

Purification and 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.

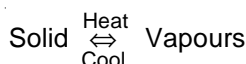
[b] Filtration of the solution : The hot saturated solution [prepared in step (a)] is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacket of the hot water funnel is heated from outside and this keeps the 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 (step c) 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



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 nonvolatile 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 decompositions 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°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 chromatography, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

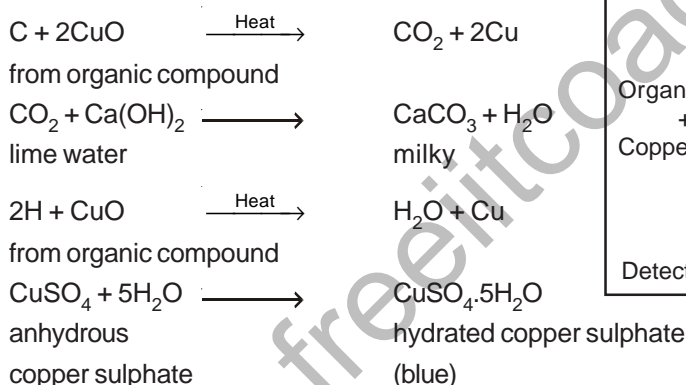
Applications of chromatographic method : This method has been used

- [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.

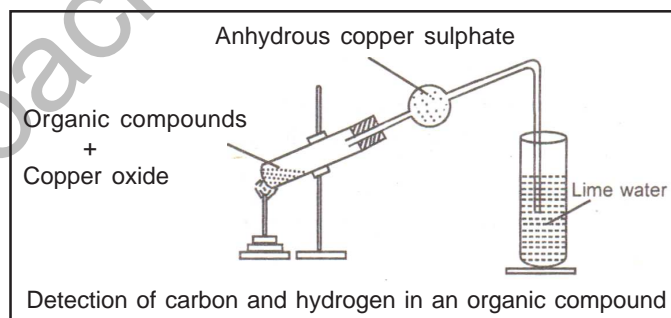
2. Qualitative Analysis :

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.

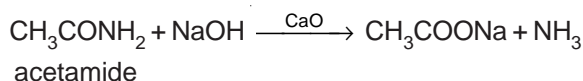


This method is known as copper oxide test.



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.



Limitation : This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberate 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 added 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 bluish green or a blue colouration confirms the presence of nitrogen in the organic compound.



from organic compound



sodium ferrocyanide



ferric ferrocyanide

(blue colour)

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



from organic

compound

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.



sod. nitroprusside

violet colouration

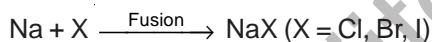
[ii] Lead acetate test : The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.



lead acetate

black

2.3 Detection of Halogens : Lasseigne's test. Sodium extract is prepared as already. During fusion, sodium will combine with the halogen (from the organic compound) to form sodium halide



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



white ppt.

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



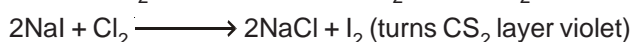
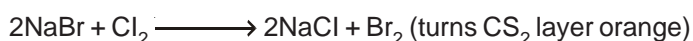
dull yellow ppt.

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



bright yellow ppt

Special test for bromine and iodine.



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 :



(from compound)



(from compound)

Procedure :

Let the mass of organic compound taken = w g

Mass of water formed = x g

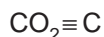
(increase in CaCl_2 U-tube)

Mass of carbon dioxide formed = y 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)



44 g of CO_2 contain C = 12 g

Y g of CO_2 contains C = $\frac{12}{44} \times y$ g

Hence
$$\text{Percentage of carbon} = \frac{12y}{44 \times w} \times 100$$

[b] Percentage of Hydrogen :

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



18g of H_2O contain H = 2g

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

$$\text{Percentage of hydrogen} = \frac{2x}{18 \times w} \times 100$$

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

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

3.2 Estimation of Nitrogen :

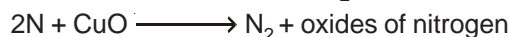
There are two methods for the estimation of nitrogen

[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.



Let the mass of organic compound = w g

The volume of nitrogen collected = $V \text{ cm}^3$

Atmospheric pressure (from barometer) = P mm of Hg

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

Aqueous tension at $t^\circ\text{C}$ = 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

$$P_1 = (P - a) \text{ mm Hg}$$

$$P_2 = 760 \text{ mm}$$

$$T_1 = (273 + t) \text{ K}$$

$$T_2 = 273$$

$$V_1 = V \text{ cm}^3$$

$$V_2 = ?$$

Applying gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(P - a) \times V \times 273}{760 (273 + t)} = x \text{ cm}^3 \text{ (say)}$$

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

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

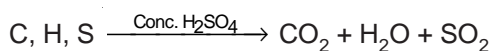
$\therefore \text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100$ $= \frac{28x \times 100}{22400 \times w}$

[ii] Kjeldahl's method : This method cannot be used for

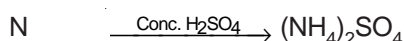
[i] Organic compounds containing nitrogen in the ring such as pyridine, quinoline, etc.

[ii] Organic compounds containing nitrogen ($-\text{NO}_2$) and diazo ($-\text{N} = \text{N}-$) groups.

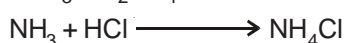
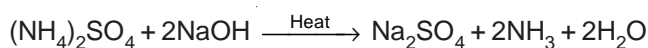
Principle : A known weight of the organic compound is heated with conc. H_2SO_4 so that nitrogen is quantitatively converted into ammonium sulphate. The solution is then heated with excess of sodium hydroxide. The ammonia evolved is passed into a known but excess volume of standard acid (HCl or H_2SO_4). 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.



(from organic compound)



(from organic compound ammonium sulphate compound)



Calculations :

Let the mass of organic compound = w g

Volume of standard acid taken = V cm³

Normality of acid = N₁

Let vol. of standard alkali used for neutralisation of unused acid = V₂cm³

Normality of standard alkali = N₂

$$\underbrace{N_1 V_1}_{\text{alkali}} = \underbrace{N_2 V_2}_{\text{acid}}$$

Let this volume of v cm³

∴ Vol. of acid used for neutralisation of ammonia = (V - v) cm³ of N₁ normality

∴ Ammonia liberated = (V - v) cm³ of N₁ solution

Now, 1000 cm³ of N₁ NH₃ solution contains nitrogen = $\frac{14(V - v) \times N_1}{1000}$ g

$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100 \\ &= \frac{14(V - v) \times N_1}{1000} \times \frac{100}{w} = \frac{1.4(V - v) \times N_1}{w} \end{aligned}$

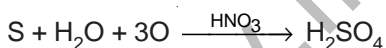
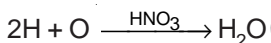
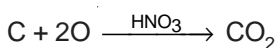
3.3 Estimation of Halogens :

Principle : A known mass of the organic substance is heated with fuming HNO₃ 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.



Halogen

Carbon, hydrogen or sulphur present in the compound will be oxidised to CO₂, H₂O and H₂SO₄ respectively.

**Calculations :**

Let the mass of organic compound 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

$\begin{aligned} \text{Percentage of halogen} &= \frac{\text{Mass of halogen}}{\text{Mass of organic compound}} \times 100 \\ \therefore &= \frac{X \times a}{(108 + X)} \times \frac{100}{w} \end{aligned}$

Here X is the atomic mass of halogen, e.g.

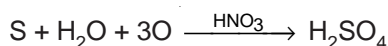
Cl = 35.5, Br = 80 (79.9 exact), I = 127 (126.9 exact)

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

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 :



ppt.

Calculations :

Let the mass of organic compound = w g

Mass of BaSO_4 formed = a g

$\text{BaSO}_4 \equiv \text{S}$

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

$$\text{Percentage of sulphur} = \frac{\text{Mass of sulphur}}{\text{Mass of organic compound}} \times 100 = \frac{32 a}{233} \times \frac{100}{w}$$

4. Determination of Molecular Mass :

Molecular mass of an organic compound can be determined by a number of methods. The principles of important methods are discussed below :

4.1 Victor Meyer's Method

Principle : A known mass of the substance is heated in the Victor Meyer's tube. The vapours produced by the substance are made to displace an equal volume of air which can be collected over water. The volume of the air displaced by vapours is measured at room temperature and atmospheric pressure. The volume is converted to volume at S.T.P. From this the weight of substance which will displace 22.4 L of vapours at S.T.P. is calculated and this gives the molecular mass.

Calculations :

First of all volume is converted to volume at S.T.P. as

Let the mass of the organic compound taken = w g

Volume of air displaced = v cm^3

Atmospheric pressure = P mm of Hg

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

\therefore Pressure of dry air = (P - a) mm of Hg

Experimental conditions

$P_1 = (P - a)$ mm

$T_1 = (273 + t)$ K

S.T.P. conditions

$P_2 = 760$ mm

$T_2 = 273$ K

$V_1 = v \text{ cm}^3$ $V_2 = ?$

Applying gas equation, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\therefore V_2 = \frac{(P - a) x v \times 273}{760 \times (273 + t)} = x \text{ cm}^3 \text{ (say)}$$

Now $x \text{ cm}^3$ of vapours at S.T.P. weight = $w \text{ g}$

22400 cm^3 of vapours at S.T.P. should weigh = $\frac{w}{x} \times 22400$

$$\therefore \boxed{\text{Molecular mass of substance} = \frac{w}{x} \times 22400}$$

4.2 Volumetric method : The volumetric method is used for determining the molecular mass of acids and bases. For example, in case of an acid, a known mass of it is dissolved in water and titrated against standard alkali solution using suitable indicator (phenolphthalein). From the volume of alkali required for neutralisation of the acid, molecular mass can be calculated.

Let the organic compound taken be $w \text{ g}$ and $V_1 \text{ cm}^3$ of N_1 alkali be used for its neutralisation.

Then $V_1 \text{ cm}^3$ of N_1 alkali = $w \text{ g}$

$$1000 \text{ cm}^3 \text{ of } 1 \text{ N alkali} = \frac{w}{V_1} \times \frac{1000}{N_1}$$

1000 cm^3 of 1 N alkali corresponds to gram equivalent of the alkali, because acid and alkali always react in equivalent proportions.

$$\text{Gram equivalent of the acid} = \frac{w}{V_1} \times \frac{1000}{N_1}$$

$$\therefore \text{Molecular mass} = \text{Eq. wt.} \times \text{Basicity} = \frac{w}{V_1} \times \frac{1000}{N_1} \times \text{Basicity}$$