QUANTITATIVE ANALYSIS

Quantitative analysis, a method employed to determine the percentage composition of elements within organic compounds, involves a systematic examination of the various elements present. Several commonly utilized methods are employed for estimating the content of different elements, encompassing

(1) Estimation of Carbon and Hydrogen

This technique involves the simultaneous estimation of carbon and hydrogen in organic compounds.

Principle: In this method, a predetermined mass of the dry organic compound is subjected to intense heating in the presence of dry cupric oxide, within an environment devoid of carbon dioxide (CO_2). The organic compound undergoes oxidation, leading to the production of carbon dioxide (CO_2) and water vapor, as depicted by the following reactions:

$$\underset{\text{From organic compound}}{C} + 2CuO \rightarrow CO_2 + 2Cu$$

$$\underset{\text{From organic compound}}{2H} + CuO \rightarrow H_2O + Cu$$

Generally speaking: $C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

The quantification of water and carbon dioxide produced during the combustion of a given organic compound is achieved through a meticulous process.

(a) Water Absorption

- The water vapor produced during the combustion is absorbed in a U-tube containing either anhydrous calcium chloride ($CaCl_2$) or anhydrous magnesium perchlorate.
- The U-tube is weighed both before and after the combustion process.

(b) Carbon Dioxide Absorption

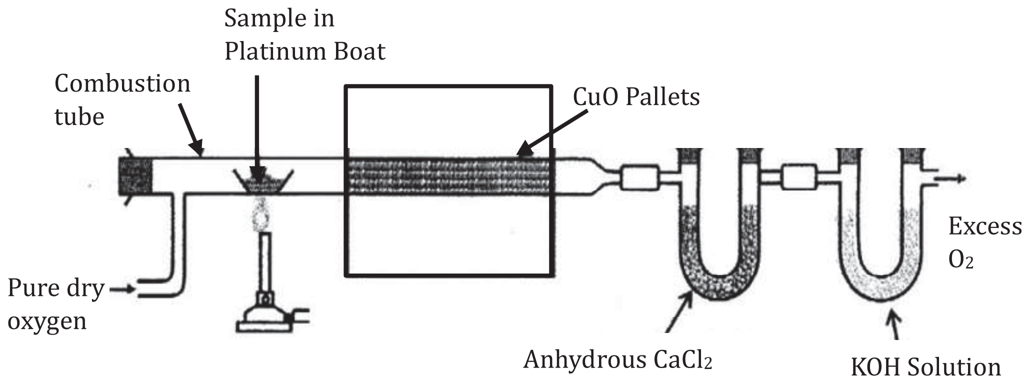
- Simultaneously, the carbon dioxide generated is absorbed in another U-tube containing a concentrated solution of potassium hydroxide (KOH).
- Similar to the water absorption step, the U-tube is weighed before and after the combustion.

(c) Mass Calculation

- The increase in the mass of the U-tube containing $CaCl_2$ provides the mass of the water produced during combustion.
- Correspondingly, the increase in the mass of the U-tube with KOH indicates the mass of the carbon dioxide produced.

By meticulously weighing the U-tubes before and after the combustion process and analyzing the resultant mass changes, the method accurately determines the masses of water and carbon dioxide produced. This stepwise approach ensures precise measurements and reliable quantitative analysis of the combustion products in the organic compound.

The equipment utilized for determining the content of carbon and hydrogen is depicted in the accompanying figure.



Calculations:
Let's consider the mass of the organic compound taken as w grams. The observed increase in the mass of the calcium chloride tube is denoted as a gram, representing the mass of the water formed during the process. Similarly, the increase in the mass of the potash bulbs is represented by b grams, indicating the mass of the liberated CO_2 gas.

(a) Calculation of % of H:

One mole of water contains two mole of hydrogen atom

$\because$ 18 g of water contains 2 g hydrogen

$\therefore$ a g of water contains $(\frac{2}{18} \times a)$ g hydrogen

Thus, The% of H $= \frac{\frac{2}{18} \times a}{w} \times 100$.

(b) Calculation of % of C:

One mole of CO_2 contains one mole of carbon atom.

$\because$ 44 g of CO_2 contains carbon = 12g

$\because$ b g of CO_2 contains carbon $= (\frac{12}{44} \times b)$ g

Hence, The % of carbon $= \frac{\frac{12}{44} \times b}{w} \times 100$

(2) Estimation of Nitrogen

Two distinct methods are employed for the estimation of nitrogen.

(a) Duma's Method

This technique is universally applicable to all organic compounds that contain nitrogen.

Principle:

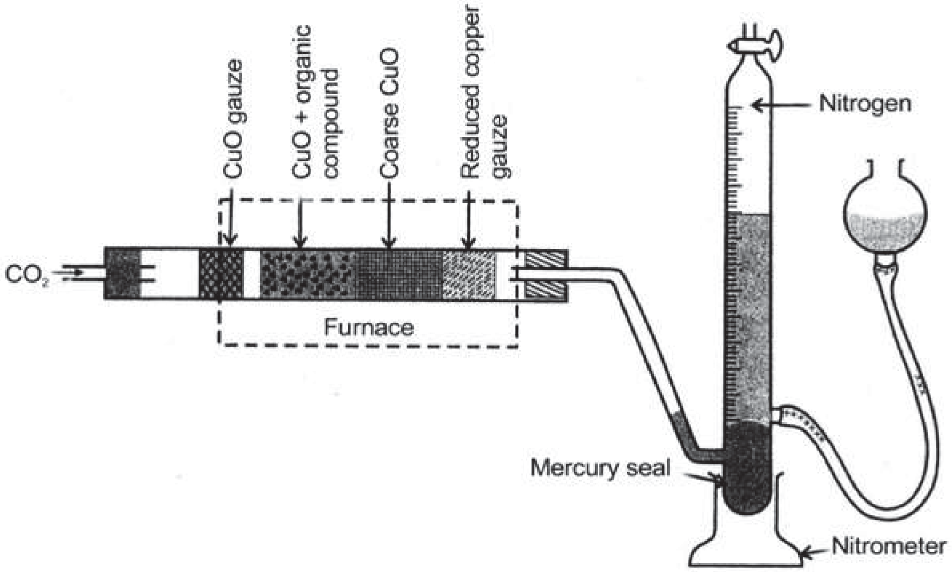
The method involves heating a known mass of the organic compound intensely with an excess of copper oxide within an atmosphere saturated with carbon dioxide. During this process, carbon undergoes oxidation to form carbon dioxide, hydrogen is converted to water, and nitrogen is released as nitrogen gas. If any nitrogen oxide is generated, it is subsequently reduced back to nitrogen by passing it over a hot, luminous copper spiral.

The chemical reactions can be described as follows:

$$C + 2CuO \rightarrow 2Cu + CO_2\uparrow$$
$$2H + CuO \rightarrow Cu + H_2O\uparrow$$
$$\text{Nitrogen} + CuO \rightarrow N_2 + \text{a little of oxide of nitrogen}$$
$$\text{Oxide of Nitrogen} + Cu \rightarrow CuO + N_2$$

In general, $C_xH_y N_z + \left(2x + \frac{y}{2}\right) CuO \rightarrow xCO_2 + \frac{y}{2} H_2O + \frac{z}{2} N_2 + \left(2x + \frac{y}{2}\right) Cu.$

All of the liberated nitrogen is then collected over a concentrated potassium hydroxide (KOH) solution, which effectively absorbs carbon dioxide (CO_2) and water vapors. The volume of nitrogen collected is measured, and the percentage of nitrogen in the organic compound is subsequently calculated.



Calculation:

Let the mass of the organic compound = w g

The volume of nitrogen collected = v ml.

Atmospheric pressure (from Barometer) = P_{mm} of Hg Room temperature = T_1K

If temperature is in °C, then T_1K = t°C + 273

Aqueous tension at T_1K = a mm of Hg

Pressure of dry nitrogen (P – a) mm of Hg

Let us Ist convert the volume of nitrogen to volume at STP.

Experimental Condition	STP Conditions
P_1 = (Pa) mm of Hg	P_2 = 760 mm of Hg
$T_1 = T_1$K	T_2 = 273 K
V_1 = v ml	V_2 = ?

According to gas equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\therefore \quad V_2 = \frac{P_1V_1 \times T_2}{P_1T_2} = \frac{(P - a) \times V \times 273}{760 \times T_1} = x \text{ ml}$$

Now, 22,400 ml of N_2 at STP will weight = 28 g

x ml of N_2 at STP will weigh = $\frac{28}{22400} \times xg$

$$\therefore \quad \% \text{ of Nitrogen} = \frac{\text{Mass of Nitrogen}}{\text{Mass of organic compound}} \times 100$$

$$\% \text{ of Nitrogen} = \frac{28\times}{22400 \times w} \times 100$$

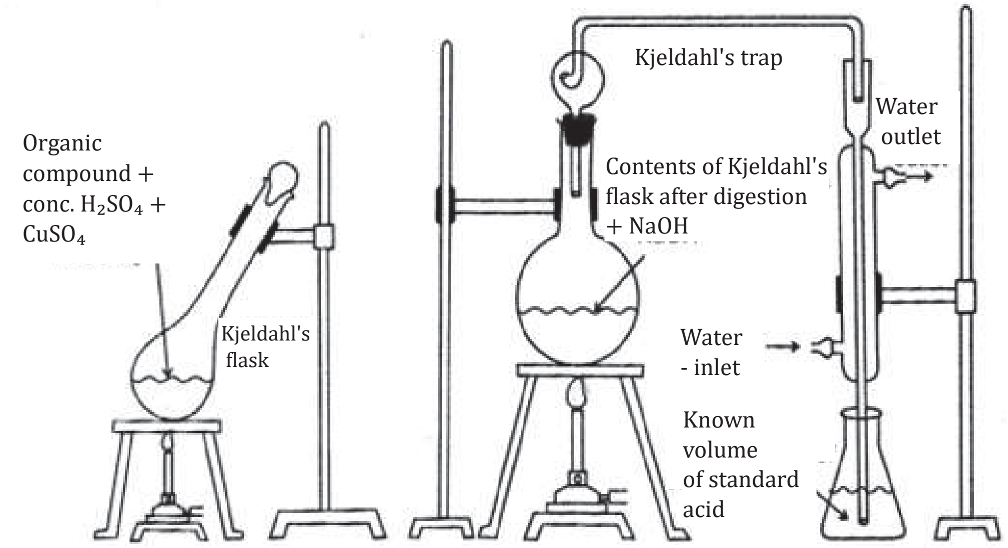
(b) Kjeldahl's Method

Kjeldahl's method, widely employed for nitrogen estimation in food, fertilizers, and pharmaceuticals, is both straightforward and convenient. However, it presents limitations, as it cannot be applied to compounds that fall under two categories:

(i) Compounds containing nitrogen within a ring structure (e.g., pyridine or quinoline).

(ii) Compounds featuring nitro ($-NO_2$) and azo ($N = N -$) groups.

The apparatus utilized in the nitrogen estimation process via Kjeldahl's method is illustrated in the accompanying figure.



Digestion (heating in Kjeldahl's flask) Kjeldahl's distillation

In this method, a known mass of the organic compound undergoes digestion with concentrated H_2SO_4 in the presence of potassium sulfate and a small amount of copper sulfate within an elongated-neck flask. The nitrogen present in the compound undergoes quantitative conversion into ammonium sulfate through the chemical reaction:

$$\underset{\text{(From organic compound)}}{N} + \text{Conc.}H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The resulting liquid is subjected to distillation with an excess of sodium hydroxide solution. The evolved ammonia is directed into a known but excess volume of standard acid (HCl or H_2SO_4), leading to the following reactions:

$$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + 2NH_3$$
$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Any unused acid is determined through titration with a standard alkali, following the reaction:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

The quantity of acid consumed in reaction with ammonia is determined, allowing the calculation of the percentage of nitrogen in the compound.

Calculation:

Let the mass of the organic compound = w g

Volume of standard H_2SO_4 of molarity M = V ml.

Now, excess acid left after absorption of NH_3, is titrated with NaOH of molarity, M.

Consequently, volume of NaOH of molarity M used for titration of excess of $H_2SO_4 = V_1$, ml

Now, V_1, ml of NaOH of molarity M $= \frac{V_1}{2}$ ml of H_2SO_4 of molarity M

$\therefore$ Volume of H_2SO_4 of molarity M left unreacted $= \frac{V_1}{2}$ ml

Volume of H_2SO_4 of molarity M used for neutralisation of $NH_3 = (V - \frac{V_1}{2})$ ml

Now, $(V - \frac{V_1}{2})$ ml of H_2SO_4 of molarity M = $2\,(V - \frac{V_1}{2})$ml of NH_3, solution of molarity M

Now, 1000 ml of 1 M NH_3, solution contain 17 g NH_3 or 14 g nitrogen.

∴ $2(V - \frac{V_1}{2})$ml of NH_3 of molarity M contains nitrogen = $\frac{14 \times M \times 2\,(V - \frac{V_1}{2})}{1000}$ grams.

Therefore, the percentage of nitrogen (% of N) in the organic compound is given by the formula:

$$= \frac{14 \times M \times 2\,(V - \frac{V_1}{2})}{1000} \times \frac{100}{w}$$

Alternatively, expressed in terms of 1% of N:

$$1\%\text{ of N} = \frac{1.4 \times 2\,(V - \frac{V_1}{2})}{W}$$