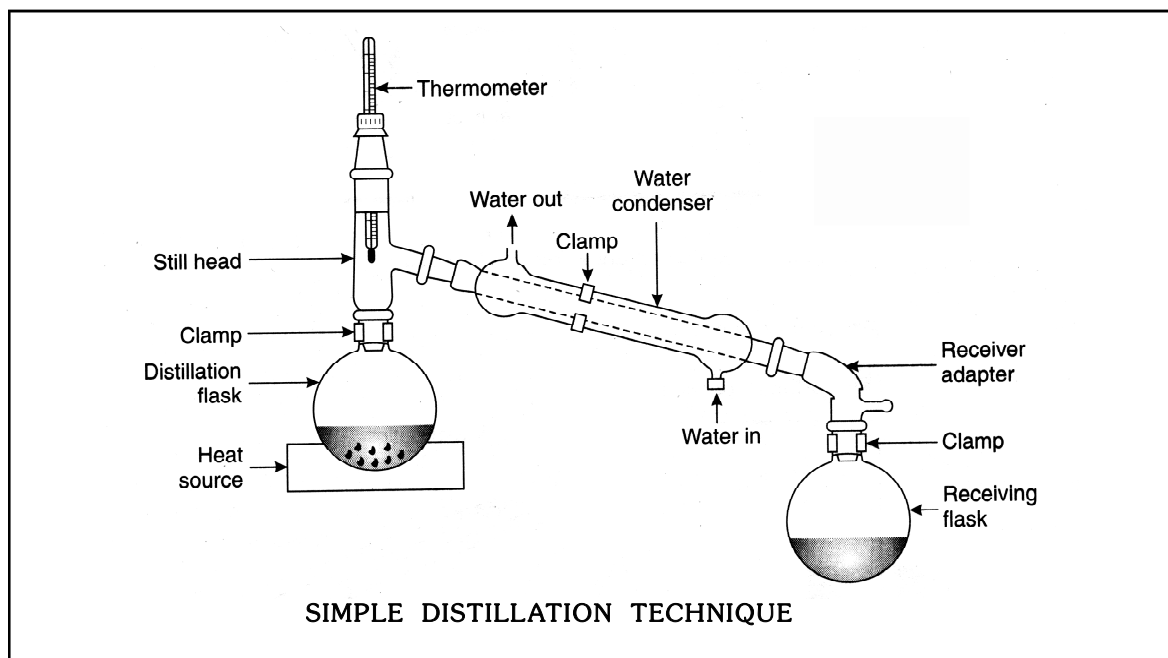
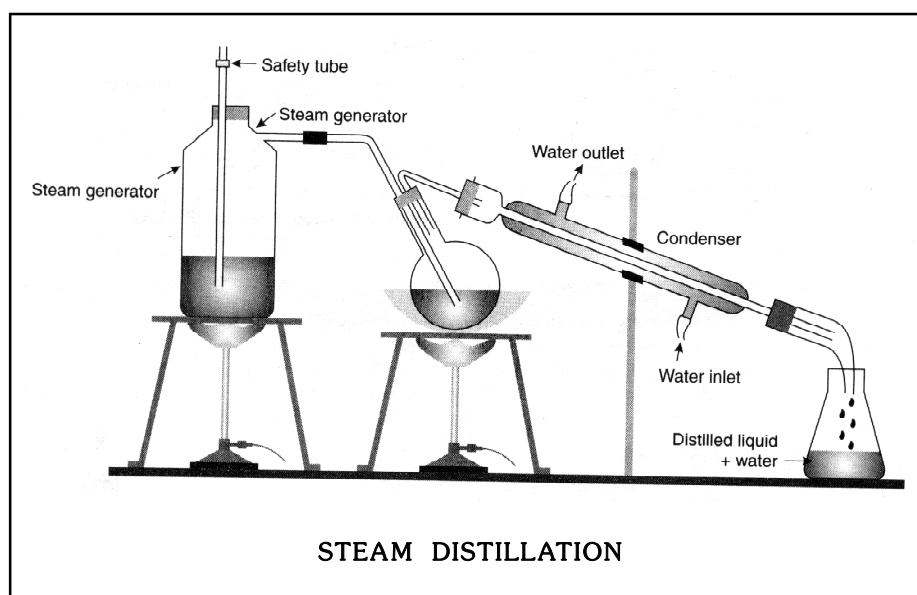
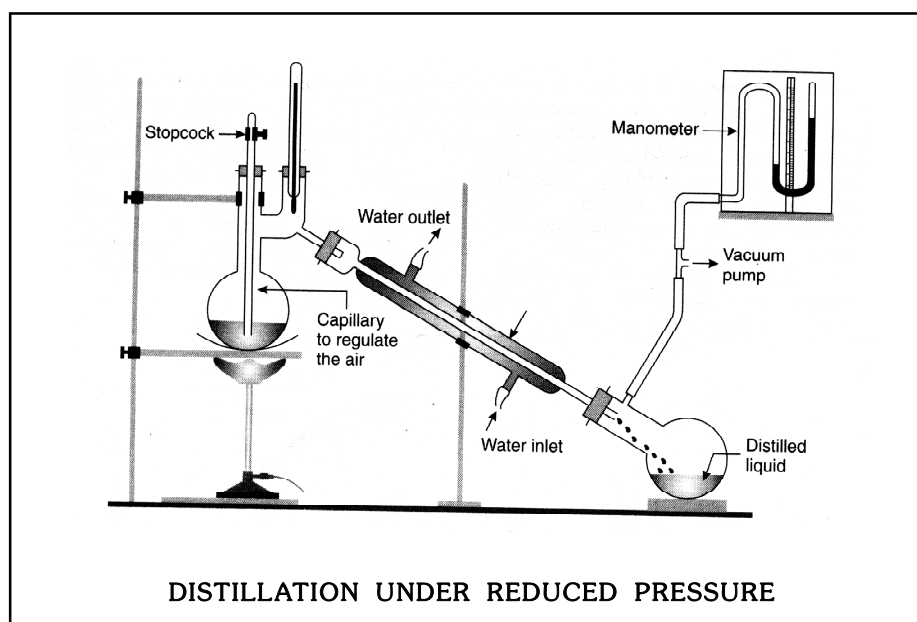
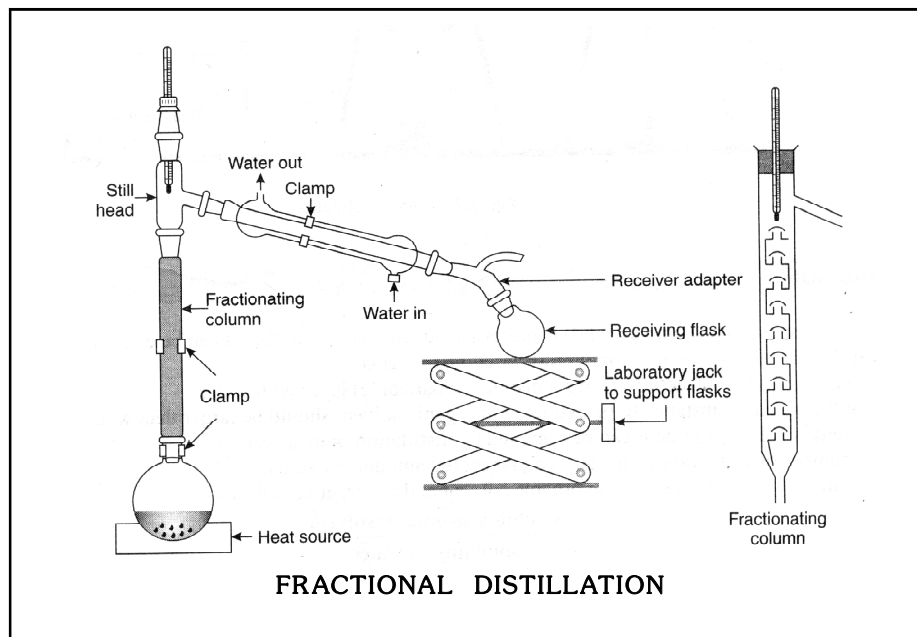


## PURIFICATION METHODS

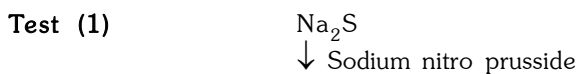
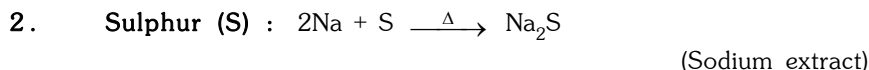
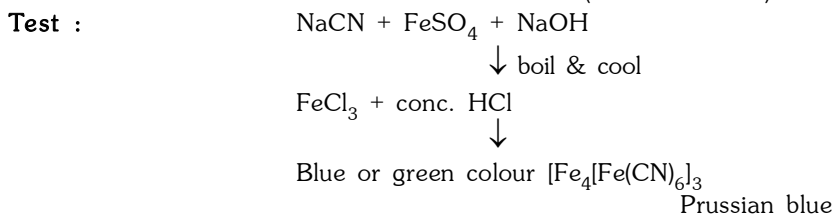
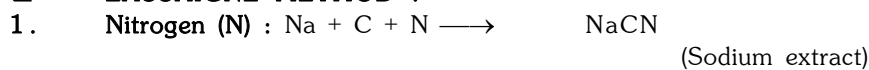
### □ Distillation Techniques :

Type	Conditions	Examples
(A) Simple distillation	(i) When liquid sample has non volatile impurities  (ii) When boiling point difference is 80 K or more.	(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K)  (ii) Mixture of Ether (BP = 308K) & Toluene (BP = 384K)  (iii) Hexane (342K) and Toulene(384K)
(B) Fractional distillation	When BP difference is 10	(i) Crude oil in petroleum industry (ii) Acetone (329) and Methyl alcohol(338K)
(C) Distillation under reduced pressure (Vacuum distillation)	When liquid boils at higher temperature and it may decompose before BP is attained.	(i) Concentration of sugar juice (ii) Recovery of glycerol from spent lye. (iii) Glycerol
(D) Steam distillation	When the substance is immiscible with water and steam volatile.  $P = P_1 + P_2$ <div style="display: flex; justify-content: space-around; font-size: small;"> <div>Vapour pressure</div> <div>Vapour pressure of Organic liquid</div> <div>Vapour pressure of water</div> </div>	(i) Aniline is separated from water (ii) Turpentine oil (iii) Nitro Benzene (iv) Bromo Benzene (v) Naphthalene (vi) o-Nitrophenol

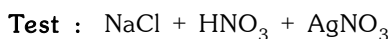
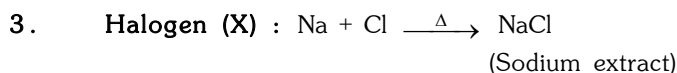
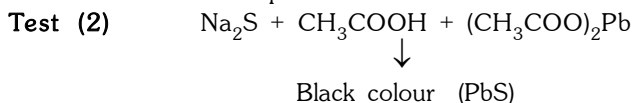




❑ **LASSAIGNE METHOD :**



A deep violet colour

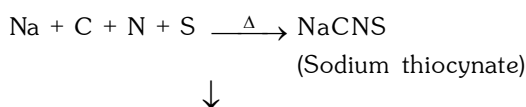


(a) White ppt soluble in aq.  $\text{NH}_3$  confirms Cl

(b) Yellow ppt partially soluble in aq.  $\text{NH}_3$  confirms Br

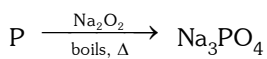
(c) yellow ppt insoluble in aq.  $\text{NH}_3$  confirms I

4. **Nitrogen and Sulphur together :**



As in test of nitrogen, instead of green or blue colour, blood red coloration confirms presence of N and S both.

5. **Phosphorous (P) :**



Solution in boiled with nitric acid and then treated with ammonium molybdate  $(\text{NH}_4)_2\text{MoO}_4$



Formation of yellow ppt indicate presence of phosphate hence phosphorous present in organic compounds.

❑ **THE QUANTITATIVE ANALYSIS :**

Quantitative analysis involves the estimation of percentage composition of various element by suitable method. The molecular mass of the compound is also determined by suitable methods. The knowledge of molecular mass and percentage composition help us to determine the molecular formula of the compound.

❑ **ESTIMATION OF CARBON AND HYDROGEN OR LIEBIG COMBUSTION METHOD :**

Organic compound + dry, black CuO

(w g)  $\downarrow$  Heat strongly in combustion tube  
 mixture of oxide

$\downarrow$  Pass through

(i) anhydrous  $\text{CuSO}_4$

(ii) anhydrous  $\text{CaCl}_2$

say increase in weight = a g

↓ Pass through

(i) KOH (aq)

(ii) Saphnolite resin

say increase in weight = b g

**For % of H** - The increase in weight is 'a' g due to the formation of H<sub>2</sub>O

∴ 18 g H<sub>2</sub>O has H = 2 g

∴ a g H<sub>2</sub>O has  $H = \frac{2a}{18}$  g

Since w g organic compound has =  $\frac{2a}{18}$  g hydrogen.

∴ 100 g organic compound has =  $\frac{2a \times 100}{18 \times w}$  g hydrogen

$$\therefore \%H = \frac{2}{18} \times \frac{\text{weight of H}_2\text{O formed}}{\text{weight of substance}} \times 100$$

**For % of C** -

The increase in wt is b g due to formation of CO<sub>2</sub>

∴ 44 g CO<sub>2</sub> has C = 12 g

∴ b g CO<sub>2</sub> has  $C = \frac{12}{44} \times b$  g

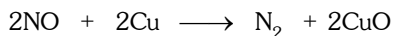
Since w g organic compound has  $\left(\frac{12}{44} \times b\right)$  g carbon

∴ 100 g organic compound has  $\frac{12}{44} \times b \times \frac{100}{w}$  g carbon

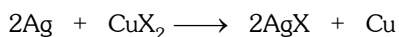
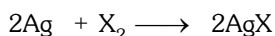
$$\therefore \%C = \frac{12}{44} \times \frac{\text{weight of CO}_2 \text{ formed}}{\text{weight of substance}} \times 100$$

**Note** : This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which on being absorbed in KOH will increase the percentage of carbon and therefore following modification should be made.

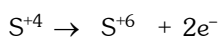
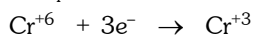
**(a) If N is also present** : The gaseous oxide mixture is first passed over heated Cu gauze which reduces all oxides of N to N<sub>2</sub> which are neither absorbed by H<sub>2</sub>O nor by KOH



**(b) If halogens are present** : A roll of silver gauze is placed at the exit end of combustion tube which retains all the halogens on itself.



**(c) If S is present** : A layer of fused lead chromate is placed near the exit end, all the oxides of sulphur are oxidised to PbSO<sub>4</sub> & left in tube itself.



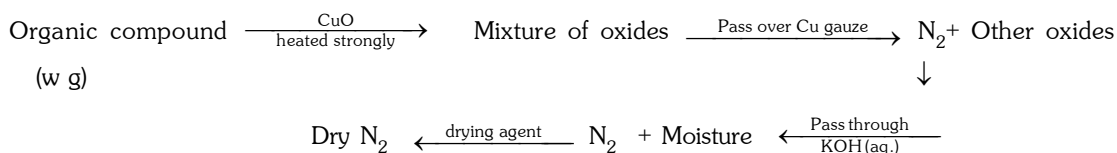
## ❑ GENERAL CONCEPT FOR DRYING AND DEHYDRATING AGENTS

- (i) Acidic oxides (non metals oxides such as  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{P}_2\text{O}_5$  etc.) are absorbed by alkali ( $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{Ca(OH)}_2$  etc.)
- (ii) Basic oxides ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  etc.) are dissolved in acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  etc.)
- (iii) Acidic oxides can not be dried by basic dehydrating agent (e.g  $\text{CaO}$ ) but they are dried by acid dehydrating agent (e.g  $\text{H}_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$  etc). However  $\text{H}_2\text{S}$  can be dried by  $\text{H}_2\text{SO}_4$  because it reacts with  $\text{H}_2\text{SO}_4$ .  

$$\text{H}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{S} + \text{SO}_2$$
- (iv) Basic substances can not be dried by acidic dehydrating agent but are dried by basic dehydrating agent (e.g  $\text{CaO}$ ). It is because  $\text{NH}_3$  is dried by  $\text{CaO}$  but not by  $\text{H}_2\text{SO}_4$ .

## ❑ ESTIMATION OF NITROGEN

### (a) Duma's method :



(Let Vml at N.T.P.)

$$\therefore 22400 \text{ ml N}_2 \text{ weigh at N.T.P.} = 28 \text{ g}$$

$$\therefore V \text{ ml N}_2 \text{ weigh at NTP} = \frac{28}{22400} \times V \text{ g}$$

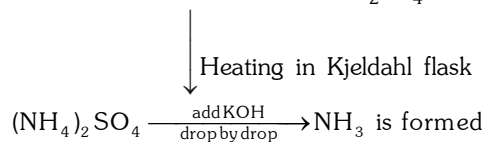
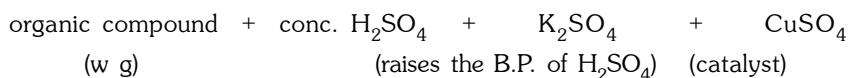
$$\text{since } w \text{ g organic compound gives } \frac{28}{22400} \times \frac{V}{w} \times 100 \text{ g}$$

$$\therefore \boxed{\% \text{N} = \frac{28}{22400} \times \frac{\text{Volume of N}_2 \text{ at NTP}}{\text{weight of the compound}} \times 100}$$

**Note :** This method can be used to estimate nitrogen in all types of organic compounds.

## ❑ KJELDAHL'S METHOD :

This method is based on the principle that a nitrogenous organic compound on heating with conc.  $\text{H}_2\text{SO}_4$  converts all its nitrogen quantitatively to ammonium sulphate ;



Pass this gas through  $V_1$  ml of  $\text{N}_1 \text{ H}_2\text{SO}_4$

Now titrate the  $\text{H}_2\text{SO}_4$  by another alkali say of  $\text{N}_2 \text{ H}_2\text{SO}_4$  ( $\text{NH}_3$  is absorbed here)

$V_2$  ml of  $\text{N}_2 \text{ ,KOH}$  are used

$$\text{Meq of H}_2\text{SO}_4 \text{ taken} = \text{N}_1 V_1$$

$$\text{Meq. of KOH used for H}_2\text{SO}_4 = \text{N}_2 V_2$$

$$\therefore \text{Meq. of H}_2\text{SO}_4 \text{ for NH}_3 = \text{N}_1 V_1 - \text{N}_2 V_2$$

$$\therefore \text{Meq. of NH}_3 \text{ formed} = (\text{N}_1 V_1 - \text{N}_2 V_2) \text{ or say NV}$$

(the difference obtained or V ml of  $\text{N H}_2\text{SO}_4$  are used to absorb  $\text{NH}_3$ )

$$\therefore \frac{W_{\text{NH}_3}}{17} \times 1000 = NV$$

$$\therefore W_{\text{NH}_3} = \frac{17}{1000} \times NV$$

Now  $\therefore 17 \text{ g NH}_3$  has 14 g Nitrogen

$$\therefore \frac{17}{1000} \times NV \text{ g NH}_3 \text{ has } \frac{14 \times 17 \times NV}{17 \times 1000} \text{ g Nitrogen}$$

$$= \frac{14NV}{1000} \text{ g Nitrogen}$$

$$\therefore w \text{ g organic compound has } \frac{14NV}{1000} \text{ g nitrogen}$$

$$\therefore 100 \text{ g organic compound has } \frac{14NV \times 100}{w \times 1000} \text{ g nitrogen.}$$

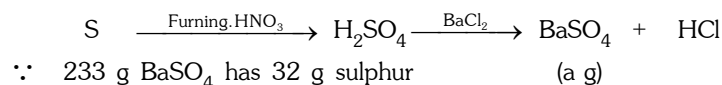
$$= \frac{1.4NV}{w} \text{ g nitrogen}$$

$$\therefore \boxed{\% \text{ Nitrogen} = 1.4 \times \frac{\text{Normality of the acid} \times \text{volume of the acid}}{\text{weight of the compound}}}$$

**Note :** This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo gp. ( $\text{--N} = \text{N--}$ ) and nitrogen in the ring (pyridine, quinole etc.). Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

#### ❑ ESTIMATION OF SULPHUR (CARIUS METHOD) :

Organic compound + con.  $\text{HNO}_3$  +  $\text{BaCl}_2 \rightarrow$  ppt ( $\text{BaSO}_4$ ) is dried and weighed say "a" g  
(w g)



$$\therefore a \text{ g BaSO}_4 \text{ has } \frac{32 \times a}{233} \text{ g sulphur}$$

$$\therefore \% \text{ of Sulphur} = \frac{32 \times a \times 100}{233 \times w}$$

$$\boxed{\% \text{ S} = \frac{32}{233} \times \frac{\text{weight of BaSO}_4 \text{ formed}}{\text{weight of compound}} \times 100}$$

#### ❑ ESTIMATION OF HALOGENS ( CARIUS METHOD) :

Organic compound + con  $\text{HNO}_3$  +  $\text{AgNO}_3 \rightarrow$  ppt ( $\text{AgX}$ ) is dried and weighed say a g

$$\% \text{ of Cl} = \frac{35.5}{143.3} \times \frac{\text{weight of AgCl}}{\text{weight of compound}} \times 100$$

$$\% \text{ of Br} = \frac{80}{188} \times \frac{\text{weight of AgBr}}{\text{weight of compound}} \times 100$$

$$\% \text{ of I} = \frac{127}{235} \times \frac{\text{weight of AgI}}{\text{weight of compound}} \times 100$$

### ❑ ESTIMATION OF PHOSPHORUS - (CARIUS METHOD) :

Organic compound + con.  $\text{HNO}_3$  + Magnesia mixture ( $\text{MgSO}_4$  +  $\text{NH}_4\text{OH}$  +  $\text{NH}_4\text{Cl}$ )  
(w g)



Precipitate is dried and ignited to give magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ) weighed say a g

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{weight of } \text{Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{weight of compound}} \times 100$$

Atomic weight of P = 31    2 = 62 g

molecular weight of  $\text{Mg}_2\text{P}_2\text{O}_7$  = 222 g

### ❑ ESTIMATION OF OXYGEN :

There is no direct formula and method for estimation of oxygen however, percentage of oxygen is calculated by

$$\% \text{ of oxygen} = 100 - [\text{Sum of the \% of all other elements}]$$

**Note** - A direct method for estimation of oxygen has been given by Alusive in 1947 known as Alusive method.

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