mass spectrometry

mass spectrometry

is used to determine the structures of organic compounds:

1. finding the molecular formula of a compound by measuring the mass of its molecular ion to a high degree of accuracy

mass spectrometry

2. finding the number of carbon atoms in a molecule by measuring the abundance ratio of its molecular ion (M) peak and the M+1 peak

mass spectrometry

3. finding whether a compound contains chlorine or bromine atoms, and if so, how many of each, by measuring the abundance ratios of the M+2 and M+4 peaks

mass spectrometry

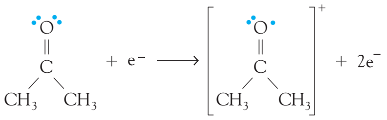
4. working out the structure of a molecule by looking at the fragments produced when an ion decomposes inside a mass spectrometer

6 Mr using mass spectrometry

If we vaporise an organic molecule and subject it to the ionising conditions inside a mass spectrometer, the mass/charge ratio (m/e) for the molecular ion can be measured, and hence the relative molecular mass can be found.

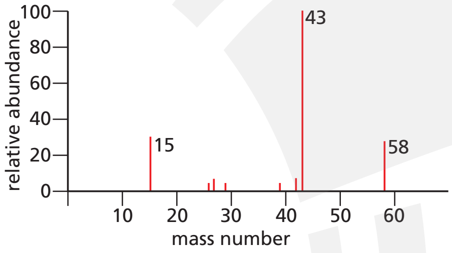
7 Mr using mass spectrometry

For example, one of the non-bonding electrons on the oxygen atom of propanone can be removed by electron bombardment, to give an ionised molecule:



The m/e ratio for the resulting molecular ion is 58.

8 Mr of propanone



9 the M+1 peak

There are two stable isotopes of carbon, ^{12}C and ^{13}C.

Their relative abundances are 98.9% for ^{12}C and 1.1% for ^{13}C.

This means that out of every 100 methane (CH_4) molecules, about 99 molecules will be $^{12}CH_4$ and just one molecule will be $^{13}CH_4$.

10 the M+1 peak

For ethane, C_2H_6, the chances of a molecule containing one ^{13}C atom will have increased to about 2 in 100,

because each C atom has a chance of 1 in 100 to be ^{13}C, and there are two of them.

11 the M+1 peak

The M peak of a molecule is due to all carbon atoms in the molecule being ^{12}C.

and the M+1 peak is due to one carbon atom being ^{13}C and the rest ^{12}C.

12 the M+1 peak

By measuring the ratio of the M to M+1 peaks, we can thus work out the number of carbon atoms the molecule contains.

The ratio approximately is **100 : 1.1(n)**
where n is the number of carbon atoms.

13 skill check 1

The molecular ion peak of a compound has an m/e value of 136, with a relative abundance of 17%, and an M+1 peak at m/e 137 where the relative abundance is 1.5%. How many carbon atoms are in the molecule?

14 skill check 2

A compound contains C, H and O atoms. Its mass spectrum has a peak at m/e 132 with a relative abundance of 43.9 and a peak at m/e 133 with a relative abundance of 2.9.

Calculate the number of carbon atoms in each molecule, and suggest its molecular formula.

15 the M+2 peak

Although fluorine and iodine each have only one stable isotope, chlorine and bromine have two. Their natural percentage abundances are shown below.

Element	Isotope	Natural abundance	Approximate ratio
chlorine	^{35}Cl	75.5	3 : 1
	^{37}Cl	24.5	
bromine	^{79}Br	50.5	1 : 1
	^{81}Br	49.5	

16 the M+2 peak

The mass spectrum of a compound containing one of these elements should therefore show two molecular ions,

one with an m/e value two mass units higher than the other.

17 the M+2 peak

The ratio of the M/(M+2) peak should reflect the natural abundances given in the table, i.e.

3:1 for chlorine;

1:1 for bromine.

18 the M+2 peak

the mass spectrum of CH_3Cl will have peaks:

for $CH_3{}^{35}Cl^+$ at m/e 50 (12 + 3 + 35 = 50) and

for $CH_3{}^{37}Cl^+$ at m/e 52 (12 + 3 + 37 = 52)

The relative abundances of the two peaks will be in the ratio 3:1 which is the ratio of the two Cl isotopes.

19 the M+2 peak

A similar situation occurs with bromine, although in this case the two molecular ion peaks will be of equal heights, since the isotopic abundance ratio is near to 1:1.

20 the M+2 peak

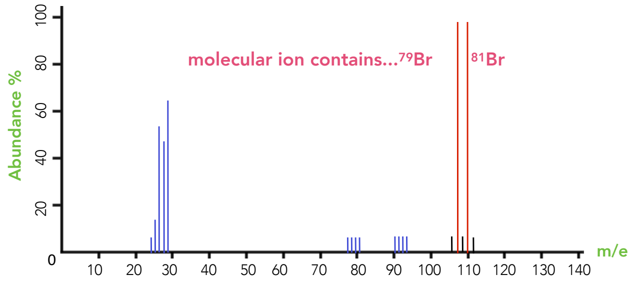
There are two peaks for the molecular ion of C_2H_5Br,

one for the molecule containing the isotope ^{79}Br (M)

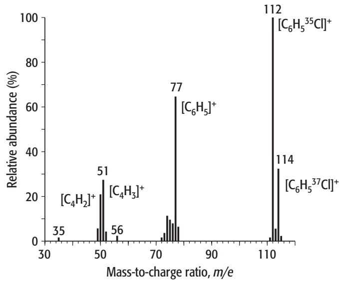
the other for the one with the ^{81}Br isotope (M + 2).

Because the two isotopes are of similar abundance, the peaks are of similar height.

21 M+2 peak examples



22 M+2 peak examples



23 The M+4 peak

If the molecule contains two chlorine atoms, (or two bromine atoms, or one of each) we should expect to see three molecular ions, at m/e values of M, M+2 and M+4.

24 The M+4 peak

Take the molecule 1,2-dibromoethane, $C_2H_4Br_2$.

Each carbon can be attached to either a ^{79}Br or a ^{81}Br atom, and there is a (roughly) equal chance of either.

We therefore arrive at the following possibilities, each of which is equally likely.

25 The M+4 peak

Formula	***m/e* value**	**Peak**
$^{79}BrCH_2CH_2{}^{79}Br$	186	M
$^{79}BrCH_2CH_2{}^{81}Br$	188	M + 2
$^{81}BrCH_2CH_2{}^{79}Br$	188	M + 2
$^{81}BrCH_2CH_2{}^{81}Br$	190	M + 4

There will thus be three molecular ion peaks, with relative abundances of 1:2:1.

26 The M+4 peak with Cl

Just as with dibromoethane, there will be four possible formulae for dichloromethane, CH_2Cl_2.

Formula	Ion reference	*m/e* value
$CH_2{}^{35}Cl^{35}Cl$	***a***	84
$CH_2{}^{35}Cl^{37}Cl$	***b***	86
$CH_2{}^{37}Cl^{35}Cl$	***c***	86
$CH_2{}^{37}Cl^{37}Cl$	***d***	88

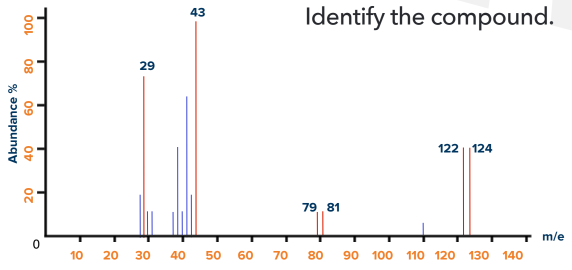
27 The M+4 peak with Cl

Formula	Ion reference	*m/e* value
$CH_2{}^{35}Cl^{35}Cl$	***a***	84
$CH_2{}^{35}Cl^{37}Cl$	***b***	86
$CH_2{}^{37}Cl^{35}Cl$	***c***	86
$CH_2{}^{37}Cl^{37}Cl$	***d***	88

The overall probabilities are therefore: 9:6:1

28 The M+4 peak with Cl

29 skill check 3



Identify the compound.

30 skill check 4

Compounds used as pesticides may contain bromine or chlorine.

(i) What would be the difference in the ratio of the M: M+2 peaks if the pesticide contained one chlorine rather than one bromine atom?

....

(ii) If a given pesticide contains **two** chlorine atoms per molecule, deduce the relative heights of the M, M+2 and M+4 peaks.

[3]

31 skill check 5

At one time, bromomethane, CH_3Br, was widely used to control insect pests in agricultural crops and timber. It is now known to break down in the stratosphere and contribute to the destruction of the ozone layer.

Samples can be screened for traces of bromomethane by subjecting them to mass spectrometry.

(i) Which peak(s) would show the presence of bromine in the compound?

....

(ii) How could you tell by studying the M and M+2 peaks that the compound contained bromine rather than chlorine?

....

....

[3]

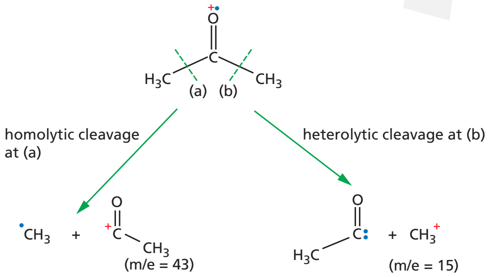
32 analysing molecular fragments

If the ionising electron beam in a mass spectrometer has enough energy, the molecular ions formed by the loss of an electron can undergo bond fission, and molecular fragments are formed.

33 analysing molecular fragments

Some of these will carry the positive charge, and therefore appear as further peaks in the mass spectrum.

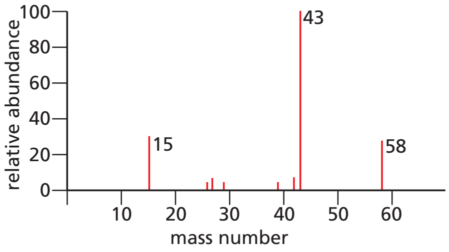
34 analysing molecular fragments



35 analysing molecular fragments

We therefore expect the mass spectrum of propanone to contain peaks at m/e = 15 and 43, as well as the molecular ion peak at 58

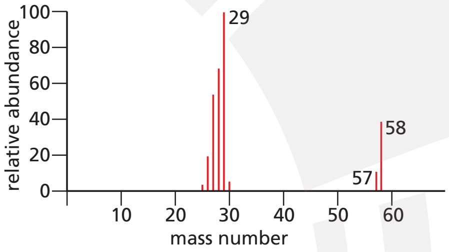
36 analysing molecular fragments



37 analysing molecular fragments

The fragmentation pattern can readily distinguish between isomers. Compare the following the mass spectrum of propanal.

38 analysing molecular fragments



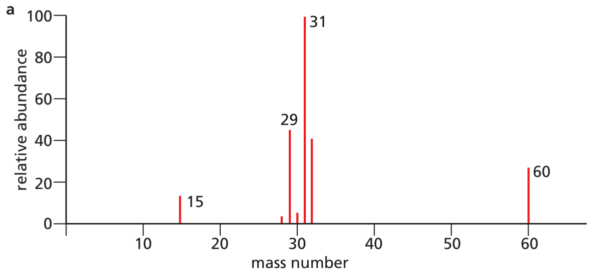
39 analysing molecular fragments

Here there is no peak at m/e = 15, nor one at m/e = 43. Instead, there is a peak at m/e = 57 and several from m/e = 26 to 29.

40 skill check 6

The following shows the mass spectra of two compounds with the molecular formula $C_2H_4O_2$. One is methyl methanoate, and the other is ethanoic acid. Decide which is which?

41 skill check 6



42 skill check 6