# PURIFICATION & CHARACTERISATION OF ORGANIC COMPOUNDS

## 1. PURIFICATION OF ORGANIC COMPOUNDS

The methods to be employed depend on the physical state of the compound.

**1.1 Crystallisation :** This method is based on the differences in the solubility of the organic compound and its impurities in a solvent.

**(a) Preparation of the solution :** Organic substance is powdered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating.

**Choice of Solvent.** The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are:

(i) The organic substance should dissolve in the solvent upon heating and it should get separated on cooling.

(ii) The solvent should not dissolve the impurities.

(iii) The solvent should not react chemically with the substance.

For example, suppose we want to purify sugar containing an impurity of common salt. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble.

**(b) Filtration of the solution.** The hot saturated solution is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacketer of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration.

**(c) Crystallisation.** The hot filtration is allowed to cool slowly and undisturbed in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed.

**(d) Separation of the crystals.** The crystals formed are separated from the mother liquor by filtration. The filtration is normally done by use of Buckner funnel and a suction pump. This enables the filtration under reduced pressure and is therefore, quite fast.

**(e) Drying of crystals.** The crystals are dried by pressing between the folds of filter paper and then placed in a steam of air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.

**1.2 Sublimation :** Certain organic solids directly change from solid to vapour state on heating. This process is called sublimation. The vapours on cooling change back to the solid form

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

The sublimation process is used for the separation of those solids which sublime on heating from non-volatile solids. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid, etc. containing non-volatile impurities.

**1.3 Distillation :** This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained. The distillate contains pure liquid while the impurities are left behind in the distillation flask **e.g.**Ether from ethyl alcohol.

**1.4 Fractional Distillation :** This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards. This method may be used to separate a mixture of acetone (b.p. 330K) and methyl alcohol (b.p. 338. K).

**1.5 Distillation under Reduced pressure (Vaccum Distillation) :** Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.

**Ex.** glycerol boils with decomposition at 563K.

**1.6 Steam distillation :** The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture. Thus, the process of steam distillations is used to purify the substances which

(i) are volatile in steam but are not miscible with water

(ii) possess sufficiently high vapour pressure at the boiling point temperature of water ($100^0$C)

(iii) contain non-volatile impurities.

The process of steam distillation can be applied for the separation of a mixture of o-nitrophenol and p-nitrophenol. In this process, water vapours carry along with them vapours of o-nitrophenol which is more volatile and they get condensed in the receiver ; p-nitrophenol with higher b.p. remains in the distillation flask. The method can also be used for the purification of impure sample of aniline.

**1.7 Chromatography :** This method is based on the differences in the rates at which the components of a mixture are adsorbed on a suitable adsorbent. There are many forms of chromatography such as column chromatograhy, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

**Applications of chromatographic method.**
This method has been used
(i) To separate ortho and para nitro-anilines.
(ii) To separate blue and red dyes.
(iii) To separate and purify plant pigments and other natural products.

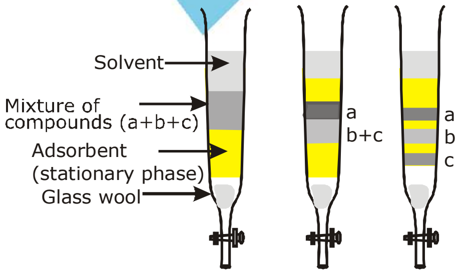
### Types of chromatography :

Based on the principle involved chromatography is classified into different categories. Two of these are.
(a) Adsorption chromatography, and
(b) Partition chromatography

### (a) Adsorption chromatography :

Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina, When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.
(i) Column chromatography, and
(ii) Thin layer chromatography.

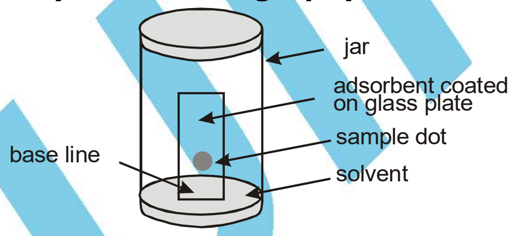
### Column chromatography:



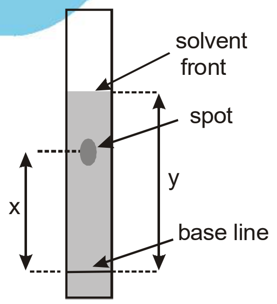
**Column chromatography. Different stages of separation of components of a mixture**

Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column

### Thin layer chromatography :



**Thin layer chromatography chromatogram being developed**



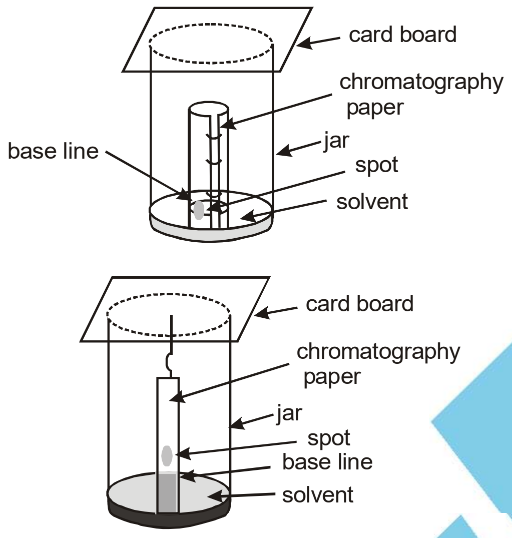
**Developed chromatogram**

Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2 mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate or chromaplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of TLC plate. The glass plate is then placed in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The ralative adsorption of each component of the mixture is expressed in terms of its **retardation factor** i.e. $R_f$ value

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

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds which are invisible to the eye but fluoresce, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine spots of compounds, which adsorb iodine will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, Amino acids may be detected by spraying the plate with ninhydrin solution

**(b) Partition Chromatography :**



**Paper chromatography chromatography paper in two different shapes**

Partition chromatography is based on continuous differential partitioning of components of mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents This solvent rises up the paper by capillary action and flows over the spot. The paper selectively ratains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

## 2. QUALITATIVE ANALYSIS

The qualitative analysis of an organic compound involves the detection of all the elements present in it.

**2.1 Detection of Carbon and Hydrogen :** A small amount of the dry and powdered substance is mixed with about double the amount of pure and dry copper oxide. The mixture is heated in a well dried hard glass tube (fig) delivery tube is packed with glass wool containing anhydrous copper sulphate (white). When the mixture is heated , the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky. The hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

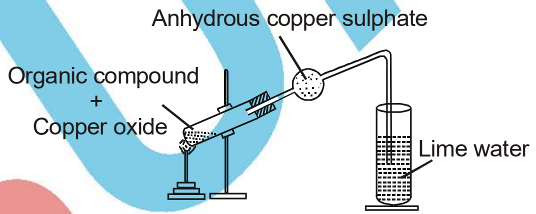


fig. Detection of carbon and hydrogen in an organic compound

$$\underset{\text{from organic compound}}{C} + 2CuO \xrightarrow{\text{Heat}} CO_2 + 2Cu$$

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

$$\underset{\text{from organic compound}}{2H} + CuO \xrightarrow{\text{Heat}} H_2O + Cu$$

$$\underset{\text{anhydrous copper sulphate (white)}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{hydrated copper sulphate (blue)}}{CuSO_4 \cdot 5H_2O}$$

This method is known as copper oxide test.

**2.2 Detection of Nitrogen :** Nitrogen in an organic compound is detected by the following tests :

**(a) Soda lime test**. A pinch of an organic compound is heated strongly with soda lime (NaOH + CaO) in a test tube. If ammonia gas evolves, it indicates nitrogen.

$$\boxed{\underset{\text{acetamide}}{CH_3CONH_2} + NaOH \xrightarrow{CaO} CH_3COONa + NH_3}$$

**Limitation :** This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberated ammonia on heating with sodalime.

**(b) Lassaigne's method :** A small piece of a 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 then cooled and filtered. The filtered liquid is known as sodium extract or Lassaigne's extract.

The Lassaigne's extract is usually alkaline. If not, it may be made alkaline by adding a few drops of a dilute solution of sodium hydroxide added to a part of sodium extract a small amount of a freshly prepared ferrous sulphate solution is and the contents are warmed. A few drops of ferric chloride solution are then added to the contents and the resulting solution is acidified with dilute hydrochloric acid. The appearance of a bluish green or a blue colouration confirms the presence of nitrogen in the organic compound. The following chemical reactions occur during the test :

$$\underset{\text{from organic compound}}{Na + C + N} \longrightarrow NaCN$$

$$\mathbf{FeSO_4} + 2NaCN \longrightarrow Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{sodium ferrocyanide}}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + \mathbf{4FeCl_3} \longrightarrow \underset{\text{ferric ferrocyanide (blue colour)}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

**2.3 Detection of Sulphur :** The sulphur in the compound reacts with sodium metal to form sodium sulphide.

$$\underset{\text{from organic compound}}{2Na + S} \longrightarrow Na_2S$$

The Lassaigne's extract is divided into two parts and following tests are performed.

**(i) Sodium nitroprusside test.** The one portion of the extract, a few drops of sodium nitroprusside are added. The appearance of violet colouration indicates sulphur.

$$Na_2S + \underset{\text{sod. nitroprusside}}{Na_2\,[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet colouration}}{Na_4[Fe(CN)_5NO.S]}$$

**(ii) Lead acetate test :** The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.

$$Na_2S + \underset{\text{lead acetate}}{Pb(CH_3COO)_2} \longrightarrow \underset{\text{black}}{PbS} + 2CH_3COONa$$

**2.4 Detection of Halogens :**

**Lassaigne's test**. Sodium extract is prepared as already. During fusion , sodium will combine with the halogen (from the organic compound) to form sodium halide

$$Na + X \xrightarrow{\text{Fusion}} NaX \ (X = Cl,\ Br,\ I)$$

(i) A white precipitate soluble in ammonium hydroxide solution indicates the presence of chlorine in the organic compound

$$NaCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl} + NaNO_3$$

(ii) A dull yellow precipitate partially soluble in ammonium hydroxide solution indicates the presence of bromine in the organic compound.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{dull yellow ppt.}}{AgBr} + NaNO_3$$

(iii) A bright yellow precipitate, completely insoluble in ammonium hydroxide solution, indicates the presence of iodine in the organic compound.

$$NaI + AgNO_3 \longrightarrow \underset{\text{bright yellow ppt}}{AgI} + NaNO_3$$

**Special test for bromine and iodine.**

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2 \quad \text{(turns } CS_2 \text{ layer orange)}$$

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2 \quad \text{(turns } CS_2 \text{ layer violet)}$$

**Test of phosphorus :**

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

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

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow$$

$$\underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

## 3. QUANTITATIVE ANALYSIS

### 3.1 Estimation of Carbon and Hydrogen :

**Principle.** A known weight of the given dry organic compound is heated strongly with dry cupric oxide in an atmosphere of air or oxygen free from $CO_2$. The carbon and hydrogen of the organic compound are oxidised to $CO_2$ and water vapour as :

$$\underset{\text{(from compound)}}{C} + 2CuO \dashrightarrow CO_2 + 2Cu$$

$2H + CuO \dashrightarrow H_2O + Cu$
(from compound)

**Procedure :**
Let the mass of organic compound taken = mg
Mass of water formed = $m_1$ g
(increase in $CaCl_2$ U-tube)
Mass of carbon dioxide formed = $m_2$ g
increase in potash tubes)

**(a) Percentage of Carbon**
We know that 1 mole of carbondioxide (44 g) contains 1 gram atom of carbon (12g).

$$CO_2 \equiv C$$

44 g of $CO_2$ contain C = 12g

$$m_2 \text{ g of } CO_2 \text{ contains } C = \frac{12}{44} \times m_2 \text{ g}$$

$$\text{Hence Percentage of carbon} = \frac{12m_2}{44 \times m} \times 100$$

**(b) Percentage of Hydrogen**
We know that one mole of water (18g) contains 2 gram atom of hydrogen (2g)

$$H_2O = 2H$$

18g of $H_2O$ contain H = 2g

$$\therefore\ m_1 \text{ g of } H_2O \text{ contains } H = \frac{2}{18} \times m_1 \text{ g}$$

$$\text{Percentage of hydrogen} = \frac{2m_1}{18 \times m} \times 100$$

Percentage of C

$$= \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Percentage of H

$$= \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of compound taken}} \times 100$$

## 3.2Estimation of Nitrogen :

There are two methods for the estimation of nitrogen
(i) Duma's method (ii) Kjeldahl's method

### (i) Duma's method :

**Principle of the method.** A known mass of an organic compound is heated with dry cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidised to carbon dioxide and water respectively while nitrogen is set free. If any oxide of nitrogen is produced during this process, it is reduced to nitrogen by passing over a heated copper gauze. The gaseous mixture is collected over an aqueous solution of KOH when all the gases except nitrogen are absorbed. The volume of nitrogen produced is measured at room temperature and atmospheric pressure. From the volume of $N_2$ produced, percentage of nitrogen in the sample can be calculated.

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$
$$2H + CuO \longrightarrow H_2O + Cu$$
$$2N + CuO \longrightarrow N_2 + \text{oxides of nitrogen}$$

Oxides of nitrogen + Cu → CuO + $N_2$
Let the mass of organic compound = wg
The volume of nitrogen collected = V$cm^3$
Atmospheric pressure (from barometer)
= P mm of Hg
Room temperature = $t^0C$
Aqueous tension at $t^0C$ = a mm of Hg
Pressure of dry nitrogen = (P – a) mm of Hg
Let us first convert the volume of nitrogen to volume at S.T.P.

| Experimental conditions | S.T.P. conditions |
|---|---|
| $P_1 = (P - a)$ mm Hg | $P_2 = 760$ mm |
| $T_1 = (273 + t)$K | $T_2 = 273$ |
| $V_1 = V\ cm^3$ | $V_2 = ?$ |

$$\text{Applying gas equation } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore\ V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(P-a) x V \text{ x } 273}{760\,(273+t)} = x \text{ cm}^3 \text{ (say)}$$

Now 22400 $cm^3$ of $N_2$ at S.T.P. weight = 28 g

$$x \text{ cm}^3 \text{ of } N_2 \text{ at S.T.P. will weigh} = \frac{28}{22400} \times xg$$

∴ Percentage of nitrogen

$$= \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \text{ x } 100 = \frac{28x \text{ x } 100}{22400 \text{ x } w}$$

**(ii) Kjeldahl's method :** This method cannot be used for
(i) Organic compounds containing nitrogen in the ring such as pyridine, quinoline, etc.
(ii) Organic compounds containing nitrogen ($-NO_2$) and diazo (-N = N-) groups.

**Principle :** A known weight of the organic compound is heated with conc. $H_2SO_4$ 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 $H_2SO_4$). 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 neutralisation of ammonia can be calculated. From this percentage of nitrogen can be calculated.

$$C, H, S \xrightarrow{\text{Conc. } H_2SO_4} CO_2 + H_2O + SO_2$$

(from organic
compound)

$$\underset{\text{(from organic compound)}}{N} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{ammonium sulphate}}{(NH_4)_2SO_4}$$

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

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

$$NH_3 + HCl \longrightarrow NH_4Cl$$

**Calculations**

Let the mass of organic compound = w g

Volume of standard acid taken = V $cm^3$

Normality of acid = $N_1$

Let vol. of standard alkali used for neutralisation of unused acid = $V_2$ $cm^3$

Normality of standard alkali = $N_2$

$$\underbrace{N_1V_1}_{\text{alkali}} = \underbrace{N_2V_2}_{\text{acid}}$$

Let this volume of v $cm^3$

∴ Vol. of acid used for neutralisation of ammonia = (V – v) $cm^3$ of $N_1$ normality

∴ Ammonia liberated = (V – v) $cm^3$ of $N_1$ solution

Now, 1000 $cm^3$ of 1N $NH_3$ solution contains nitrogen = 14 g

(V – v) $cm^3$ of $N_1$ $NH_3$ solution contains nitrogen

$$= \frac{14(V-v)\times N_1}{1000}\,g$$

Percentage of nitrogen

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

$$= \frac{14(V-v)\times N_1}{1000} \times \frac{100}{w} = \frac{1.4(V-v)\times N_1}{w}$$

### 3.3 Estimation of Halogens :

**Carius method :**

**Principle :** A known mass of the organic substance is heated with fuming $HNO_3$ in a Carius tube. The silver halide so obtained is separated, washed, dried and weighed. From the weight of silver halide formed, the percentage of halogen can be calculated.

$$\underset{\text{Halogen}}{X} + AgNO_3 \longrightarrow AgX$$

Carbon, hydrogen or sulphur present in the compound will be oxidised to $CO_2$, $H_2O$ and $H_2SO_4$ respectively.

$$C + 2O \xrightarrow{HNO_3} CO_2$$

$$2H + O \xrightarrow{HNO_3} H_2O$$

$$S + H_2O + 3O \xrightarrow{HNO_3} H_2SO_4$$

**Calculations :**

Let the mass of organic compound be w g

Mass of silver halide formed = a g

Now, AgX = X

108 + X parts by weight of silver halide contains X parts by weight of halogen (X is its atomic mass)

(108 + X) g of silver halide give halogen

= X a g of silver halide will give halogen

$$= \frac{X}{(108+X)} \times a\,g$$

∴ Percentage of halogen

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

$$= \frac{X \times a}{(108+X)} \times \frac{100}{w}$$

Here X is the atomic mass of halogen, e.g. Cl = 35.5 , Br = 80 (79.9 exact), I = 127 (126.9 exact)

Percentage of halogen

$$= \frac{\text{Atomic mass of halogen} \times \text{Mass of silver halide}}{(108 + \text{At. mass of halogen}) \times \text{Mass of organic substance}} \times 100$$

### 3.4 Estimation of Sulphur

Sulphur is estimated by Carius method.

**Principle :** A known mass of the organic compound is heated with fuming $HNO_3$ in a sealed tube when sulphur is quantitatively converted into sulphuric acid. It is then precipitated with barium chloride as barium sulphate. The precipitate is filtered, washed, dried and weighed. From the weight of $BaSO_4$ formed, the percentage of sulphur can be calculated. The main reactions are :

$$S + H_2O + 3O \xrightarrow{HNO_3} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{ppt.}}{BaSO_4}$$

**Calculations :**

Let the mass of organic compound = w g

Mass of $BaSO_4$ formed = a g

$BaSO_4 \equiv S$

137 + 32 + 64 = 32

= 233

233 g of $BaSO_4$ contain sulphur = 32 g

a g of $BaSO_4$ will contain sulphur = $\frac{32 \times a}{233}$ g

Percentage of sulphur

$$= \frac{32a}{233} \times \frac{100}{w}$$

## SOLVED PROBLEMS

**Ex.1** ***Liquid which decompose below their normal boiling points can be distilled at lower temperature by-***
***(A) Increasing the pressure***
***(B) Decreasing the pressure***
***(C) Heating in water bath***
***(D) Heating in sand bath*** ***Ans.(B)***

**Sol.** B.pt. gets lowered at low pressure.

**Ex.2** ***A bottle containing two immiscible liquids is given to you. They may be separated by using a-***
***(A) Fractionating coloumn***
***(B) Separating funnel***
***(C) Vacuum distillation***
***(D) Steam distillation*** ***Ans.(B)***

**Sol.** Being immiscible liquids, they form different layers.

**Ex.3** ***In Lassaigne's test for nitrogen, the blue colour is due to the formation of-***
***(A) Ferric ferrocyanide***
***(B) Potassium ferrocyanide***
***(C) Sodium ferrocyanide***
***(D) Sodium cyanide*** ***Ans.(A)***

**Sol.** In Lassaigne's test substance is heated strongly with sodium metal then water extract is boilded with alkaline $FeSO_4$ solution and after cooling $FeCl_3$ solution and excess of HCl is added in it. If prussian blue or green ppt. is obtained then Nitrogen is confirmed-

$Na + C + N \longrightarrow NaCN$

$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$

$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$

sodium ferrocyanide prussian blue or green
(ferric ferrocyanide)

**Ex.4** ***In sodium fusion test of organic compounds, the nitrogen of an organic compound is converted to-***
***(A) Sodamide*** ***(B) Sodium cyanide***
***(C) Sodium nitrite*** ***(D) Sodium nitrate***
***Ans. (B)***

**Sol.** $Na + C + N \xrightarrow{\text{fusion}} NaCN$

**Ex.5** ***Liebig method is used for the estimation of-***
***(A) Nirogen*** ***(B) Sulphur***
***(C) Carbon and Hydrogen***
***(D) Halogens*** ***Ans. (C)***

**Sol.** Liebig method is used for the estimation of carbon and hydrogen.

**Ex.6** ***The quantitative determination of halogen in an organic compound is known as-***
***(A) Dumas method*** ***(B) Carius method***
***(C) Kjeldahl method*** ***(D) Leibig method***
***Ans.(B)***

**Sol.** The quantitative determination of halogen in an organic compound is called as carius method.

**Ex.7** ***0.2475g of an organic compound gave on combustion 0.4950g of carbon dioxide and 0.2025 g of water. The percentage of carbon and hydrogen are-***
***(A) 54.54, 9.09*** ***(B) 52.54, 8.09***
***(C) 120, 5.8*** ***(D) None*** ***Ans. (A)***

**Sol.** Wt. of organic compound = 0.2475 g
Wt. of $CO_2$ produced = 0.4950 g
Wt. of $H_2O$ produced = 0.2025 g
Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen

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

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

**Ex.8** ***0.257 g of an organic substance was heated with conc $H_2SO_4$ and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 ml of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralisation at the end of the*** process. ***The percentage of nitrogen in the compound is-***
***(A) 14.6*** ***(B) 18.0*** ***(C) 17.0*** ***(D) 15.5***
***Ans.(A)***

**Sol.** Volume of $\frac{N}{10}$ HCl taken = 50ml

Volume of $\frac{N}{10}$ NaOH used for neutralisation of unused acid = 23.2 ml

Now $N_1 V_1(NaOH) = N_2V_2(HCl)$

23.2 ml of $\frac{N}{10}$ NaOH ≡ 23.2 ml of $\frac{N}{10}$ HCl

∴ Volume of $\frac{N}{10}$ HCl unused = 23.2 ml

∴ Volume of N/10 HCl required for neutralization of $NH_3$ = 50 - 23.2 = 26.8 ml

26.8 ml of $\frac{N}{10}$ HCl = 26.8 ml of N/10 $NH_3$

1000 ml of 1N $NH_3$ solution contains nitrogen = 14 g

26.8 ml of $NH_3$ solution contains nitrogen

$$= \frac{14 \times 26.8}{10 \times 1000}$$

Percentage of nitrogen

$$= \frac{14 \times 26.8 \times 100}{10 \times 1000 \times 0.257} = 14.6\%$$