Mass spectrometry

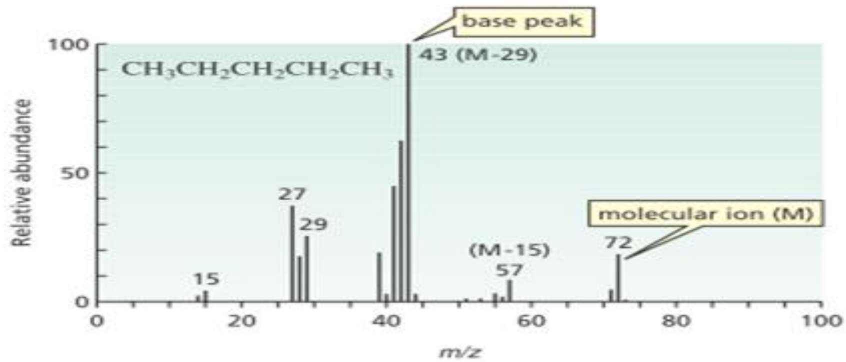
is a powerful technique , that allows us to determine the **molecular mass** and the **molecular formula** of a compound, as well as certain **structural features** of the compound.

Principle of operation

In mass spectrometry, a small sample of a compound is introduced into an instrument called a mass spectrometer, where it is vaporized and then ionized by bombarding a molecule with high energy electron beam (70 eV) usually around 1600 kcal/mol, When a high–energy electron strikes the molecule, it causes one of the electrons in the molecule to be ejected. This technique, called **electron impact ionization** (**EI**), generates a high-energy intermediate that is both a
radical and a cation (molecularmolecular ion: radical cation (M)+•).

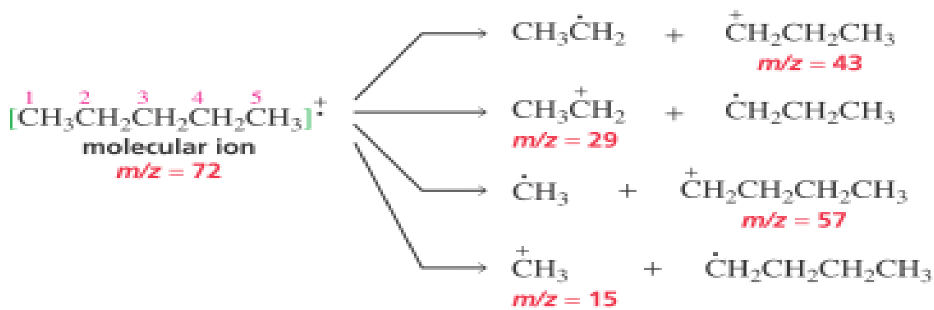
Therefore, many of the molecular ions break apart into **cations, radicals, neutral molecules, and other radical cations.** The bonds most likely to break are the weakest ones and those that result in the formation of the most stable products. All the positively charged fragments of the molecule accelerated toward collector and to the detector .Whereas, neutral fragments are not accelerated, they are eventually pumped out of the spectrometer. The mass spectrometer records a mass spectrum a graph of the relative abundance of each fragment plotted against its (m/z) value. Because the charge (z) on essentially all the fragments that reach the collector plate is (+1), (m/z) is the molecular mass (m) of the fragment. Remember that only positively charged species reach the collector.

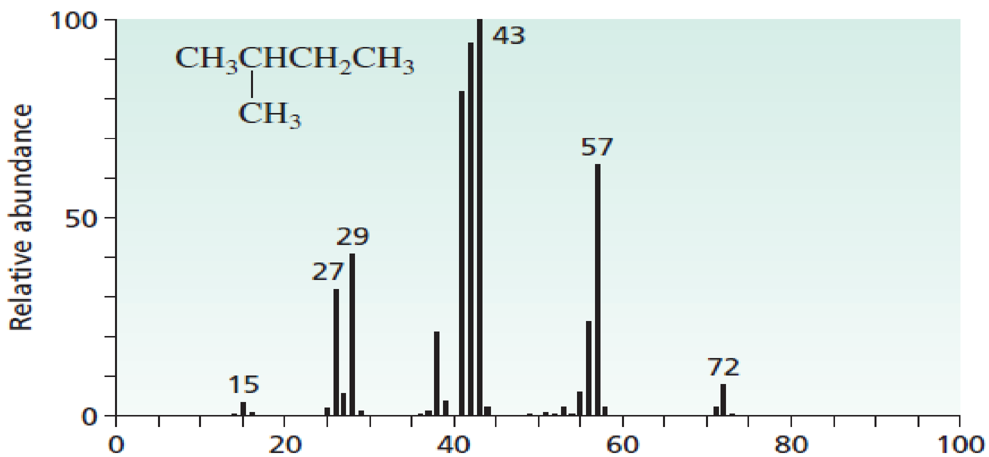
For example: The mass spectrum of pentane, shown as a bar graph and in tabular form. The base peak (relative intensity of 100%) represents the fragment that appears in greatest abundance. The (m/z) value of the molecular ion gives the molecular mass of the compound.



m/z	Relative abundance
73	0.52
72	18.56
71	4.32
57	11.20
43	100.00
42	55.27
41	37.93
39	12.44
29	26.65
28	17.75
27	31.22
15	4.22
14	2.56

The way a molecular ion fragments depends on the strength of its bonds and the stability of the fragments.

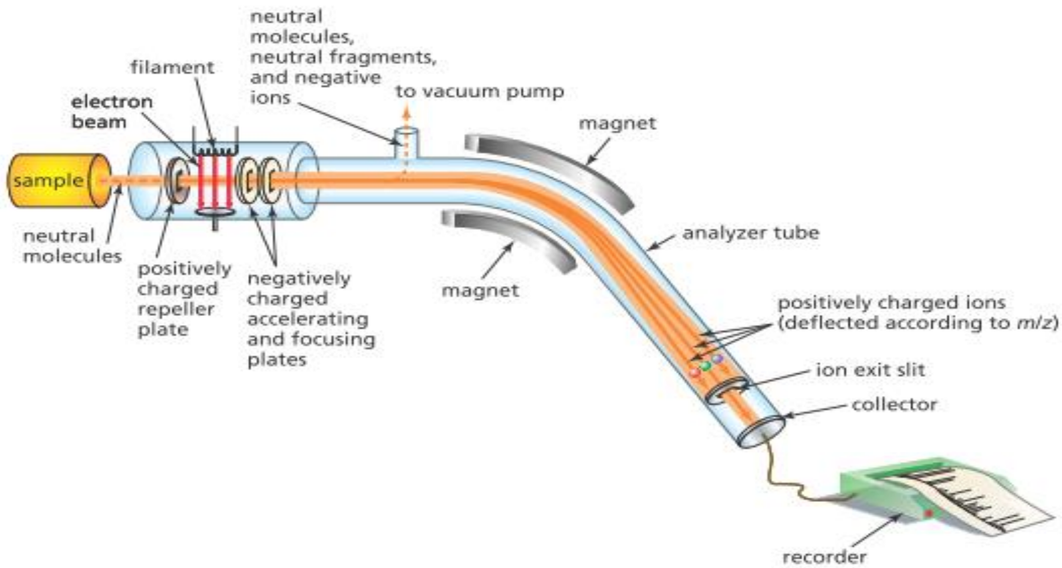




Instrumentation:

There are different types of mass spectrometer; each has different advantages, draw-backs and applications. All consist of five major sections linked together (figure below):

Inlet – Ionization source – Analyzer – Detector- Computer system.



A sample studied by mass spectrometry may be a gas, a liquid, or a solid. Enough of the sample must be converted to the vapor state to obtain the stream of molecules that must flow into the ionization chamber. With gases, of course, the substance is already vaporized, so a simple inlet system can be used.

The same system can be used for volatile liquids or solids. For less-volatile materials, the system can be designed to fit within an oven, which can heat the sample to increase the vapor pressure of the sample. Care must be taken not to heat any sample to a temperature at which it might decompose.

With nonvolatile samples, other sample inlet systems must be used. A common one is the direct probe method. The sample is placed on a thin wire loop or pin on the tip of the probe, which is then inserted through a vacuum lock into the ionization chamber. The sample probe is positioned close to the ion source. The probe can be heated, thus causing vapor from the sample to be evolved in proximity to the ionizing beam of electrons.

The most versatile sample inlet systems are constructed by connecting a chromatograph to the mass spectrometer such as:

Gas chromatography–mass spectrometry (GC-MS) and high-performance liquid chromatography–mass spectrometry (HPLC-MS, or more simply LC-MS).

Isotope ratio data

A method of determining molecular formulas is to examine the relative intensities of the peaks due to the molecular ion and related ions that bear one or more heavy isotopes (the molecular ion cluster), determination of M+1, M+2, and M+4……depending on the table of relative abundances (table below). The advantages of this method is that, does not require the much more expensive high-resolution instrument. This method is useless, of course, when the molecular ion peak is very weak or does not appear.

NATURAL ABUNDANCES OF COMMON ELEMENTS AND THEIR ISOTOPES

Element	Relative Abundance					
Hydrogen	^{1}H	100	^{2}H	0.016		
Carbon	^{12}C	100	^{13}C	1.08		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.20
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.10	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.40
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98.0
Iodine	^{127}I	100				

The relative intensities of M + 1 and M + 2 peaks can be estimated quickly using simplified calculations. The formula to calculate the M + 1 peak intensity (relative to M+= 100) for a given formula is found in Equation (1) . Similarly, the intensity of an M + 2 peak intensity (relative to M+= 100) may be found by using equation (2):

$$[M+1] = (\text{number of C} \times 1.1) + (\text{number of H} \times 0.015) + (\text{number of N} \times 0.37) + (\text{number of O} \times 0.04) + (\text{number of S} \times 0.8) + (\text{number of Si} \times 5.1) \quad \text{……eq.1}$$

$$[M+2] = \frac{(\text{number of C} \times 1.1)^2}{200} + (\text{number of O} \times 0.2) + (\text{number of S} \times 4.4) + (\text{number of Si} \times 3.4) \quad \text{…..eq.2}$$

Q1: Calculate the M+1 and M+2 of propene and diazimethane, CO, N2 and ethene?

Problem: Calculate the M+1 and M+2 of C7H16 ? Mw= 100.

M+1% = 1.1x 7 + 16x 0.015 = 7.7

M+2%= $(M+1)^2/200= 7.7^2/200= 0.3$

Thus:			
	base peak	100	100%
	M+1	101	7.7%
	M+2	102	0.3%

Q2/ Mw=18, M+1=0 and M+2=0.2 deduce the structure?

Q3/ Calculate the M+1 and M+2 of C3H6O?

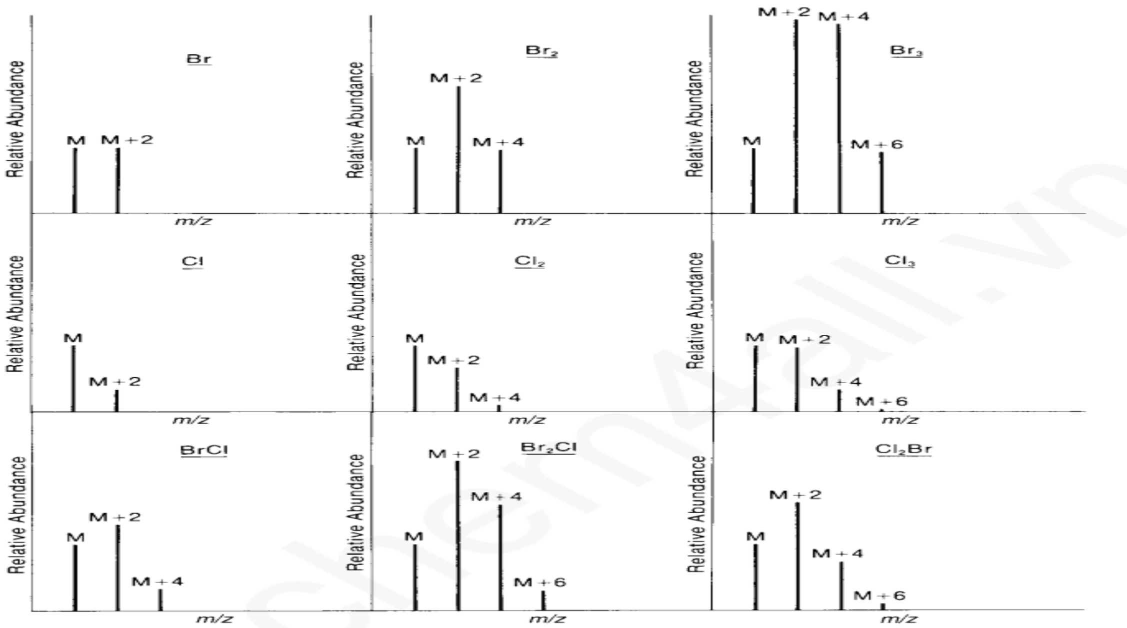
When chlorine or bromine is present, the M + 2 peaks become very significant. The heavy isotope of each of these elements is two mass units heavier than the lighter isotope. The natural abundance of 37Cl is 32.5% that of 35Cl, and the natural abundance of 81Br is 98.0% that of 79 Br. When either of these elements is present, the M + 2peak become quite intense. If a compound contains two chlorine or bromine atoms a distinct M+2 and M+4 should be observed. Table below:

	Relative Intensities			
Halogen	***M***	***M + 2***	***M + 4***	***M + 6***
Br	100	97.7		
Br_2	100	195.0	95.4	
Br_3	100	293.0	286.0	93.4
Cl	100	32.6		
Cl_2	100	65.3	10.6	
Cl_3	100	97.8	31.9	3.47
BrCl	100	130.0	31.9	
Br_2Cl	100	228.0	159.0	31.2
Cl_2Br	100	163.0	74.4	10.4

Q4/ Calculate the M+1 and M+2 of MeBr?

Q5/ Deduce the MF of the compound that has: Mw:

132:100%, 133:2.2%, 134:100%, 135:2.25, 136:34%,137: 0.8%, 138: 4.4%.



Q6/ Deduce the MF of the compound that has

Mw: 157 =100% , M+1: 158=8.264%,   M+2: 159=33%.

Because M+1= 8.248 means less than eight carbons

7x 1.1= 7.7   7x12= 84

8.248-7.7= 0.548

0.548-0.38= 0.168 for 1N   14

0.168-0.04= 0.128 for O   16

0.128 = 8x0.016 for 9H   9

123

158-123= 35 for 1Cl

M+2= 33%   33-32.5= 0.5 for C and O.

The MF= C7H8NOCl

M+1:

C: 7.7 x 1.1= 7.7

N: 1x 0.38= 0.38

O: 1x0.04 = 0.04

H: 8x 0.016= 0.128

M+1= 8.248

M+2=

C: $(7.7)^2/200$= 0.3

O: 1x 0.2= 0.2

Cl: 1x 32.5= 32.5

M+2= 33%

Q7/ Deduce the MF of the compound that has: Mw: 156=24.4%, 157= 1.3%, 158=15.8%, 160=2.6%

Q8/ An unknown substance shows a molecular ion peak at mle = 170 with a relative intensity of 100.TheM+ 1peak has an intensity of 13.256, and the M+ 2 peak has an intensity of 1.00. What is the molecular formula of the unknown?

Q9/ An unknown hydrocarbon has a molecular ion peak at m/e = 84, with a relative intensity of 31.3. TheM+1peak has a relative intensity of 2.06, and theM+ 2 peak has a relative intensity of 0.08.What is the molecular formula for this substance?

Q10/ An unknown substance has a molecular ion peak at m/e = 107, with a relative intensity of 100.The relative intensity of theM+ 1peak is 8.00, and the relative intensity of the M+ 2 peak is 0.30.What is the molecular formula for this unknown?

Q4/ The mass spectrum of an unknown liquid shows a molecular ion peak at m/e = 78, with a relative intensity of 23.6. The relative intensities of the isotopic peaks are as follows.

m/e =79	Relative intensity= 0.79
80	7.55
81	0.25

What is the molecular formula of this unknown?

Q11/ An unknown compound has the mass spectrum shown,deduce the structure.