

Purification and Characterisation of Organic Compounds

Purification of Organic Compounds

Organic compounds extracted from a natural source or synthesized in the laboratory requires purification. Various methods are used for the purification and are based on the nature of the compound and the impurity present in it. The purity of a compound is ascertained by determining its melting point or boiling point or by chromatographic and spectroscopic techniques.

Methods of Purification of Solids

- (i) **Crystallisation** In this process, a saturated solution of impure substance is prepared in hot solvent and heated with animal charcoal which adsorbs the impurities. The solution is filtered and filtrate on cooling deposits crystals of pure compound. Success of the process depends upon the selection of the solvent. The impurities must be least soluble.

┌ A process in which crystal formation is initiated by adding crystals of pure substance, is known as **seeding**. ─┐

- (ii) **Fractional crystallisation** It is based on the different solubilities of different compounds in a solvent. The compound having less solubility crystallises out first on cooling leaving behind others in solution. Sometimes mixture of two solvents, e.g. alcohol and water, chloroform and petroleum ether, give better results.

- (iii) **Sublimation** Some solids directly convert into vapours when heated without converting into liquid. These are known as sublimate and this process is called sublimation. The substances which sublime can be purified by this method provided the impurities present does not sublime. Camphor, naphthalene and anthracene are purified by sublimation.

Methods of Purification of Liquids

- (i) **Simple distillation** The vaporisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation. The liquids boiling under ordinary conditions of temperature and pressure without decomposition and containing non-volatile impurities are purified by simple distillation.
- (ii) **Fractional distillation** It is employed for separating mixture of two or more volatile liquids having boiling points close to each other, e.g. acetone (boiling point 60°C) and methanol (boiling point 65°C). Components of petroleum are separated by this method. The vapours of the liquids are passed through the fractionating column which provides greater space for their cooling. The vapours of high boiling substance condense and fall back into distillation flask.
- (iii) **Distillation under reduced pressure or vacuum distillation** Some liquids decompose when heated to their boiling points, e.g. glycerol. Such liquids can be purified by distillation under reduced pressure much below than their boiling points.
- (iv) **Steam distillation** The liquids insoluble in water, steam volatile in nature, having high molecular weight and high vapour pressure are purified by steam distillation provided the impurities present are not steam volatile. The liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p). i.e. $p = p_1 + p_2$. Since, p_1 is lower than, p the organic liquid vaporises at lower temperature than its boiling point. e.g. *o*-hydroxy acetophenone and *p*-hydroxy acetophenone are separated by this method.
- (v) **By separating funnel** In this method, a mixture of two immiscible liquids can be separated and the process is also called differential extraction.

Chromatographic Method

It was discovered by **Tswett** (1906).

It is based upon the principle of selective adsorption of various components of a mixture between the two phases : stationary or fixed phase and mobile phase.

The various chromatographic techniques are:

1. Adsorption Chromatography

Stationary phase – solid or ion exchange resin. Mobile phase –liquid or gas.

It includes liquid-solid chromatography, gas-solid chromatography or ion exchange chromatography.

Two types of chromatographic techniques based on the principle of differential adsorption are as follows.

(a) Column Chromatography

It is an example of adsorption chromatography. Adsorbents used are alumina, silica gel, cellulose powder, animal charcoal, keiselguhr etc.

Liquid solvents used are benzene, petroleum ether, alcohol etc.

When the solvent is poured over the mixture present at the top of a column packed with adsorbent, the components are separated into number of layers called **zones**, **bands** or **chromatograms** due to preferential adsorption.

(b) Thin Layer Chromatography

It involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. The 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 chromoplate.

The solution of the mixture to be separated is applied as 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 solvent rises up the plates, the component of mixture moves up along with the eluant to different distance depending on their degree of adsorption and separation takes place.

Retardation Factor i.e. R_f Value

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

2. Partition Chromatography

Fixed phase-liquid supported on inert solid. Mobile phase –liquid or gas.

This process is known as liquid-liquid partition chromatography or liquid-gas partition chromatography on the basis of its different phases.

3. Paper Chromatography

The principle of paper chromatography is based on the fact that solutes have the capacity to migrate through filter paper at different rates as a solution is drawn into strip of paper by capillary action.

In paper chromatography, the dissolved substance is applied as a small spot about 2-3 cm from the edge of a strip or square of filter paper and is allowed to dry. This strip is then suspended in a large close container where atmosphere is saturated with the solvent system. The end containing the sample is dipped into the mobile phase which has already been saturated with the stationary phase. When the solvent front has reached at the other end of the paper, the strip is removed and the zones are located by analytical methods.

┌ The ratio of the distance travelled by a component to the distance travelled by the solvent front is characteristic of each component and is known as the R_f value.

$$R_f = \frac{\text{distance in cm from starting line to the centre of zone}}{\text{distance in cm from starting line to the solvent front}}$$

Elution The continuous pouring of solvent from the top of the column is known as elution or running of column. Solvent is known as **eluant**.

The most weakly adsorbed component is eluted first by least polar solvent while more strongly adsorbed component is eluted later by highly polar solvents.

Chemical Methods of Purification

The substance to be purified is treated with a suitable chemical reagent to form a stable derivative. It is then separated by suitable method and decomposed to get the pure compounds.

Examples

- (i) Mixture of amines (1° , 2° and 3°) is separated by **Hinsberg's method**.
- (ii) Acetic acid from pyroligneous acid is separated by forming calcium salt.

(iii) Acids are separated by forming sodium derivatives with NaHCO_3 .

(iv) Absolute alcohol is obtained from rectified spirit by quick lime process and azeotropic distillation.

Azeotropic Distillation

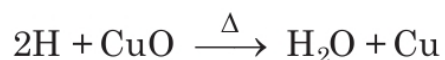
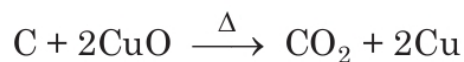
Azeotropes are constant boiling mixtures which distil off without any change in composition at a fixed temperature. Therefore, **components of an azeotropic mixture cannot be separated by fractional distillation**. A very common example of azeotropic mixture is rectified spirit which contains 95.87% ethyl alcohol and 4.23% water by weight which boils at 351.1 K.

Such mixtures are separated by adding another component which generate a new lower boiling azeotrope that is heterogeneous (i.e. producing two immiscible liquid phases). e.g. C_6H_6 is added to H_2O and ethyl alcohol azeotrope to separate them.

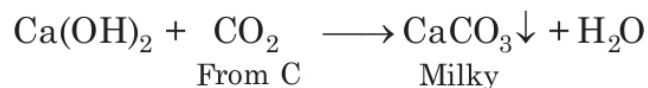
Qualitative Analysis of Organic Compounds

1. Detection of Carbon and Hydrogen

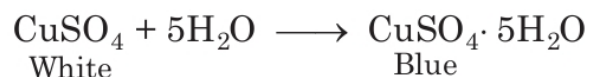
This is done by heating the given organic compound with dry cupric oxide in a hard glass test tube when carbon present is oxidised to carbon dioxide and hydrogen is oxidised to water.



Carbon dioxide turns lime water milky.



Water condenses on the cooler parts of the test tube and turns anhydrous copper sulphate blue.



Lassaigne's Test

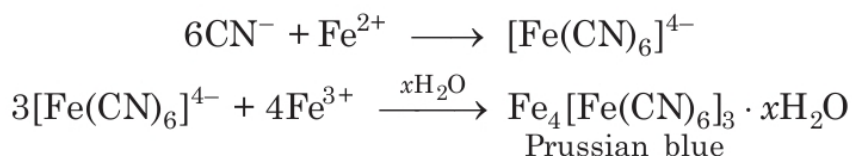
The organic compound is fused with a small piece of Na metal. When element (N, S, X) of the organic compound combine to give NaCN , Na_2S or NaX , the red hot tube is plunged in distilled water, boiled and filtered. The filtrate is called **Lassaigne's extract** or **sodium extract**. The Lassaigne's extract is usually alkaline. If not, it is made

alkaline by adding a few drops of a dilute solution of sodium hydroxide. The purpose of fusing the organic compounds with sodium metal is to convert halogens, N, S, P etc., present in the organic compound to their corresponding soluble sodium salts (ionic compounds).



1. Detection of Nitrogen

To a part of this Lassaigne's extract a few drops of a freshly prepared solution of ferrous sulphate is added, because a dilute solution of FeSO_4 after a long time oxidise to basic ferric sulphate which is useless for analysis. The contents are warmed a little, cooled and then acidified with dil. H_2SO_4 . Appearance of a green or Prussian blue colouration indicates the presence of nitrogen.



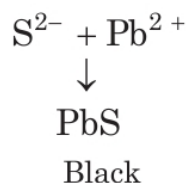
If S is also present alongwith N, a red colour in place of Prussian blue in the test of nitrogen appears, due to the formation of $\text{Fe}(\text{SCN})^{2+}$.

Hydrazine does not give Lassaigne's test for nitrogen since it does not contain carbon. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or preferably starch (which contains C but not N, S, halogens etc.) is added. Under these conditions, C of starch or charcoal combines with N of the compound to form NaCN which will now give a positive test for nitrogen.

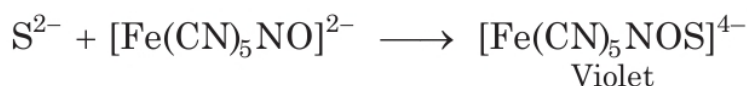
┌ Lassaigne's test is not shown by diazonium salts because diazonium salts usually lose N_2 on heating much before they have a chance to react with fused sodium metal. ┐

2. Detection of Sulphur

- (i) Sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of PbS indicates the presence of sulphur.

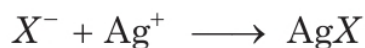


- (ii) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.



3. Detection of Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.



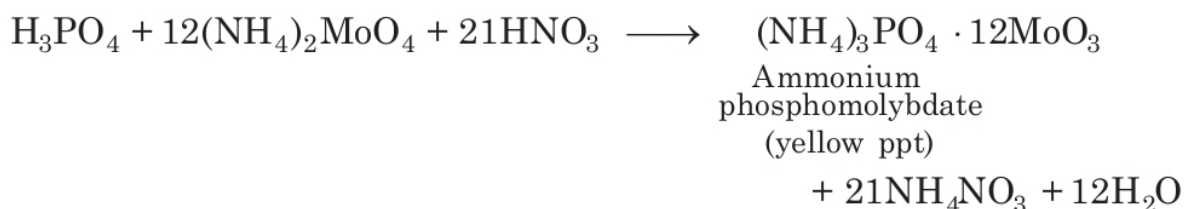
X represents a halogen —Cl, Br, or I.

AgCl-white ppt, AgBr-dull yellow ppt, AgI-bright yellow ppt.

Note *Beilstein test is also a test for halogen but it is not a confirmatory test.*

4. Detection of Phosphorus

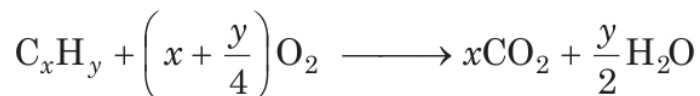
The compound is heated with an oxidising agent (sodium peroxide). By this the phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.



Quantitative Estimation of Elements

1. Estimation of Carbon and Hydrogen (Liebig's Method)

When a known mass of organic compound is strongly heated with dry CuO, C and H present are quantitatively oxidised to CO₂ and H₂O respectively.



By knowing the amount of CO₂ and H₂O from known weight of organic compound, the percentage of carbon and hydrogen can be computed.

The water is absorbed in anhydrous CaCl₂.

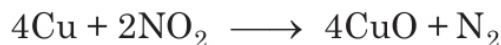
The carbon dioxide is absorbed in concentrated solution of KOH.

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{\text{mass of CO}_2 \times 100}{\text{mass of organic substance}}$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O} \times 100}{\text{mass of organic substance}}$$

On heating with CuO, elements other than C and H are also modified as follows :

When organic compound contains nitrogen, the oxides of nitrogen (NO, N₂O etc.) are absorbed by caustic potash. These are removed by the use of bright copper gauge.



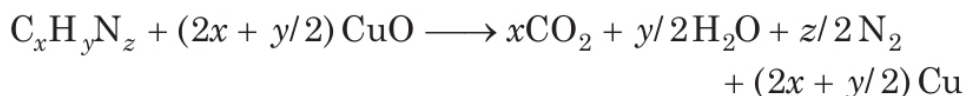
Nitrogen is not absorbed by KOH solution.

┌ When organic compound contains halogens, they are removed by using silver gauge by forming non-volatile silver halide.
When sulphur is present, it is removed by forming lead sulphate by using fused lead chromate and halogens form lead halides. ┐

Estimation of Nitrogen

(i) **Duma's method** This method is used for nitrogenous compounds. Though tedious but it is better than Kjeldahl's method.

In this method, the nitrogenous compound is heated strongly with CuO in the atmosphere of CO₂ and the mixture obtained is passed over a roll of heated bright Cu gauze. The oxides of nitrogen again reduce to N₂. The resultant mixture is passed in KOH. All gases except N₂ are fairly absorbed. Nitrogen is collected over KOH and its volume at NTP is measured.

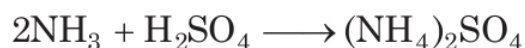
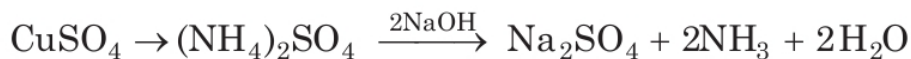


$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{28 \times \text{volume of N}_2 \text{ at NTP} \times 100}{22400 \times \text{wt. of organic compound}} \\ &= \frac{\text{mass of nitrogen} \times 100}{\text{mass of organic substance}} \end{aligned}$$

(ii) Kjeldahl's method

In this method, nitrogen containing compound is heated with conc. H_2SO_4 . The acid mixture obtained is then heated with excess of NaOH . The liberated ammonia gas is absorbed in an excess of standard solution of H_2SO_4 . The amount of NH_3 produced is determined by estimating the amount of H_2SO_4 consumed in reaction.

Organic compound + conc. H_2SO_4 + (small amount of K_2SO_4 and



Ammonia is passed through H_2SO_4 or HCl of known volume and normality. The volume of acid neutralised by NH_3 is calculated by neutralising the acid left by NaOH solution.

$$\text{Percentage of nitrogen} = \frac{1.4 \times N \times V}{\text{mass of organic compound}}$$

N = normality of acid

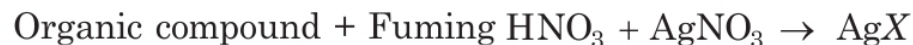
V = volume of acid in mL neutralised by ammonia.

(In practice, K_2SO_4 is added to raise the boiling point of H_2SO_4 and CuSO_4 is added to catalyse the reaction).

Kjeldahl's method is not reliable as results obtained are generally low. It cannot be applied to compounds containing nitrogen directly linked to oxygen or nitrogen such as nitro, nitroso, azo and nitrogen present in ring as in pyridine.

Estimation of Halogen (Carius Method)

In this method, halogen containing compound is heated with fuming HNO_3 in presence of AgNO_3 contained in carius tube. On heating, C and H are oxidised to CO_2 and H_2O and halogen present forms AgX .



It is estimated gravimetrically.

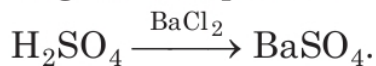
Percentage of halogen

$$= \frac{\text{Atomic mass of halogen atom} \times \text{mass of AgX} \times 100}{\text{mol. mass of AgX} \times \text{mass of organic compound}}$$

Estimation of Sulphur

In this method, sulphur containing compound is heated in carius tube with Na_2O_2 or fuming HNO_3 . On heating S is oxidised to H_2SO_4 . It is precipitated as BaSO_4 by adding excess of BaCl_2 solution in water.

Organic compound + Oxidising agent (Na_2O_2 or fuming HNO_3) \rightarrow



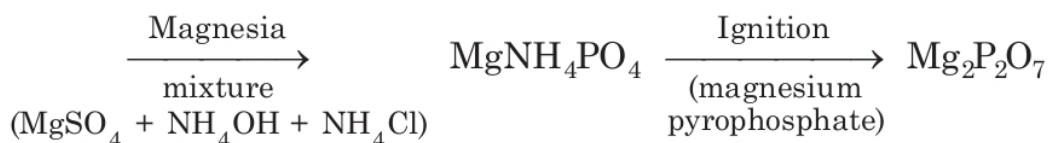
It is estimated gravimetrically,

$$\text{Percentage of sulphur} = \frac{32 \times \text{mass of BaSO}_4 \times 100}{233 \times \text{mass of organic compound}}$$

Estimation of Phosphorus

In this method, organic compound is heated with fuming HNO_3 that converts 'P' present in compound to phosphoric acid. It is precipitated as $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ by adding NH_3 and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as MgNH_4PO_4 by adding magnesia mixture which on ignition yields $\text{Mg}_2\text{P}_2\text{O}_7$.

Organic compound + Fuming nitric acid $\rightarrow \text{H}_3\text{PO}_4$



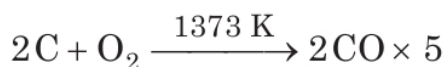
$$\text{Percentage of phosphorus} = \frac{62 \times \text{mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{222 \times \text{mass of organic compound}}$$

Now a days CHN elemental analyser is used to estimate the C, H and N in the organic compound.

Estimation of Oxygen

The mixture of gaseous product containing oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

Compound $\xrightarrow{\text{Heat}} \text{O}_2 + \text{Other gaseous products}$



$$\therefore \text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{88 \times m} \%$$

m = mass of organic compound taken.

m_1 = mass of carbon dioxide produced.