UNIT 17

QUALITATIVE ANALYSIS
(Mass Spectrometry)

Student Learning Outcomes (SLOs)

- Analyse mass spectra in terms of m/ e values and isotopic abundances.
- Calculate the relative atomic mass of an element given the relative abundance of it's isotopes or it's mass spectrum.
- Deduce the molecular mass of an organic molecule from the molecular ion peak in the mass spectrum.
- Suggest the identity of molecules by simple fragmentation in a given mass spectrum.
- Deduce the number of C atoms "n" in a compound using the M+1 peak and the formula:

$$\text{Number of carbon-atoms} = \frac{\text{relative intensity of M+1 peak}}{0.01107 \times \text{relative intensity of } M^+}$$

- Deduce the presence of chlorine and bromine atoms in a compound using M+. peak in mass spectrum.

General uses and instrumentation of Mass Spectrometry have already been discussed in grade XI. It is a very useful tool to analyse the number of isotopes of an element and their relative abundances. Furthermore, it is also used to determine the molecular masses and help in the structure determination of organic molecules, especially organic molecules. Another advanced benefit of mass spectrometry is the study of reaction mechanisms by finding fragmental masses of molecular fragment cations and intermediate cations formed during the reaction.

17.1 How to analyse a number of isotopes and their relative abundances of isotopes?

The number of peaks that appear on a proper m/z value in the mass spectrum tells us about the number of isotopes. For example, two peaks are seen in the mass spectrum of chlorine which shows that there are two isotopes of chlorine present in the natural sample. Similarly, three peaks in the hydrogen spectrum tell us about three isotopes of hydrogen namely protium, deuterium and tritium.

Secondly, the height of each peak tells us about the relative abundances of each isotope in terms of percentage.

17.2 Calculation of relative atomic masses:

The relative atomic mass of an element can be calculated by the given formula using the relative abundance of each isotope with its m/z value.

$$\text{Relative (avg.) atomic mass} = \frac{\sum \text{(mass number)} \times \text{(isotope abundance)}}{100}$$

For example, the study of the Boron(z=5) spectrum tells the number of isotopes with relative abundances of isotopes are as follows:

Mass number of boron =10

Relative abundance of boron=19.90%

Mass number=11

Relative abundance B-11= 80.10%

It's average atomic mass can be calculated by putting this information in the formula.

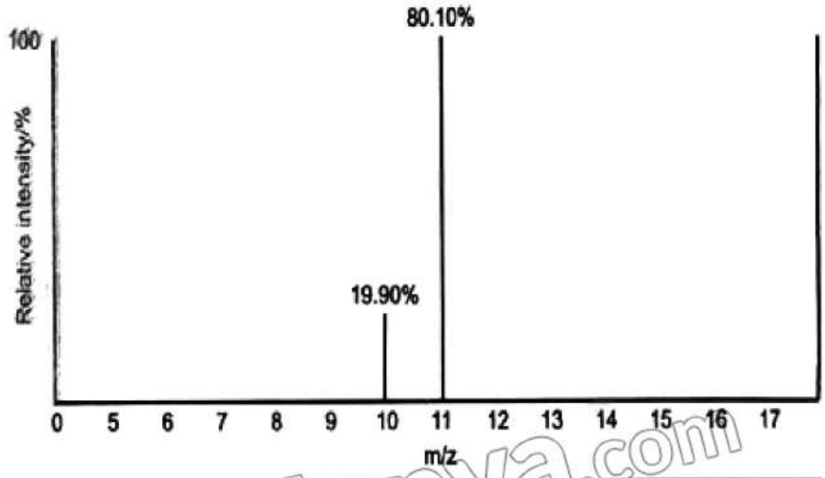


Fig 17.1: Mass spectrum of boron

$$\text{Avg. Atomic mass of Boron} = \frac{(10 \times 19.90) + (11 \times 80.10)}{100} = 10.801\text{amu}$$

CONCEPT ASSESSMENT EXERCISE 17.1

Question: Using the given spectrum, calculate the average atomic mass of the element and find out to which element this spectrum belongs. You can take the help of the periodic table.

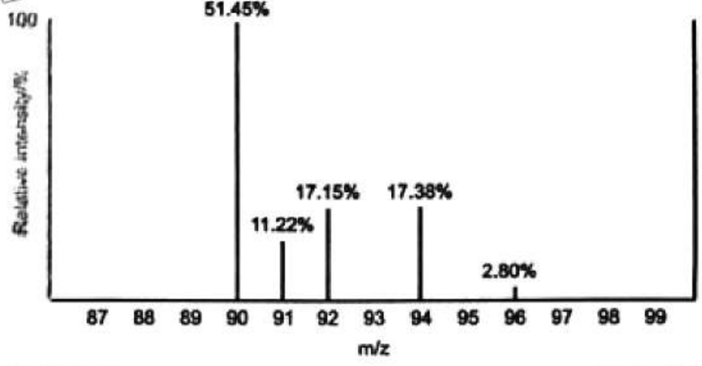


Fig 17.2:

17.3 Determination of molecular mass by molecular ion peak

The first thing to do is the identification of the molecular ion peak (M^+). The molecular ion peak is the peak in a mass spectrum that represents the molecular ion (symbol: M^+ peak). The molecular ion peak is the point with the largest mass-to-charge ratio after excluding any peaks caused by the presence of heavier isotopes. Then you check the m/z value of the molecular ion peak. Another important characteristic peak of a compound in mass spectrum is base peak. The base peak is due to the most abundant ion of the molecule which is given abundance of 100. The peak corresponding to the most abundant ion is called base peak.

The value of m/z of molecular ion peak is equal to the molecular mass because most of the ions carry +1 charge. If isotopes are present with greater mass but less relative abundance their peaks will arise at a greater m/z. For example, if an organic compound has ^{13}C isotope a smaller peak at (M+1) one m/z greater than the molecular ion peak.

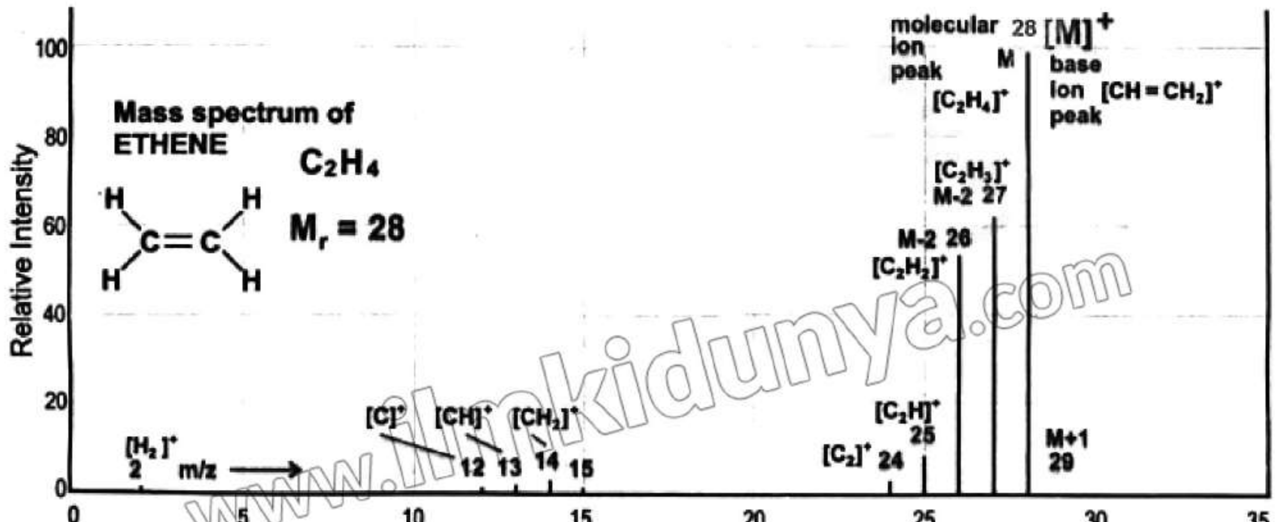


Fig 17.3 Mass spectrum of ethene

For example, the molecular ion or heaviest peak for hexane appears at 86 m/z. Let us explain the mass spectrum of the ethene molecule. In the figure the molecular ion peak appears at m/z= 28 which is equivalent to the molecular mass of ethene. The peak at 29 is the M+1 peak due to one of carbon in ethene that is C-13 isotope having 1% abundance. The peak is at m/z=30 is the M+2 peak due to the presence of both carbons as C-13 in ethene. M+2 peak usually much smaller than M+1 and M peaks. The other peaks are formed by all those fragment ions formed during the process of mass Spectrometry.

17.4 Identification of a molecule by fragmentation pattern

By the impact of electrons from the electron gun onto the molecules, molecule undergoes fragmentation. Dissociation of the bond depends on the type of functional group, usually the weakest bond breaks and the most stable fragments are formed. Among the fragments only cations are carried to the detector. In the mass s Mass spectrum of n-pentane s usually the fragments of m/z=15 and m/z=14 are formed corresponding to the (CH_3^+) methyl cation. Similarly, m/z=29 peak also appears which represents ethyl ($CH_3CH_2^+$) cation and m/z=43 for the propyl cation($CH_3CH_2CH_2^+$).

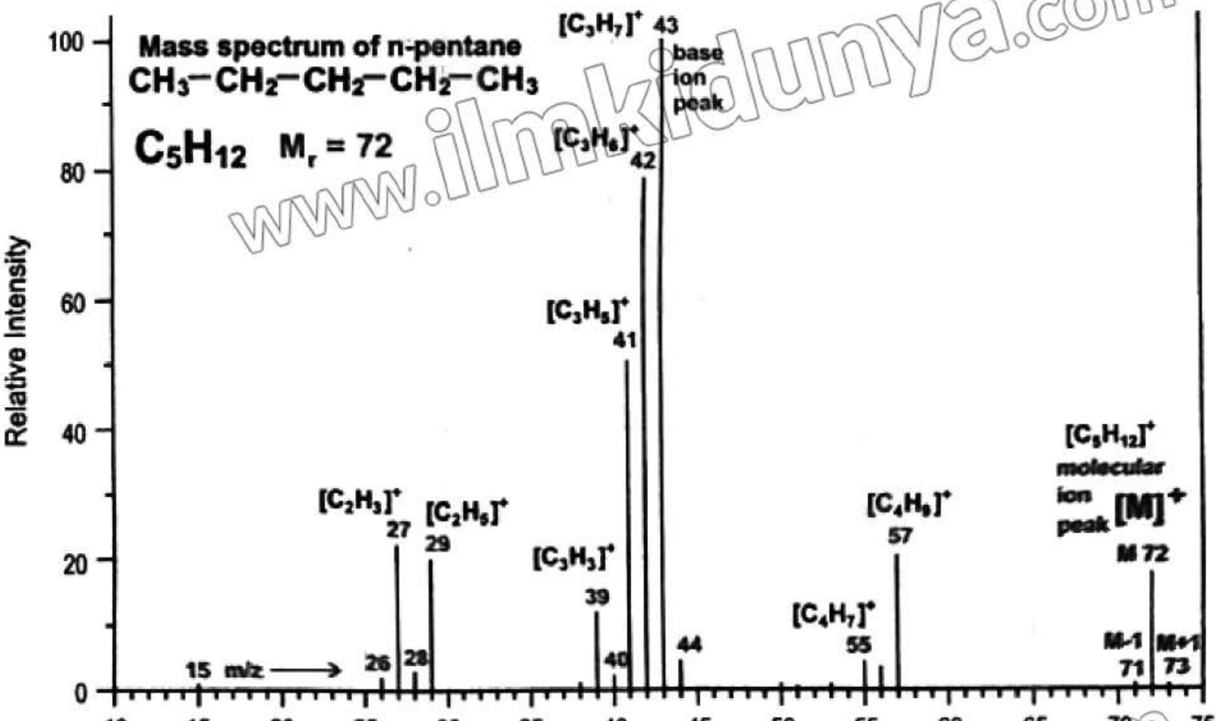


Fig 17.4: Mass spectrum of n-pentane

m/z=41 peak is formed 2 Hydrogen atoms from propyl cation to form propylene cation ($^+CH_2CH{=}CH_2$). Some stable ions are also formed by the rearrangement of unstable ions.

In the above fragmentation pattern of n-pentane given in the figure shows that molecular ion peak is formed at m/z=72. This molecular ion is fragmented by electron impact into ethyl radical and propyl cations. There are equal chances of the formation of ethyl cation(m/z=29) and propyl radical. During this fragmentation, CH_3^+ is also formed giving a peak at m/z=15. Thus the fragmentation pattern in the mass spectrum and molecular ion peak give considerable clues regarding the molecular structure.

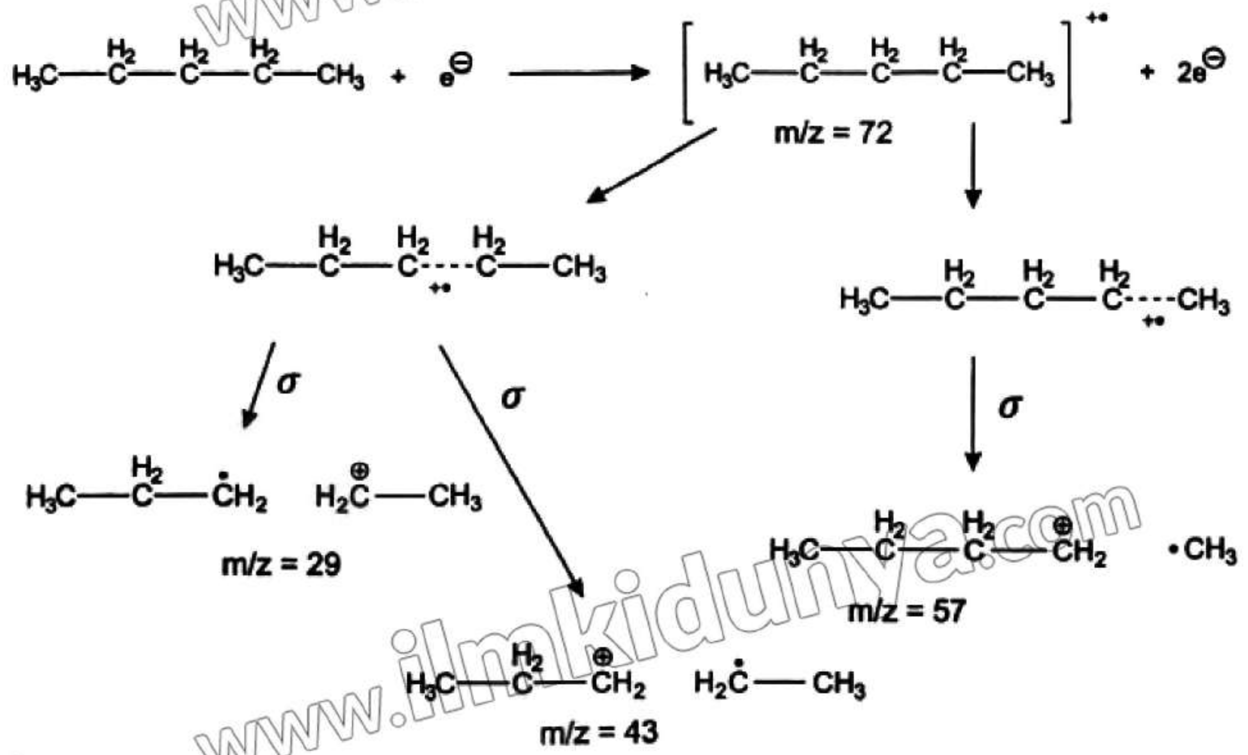


Fig 17.5: fragmentation pattern of n-pentane

Similarly for functional groups like alcohols, a peak with one less than the molecular ion peak M-1 appears by the loss of hydrogen from the OH group. By the loss of the OH group M-17 peak is obtained, this OH group can be a cation OH^+ giving rise to a peak at m/z=17 as well.

17. 5 Deduction of C-number in a molecule:

From intensities of the molecular ion and molecular ion plus one (M^+ +1), we can calculate the number of carbon atoms in a molecule by using the formula:

$$\text{Number of carbon-atoms} = \frac{100 \times \text{abundance of M+1 peak}}{1.1 \times \text{abundance of } M^+ \text{ peak}}$$

Example: Determine the molecular formula of a molecule with a molecular ion peak of relative abundance of 27.32% and M+1 peak with a relative intensity of 2.10%.

Solution: By putting the values of relative intensities in the above formula we get:

$$\text{Number of carbon-atoms} = \frac{100 \times 2.10}{1.1 \times 27.32}$$

$$6.94 \cong 7$$

So there are seven carbon atoms in this molecule.

17.6 Deduction of the presence of Chlorine and Bromine in a molecule

Both Chlorine and Bromine have considerable relative abundances of their heavier isotopes, so they can be recognised by peaks of greater m/z in their mass spectra.

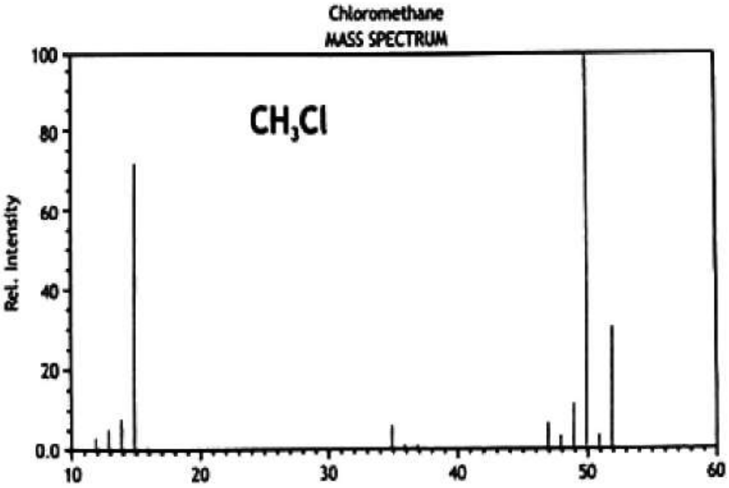


Fig 17.6: Mass spectrum of methyl chloride

Chlorine: The molecular ion peak (M^+) of chlorine appears at m/z = 35 due to greater relative abundance (75.77%). We get an additional peak of one-third height at M+2 due to the presence of heavy isotope Cl-37 with a relative abundance of 24.23%. The height of this peak confirms the presence of Chlorine.

The above spectrum of chloromethane shows the molecular ion peak at m/z=50 which is equivalent to molecular mass of CH_3Cl. Another considerable peak at m/z=52 represents the presence of heavy isotope Cl-37 with a relative abundance one third of the molecular ion peak.

Bromine: The two isotopes of bromine i.e. Br-79 and Br-81 have relative abundances of 50.50% and 49.50%, respectively. We should get molecular ion peak (M^+) at m/z=79 and another peak of approximately the same height at m/z= 81. This is the M+2 peak. As it is obvious from the mass spectrum of Bromoethane molecular ion peak appeared at m/z=108 which is equivalent to its molecular mass and the M^{+2} peak is slightly smaller at m/z= 110 representing the presence of heavier isotope Br-81.

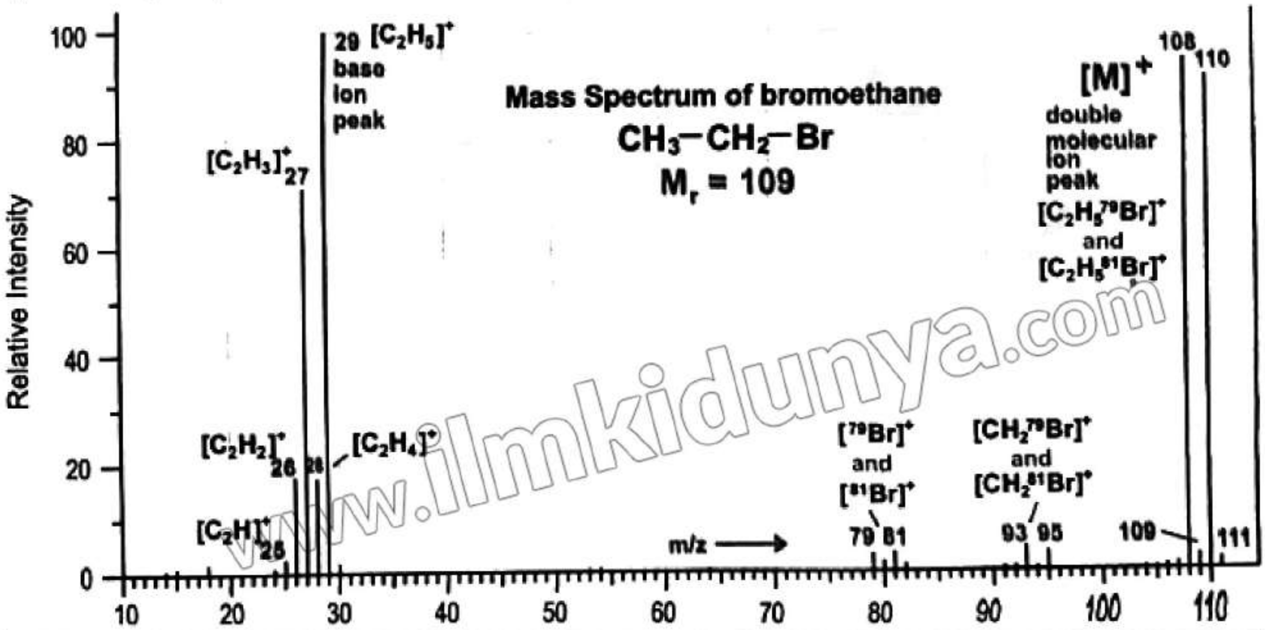


Fig 17.7: Mass spectrum of ethyl bromide

KEY POINTS

- Mass Spectrometry is a very useful tool to analyse relative abundances of the isotopes of an element in a compound.
- The number of peaks that appear on a proper m/z value in the mass spectrum tells us about the number of isotopes.
- The height of each peak tell us about the relative abundances of each isotope in terms of percentage.
- The molecular ion peak is the peak in a mass spectrum that represents the molecular ion (symbol: M^{+} Peak).
- By the impact of electrons from the electron gun on to the molecules, molecule undergoes fragmentation.
- We can calculate number of carbon atoms in a molecule by using a formula using the information obtained by mass spectrum.

References:

1. Mass Spectrometry by Jürgen H Gross, 2004
2. Introduction to spectroscopy byDonald L Pavia, 2008
3. Spectra imagine courtesy by Google images

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which is not the field of mass spectrometry?

a) Molecular mass

b) Relative abundance of isotopes

c) Concentration of molecules in a sample

d) Molecular structure elucidation

ii. Average atomic mass of an element can be calculated by using:

a) IR spectroscopy

b) b. UV visible spectroscopy

b) Mass spectrometry

c) d. Nuclear magnetic resonance spectroscopy

iii. Molecular mass of a compound cannot be deduced by:

a) Molecular ion peak b) Base peak

c) M+1peak d) M+2 peak

iv. Why is m/z value taken equivalent to mass?

a) Charge is zero b) Charge of ions is equal to+1

c) Charge of irons is equal to -1 d) Mass is very high as compared to charge

v. Fragments in mass spectrum are formed by the:
   a) Impact of electrons
   b) Impact of protons
   c) Chemical rearrangements
   d) Both A and C

vi. Bromine can be recognised by:
   a) Molecular ion peak
   b) M+1 peak
   c) M+2 peak
   d) M-1 peak

1. Short Answer Questions

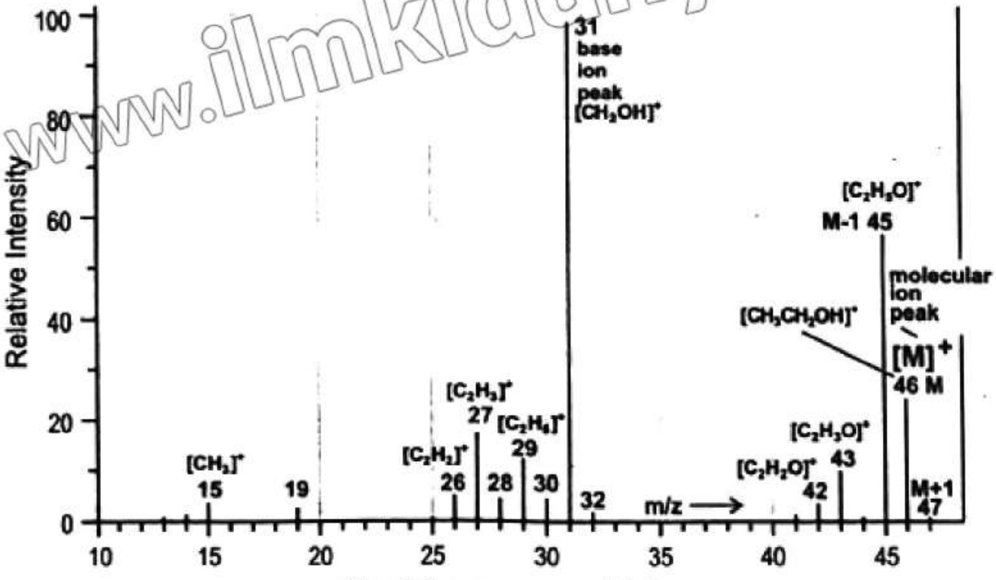
i. How can you calculate average atomic mass of an element using relative abundance is of all isotopes?

ii. How the number of carbon atoms in a molecule can be calculated by using intensities of the peaks in mass spectrum?

iii. How can you identify the presence of chlorine and bromine in the molecule using mass spectrum?

iv. What is the role of molecular ion peak in the determination of molecular mass of a substance?

v. Observe following mass spectrum of an organic compound "g" carefully and answer the given questions.



MS of the compound "g"

a. Write few reactions that help to understand the fragmentation pattern of the sample molecule "g" whose MS is given.

b. Why is the peak at m/z 47 is not the molecular ion peak?

c. What do you mean by a base-peak?

d. What is the structural formula of the molecule g?

2. Long Answer Questions

i. Analyse in detail, the information obtained by the fragmentation pattern in mass spectrum, used for the structural elucidation of a molecule.