

Introduction

Analytical chemistry

"The branch of chemistry that deals with separation and analysis of a sample to identify its components is called analytical chemistry."

The separation is carried out prior to qualitative and quantitative analysis.

- **Qualitative analysis** provides the identity of a substance (composition of chemical species).
- **Quantitative analysis** determines the amount of each components present in the sample.

Hence, in this branch different techniques and instruments used for analysis are studied. The scope of this branch covers food, water, environmental and clinical analysis.

CLASSICAL METHOD OF ANALYSIS

Exercise: Q.3(1) What is combustion analysis? Describe its different steps.

Combustion Analysis and determination of Molecular Formula

Empirical and molecular formulas for compounds that contain only carbon and hydrogen (C_xH_y) or carbon, hydrogen, and oxygen ($C_xH_yO_z$) can be determined with a process called combustion analysis. The sole products will be CO_2 and H_2O and these two products of combustion are separately collected.

Procedure:

The steps for this procedure are:

- Weigh a sample of the compound to be analyzed and place it in the apparatus shown in the image below.
- Burn the compound completely. The only products of the combustion of a compound that contains only carbon and hydrogen (C_xH_y) or carbon, hydrogen, and oxygen ($C_xH_yO_z$) are carbon dioxide and water.



- The H_2O and CO_2 are drawn through two tubes. One tube contains a substance that absorbs water, and the other contains a substance that absorbs carbon dioxide. Weigh each of these tubes before and after the combustion. The increase in mass in the first tube is the mass of H_2O that formed in the combustion, and the increase in mass for the second tube is the mass of CO_2 formed.
- Assume that all the carbon in the compound has been converted to CO_2 and trapped in the second tube. Calculate the mass of carbon in the compound from the mass of carbon in the measured mass of CO_2 formed.

$$\% \text{ of C} = \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times \frac{12}{44} \times 100$$

- Assume that all of the hydrogen in the compound has been converted to H_2O and trapped in the first tube. Calculate the mass of hydrogen in the compound from the mass of hydrogen in the measured mass of water.

$$\% \text{ of H} = \frac{\text{Mass of } H_2O}{\text{Mass of organic compound}} \times \frac{2.016}{18} \times 100$$

- If the compound contains oxygen as well as carbon and hydrogen, calculate the mass of the oxygen by subtracting the mass of carbon and hydrogen from the total mass of the original sample of compound.
- Use this data to determine the empirical and molecular formulas in the usual way.

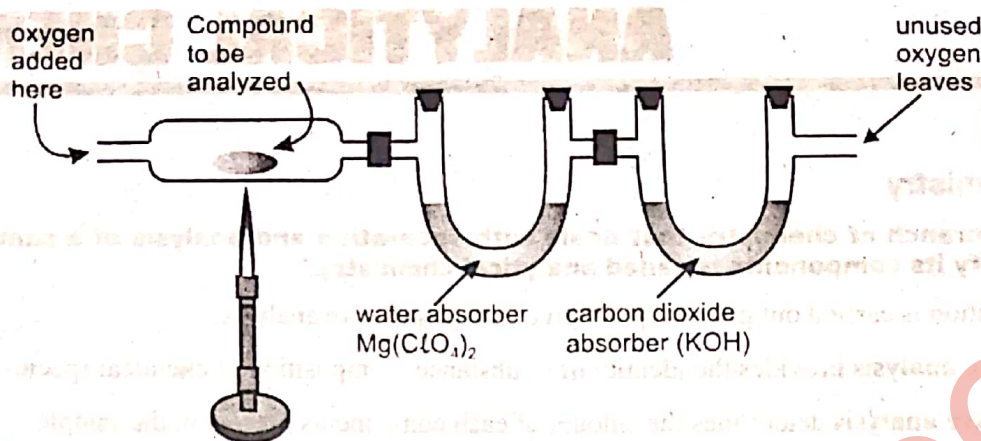


Fig 24.1: Apparatus for combustion analysis.

Apparatus for Combustion Analysis:

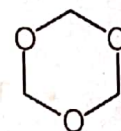
A compound containing carbon and hydrogen (C_aH_b) or carbon, hydrogen, and oxygen ($C_aH_bO_c$) is burned completely to form H_2O and CO_2 . The products are drawn through two tubes. The first tube absorbs water, and the second tube absorbs carbon dioxide.

To illustrate how empirical and molecular formulas can be determined from data derived from combustion analysis, let's consider a substance called trioxane. Formaldehyde, CH_2O , is unstable as a pure gas, readily forming a mixture of a substance called trioxane and a polymer called paraformaldehyde. That is why formaldehyde is dissolved in a solvent, like water, before it is sold and used. The molecular formula of trioxane, which contains carbon, hydrogen, and oxygen, can be determined using the data from two different experiments. In the first experiment, 17.471 g of trioxane is burned in the apparatus shown above, and 10.477 g H_2O and 25.612 g CO_2 are formed. In the second experiment, the molecular mass of trioxane is found to be 90.079.

Q. How will you determine the molecular formula of a compound?

Ans. We can get the molecular formula of a compound from its empirical formula and its molecular mass. To get the empirical formula, we need to determine the mass in grams of the carbon, hydrogen, and oxygen in 17.471 g of trioxane. Thus, we need to perform these general steps.

- First, convert from the data given to grams of carbon, hydrogen, and oxygen.
- Second, determine the empirical formula from the grams of carbon, hydrogen, and oxygen.
- Third, determine the molecular formula from the empirical formula and the given molecular mass.



Because we assume that all the carbon in trioxane has reacted to form CO_2 , we can find the mass of carbon in 17.471 g trioxane by calculating the mass of carbon in 25.612 g CO_2 .

$$\text{Weight of carbon} = 25.612 \text{ g } CO_2 \left(\frac{1 \text{ mol } CO_2}{44.010 \text{ g } CO_2} \right) \left(\frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \right) \left(\frac{12.011 \text{ g C}}{1 \text{ mol C}} \right) = 6.9899 \text{ grams of carbon}$$

Because we assume that all of the hydrogen in trioxane has reacted to form H_2O , we can find the mass of hydrogen in 17.471 g trioxane by calculating the mass of hydrogen in 10.477 g H_2O .

$$\text{Weight of hydrogen} = 10.477 \text{ g } H_2O \left(\frac{1 \text{ mol } H_2O}{18.0153 \text{ g } H_2O} \right) \left(\frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \right) \left(\frac{1.00797 \text{ g H}}{1 \text{ mol H}} \right) = 1.1724 \text{ grams of carbon}$$

Because trioxane contains only carbon, hydrogen, and oxygen, we can calculate the mass of oxygen by subtracting the masses of carbon and hydrogen from the total mass of trioxane.

$$\text{Weight of oxygen} = 17.471 \text{ g trioxane} - 6.9899 \text{ g C} - 1.1724 \text{ g H} = 9.309 \text{ grams of oxygen}$$

We now calculate the empirical formula.

$$\text{No. of mols of carbon C} = 6.6899 \text{ gC} \left(\frac{1 \text{ mol C}}{12.011 \text{ gC}} \right) = 0.58196 \text{ mol C} \div 0.5818 \approx 1 \text{ mol C}$$

$$\text{No. of mols of hydrogen H} = 1.1724 \text{ gH} \left(\frac{1 \text{ mol H}}{1.00797 \text{ gH}} \right) = 1.163 \text{ mol H} \div 0.5818 \approx 2 \text{ mol H}$$

$$\text{No. of mols of oxygen O} = 9.309 \text{ gO} \left(\frac{1 \text{ mol O}}{15.9994 \text{ gO}} \right) = 0.5818 \text{ mol O} \div 0.5818 \approx 1 \text{ mol O}$$

The empirical formula is CH₂O, which can be used to calculate the molecular formula.

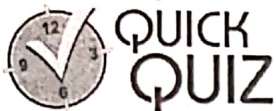
$$\begin{aligned} \text{Empirical formula mass} &= 1(12.011) + 2(1.00794) + 1(15.9994) \\ &= 30.026 \end{aligned}$$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{90.079}{30.026} \approx 3$$

Molecular formula C₃H₆O₃

Drawback:

The classical method i.e. combustion analysis is only limited to those organic compounds which contain carbon, hydrogen and oxygen. So there is a need of such methods which explain/find all types of atoms/elements present in an organic compounds. So now modern methods are used which are being discussed in next topic.



1. Give difference between qualitative and quantitative analysis.

Ans. Quantitative analysis:

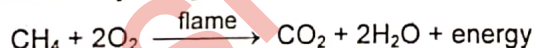
It is the study that provides the information about the amount of the components present in a given sample. e.g. sea water contains 9g/L NaCl.

Qualitative analysis:

It is the study that provide the information about the composition of chemicals present in a given sample e.g. egg contains calcium, water, proteins etc.

2. Name the products obtained by complete combustion of hydrocarbon.

Ans. The compounds obtained by complete combustion of hydrocarbons are CO₂ and water.



But in the limited supply of oxygen carbon monoxide is formed instead of carbon dioxide.

3. How mass of oxygen is calculated if it also present along with carbon and hydrogen.

Ans. In combustion analysis, a known amount of organic compound is burnt in free supply of oxygen. The carbon and hydrogen of the organic compound is converted into CO₂ and H₂O respectively. But as oxygen gas is also provided from the external source to burn the organic compound, so we cannot measure the %age of oxygen present in the compound directly. However it is determined by method of difference.

$$\% \text{ age of O} = 100 - (\% \text{ age of C} + \% \text{ age of H})$$

4. Give general steps use to calculate empirical formula.

Ans. The steps involved in determination of empirical formula are:

- Determine the percentage composition of each element in a substance.
- Divide the percentage of each element by its atomic mass to get the number of moles.
- Divide the moles of each element by the smallest number of moles to get atomic ratios.
- If atomic ratios are not in simple whole number, and then multiply with a small suitable number to get whole number ratio. Thus empirical formula is obtained.

5. Give drawback of combustion analysis.

Ans. Drawback of combustion analysis:

- Combustion analysis is only limited to those organic compounds which contain carbon, hydrogen and oxygen.
- It is a destructive technique, Sample cannot be recovered.

Modern Methods of Analysis

Q. What is spectroscopy?

Ans. Spectroscopy involved using instruments to examine the radiation emitted or absorbed by chemicals giving information about their molecular structure.

Spectroscopy

The branch of science which describes the interactions of electromagnetic radiation with matter is known as spectroscopy. It means, it is the area of study that represents molecular structure with electromagnetic radiation. Electromagnetic radiation is form of energy commonly known as radiation energy such as light energy. According to quantum mechanics, electromagnetic radiation has the properties of both a wave and a particle, like discrete packet of energy, called quanta or photons. An electromagnetic radiation can be characterized in different ways.

Wavelength

The distance between two successive crests or troughs of a wave in a beam of radiation is called wavelength and is denoted by λ (lambda). The units commonly used for wavelength are angstrom, nanometer, micrometer and meter. ($1\text{m} = 10^6 \mu\text{m} = 10^9 \text{nm} = 10^{10} \text{\AA}$)

Frequency

The number of waves passing through a point on the path of a beam of radiation per second is called frequency and is denoted by ν (nu). It is expressed in hertz (Hz) or cycles per second (cps). ($1 \text{ Hz} = 1 \text{ cps}$).

Wave number

It is the number of waves passing per centimeter. A common unit for $\bar{\nu}$ is the reciprocal centimeter (cm^{-1}).

Energy

Electromagnetic radiation can be characterized in terms of energy possessed by each photon of radiation. The SI unit is joule (J). Each photon has an energy which is proportional to the frequency of light.

Cosmic rays, gamma rays, X-rays, ultraviolet, visible light, infrared rays, microwaves and radio waves, all are electromagnetic radiation. Electromagnetic spectrum covers a wide range of wavelengths and radiations of different wavelengths have different characteristics. The whole electromagnetic spectrum can be conveniently divided into several regions, each region can be defined by the limits of any of the four parameters, i.e., wavelength, frequency, wave number or energy.

Table 24.1 Ranges of electromagnetic radiations in spectral region

Spectrum region	Wavelength	Frequency (Hz)	Wavenumber (cm^{-1})	Energy (J)
Cosmic rays	10^{-6}\AA	3×10^{22}	10^{12}	2×10^{-11}
	10^{-3}\AA	3×10^{21}	10^{11}	2×10^{-12}
Gamma rays	10^{-1}\AA	3×10^{19}	10^9	2×10^{-14}
	10^{-4}\AA			
X-rays	100\AA (10 nm)	3×10^{16}	10^6	2×10^{-17}
Ultraviolet	400 nm	7.5×10^{14}	2.5×10^4	5×10^{-19}
Visible	800 nm	3.8×10^{14}	1.3×10^4	2.5×10^{-19}
Infrared	$10^3 \mu\text{m}$	3×10^{11}	10	2×10^{-22}

Microwave	$10^6 \mu\text{m}$ (1m)	3×10^8	10^{-2}	2×10^{-25}
Radio wave	10^3 m	3×10^5	10^{-5}	2×10^{-28}

Principle of Spectroscopy

All organic compounds interact with electromagnetic radiation, that is, they absorb energy. When a molecule absorbs energy, a transformation occurs. Lower energy radiation may cause a molecular rotation, or a bond vibration. Higher energy radiation may cause the promotion of electrons to higher energy levels or bond cleavage.

Whether the transformation involves molecular rotation, bond vibration, or electronic transition, the molecule absorbs only the wavelength, of radiation with exactly the energy necessary for the transition. The absorption of wavelengths of radiation is selective for a particular transition which depends on the structure of the molecule. By measuring the absorption spectra of known compounds we can correlate the wavelengths of energy absorbed with characteristic structure feature. This information is then used to determine the structure of unknown compounds.

Spectrophotometer

The instrument used to measure the amount of electromagnetic radiation absorbed by a compound is called spectrophotometer or spectrometer. It consists of light source of radiation, with a prism that can select the desired wavelengths which are passed through a sample of the compound being investigated. The radiation that is absorbed by the sample is detected and is recorded on a chart against the wavelength or wave number. Absorption peaks are plotted as minima in infrared, and usually as maxima in ultraviolet spectroscopy.

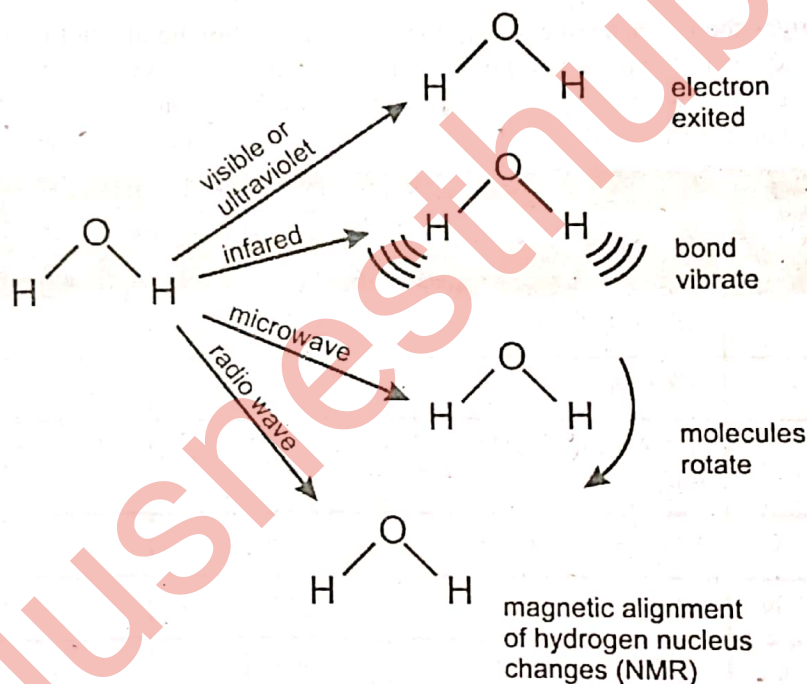
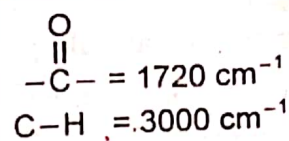
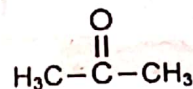
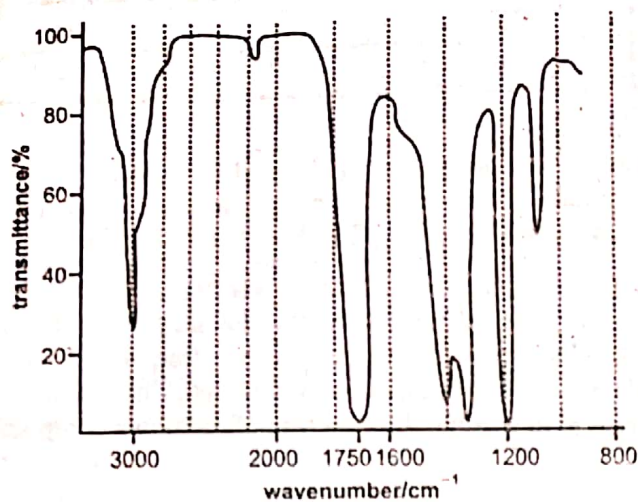


Fig 24.2 effect of different types of radiation on the water molecule

Infrared Spectroscopy (IR)

Infrared Spectroscopy

Wavelengths in IR region extends from 2.5 to $16 \mu\text{m}$ (4000 to 625 cm^{-1}). Although this radiation is weak, it does supply sufficient energy for bonds in the molecule to vibrate. The molecular motion that is affected by the absorption of quanta of the infrared radiation is the vibrational motion. The studies of vibrational spectra of molecules lead to the information on the flexibility of the molecules. The small displacement of the constituent atoms from their equilibrium positions can be seen in term of vibrational motion of the atoms. Such changes in the bond-length produce a change in the dipole moment of a heteronuclear molecule and if the oscillating dipole couples with the electrical field of the radiation an exchange of energy takes place. For example, below is the spectrum of propanone (CH_3COCH_3).



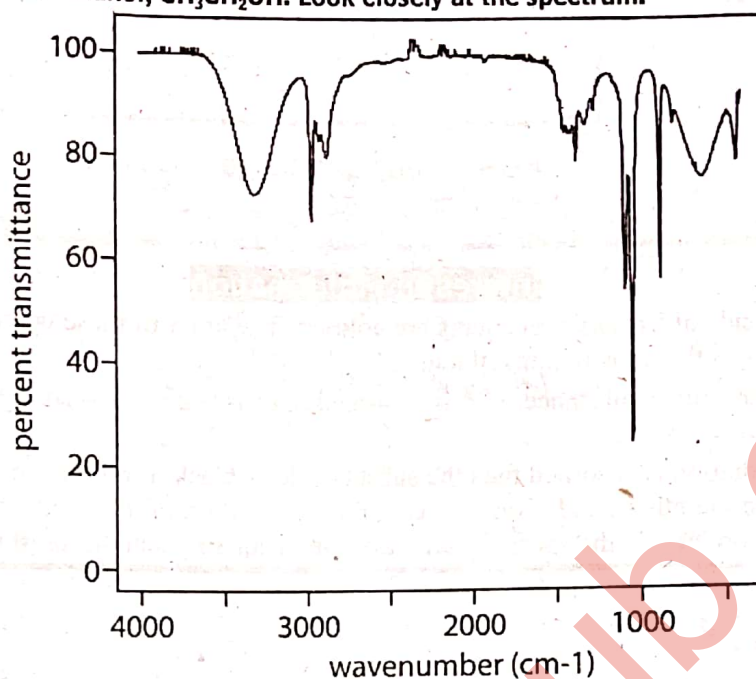
The infrared s-spectrum of propanone.

We will see that the spectrum is quite complicated even though propanone is a simple molecule with only three types of bond. The complexity arises because each bond can vibrate in a number of different ways and the vibrations can interact with each other. Nevertheless it is possible to see some characteristic peaks of absorption which we can use to identify functional groups in the molecule.

The following gives the characteristic absorption of some common bonds. In the spectrum of propanone in figure above the strong peak at about 1720cm^{-1} corresponds to the $\text{C}=\text{O}$ bond. The weaker absorption at 3000cm^{-1} corresponds to the $\text{C}-\text{H}$ bond. This peak is weaker even though there are more H atoms in the molecule: in IR spectroscopy the strength of the peak is a characteristic of the bond itself not of the number of bonds present.

Bond	Compound it is in	Absorption / cm^{-1}	Intensity (M=medium, S=strong)
C - H	Alkanes, alkenes, arenes	2840 to 3095	M/S
C = C	Alkenes	1610 to 1680	M
C = O	Aldehydes, ketones, acids, esters	1680 to 1750	S
C - O	Alcohols, ethers, esters	1000 to 1300	S
C \equiv N	Nitriles	2200 to 2280	M
C - Cl	Chloro compound	700 to 800	S
O - H	Free	3580 to 3670	S
	Hydrogen-bonded in alcohols, phenols	3230 to 3550	S (broad)
	Hydrogen-bonded in acids	2500 to 3300	M (broad)
N - H	Primary amines	3100 to 3500	S

Figure shows the IR spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$. Look closely at the spectrum.



1. What bond gives rise to the peak just below 3000cm^{-1} ?

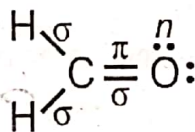
Ans. Below 3000cm^{-1} is the region which is for C-H stretching vibration in IR spectra.

2. What bond gives rise to the peak at about 3400cm^{-1} ?

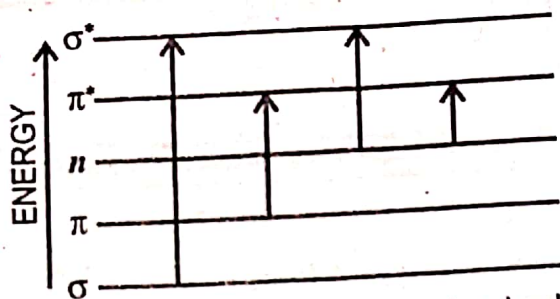
Ans. 3400cm^{-1} is a region for a sharp peak of -OH stretching vibration.

Visible and Ultraviolet Spectroscopy (UV-VIS)

In ultraviolet-visible spectroscopy, the absorption of ultraviolet (200-400 nm) and visible (400-750 nm) radiation by molecules is associated with the extraction of loosely held electrons (such as unshared electrons or electrons in a π bond) from a lower-energy, occupied molecular orbital (MO) to a higher energy unoccupied molecular orbital (MO^*). There are three kinds of electrons, these in δ bonds, these in π bonds and unshared electrons which are denoted by the letter, 'n' for nonbonding e.g.



On absorbing energy any of these electrons can enter excited states, which are either anti-bonding σ^* or π^* . All molecules have σ and σ^* orbitals, but only those with π orbitals have π^* orbitals. Only the $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and more rarely the $n \rightarrow \sigma^*$ excitations occur in the near ultraviolet and visible regions, which are the available regions for ordinary spectrophotometers. The energy required for $\sigma \rightarrow \sigma^*$ transition is very high and therefore, occurs it, in the vacuum UV region (below 200 nm) which is not usually accessible in most UV-Vis) spectrophotometers. The relative energy for 3 electrons transitions detectable by UV spectrophotometer in order of increasing ΔE is $n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^*$. In fact, the absorption of UV-Vis radiation by a molecule results in the electronic transition from highest occupied MO to the lowest unoccupied MO (molecular orbital).



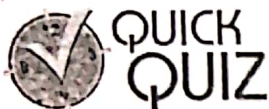
Relative energy changes involved in various electronic transitions

Interesting Information

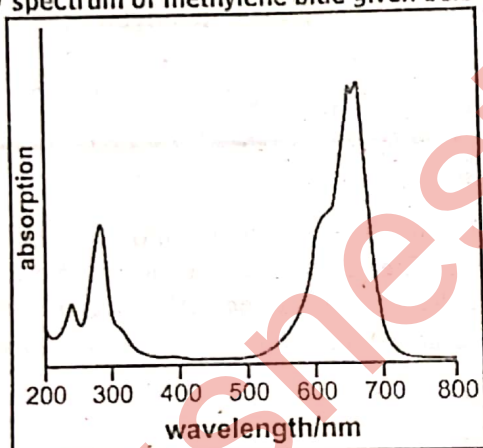
Most of the compounds of transition elements are colored. The color of these compounds can often be related to incompletely filled d-orbitals in the transition metal ion.

In general, when light hits a substance, part is absorbed, part is transmitted (if the substance is transparent) and part may be reflected.

If all the incident radiation is absorbed then the substance look black. If all the incident radiation is reflected then the substance look white. On the other hand if only a very small proportion of the incident white light is absorbed and if all the radiation in the visible region of the spectrum are transmitted equally then the substance will appear colorless.



Look at the visible/UV spectrum of methylene blue given below:



The visible / UV spectrum of methylene blue

Color	Wavelength
violet	380–450 nm
blue	450–495 nm
green	495–570 nm
yellow	570–590 nm
orange	590–620 nm
red	620–750 nm

1. What colours of visible light does methylene blue absorb? *→ red*

Ans. Methylene blue absorb red colour radiations in the range of 650-800nm.

2. Explain why methylene blue has a blue colour. *→ bc it emit*

Ans. When white light shines on methylene blue, some of the electrons in the dye molecules become excited. The electrons absorb certain frequencies of light radiation and change their energy level. The radiation they absorb to be in the red end of the spectrum. Removing red from the white light makes it look blue.

3. How can we get information about a compound using UV/visible spectroscopy?

Ans. UV-visible (UV-vis) spectroscopy has been applied in numerous ways to facilitate qualitative and quantitative analysis as well as structure determination and online reaction monitoring in a wide range of environments.

4. Give colour of following wavelength (i) 600-620 (ii) 490-520

Ans. (i) The colour of the above mentioned wavelengths would be orange.

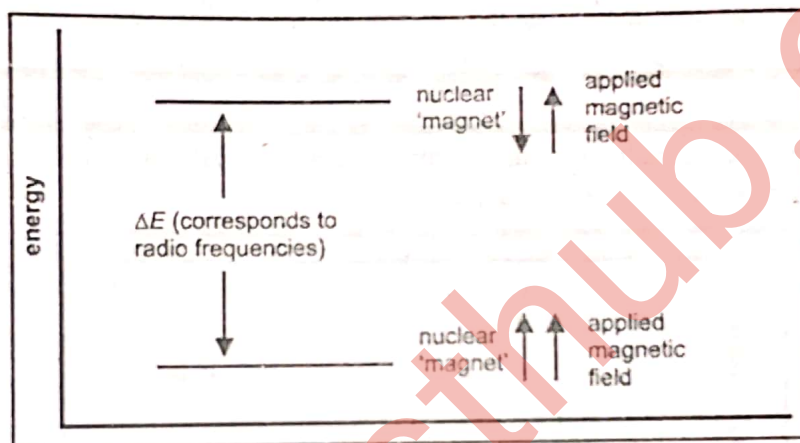
(ii) The colour of the above mentioned wavelengths would be green.

NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear magnetic resonance (NMR), as the name implies, is concerned with the magnetic properties of certain atomic nuclei. All nuclei carry a charge, and some of them also spin about their axes in a manner that is analogous to that in which electrons spin about their axis. The nuclei, whose spin quantum number is zero, do not spin. The symbol I is used to denote the spin quantum number of a nucleus.

The Nuclear Magnet

A spinning charge, whether positive or negative, consisting of a circular current which generates a magnetic dipole along the spin axis. Since all nuclei carry a charge, a spinning nucleus behaves as a tiny bar magnet, called nuclear magnet, placed along the spin axis, and has a characteristic magnetic moment, μ . In the absence of an external magnetic field, the nuclear magnets are oriented in a random fashion. However, if they are placed under the influence of a uniform external magnetic field, they can take up different orientations with respect to the applied magnetic field in a quantized system. According to the quantum mechanics, the number of possible orientations of a nuclear magnet in an applied magnetic field is determined by the spin quantum number of the nucleus and is given by $(2I + 1)$.



Two alignment of the nuclear magnet in an external magnet field. The energy difference between the two orientations is the basis of the technique of NMR

The absorption of electromagnetic radiation by a nucleus, to induced spin-flipping will take place when the frequency of the electromagnetic radiation is exactly equal to the precessional frequency of the nucleus, i.e., the two frequencies are in resonance; hence the term nuclear magnetic resonance (NMR).

Instrumentation

There are two types of spectrophotometers which are commonly used for the NMR study:

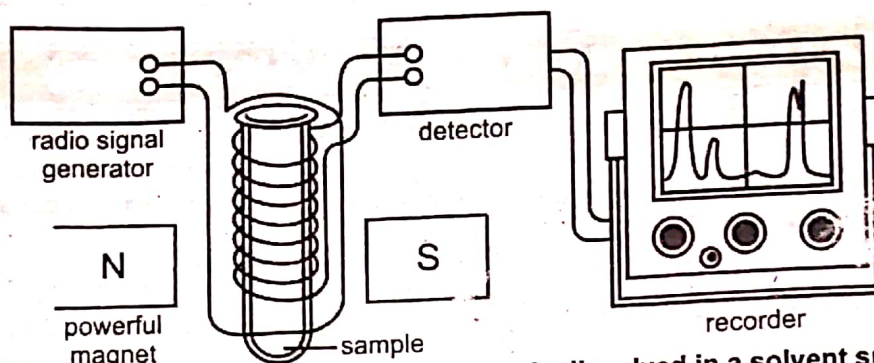
$$\nu = \frac{\gamma H_0}{2\pi}$$

(i) Continuous Wave (CW) NMR spectrophotometer

In CW-NMR spectrophotometer, the frequency of the electromagnetic radiation is kept constant and the strength of the applied magnetic field is gradually varied to sequentially bring the precessional frequencies of all the nuclei in response with the frequency of the electromagnetic radiation. The spectrum is recorded directly as absorption versus frequency, and it takes several minutes to complete.

(ii) Fourier Transform (FT) NMR spectrometer

In the FT-NMR spectrophotometer, the strength of the applied magnetic field is kept constant and the radio-frequency is applied as a single short-duration (microseconds) powerful pulse (a burst of radio-frequency energy) which effectively covers the whole frequency range to be studied. The signal detected in this case is recorded, digitized and stored in a computer as an array of numbers. Fourier Transformation (a mathematical treatment form as a CW spectrum). In the CW-NMR spectrophotometer, we measure the radiant energy which is absorbed, whereas in the FT-NMR spectrophotometer it is the energy emitted by the relaxing nuclei which is measured. Thus, the CW-NMR experiment provides an absorption spectrum, whereas the pulsed FT-NMR experiment provides an emission spectrum.



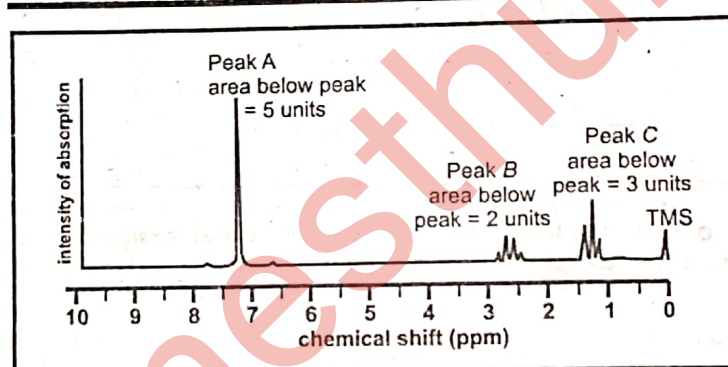
A simplified NMR spectrometer. The sample is dissolved in a solvent such as H_2O or CCl_4 which does not have nuclear magnetic properties.

Usefulness of NMR

- The technique of NMR is particularly useful for identifying the number and type of hydrogen atoms (^1H) in a molecule.
- It is also used to find the position of carbon atoms. The common isotope of carbon, ^{12}C does not have a nuclear magnet but natural carbons contains 1% of the ^{13}C isotope which does show magnetic behavior and can be identified using NMR.

Q. What is n + 1 rule?

Ans. n + 1 rule is used to determine the multiplicity and splitting patterns of peaks in ^1H NMR. Where n = number of neighbouring protons (on adjacent carbon)



The proton NMR spectrum of ethylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$

Examples:

The above figure shows the NMR spectrum of ethylbenzene $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$. This is a proton NMR spectrum: the frequencies correspond to the absorption of energy by ^1H nuclei, which are protons. Notice that there are three major peaks of differing heights. Each peak corresponds to H atoms in a different molecular environment. This area under each peak is proportional to the number of that type of H atom in the molecule. The largest peak (A) corresponds to the 5 H atom since C_6H_5 , the benzene ring. The second largest (C) corresponds to the 3 H atoms in the $-\text{CH}_3$ group and the third peak (B) corresponds to the 2 H atoms in the CH_2 group.

The H atoms in a particular type of environment have similar positions in the NMR spectrum. Normally this position is measured as a chemical shift, from a fixed reference point. The reference point normally used is the absorption of a substance known as TMS (tetramethylsilane). The chemical shift of TMS is set at zero.

Q. Why we use TMS as reference compound for ^1H NMR spectroscopy?

Ans. TMS stands for tetramethylsilane, $\text{Si}(\text{CH}_3)_4$. This non-toxic and uncreative substance is chosen as the NMR reference because its protons give a single peak that is well separated from the peaks found in the NMR spectra of most organic compounds.

QUICK QUIZ

1. Which type of nucleus has magnetic field?

Ans. The nucleus which has odd number of protons and neutrons has nuclear magnetic field. While in case of even number of protons and neutrons the opposite field of pair cancels out each other and no overall field in this case.

2. What happens when a magnetic nucleus is placed in magnetic field?

Ans. When a magnetic nucleus is placed in magnetic field the nuclear magnet will be align with applied magnetic field. This alignment may be.

- Of low energy along the applied magnetic field.
- Of high energy which is against of applied magnetic field.

3. What is nuclear magnetic resonance spectroscopy?

Ans. Certain nuclei (^1H , ^{13}C , ^{15}P) are placed in a strong magnetic field and radio frequency is applied to flip the spin of these nuclei. Since these nuclei absorb certain radio waves to flip their spin, that radio frequency is observed on NMR spectrum and this absorbed frequency depends on the applied magnetic field and environment of the protons. In this way one can examine the structure of the organic molecule. Such technique is called NMR spectroscopy.

4. What information is obtained from NMR spectrum?

Ans. NMR spectrum gives following information

- Total number of protons in the organic molecule.
- How many different types of protons are present according to their environment.
- Position of the different protons.
- Their connectivity sequence.

5. What information's are obtained from numbers of peaks and area under peaks in NMR spectrum?

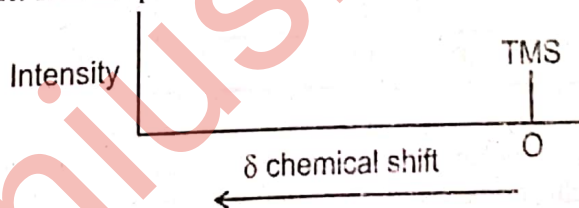
Ans. The information obtained from:

- Number of peaks:** Type of the some nuclei with different environments.
- Area under peak:** Number of spinning nuclei of a particular environment.

6. What is NMR reference?

Ans. The NMR references includes:

- **Chemical shift:** Difference among environments starting from a reference point.
- **Reference point:** It is the point for the absorption of tetramethylsilane (TMS) considered at reference zero point.



7. Why splitting of peaks occur?

Ans. Since every nucleus possess magnetic field and have influence on the neighbouring protons (vicinal protons). When external magnetic field is applied then a nucleus feels two types of magnetic field

- Applied magnetic field
- The magnetic field due to its neighbouring protons.

Such type of protons which have effects on the magnetic fields of each others are called magnetically coupled nuclei. Due to this magnetically coupling a proton signal split and this splitting depends on the number of vicinal protons.

Exercise: Q.3(5) Discuss the general principle and instrumentation of Atomic Emission Spectroscopy.

Atomic Emission Spectroscopy

Atomic emission spectroscopy pertains to electronic transitions in atoms. Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states.

Principle

The source vaporizes the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy, E_2 undergoes a transition to a state of lower energy E_1 and a photon of energy $h\nu$ is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

Types of Spectrum

Spectrum may be classified as:

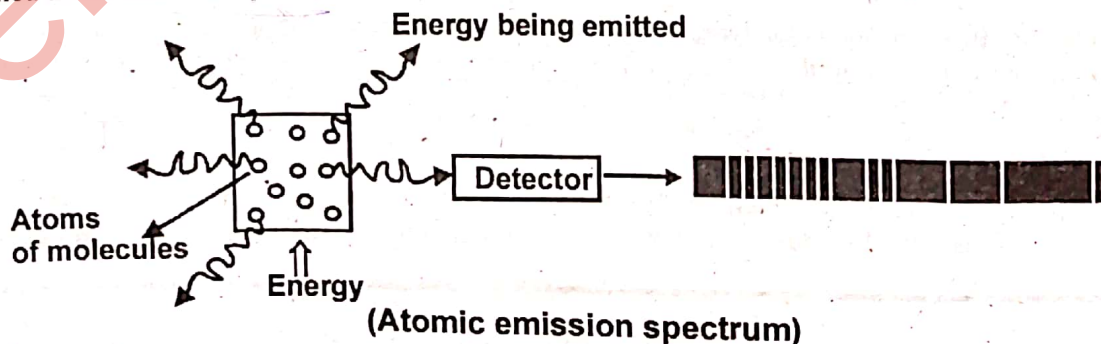
1. Continuous Emission Spectrum
2. Line or Atomic Emission Spectrum

The approximate wavelengths of visible radiation of different colours

Colour	Approximate wavelength / nm
Infrared	Above 800
Red	650-800
Orange	595-650
Yellow	580-595
Green	500-580
Blue-green	490-500
Green-blue	480-490
Blue	435-480
Violet	400-435
Ultraviolet	Below 400

Atomic or Line Emission Spectrum

When an element is vapourized in a flame, or in an electric arc or in a discharge tube, it emits a light of characteristic colour. The resolution of ray of this light produces coloured lines separated by dark spaces. This type of separation is called a line emission spectrum.



Each element has its own characteristic colour by which it can be identified:

Elements	Colour in Bunsen flame
Na	Yellow
Sr	Red
K	Violet

Elements	Glowing Colour
Ne	Orange red
He	Orange pink
H ₂	Orange red & blue
Cl ₂	Orange green

The lines in the spectrum of an element are not haphazardly distributed but they occur in groups or series. In series the separation between them decreases regularly as their wave length decreases. At a certain limiting value, the spectrum becomes continuous.

Advantages of Emission Spectroscopy

Emission method is extremely important in analysis like:

- (i) This technique is highly specific
- (ii) This method is extremely sensitive. With this technique all metallic elements can be detected even if they are present in very low concentration.
- (iii) Even metalloids have been identified by this technique.
- (iv) This analysis can be performed either in solid or liquid state with almost equal convenience.
- (v) This technique requires minimum sample preparation as a sample can be directly introduced into the spark.
- (vi) The technique provides results very rapidly. If automated, time required is just 30 sec to one minute.
- (vii) This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, environmental and biological samples.

Disadvantages of Emission Spectroscopy

- (i) The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.
- (ii) Recording is done on a photographic plate which takes some time to develop, print and interpret the results.
- (iii) Radiation intensities are not always be reproducible.
- (iv) Relative error exceeds 1 to 2 %.
- (v) The accuracy and precision are not high.

Applications:

- (i) Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, V, Pb, Bi, P and Mo in iron and steel in metallurgical processes.
- (ii) Alloys of Zn, Cu, Pb, Al, Mg and Sn have been analyzed.
- (iii) Lubricants oils have been analyzed for Ni, Fe, Cr, Mn, Si, Al and so on. If the concentration of metal in lubricating oil has increased during use, it indicates excessive wear and tear need for engine overhaul.
- (iv) In petroleum industry oil is analyzed for V, Ni, Fe the presence of which makes fuel poor.
- (v) Solid samples and animal tissues have been analyzed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc.
- (vi) Emission spectroscopy has been used to detect 40 elements in plants and soil. Thus metal deficiency in paints and oil can be diagnosed.

The following materials have been analysed by emission spectroscopy:

- Trace and major constituents in ceramics.
- Traces of Co, Ni, Mo and V in Graphite.
- Trace metal impurities in analytical reagents.
- Trace of Ca, Cu, Zn in blood.
- Zinc in pancreatic tissues,

1. Define atomic emission spectroscopy.

Ans. Atomic emission spectroscopy pertains to electronic transitions in atoms which use an excitation source like flame sparks and concerned with the characteristic radiations produced when atoms are excited.

2. What is meant by excitation of molecule?

Ans. When a gaseous sample is introduced it absorbs energy as a result excitation of electrons occurs from lower energy levels to higher energy level which is known as excitation.

3. Name those elements which can analyze by emission spectroscopy.

Ans. A number of elements can analyze by emission spectroscopy due to their characteristic emissions are Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, Pb, Bi, P, Mo, V, Na, K and Zn.

4. How emission spectroscopy apply in metallurgy?

Ans. Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, V, Pb, Bi, P and Mo in iron and steel metallurgical processes.

Exercise: Q.3(6) What is the basic principle of Atomic Absorption Spectroscopy? Describe the instrumentation used.

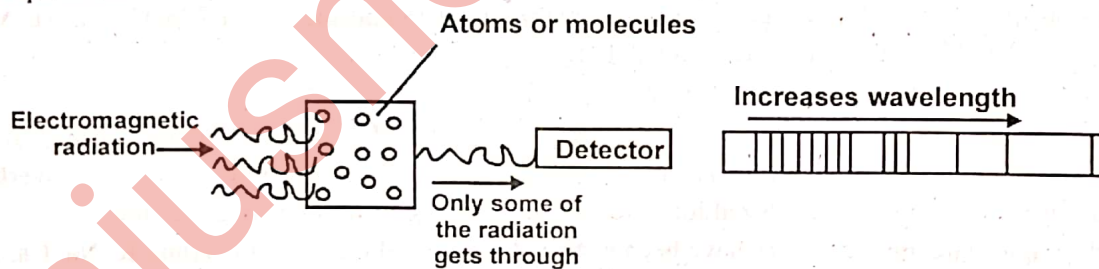
Atomic Absorption Spectroscopy (AAS)

The technique has been particularly useful in the determination of trace metals in liquids. The versatility of AAS can be realized from the fact that 60-70 elements have been analyzed by this method in concentration as low as 1 ppm. The greatest advantage of AAS is the analysis of one metal in the presence of another metal, thus saving time and eliminating error.

Principle

When white light is allowed to pass a sample of a substance, it may absorb radiation of a particular wave length. There will be a dark space in the continuous spectrum of white light for that particular wave length. This spectrum is called a line or atomic absorption spectrum.

A substance which absorbed a particular radiation in normal state will emit the radiation in excited state. The emission lines and absorption lines will be exactly at the same place in the spectrum. For example H_2 gas gives red colour spectrum in excited state. In normal state it absorbs the red colour. Thus there will be a dark line in place of red colour in the continuous spectrum.



(Atomic absorption spectrum)

Applications of Atomic Absorption Spectroscopy (AAS)

- (1) The AAS technique has become the most powerful tool of analysis. The method is well-suited to the analysis of a substance at low concentration
- (2) It has several advantages over conventional absorption or emission spectroscopic methods.
- (3) AAS methods are highly specific, hence analysis of a metal from a complex mixture is possible and a high energy source needs not be employed.
- (4) The technique is firmly established in analytical chemistry, ceramics, mineralogy, biochemistry, metallurgy, water supplies and soil analysis.


**QUICK
QUIZ**

1. Give principle of atomic absorption spectroscopy.

Ans. Principle of AAS:

Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usually visible by neutral atoms in the gaseous states. If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground state atoms present in the flame. This is the underlying principle of AAS.

2. Give few applications of Atomic absorption spectroscopy.

Ans. Applications of Atomic Absorption Spectroscopy (AAS)

- (5) The AAS technique has become the most powerful tool of analysis. The method is well-suited to the analysis of a substance at low concentration
- (6) It has several advantages over conventional absorption or emission spectroscopic methods.
- (7) AAS methods are highly specific, hence analysis of a metal from a complex mixture is possible and a high energy source needs not be employed.
- (8) The technique is firmly established in analytical chemistry ceramics mineralogy, biochemistry, metallurgy, water supplies and soil analysis.

Exercise: Q.3(7) What is the basic principle of Mass Spectrometer? How does it work?

MASS SPECTROMETRY (MS)

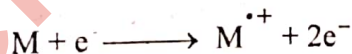
The mass spectrometer is an instrument which turns atoms and molecules into ions and measures their mass.

In 1919, Aston invented the mass spectrometer. This gave chemists a reliable and accurate method of comparing the relative masses of atoms. At one time, the relative masses of atoms were known as atomic weights, but nowadays we refer to them as relative atoms masses.

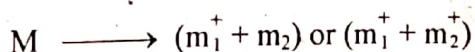
Mass spectrometry is an analytical technique which involves the production of gaseous ions from the substance under investigation, their separation according to their mass-to-charge ratio (m/e) and the measurement of the relative abundance of these ions. In this technique, no absorption of light is involved. This is why it is commonly called spectrometry instead of spectroscopy. It is called spectroscopy because the ultimate result is obtained in the form of a 'spectrum' as in the case of other spectroscopic techniques.

Basic Principle

In mass spectrometry, as organic molecule under high vacuum is bombarded with an electron of energy greater than the ionization energy of the molecule; the ionization energy of most of organic molecules is around 10 eV (964 kJmol^{-1}). As a result of this, one of the electrons of the molecule is dislodge and a singly charged molecular ion is produced. The molecular ion which is produced in this primary process is a radical cation, i.e., it has an unpaired electron is positively charged.



The sample in vapour state is usually subjected to a beam of electrons of 70 eV energy. These highly energetic electrons not only ionize the organic molecules but also impart a large amount of energy to the molecular ions. A molecular ions generally dissociates into fragments called fragment ions.



The positively charged ions are separated by deflection in a variable magnetic field. The ions are directed into an analyzer tube surrounded by a magnet. The magnet deflects the ions from their original path causing them to adopt a circular path the radius of which depends on the mass-to-charge ratio (m/z) of the ions. The ion beam of a particular m/z

can be selectively focused through a narrow slit on to an ion collector where it generates a current proportional to the relative abundance of the ions in the beam, which is recorded as a spectrum. The mass spectrum in fact, is a plot of the relative intensity of the ions against their dimensionless m/z value. The doubly charged ions are deflected much more than the singly charged ions and appear in the mass spectrum at half the m/z value ($m/2z$) of the singly charged ions of the same mass. For example, a doubly charged ion of mass 90 give rise to a peak at m/z 45.

Instrumentation and working

The basic idea of a mass spectrometer can be demonstrated using the apparatus. Wooden balls of different sizes but with identical iron cores roll down a sloping plane. At the bottom of the slope a powerful magnet attracts the iron cores and the moving balls are deflected.

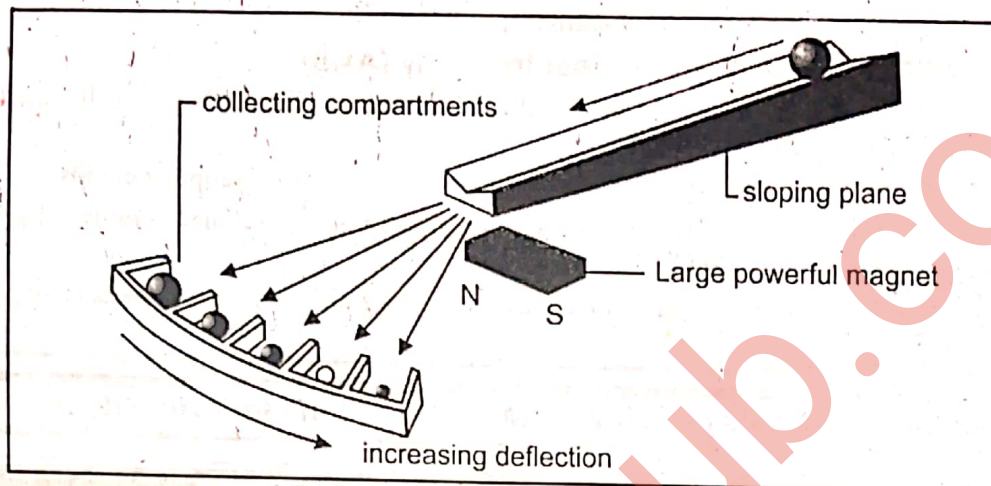


Fig 24.11 A simple model to illustrate the working of a mass spectrometer

As the balls have identical iron cores, they are all attracted equally by the magnet. But the smaller balls are lighter and therefore they are deflected the most. The balls collect in different compartments depending on their mass. All balls of the same mass collect in the same compartment. Using this simple apparatus, it is possible to separate the different sized balls according to their mass and to find the relative numbers of each present.

A real mass spectrometer according works in a similar fashion to this simple model. It separates atoms according to their mass and shows the relative numbers of the different atoms present. Before the atoms can be deflected and separated, they must be converted to positively charged ions.

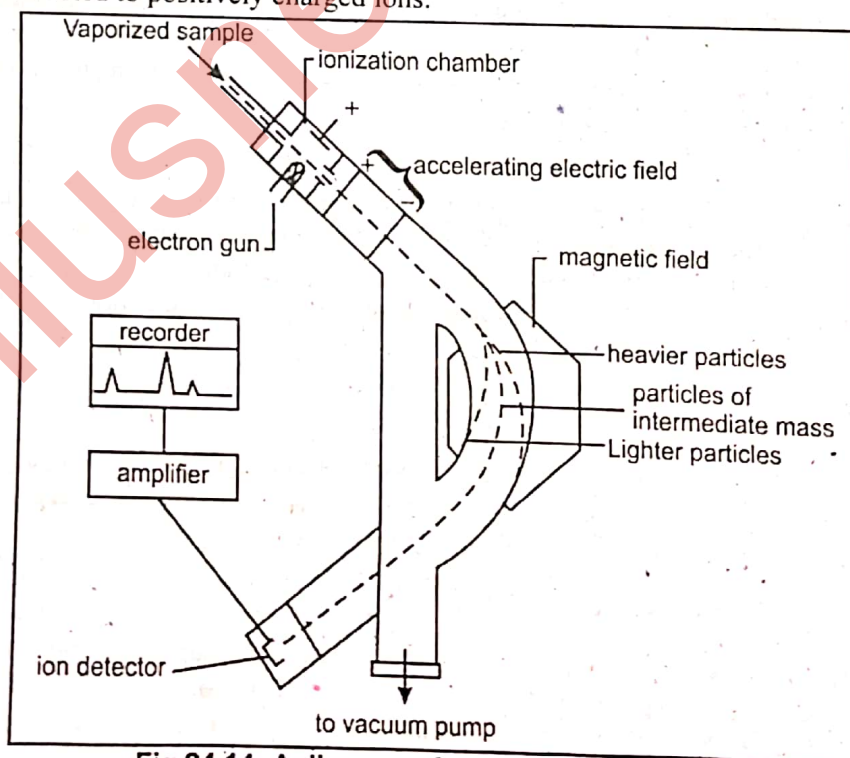


Fig 24.14: A diagram of a mass spectrometer.

Figure shows a simple mass spectrometer. There are five main stages.

1. Vaporization – the sample of elements is vaporized.
2. Ionization – positive ions are obtained from the vapor.
3. Acceleration – the positive ions are accelerated by an electric field.
4. Detection – the ions are detected and a record is made.



QUICK QUIZ

1. Why does the magnet have the same attraction for all the balls?

Ans. Magnet has same attraction for all balls because they all are of iron core with equal attractions.

2. Which size of ball will be deflected the most? Why?

Ans. Small balls will be deflected more due to lighter frictionless mass comparative to large balls



QUICK QUIZ

Look closely at given figure:

1. How many different ions are detected in the mass spectrum of naturally occurring magnetism?

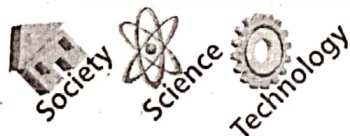
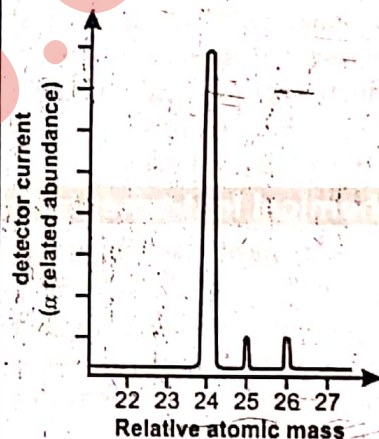
Ans. The above mass spectrum shows three peaks at different relative masses hence it should contain three different ions.

2. What are the relative masses of these different ions?

Ans. The graph shows that they have relative masses of 24, 25 and 26 in mass spectrum.

3. What are the relative proportions of these different ions?

Ans. The intense peak of ions having mass 24 is the most abundant ion (71%), while the relative masses 25 (10%) and 26 (11%) are of low abundance.



1. Temperature Variations Within A Flame

There are four different parts or zones of a flame i.e.

Blue zone (a zone of complete combustion)

Dark zone (a zone where no combustion occurs)

Luminous zone (a zone of partial or incomplete combustion)

Non-luminous zone (a zone of complete combustion)

Luminous zone where incomplete combustion takes place has the temperature between 600-850°C (1,112-1,562 °F).

Non luminous zone where complete combustion takes place has the temperature of about 2000°C (3,632 °F).

In fires (particularly house fires), the cooler flames are often red and produce the most smoke. Here the red color compared to typical yellow color of the flames suggests that the temperature is lower. This is because there is a lack of oxygen in the room and therefore there is incomplete combustion and the flame temperature is low, often just 600-850 °C (1,112-1,562 °F). This means that a lot of carbon monoxide is formed (which is a flammable gas if hot enough) which is when in Fire and Arson investigation there is greatest risk of backdraft. When this occurs flames get oxygen, carbon monoxide combusts and temporary temperatures of up to 2,000 °C (3,632 °F) occur.

Flame temperatures of common items include a candle at $1,400^{\circ}\text{C}$ ($2,600^{\circ}\text{F}$), a blow torch at around $1,600^{\circ}\text{C}$ ($2,900^{\circ}\text{F}$) a propane torch at $1,995^{\circ}\text{C}$ ($3,620^{\circ}\text{F}$), or a much hotter oxyacetylene combustion at $3,000^{\circ}\text{C}$ ($5,400^{\circ}\text{F}$).

2. Forensic Chemistry And Problem Solving Skill

Forensic chemistry is the application of chemistry to criminal investigation. This major is recommended for individuals who wish to pursue a career in criminal investigation, in the laboratory analysis of forensic evidence, or pursue graduate study in forensic science. This course of study would also develop the analytical skills required for careers in other areas of civil law such as environmental pollution, accident investigation and product liability. Due to the nature of forensic investigations, the forensic chemist requires a strong background in chemical analysis and problem solving skill and must be able to effectively communicate the results of laboratory analysis in reports and in the courtroom. So a forensic chemist must have a strong theoretical and experimental background in analytical chemistry as well as in problem solving skills.

Forensic chemists must have good attention to detail and superior problem-solving skills. They need critical thinking abilities to solve crime puzzles based on fragmentary evidence. Forensic chemists must take accurate notes and make accurate records of their findings. They need strong writing skills to produce clear reports on highly technical subjects so that others can understand.

Analytical measurements are essential to everyday life, required to determine the composition and control the quality of many products, to protect the environment and to monitor health. Consequently Analytical Chemistry has a major impact, not only in chemistry, but also in fields such as biochemistry, and the forensic, food, environmental and pharmaceutical sciences. Forensic chemistry is the application of analytical chemistry to the law and involves the examination of physical traces, such as body fluids, bones, fibres and drugs. Success in analytical chemistry requires the ability to make rigorous measurements, an appreciation of the principles and practice of modern instrumentation, and a problem-solving approach.

3. Chemical Instrumentation And Technology

Chemical instruments are used extensively in research and development activities, laboratories being one of the major users. Use of chemical instruments for disease diagnosis is on a rise.

Chemical equipment market is growing at a rapid rate due to the continuous requirement of these instruments in pharmaceutical and biotechnology industries. Besides the increase in number of biotechnology firms worldwide, advances in life science research and technology innovations with human genome mapping, and emergence of proteomics have enabled industry growth; as such high-end research projects require quality instruments with high throughput capacity. All these factors are driving the life science and chemical instrumentation market.

The global life science and chemical instrumentation market was estimated to be \$30.2 billion in the year 2011 and is expected to grow at a CAGR of 8.4% from 2011 to 2016 to reach \$45.2 billion.

4. Connection Between Chromatography And MS

Chromatography is the collective term for a set of laboratory techniques for the separation of mixtures and for the detection of small amounts of materials present in those mixtures. The mixture is dissolved in a fluid called the mobile phase, which carries it through a structure holding another material called the stationary phase. The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation.

Mass spectrometry (MS) is an analytical technique that measures the mass-to-charge ratio of charged particles. It is used for determining masses of particles, for determining the elemental composition of a sample or molecule, and for elucidating the chemical structures of molecules, such as peptides and other chemical compounds. MS works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances, even present in small amounts, within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. GC-MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification. GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample.

Liquid chromatography-mass spectrometry (LC-MS, or alternatively HPLC-MS) is a chemistry technique that combines the physical separation capabilities of liquid chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry. LC-MS is a powerful technique used for many applications which has very high sensitivity and selectivity. Generally its application is oriented towards the general detection and potential identification of chemicals in the presence of other chemicals (in a complex mixture). Preparative LC-MS system can be used for fast and mass directed purification of natural-products extracts and new molecular entities important to food, pharmaceutical, agrochemical and other industries. The limitations of LC-MS in urine analysis drug screening is that it often fails to distinguish between specific metabolites, in particular with hydrocodone and its metabolites. LC-MS urine analysis testing is used to detect specific categories of drugs. However, gas chromatography (GC-MS) should be used when detection of a specific drug and its metabolites is required.

KEY POINTS

- The empirical formula of an organic compound can be found by analysis of its combustion products
- The molecular formula of a compound can be found from the empirical formula once the relative molecular mass is unknown.
- The structural formula shows the precise arrangement of atoms. It can be found from knowledge of some of the properties of the compound or by using instrumental methods, particularly mass spectrometry, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR).
- The instrument that is used to measure the amount of electromagnetic radiation absorbed by an organic molecule is called Spectrophotometer or Spectrometer.
- Absorption of infrared radiation causes covalent bonds within the molecule to be promoted from one vibrational energy level to a higher vibrational energy level.
- Stronger bonds require greater energy to vibrate. Therefore such bonds absorb infrared radiation of shorter wavelengths.
- Different functional groups absorb infrared radiation at different wavelengths and their presence or absence in a molecule can be determined by examination of an IR spectrum.
- No two compounds have exactly identical infrared spectra.
- Absorption of ultraviolet visible radiation causes electrons within molecules to be promoted from one energy level to a higher electronic energy level.
- If an organic compound does not absorb UV-Vis radiation it means that the compound does not contain conjugated double bonds.
- If an organic compound absorbs UV-Vis radiation it means that the compound contains a carbonyl group or conjugated double bonds. For example, conjugated dienes, carbonyl compounds and aromatic compounds all absorb in the UV-Vis region.
- Absorption of radio waves in the presence of a magnetic field causes nuclei within molecules to be promoted from one spin energy level to a higher spin energy level.
- The number of signals in the NMR spectrum corresponds to the number of different types of protons in the molecules.
- The position (chemical shift) of each signal gives information about the structural environment of the protons.
- The relative areas (Interrogation) under the signals give the ration of the numbers of each type of protons in the molecule. If the molecular formula is known, the actual number of each type of protons can be determined.
- The splitting pattern of each signal gives us the number of protons on neighboring carbons. The number of peaks into which a signal is split a signal is split is one more than the total number of protons on directly adjacent carbons.
- Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states.
- Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usually visible by neutral atoms in the gaseous states. If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground state atoms present in the flame.

- Mass spectroscopy involves organic molecules being bombarded by a very high-energy electron beam.
- The peak of highest intensity in a mass spectrum is referred to as the base peak.
- Fragmentation processes can produce numerous fragments from which the structures of organic molecules can be deduced.
- When one electron is removed from a molecule, a molecular ion is produced. The m/e value of the molecular ion peak is the molecular weight of the compound being investigated. The molecular weights obtained by mass spectroscopy are extremely accurate.

EXERCISE

Q1. Multiple Choice Questions. Encircle the correct answer:

- ★ Read the question carefully.
- ★ Try to answer the question yourself before reading the answer choices.
- ★ Guess only if you can eliminate one or more answer choices.
- ★ Drawing a picture can help.
- ★ Don't spend too much time on any one question.
- ★ In-depth calculations are not necessary; approximate the answer by rounding.

- (1) Which of the following techniques does not involve electromagnetic radiations?
 - (a) infrared spectroscopy
 - (b) NMR spectroscopy
 - (c) mass spectroscopy
 - (d) all of these involve electromagnetic radiations
- (2) Which region of the electromagnetic spectrum is involved in the electronic excitations?
 - (a) ultraviolet
 - (b) visible
 - (c) both of these
 - (d) none of these
- (3) Which of the following techniques is different from the others as regards the basic principle?
 - (a) ultraviolet spectroscopy
 - (b) visible spectroscopy
 - (c) electronic spectroscopy
 - (d) none of these
- (4) Which of the following is used as a source of visible radiations?
 - (a) tungsten filament lamp
 - (b) hydrogen discharge lamp
 - (c) deuterium discharge lamp
 - (d) All of these
- (5) What is the wavelength range of the ordinary infrared region?
 - (a) 0.8-2.5 μm
 - (b) 2.5-16 μm
 - (c) 16-1000 μm
 - (d) 400-800 nm
- (6) The position of an infrared absorption band is commonly expressed by:
 - (a) wavelength
 - (b) wave number
 - (c) both of these
 - (d) none of these
- (7) Which of the following is not used as a source of infrared radiations?
 - (a) nernst filament
 - (b) tungsten filament
 - (c) globar
 - (d) none of these
- (8) Which region of the electromagnetic spectrum is involved in mass spectrometry?
 - (a) visible
 - (b) microwave
 - (c) radiowave
 - (d) none of these
- (9) Mass spectroscopy is an analytical technique which involves:
 - (a) production of gaseous ions from the sample
 - (b) separation of the gaseous ions
 - (c) measurement of the relative abundance of the gaseous ions
 - (d) all of these
- (10) Mass spectrometry can be used to determine:
 - (a) molecular weight
 - (b) molecular formula
 - (c) molecular structure
 - (d) all of these
- (11) Which of the following species is detected in the mass spectrometer?
 - (a) positively charged species
 - (b) radicals
 - (c) neutral molecules
 - (d) all of these

- (12) Which of the following species is produced in the ionization chamber of a mass spectrometer?
 (a) positively charged species (b) radicals
 (c) neutral molecules (d) all of these
- (13) Which kind of information about a positively charged species obtained from a mass spectrum?
 (a) molecular weight (b) relative abundance (c) both of these (d) none of these
- (14) What kind of sample can be studied in a mass spectrometer?
 (a) a gas (b) a liquid (c) a solid (d) all of these
- (15) Near ultraviolet region of these electromagnetic spectrum generally lies between:
 (a) 10-200 nm (b) 200-400 nm (c) 400-750 nm (d) 300-500 nm
- (16) Far ultraviolet or vacuum ultraviolet region generally lies between.
 (a) 10-200 nm (b) 200-400 nm (c) 400-750 nm (d) 300-500 nm
- (17) Far infrared region of the electromagnetic radiation generally lies between:
 (a) 50-200 μm (b) 100-400 μm (c) 50-1000 μm (d) 1-20 μm

SOLVED EXERCISE MCQs

Q. No	Answer	Reason
(1)	(c) Mass spectroscopy (mass spectrometry).	Because mass spectrometry uses beam of high energy electrons.
(2)	(c) Both of these.	Both UV and visible radiations can change electronic level by different electronic excitations.
(3)	(d) None of these.	All of above techniques are based upon principle of electronic excitations.
(4)	(a) Tungsten filament lamp.	Because tungsten (W) is a metal known for the production of high energy electronic beam.
(5)	(b) 2.5 – 16 μm	It is the ordinary IR region.
(6)	(b) Wave number	It is the common position expression of IR absorption bond.
(7)	(b) Tungsten filament	Tungsten filament is used as a source of IR or visible light.
(8)	(d) None of these.	Mass spectrometry is the technique in which no radiations are used for analysis.
(9)	(d) All of these.	Because all of these involved in mass spectrometry.
(10)	(a) Molecular weight.	Mass spectrometry is used for determining the relative mass and abundance of a compound.
(11)	(a) Positively charged species.	In mass spectrometry only positively charged ions are allowed to hit the detector to find their mass.
(12)	(a) Positively charged species.	In ionization chamber the high energy electrons hit the compound and knock out its valence electron, as a result cations are formed.
(13)	(c) Both of these.	Mass spectrum gives information about the molecular weight and relative abundance.
(14)	(d) All of these.	All type of compounds can be analyzed by spectrometer but they need to introduce in form of gas.
(15)	(b) 200 – 400 nm.	This is the region near to UV region.
(16)	(a) 10 – 200nm.	It is the region lies far from UV region.
(17)	(c) 50-1000 μm	It is the for infrared region of EMR.

SHORT ANSWERS QUESTIONS

2. Give brief answers for the following questions.

(i) What is spectroscopy? Underline its principle.

Ans. Spectroscopy

It is the branch of chemistry which deals about the interaction of light with matter. Spectroscopy involved using an instrument determining the structure, mass and percent abundance of elements by emission or absorption of light.

Principle:

The source vaporizes the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy, E_2 undergoes a transition to a state of lower energy E_1 and a photon of energy $h\nu$ is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

(ii) What is meant by wavelength and frequency?

Ans. Wave length (λ):

It is the distance between two adjacent crests or troughs in a beam of radiation.



It is measured in Pico meter, angstrom or nm.

$$1\text{Å} = 10^{-10}\text{m}, 1\text{nm} = 10^{-9}\text{m}, 1\text{pm} = 10^{-12}\text{m}$$

Frequency (ν):

It is the number of waves passing through a given point in one second.

It is represented as ν and units are cycles S^{-1}

$$1\text{Hz} = 1\text{ cycle } \text{S}^{-1}$$

(iii) What is spectrometer? Briefly discuss its working.

Ans. Spectrometer:

It is an instrument used to measure the amount of radiations absorbed and emitted by a compound under analysis.

Working of spectrometer:

In spectrometer the electromagnetic radiations are passed through a sample under analysis. The instrument records the difference between incident light and emitted light and gives the information about the compound in form of a spectrum.

(iv) How will you distinguish between (i) 1,3-Pentadiene and 1,4-Pentadiene (ii) Benzene and anthracene by UV-spectroscopy?

Ans. (i) 1, 3-Pentadiene and 1, 4-Pentadiene:

We can differentiate between these two on the basis of their UV – absorption spectrum. Conjugated systems absorb high wavelength and 1, 3-Pentadiene is a conjugated system and it will absorb higher wavelength with high λ_{max} than isolated system in 1, 4 pentadiene.



1, 3-Pentadiene

(Conjugated)

(high absorption)

$$\lambda_{\text{max}} = 223 \text{ nm}$$



1, 4-Pentadiene

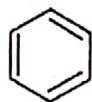
(Isolated)

(low absorption)

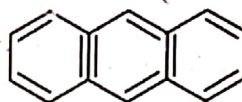
$$\lambda_{\text{max}} = 178 \text{ nm}$$

(ii) **Benzene and anthracene:**

Anthracene is a highly conjugated system having three merged benzene rings hence will show high absorption as compared to less conjugated benzene.



Benzene



Anthracene

(v) **Two isomeric dienes (X) and (Y), having the molecular formula C_5H_8 , absorb at λ_{max} 223nm and λ_{max} 178nm respectively. Write the structures of the two isomers.**

Ans. As X is absorbing longer wavelength radiation indicates the presence of conjugation while shorter wavelength radiation in Y indicated that such type of conjugation is not present in the structure of Y. Therefore the possible structures for X and Y could be

Structure of X



1, 3-Pentadiene

(Conjugated)

(high absorption)

$$\lambda_{\text{max}} = 223 \text{ nm}$$

Structure of Y



1, 4-Pentadiene

(Isolated)

(low absorption)

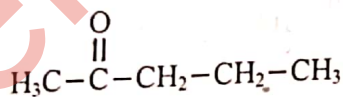
$$\lambda_{\text{max}} = 178 \text{ nm}$$

(vi) **Give significant application of Atomic Absorption Spectroscopy (AAS).**

- Ans.**
- (a) It is used to analyze the substance having low concentrations.
 - (b) This method is used to analyze an ion of a complex compound.
 - (c) Atomic absorption spectroscopy is used in analytical chemistry of mineralogy, biochemistry, metallurgy, soil analysis etc.
 - (d) It is used in clinical chemistry to analyze metals in biological fluids and tissues.
 - (e) It is used for the analysis of metal contents in water.

(vii) **How will you distinguish between 2-Pentanone and 3-Pentanone by using mass spectra?**

Ans. Each compound has a sharp major peak of fragment cation in mass spectra. This characteristic peak for 2-Pentanone will be at $m/e = 43$ and at $57 m/e$ for 3-pentanone.

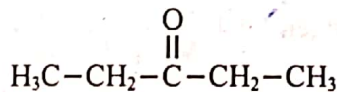


2-Pentanone

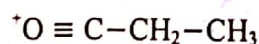
Its due to fragment



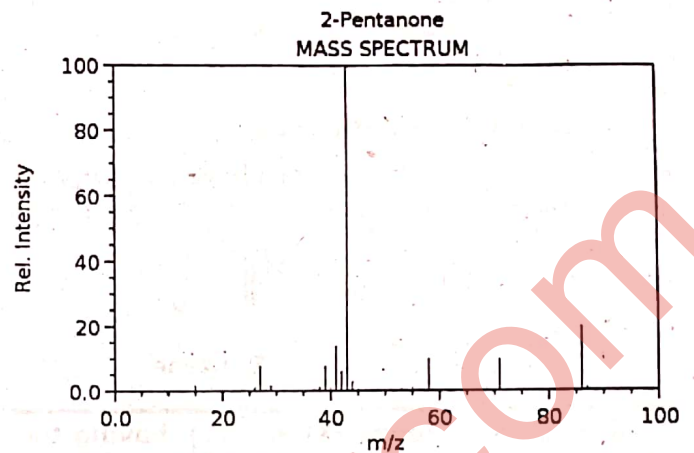
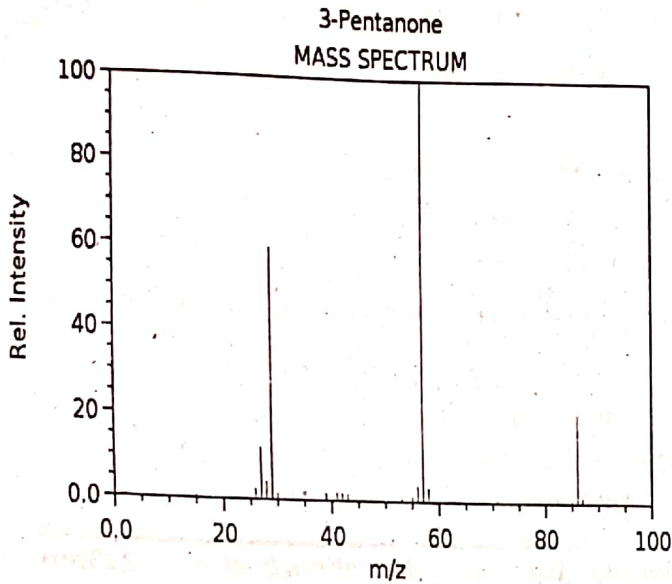
$$\frac{\text{Mass}}{e} = 43$$



3-Pentanone



$$\frac{\text{Mass}}{e} = 57$$



Q.3. Give detailed answers for the following questions.

Q.3.(2) An organic compound consists of carbon, hydrogen and oxygen was subjected to combustion analysis. 0.5439g of the compound gave 1.039g of CO₂, 0.6369g of H₂O. Determine the empirical formula of the compounds.

Ans. Given data

Mass of organic compound = 0.5439g

Mass of carbon dioxide = 1.039g

Mass of water = 0.6369g

$$C = \frac{\text{mass of CO}_2}{\text{mass of compound}} \times 100$$

Required

Empirical formula of the compound = ?

Solution

Percentage composition of the sample

$$\% \text{ of carbon} = \frac{\text{Mass of CO}_2}{\text{Mass of organic compound}} \times \frac{12}{44} \times 100$$

$$= \frac{1.039\text{g}}{0.5439\text{g}} \times \frac{12.00}{44.00} \times 100 = 52.08\%$$

$$\% \text{ of hydrogen} = \frac{\text{Mass of H}_2\text{O}}{\text{Mass of organic compound}} \times \frac{2.016}{18} \times 100$$

$$= \frac{0.6369\text{g}}{0.5439\text{g}} \times \frac{2.016}{18} \times 100 = 13.11\%$$

$$\% \text{ of oxygen} = 100 - (\% \text{ of C} + \% \text{ of H})$$

$$= 100 - (52.08 + 13.11) = 34.77\%$$

Number of gram atoms

$$\text{Gram atoms of element} = \frac{\% \text{ of element}}{\text{Atomic mass of element}}$$

$$\text{Gram atoms of C} = \frac{52.08}{12} = 4.34 \text{ gram atoms}$$

$$\text{Gram atoms of H} = \frac{13.11}{1.008} = 13.00 \text{ gram atoms}$$

$$\text{Gram atoms of O} = \frac{34.77}{16.00} = 2.17 \text{ gram atoms}$$

$$4.34 : 13 : 2.17$$

Atomic ratio

$$\text{Atomic ratio of element} = \frac{\text{Gram atoms of element}}{\text{Smallest number}}$$

$$\text{Atomic ratio of C} = \frac{4.34}{2.17} = 2$$

$$\text{Atomic ratio of H} = \frac{12.13}{2.17} = 6$$

$$\text{Atomic ratio of O} = \frac{2.17}{2.17} = 1$$

$$\text{Empirical formula } \text{C}_2\text{H}_6\text{O}$$

3. The combustion analysis shows that organic compounds contain 65.44% carbon, 5.50% hydrogen and 29.06% of oxygen. What is empirical formula? If the molecular mass of this compound is $110.15 \text{ gmole}^{-1}$ then calculate molecular formula of given organic compound.

Ans. Given data

$$\text{Percentage of carbon} = 65.44\%$$

$$\text{Percentage of hydrogen} = 5.50\%$$

$$\text{Percentage of oxygen} = 29.06\%$$

$$\text{Molecular Mass} = 110.15 \text{ g/mole}$$

Required

$$\text{Empirical formula} = ?$$

$$\text{Molecular formula} = ?$$

Solution

Number of Gram atoms

$$\text{Gram atoms of element} = \frac{\text{Percentage of element}}{\text{Atomic mass of element}}$$

$$\text{Gram atoms of C} = \frac{65.44}{12} = 5.45 \text{ gram atoms}$$

$$\text{Gram atoms of H} = \frac{5.50}{1.008} = 5.45 \text{ gram atoms}$$

$$\text{Gram atoms of O} = \frac{29.06}{16.00} = 1.82 \text{ gram atoms}$$

Atomic ratio

$$\text{Atomic ratio of element} = \frac{\text{number of gram atoms of element}}{\text{Smallest number}}$$

$$\text{Atomic ratio of C} = \frac{5.45}{1.82} = 3$$

$$\text{Atomic ratio of H} = \frac{5.45}{1.82} = 3$$

$$\text{Atomic ratio of O} = \frac{1.82}{1.82} = 1$$

Empirical formula of the compound

C, H and O are present in the compound in the ratio of 3: 3: 1 so the empirical formula C_3H_3O .

Molecular formula

In order to determine the molecular formula, first calculate the empirical formula mass.

$$\text{Empirical formula Mass of } C_3H_3O = 12 \times 3 + 1.008 \times 3 + 16 \times 1 = 55.05 \text{ g mol}^{-1}$$

$$\text{Molecular Mass} = 110.15 \text{ g mol}^{-1}$$

$$n = \frac{\text{Molecular Mass}}{\text{Empirical formula mass}} = \frac{110.15}{55.05} = 2$$

$$\text{Molecular formula} = n \times (\text{Empirical formula})$$

$$= 2 \times C_3H_3O$$

$$= C_6H_6O_2$$

