecular mass of chloroplatinate} = 2E + 2 + 195 + (35.5 \times 6) = 2E + 410$$



## Purification of Organic Compounds & Practical Organic Chemistry

One molecule of chloroplatinate on heating gives one atom of platinum.



$$\frac{\text{Weight of the salt}}{\text{Molar mass of the salt}} = \frac{\text{Weight of platinum}}{\text{Atomic mass of platinum}}$$

$$\frac{w}{2E + 410} = \frac{x}{195}$$

$$2E = \left[ \left( \frac{w}{x} \times 195 \right) - 410 \right].$$

$$\text{Molecular mass of base} = \frac{n}{2} \times \left[ \left( \frac{w}{x} \times 195 \right) - 410 \right] \quad (\text{where } n \text{ is the acidity of base})$$

### 4.3 Relative Lowering of Vapour Pressure Method

The molecular weight ( $M_1$ ) of a non-volatile organic compound can be determined by measuring the relative lowering of vapour pressure of a solvent caused by dissolving a known mass of the solute (non-volatile organic compound) in a given mass of the solvent.

$$\text{Relative lowering of vapour pressure} = \frac{P^\circ - P_s}{P^\circ} \approx \frac{w_1}{M_1} \times \frac{M_2}{W_2} \quad (\text{for very dilute solutions})$$

where  $P^\circ$  = Vapour pressure of solvent in pure state,

$P_s$  = Vapour pressure of solution,

$w_1$  = Weight of non-volatile organic compound,

$M_1$  = Molecular weight of non-volatile organic compound,

$W_2$  = Weight of solvent

and  $M_2$  = Molecular weight of solvent.



### 4.4 Elevation of Boiling Point Method

The molecular weight ( $M_1$ ) of a non-volatile organic compound can be determined by measuring the elevation in boiling point of a solvent caused by dissolving a known mass of the solute (non-volatile organic compound) in a given mass of the solvent.

$$\text{Elevation in boiling point} = \Delta T_b = T_{\text{soln}} - T_{\text{solvent}} = K_b \times \frac{w_1 \times 1000}{M_1 \times W_2}$$

where  $K_b$  = Molal elevation constant or ebullioscopic constant,

$w_1$  = Weight of non-volatile organic compound,

$M_1$  = Molecular weight of non-volatile organic compound and

$W_2$  = Weight of solvent.

### 4.5 Freezing Point Depression Method

The molecular weight ( $M_1$ ) of a non-volatile organic compound can be determined by measuring the depression in freezing point of a solvent caused by dissolving a known mass of the solute (non-volatile organic compound) in a given mass of the solvent.

$$\text{Depression in freezing point} = \Delta T_f = T_{\text{solvent}} - T_{\text{soln}} = K_f \times \frac{w_1 \times 1000}{M_1 \times W_2}$$

where  $K_f$  = Molal depression constant or cryoscopic constant,

$W_1$  = Weight of non-volatile organic compound,

$M_1$  = Molecular weight of non-volatile organic compound and

$W_2$  = Weight of solvent.

## 5. Determination of Empirical And Molecular Formula

The empirical formula of a compound is defined as the simplest formula that gives the ratio of atoms of the various elements in a molecule. This is calculated from the percentage composition of the elements.

The molecular formula of the compound gives the actual number of atoms of each element present in a molecule of the compound.

## Purification of Organic Compounds & Practical Organic Chemistry

Molecular formula = Empirical formula  $\times$  n (where n is an integer)

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

### Illustration 3.

0.2 g of an organic monobasic acid gave 0.509 g of CO<sub>2</sub> and 0.08856 g of water on complete combustion. 0.244 g of the acid required for neutralization 20 ml of N/10 alkali. Determine the molecular formula of the acid.

### Solution:

$$\text{Weight of carbon in the organic acid} = 0.509 \times \frac{12}{44} = 0.1388 \text{ g}$$

$$\text{Percentage of carbon in the organic acid} = \frac{0.1388}{0.2} \times 100 = 69.4$$

$$\text{Weight of hydrogen in the organic acid} = 0.08856 \times \frac{2}{18} = 0.00984 \text{ g}$$

$$\text{Percentage of hydrogen in the organic acid} = \frac{0.00984}{0.2} \times 100 = 4.92$$

$$\text{Percentage of oxygen} = 100 - (69.4 + 4.92) = 25.68$$

$$\text{Equivalents of acid} = \text{Equivalents of alkali} = 20 \times \frac{1}{10} \times 10^{-3}$$

$$\text{Moles of organic acid} = 20 \times \frac{1}{10} \times 10^{-3} = 0.002$$

(monobasic acid  $\therefore$  n = 1)

$$\text{Molecular weight of acid} = \frac{0.244}{0.002} = 122$$

Element	Percentage weight	% weight / Atomic weight	Whole number ratio
Carbon	69.4	$\frac{69.4}{12} = 5.78$	$\frac{5.78}{1.605} = 3.6$

## Purification of Organic Compounds & Practical Organic Chemistry

Hydrogen	4.92	$\frac{4.92}{1} = 4.92$	$\frac{4.92}{1.605} = 3.06$
Oxygen	25.68	$\frac{25.68}{16} = 1.605$	$\frac{1.605}{1.605} = 1$

∴ Empirical formula is  $C_{3.6}H_{3.06}O_1$  or  $C_7H_6O_2$

Molecular formula =  $(C_7H_6O_2)_n$

$$(C_7H_6O_2)_n = 122$$

$$[(12 \times 7) + (1 \times 6) + (16 \times 2)] n = 122$$

$$n = 1$$

Hence, Molecular formula =  $n \times$  empirical formula =  $C_7H_6O_2$

## 6. Separation of Mixtures of Organic Compounds

When it is required to identify the constituents of a mixture of organic substances, it is necessary to separate each component from the mixture and to isolate it in a pure state before proceeding with the examination. To identify the constituents of a mixture without separating them is an extremely difficult feat.

Owing to the great number of possibilities, no definite rule for procedure can be laid down and advantage will have to be taken of any facts that emerge in the preliminary examination. The preliminary examination of the mixture should include the physical state of the sample, its behaviour on distillation, determination of the elements present, behaviour on ignition, its solubility in water and whether an acid or an alkaline reaction is given.

If the mixture appears to contain some volatile liquid, it may be heated on the water-bath in a distilling flask attached to a condenser until no more of the liquid passes over. The residue in the flask or the original mixture (if it is solid) is treated with an excess of dry ether, any insoluble portion being filtered off and washed with the same solvent, the washings being added to the filtrate. By this means the majority of salts, carbohydrates

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

and other polyhydroxylic compounds, sulphonic acids and similar substances insoluble in ether, may be separated from the main portion. Such a residue is to be examined independently, extraction with cold methyl alcohol being carried out as a preliminary step towards further separation.

If the mixture have been found to contain nitrogen, the ethereal solution is shaken in a separating funnel with dilute sulphuric acid. In the absence of nitrogen, this operation can be omitted. By this means basic substances are removed from the mixture on separating the aqueous and ethereal layers. The bases may be recovered by rendering the aqueous solution alkaline and again extracting with ether.

The ethereal solution after this treatment should be washed with a small quantity of water, the washings being discarded-and shaken with dilute caustic soda solution. This has the effect of removing all compounds of an acidic character. The treatment of the aqueous portion will be discussed below.

The ether now contains only neutral substances. From these any aldehydic and most of the ketonic compounds can be removed by shaking with a concentrated solution of sodium bisulphite. The aldehydes and ketones can be recovered from the resulting precipitate or aqueous solution by acidification with dilute sulphuric acid followed by distillation, extraction or filtration.

The alkaline solution containing the acidic substances should be saturated with carbon dioxide and extracted with ether. By this procedure all phenolic compounds, which contain no carboxyl or nitro groups, oximes and similar weak acids are, liberated and pass into the ether layer. On adding dilute sulphuric acid until evolution of carbon dioxide ceases, carboxylic acids and nitrophenols are liberated and can be isolated by extraction, filtration or distillation.

At this stage all ethereal solutions should be evaporated, condensed and thus recovered. All residues should be tested afresh for constituent

## **Purification of Organic Compounds & Practical Organic Chemistry**

---

elements. The results of the above operations are briefly summarized in the scheme shown below.

The various fractions denominated (I), (II), etc., may contain the following types of compound.

(I) Hydrocarbons, ethers, alcohols, ketones, esters, aliphatic halogen compounds and conceivably aldehydes, acetals, nitriles, aliphatic amines, alkyl nitrates and nitrites whose boiling points lie below 100°C.

(II) Salts of organic bases with mineral acids, carbohydrates and other polyhydroxylic compounds, amino acids, sulphonic acids of all types.

(III) Aliphatic and aromatic primary, secondary, and tertiary amino compounds, possibly some amides also.

(IV) Aldehydic and ketonic compounds containing no groups, which would have placed them in another fraction.

(V) Hydrocarbons, ethers, alcohols, higher ketones, esters and aliphatic or aromatic halogen compounds, not included in other fractions.

(VI) Simple and substituted phenols, keto–enolic substances.

(VII) Carboxylic acid, nitrophenols (in which the nitro groups are present in either *ortho* or *para* position).

Much information as to the nature of the constituents may be obtained by the mere performance of the above separations.

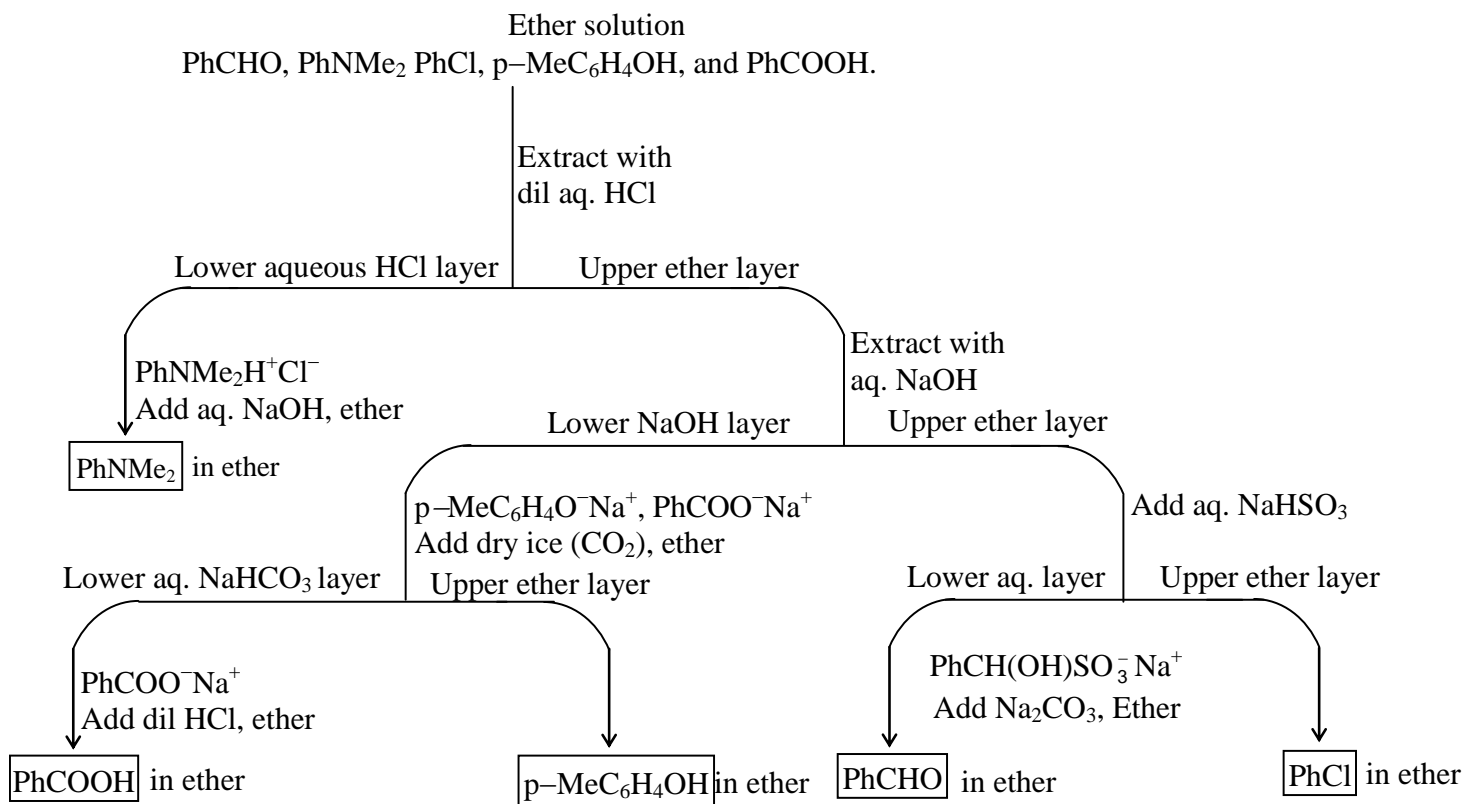
For further separation of the individual substances contained in the different fractions no definite scheme can be drawn up, but can be detected by some characteristic reactions and characteristic derivative formations.

## Purification of Organic Compounds & Practical Organic Chemistry

### Illustration 4.

Draw a flow diagram for the separation and recovery in almost quantitative yield of a mixture of the water-insoluble compounds PhCHO, PhNMe<sub>2</sub>, PhCl, p-MeC<sub>6</sub>H<sub>4</sub>OH and PhCOOH.

### Solution:



### Illustration 5.

0.21 g of an organic compound gave on combustion 0.462 g of carbon dioxide and 0.1213 g of water. Calculate the percentage of carbon and hydrogen in it.

### Solution:

$$\% \text{ of carbon in the organic compound} = \frac{0.462 \times 12}{44 \times 0.21} \times 100 = 60\%$$

$$\text{and } \% \text{ of hydrogen in the organic compound} = \frac{0.1213 \times 2}{18 \times 0.21} \times 100 = 6.41\%$$

## Purification of Organic Compounds & Practical Organic Chemistry

### Illustration 6.

0.9 g of an organic compound containing only carbon, hydrogen and nitrogen on combustion, gave 2.2 g of carbon dioxide and 0.6 g of water. What is the empirical formula of the compound?

#### Solution:

$$\text{Weight of carbon} = \frac{12}{44} \times 2.2 = 0.6 \text{ g}$$

$$\text{Weight of hydrogen} = \frac{2}{18} \times 0.6 = 0.0667 \text{ g}$$

$$\text{Weight of carbon + hydrogen} = 0.6667 \text{ g}$$

$$\text{Weight of nitrogen} = 0.9 - 0.6667 = 0.2333 \text{ g}$$

Element	Weight	Weight/Atomic Weight	Whole number ratio
Carbon	0.6	$\frac{0.6}{12} = 0.05$	$\frac{0.05}{0.0167} = 3$
Hydrogen	0.0667	$\frac{0.0667}{1} = 0.0667$	$\frac{0.0667}{0.0167} = 4$
Nitrogen	0.2333	$\frac{0.2333}{14} = 0.0167$	$\frac{0.0167}{0.0167} = 1$

∴ Empirical formula = C<sub>3</sub>H<sub>4</sub>N

### Illustration 7.

0.45 g of an organic compound gave on combustion 0.792 g of CO<sub>2</sub> and 0.324 g of water. 0.24 g of the same substance was Kjeldahlised and the ammonia formed was absorbed in 100 ml of N/8 H<sub>2</sub>SO<sub>4</sub>. The excess acid required 154 ml of N/20 NaOH for complete neutralization. Calculate the empirical formula of the compound.



### Solution:

#### Percentage of carbon:

44 g of  $\text{CO}_2$  contains = 12 g of C

$$\therefore 0.792 \text{ g of } \text{CO}_2 \text{ contain} = \frac{12 \times 0.792}{44} = 0.216 \text{ g of C}$$

$$\therefore \text{percentage of C in the organic compound} = \frac{0.216}{0.45} \times 100 = 48$$

#### Percentage of hydrogen:

18 g of  $\text{H}_2\text{O}$  contains = 2 g of H

$$\therefore 0.324 \text{ g of } \text{H}_2\text{O} \text{ contain} = \frac{2 \times 0.324}{18} = 0.036 \text{ g of H}$$

$$\therefore \text{percentage of H in the organic compound} = \frac{0.036}{0.45} \times 100 = 8$$

#### Percentage of nitrogen:

$$\text{Initial equivalents of acid taken} = 100 \times \frac{1}{8} \times 10^{-3}$$

$$\text{Equivalents of excess of acid} = \text{Equivalents of NaOH} = 154 \times \frac{1}{20} \times 10^{-3}$$

Equivalents of acid used with ammonia =

$$\left[ \left( 100 \times \frac{1}{8} \times 10^{-3} \right) - \left( 154 \times \frac{1}{20} \times 10^{-3} \right) \right] = 4.8 \times 10^{-3}$$

Equivalents of ammonia reacted =  $4.8 \times 10^{-3}$  = Moles of  $\text{NH}_3$  reacted  
= Moles of  $\text{NH}_3$  produced.

$$\text{Mass of nitrogen present in compound} = 4.8 \times 10^{-3} \times 14 = 0.0672 \text{ g}$$

$$\therefore \text{percentage of nitrogen in organic compound} = \frac{0.0672}{0.24} \times 100 = 28$$

$$\text{Percentage of oxygen} = 100 - (48 + 8 + 28) = 16$$

## Purification of Organic Compounds & Practical Organic Chemistry

To determine empirical formula:

Element	Percentage weight	% weight/amount	Whole number ratio
Carbon	48	$\frac{48}{12} = 4$	$\frac{4}{1} = 4$
Hydrogen	8	$\frac{8}{1} = 8$	$\frac{8}{1} = 8$
Nitrogen	28	$\frac{28}{14} = 2$	$\frac{2}{1} = 2$
Oxygen	16	$\frac{16}{16} = 1$	$\frac{1}{1} = 1$

∴ Empirical formula = C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O

### Illustration 8.

0.492 g of an organic compound gave 0.396 g of carbon dioxide and 0.2028 g of water on combustion. 0.37 g of the compound gave 0.639 g of silver bromide. What is the molecular formula of the compound if its vapour density is 54.5?

### Solution:

$$\text{Weight of carbon in the organic compound} = \frac{0.396 \times 12}{44} = 0.108 \text{ g}$$

$$\text{Percentage of carbon in the organic compound} = \frac{0.108}{0.492} \times 100 = 21.95\%$$

$$\text{Weight of hydrogen in the organic compound} = \frac{0.2028 \times 2}{18} = 0.02253 \text{ g}$$

$$\text{Percentage of hydrogen in the org. compound} = \frac{0.02253}{0.492} \times 100 = 4.58\%$$

$$\text{Percentage of bromine in the org. compd.} = \frac{80}{188} \times \frac{0.639}{0.37} \times 100 = 73.47\%$$

## Purification of Organic Compounds & Practical Organic Chemistry

Element	Percentage weight	% weight/atomic weight	Whole number ratio
Carbon	21.95	$\frac{21.95}{12} = 1.83$	$\frac{1.83}{0.9183} = 2$
Hydrogen	4.58	$\frac{4.58}{1} = 4.58$	$\frac{4.58}{0.9183} = 5$
Bromine	73.47	$\frac{73.47}{80} = 0.9183$	$\frac{0.9183}{0.9183} = 1$

$\therefore$  Empirical formula =  $\text{C}_2\text{H}_5\text{Br}$

Molecular formula =  $(\text{C}_2\text{H}_5\text{Br})_n$

Molecular weight =  $2 \times \text{vapour density} = 2 \times 54.5 = 109$

$$(\text{C}_2\text{H}_5\text{Br})_n = 109$$

$$[(2 \times 12) + (5 \times 1) + 80] n = 109, \quad n = 1$$

$\therefore$  Molecular formula is  $\text{C}_2\text{H}_5\text{Br}$ .

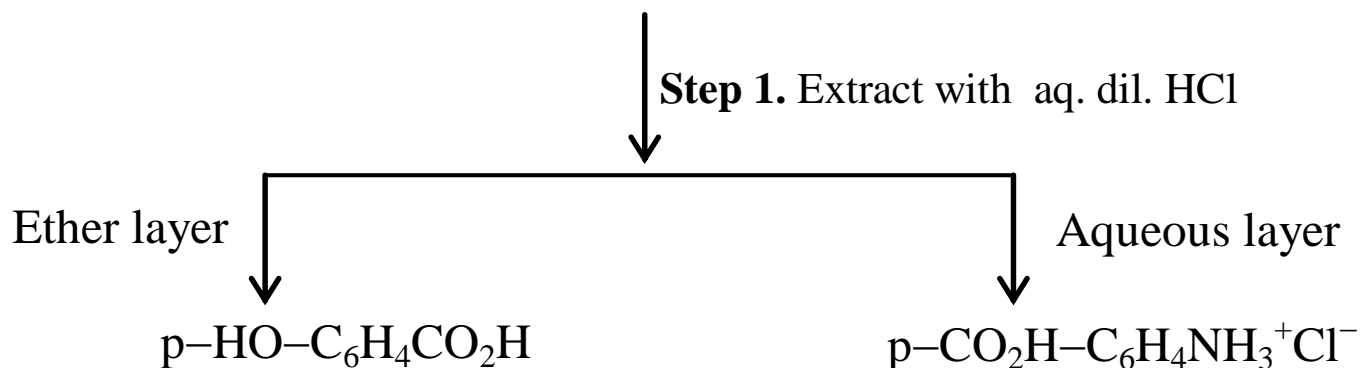
### Illustration 9.

A mixture of p-amino benzoic acid and p-hydroxy benzoic acid is taken in diethyl ether. How will you separate them (in not more than three steps)? Write the reagents and all the required conditions to separate them. Give confirmatory test for the presence of each functional group.

### Solution:

p-amino benzoic acid, p-hydroxy benzoic acid

(in ether)



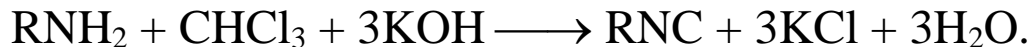
## **Purification of Organic Compounds & Practical Organic Chemistry**

---

Separate the two layers using separating funnel.

Step 2. Basification of aqueous layer with NaOH.

Test for  $-\text{NH}_2$  group: When compound containing  $-\text{NH}_2$  group is heated with  $\text{CHCl}_3$  and KOH, a very pungent smell of isocyanide is obtained.



Test for  $-\text{COOH}$  group: The compound containing  $-\text{COOH}$  group gives brisk effervescence on treatment with  $\text{NaHCO}_3$  solution due to evolution of  $\text{CO}_2$ .

Test for  $-\text{OH}$  group: A blue or green colouration is obtained when the compound is treated with neutral  $\text{FeCl}_3$  solution.