

## 8. MASS SPECTROMETRY

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### INTRODUCTION

Mass or molecular weight of a compound can be found in several ways. One such technique is using Mass Spectrometer. Not only for determination of Mass, but the technique can be used for structure elucidation, Quantitative analysis and even advanced studies could be done by using Mass spectrum of a compound.

### PRINCIPLE

Mass spectra is also called as Positive ion spectra or line spectra. Unlike other kinds of spectroscopy, we **do not** use any Electro Magnetic Radiation (**EMR**) for excitation. We use electron bombardment to convert a neutral molecule to a positive charged one. Also there is **no ground** or **excited state** like other types of spectroscopy.

Obtaining mass spectra consists of **2 steps**:

1. Conversion of neutral molecule into a charged molecule, preferably to a positively charged molecule.
2. Separation of the positively charged fragments formed, based on their masses, by using electrical or magnetic field or both.

The sample is bombarded with high energy electron beam (70eV), where an electron is knocked off from every molecule. Hence the molecule

becomes positively charged. When a positive potential (accelerating potential) is applied, as the molecules are positively charged, they get repelled and travel with great speed, in a straight path.

Potential energy = Kinetic energy of molecule

$$eV = \frac{1}{2} mv^2$$

where  $e$  = charge of ion

$V$  = acceleration voltage

$m$  = mass

$v$  = velocity after acceleration

When a magnetic field or an electric field is applied, the positive charged fragments which were travelling in straight path, now travels in a curved path. When they travel in a curved path under the influence of mag.field, the fragments are separated into different masses because the radius of curvature depends upon their respective masses.

Under magnetic field,

$$Hev = \frac{mv^2}{r}$$

$$\therefore v = \frac{reH}{m}$$

where  $r$  = radius of ion path

$H$  = strength of mag. field

$e, m, v$  = as described earlier

Substituting the value of  $v$  in the first equation, (i.e.  $eV = \frac{1}{2}mv^2$ ),

$$eV = \frac{1}{2} \times m \times \left( \frac{reH}{m} \right)^2$$

On simplifying, 
$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$

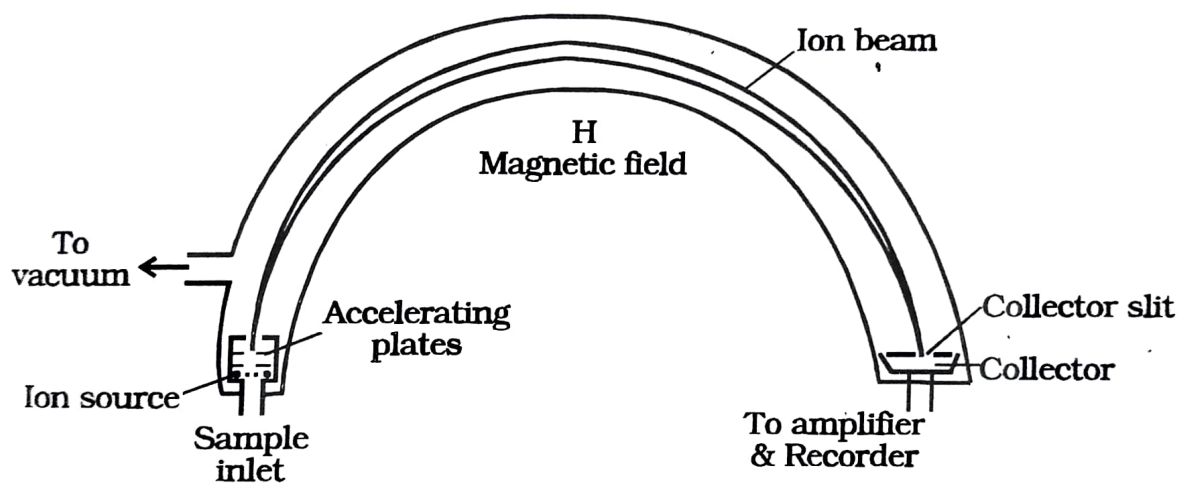
$$\frac{m}{e} \propto r^2 \text{ since } H \text{ \& } V \text{ are maintained constant}$$

$$\therefore \text{Mass} \propto (\text{radius of ion path})^2, \text{ since } e = 1 \text{ (unit positive Charge)}$$

## INSTRUMENTATION

The diagram of a single focussing, Electron impact Mass Spectrometer is shown in Fig 8.1.

**Fig 8.1. Electron impact Mass Spectrometer (single focussing)**

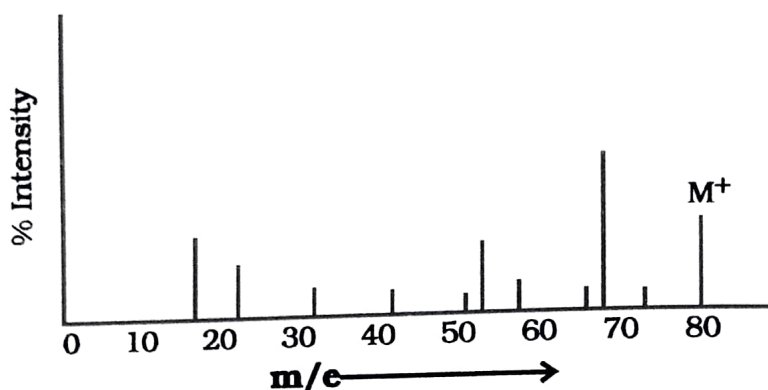


It has a horse shoe shaped glass tube which is evacuated. It has sample inlet, electron bombarding source and accelerating plates on one end. At the other end, collector slit is present. At the curvature of the tube, there is provision to apply electrical or magnetic field.

Sample in the form of vapour is allowed through sample inlet. This sample is bombarded with electron beam at 70eV. This knocks off one electron from every molecule. As these molecules become positive charged, they are accelerated by accelerating plates which also have positive charge. These accelerated molecules travel in a straight path. But because of the application of either electrical field or magnetic field, they travel in curved path. When they travel in curved path, the positive charged molecular ions are separated according to their mass  $\left(\frac{m}{e} \propto r^2\right)$ . These separated ions are

collected using a collecting slit. The different fragments fall on detector and a mass spectrum is recorded (Fig 8.2).

**Fig 8.2. Mass spectral pattern**



## TYPES OF MASS SPECTROMETERS

1. **Electron impact Mass Spectrometer (EIMS):** which is of 2 types
  - a. **Single focussing type** - Where only magnetic field is used for separation of fragments of different masses. These have resolution of 3000, which means that it is possible to record mass of two components/fragments with a difference of 0.0003 (or 1/3000).
  - b. **Double focussing type** - where magnetic field as well as electrical field is used successively to separate the fragments of different masses with a difference of even 0.000025 (Resolution = 40,000).
2. **Chemical ionisation Mass Spectrometer (CIMS):** in which a reactant gas is used to obtain positive charged ions from neutral molecule. (eg.) Methane, Ammonia or Isobutane is used as reactant gas.
3. **Field Ionisation Mass Spectrometer**
4. **Field desorption technique**
5. **Plasma desorption technique**
6. **Laser Mass Spectrometer** (Laser induced ionisation or Laser desorption ionisation).



## TYPES OF PEAKS

1. **Parent peak, Mass peak or molecular ion peak:** (often called  $M^+$  or  $P^+$ ). The peak normally with highest  $m/e$  value (x-axis) is called as  $M^+$ .
2. **Base peak:** The most intense peak (tallest on y-axis) is called as base peak.
3. **M+1 peak:** It occurs due to the presence of  $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{15}\text{N}$ ,  $^{33}\text{S}$
4. **M+2 peak:** It occurs due to the presence of  $^{18}\text{O}$ ,  $^{34}\text{S}$ ,  $^{37}\text{Cl}$ ,  $^{81}\text{Br}$

## APPLICATIONS

1. **Structure elucidation:** Using Nitrogen rule, peak matching, fragmentation pattern of compound and % abundance of isotopes, structure elucidation of organic compounds can be done.
2. **Detection of impurities:** Impurities present can be detected by the additional peaks, highest value of mass peaks than compound itself, and from the fragmentation pattern.
3. **Quantitative analysis:** The intensity of peaks correspond to the proportion of fragments. By comparing with standard drug, the quantity of sample can be estimated.
4. **Drug metabolism studies:** By recording the mass spectrum of metabolite and that of pure drug, the metabolism of the drug can be known.
5. **Clinical, Toxicological and Forensic applications:** Very minute quantities of the drug can be used to find out mass and hence the substance can be identified from the mass spectral pattern.