22.2 MASS SPECTROMETRY- NOTES

🎯 Learning outcomes

Candidates should be able to:

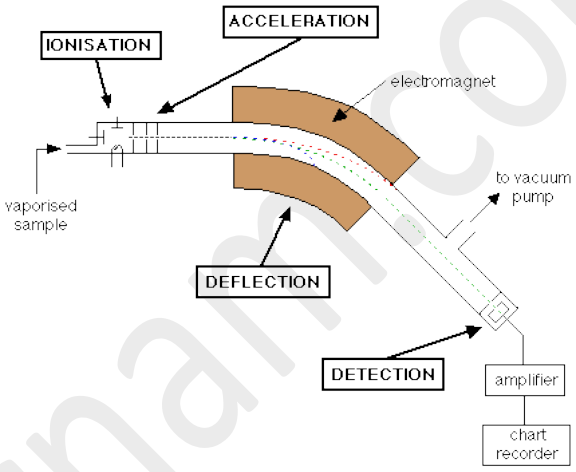
1. analyse mass spectra in terms of *m*/*e* values and isotopic abundances (knowledge of the working of the mass spectrometer is not required)
2. calculate the relative atomic mass of an element given the relative abundances of its isotopes, or its mass spectrum
3. deduce the molecular mass of an organic molecule from the molecular ion peak in a mass spectrum
4. suggest the identity of molecules formed by simple fragmentation in a given mass spectrum
5. deduce the number of carbon atoms, *n*, in a compound using the M +1 peak and the formula

   n =100 × abundance of M +1 ion/(1.1 × abundance of M + ion)
6. deduce the presence of bromine and chlorine atoms in a compound using the M +2 peak

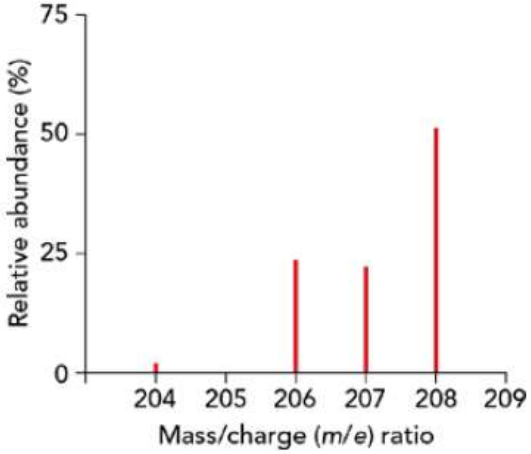
Introduction

A mass spectrometer can be used to measure the mass of each isotope present in an element. It also compares how much of each isotope is present: the relative abundance (**relative isotopic abundance**).

A mass spectrometer is a large and complex instrument.



The mass spectrum produced shows the relative abundance (isotopic abundance) on the vertical axis and the mass to ion charge ratio (*m /e*) on the horizontal axis. Figure 3.4 shows a typical mass spectrum for a sample of lead. Table 3.1 shows how the data is interpreted.



For singly positively charged ions, the (*m/e*) values give the nucleon number of the isotopes detected. In the case of lead, the table below shows that 52% of the lead is an isotope with an isotopic mass of 208. The rest is lead-204 (2%), lead-206 (24%) and lead-207 (22%).

Isotopic mass	Relative abundance / %
204	2
206	24
207	22
208	52
total	100

Determination of A_r from mass spectra

We can use the data obtained from a mass spectrometer to calculate the relative atomic mass of an element very accurately. To calculate the relative atomic mass, we follow this method:

- multiply each isotopic mass by its percentage abundance
- add the figures together
- divide by 100.

We can use this method to calculate the relative atomic mass of neon from its mass spectrum, shown in Figure below.

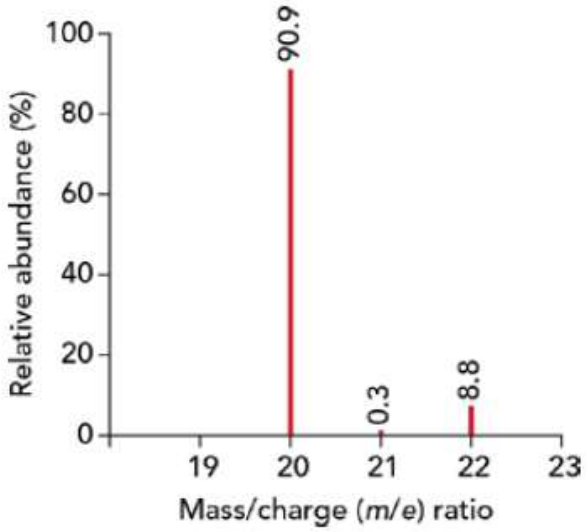


Figure: mass spectrum of Neon

The mass spectrum of neon has three peaks: ^{20}Ne (90.9%), ^{21}Ne (0.3%) and ^{22}Ne (8.8%).

$$A_r \text{ of neon} = \frac{(20 \times 90.9) + (21.0 \times 0.3) + (22 \times 8.8)}{100} = 20.2$$

Note that this answer is given to 3 significant figures, which is consistent with the data given.

A high-resolution mass spectrometer can give very accurate relative isotopic masses. For example, ^{16}O = 15.995 and ^{32}S = 31.972. Because of this high level of precision, chemists can distinguish between molecules such as SO_2 and S_2, which appear to have the same relative molecular mass.

Identification of an organic compound using mass spectrometry

The main use of mass spectrometry is in the identification of organic compounds. As in other forms of spectroscopy, a substance can be identified by matching its spectrum against the spectra of known substances stored in a database. This technique is known as 'fingerprinting'.

The high-energy electrons knock electrons from the molecules and break covalent bonds, fragmenting the molecule. Figure below shows the mass spectrum produced by propanone, CH_3COCH_3.

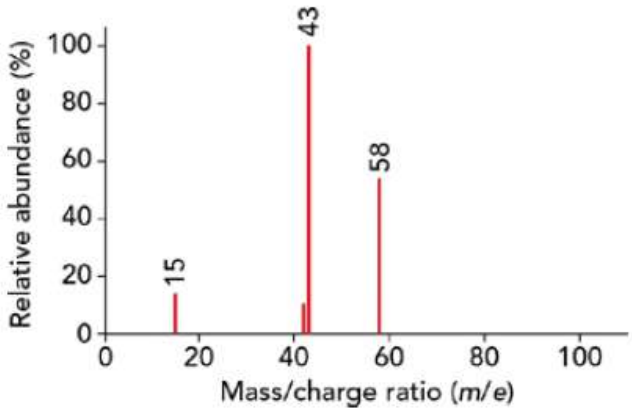
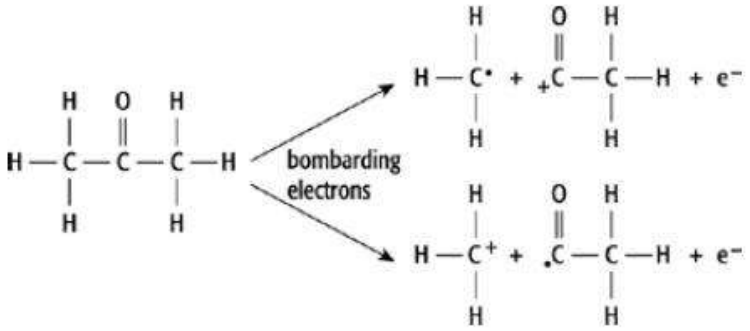


Fig: mass spectrum of Propanone (CH_3COCH_3)

The peak at the highest mass-to-charge ratio is caused by the **molecular ion** (M^+). This ion is formed by the sample molecule with one electron knocked out. It gives us the relative molecular mass of the sample.

We can assume the ions detected carry a single positive charge, so the reading on the horizontal axis gives us the mass. In the case of propanone, CH_3COCH_3, the molecular ion has a relative mass of 58.0. This corresponds to $CH_3COCH_3^+$, with a mass of (3 × 12.0) + (1 × 16.0) + (6 × 1.0).

We also get large peaks at 15 and 43 on the mass spectrum. These peaks are due to fragments that are produced when propanone molecules are broken apart by the electron bombardment. Knowing the structure of propanone, we should be able to identify the fragment responsible for each peak.



Molecular ion, *M*+, is formed when one electron is removed from a molecule to form an ion with a single positive charge e.g. $CH_4 \rightarrow CH_4^+ + e^-$. Remember that no atoms are removed.

Remember that fragmentation (breaking apart) of a compound in a mass spectrometer causes certain bonds to break. You can deduce what the fragment is by adding up the atomic masses of carbon, hydrogen and/or other atoms. So, a fragment of *m/e* 15 is C + 3H = 12 + (3 × 1) which is $^+CH_3$ and a fragment of *m/e* 43 could be $^+C_3H_7$ or CH_3CO^+.

The breaking of single bonds, such as C—C, C—O or C—N, is the most common cause of fragmentation.

These fragments are very common in mass spectra of organic compounds.

Mass	Fragment
15	$^+CH_3$
28	^+CO or $C_2H_4^+$

29	**$CH_3CH_2^+$**
43	**$C_3H_7^+$ or CH_3CO^+**

Deduce the number of carbon atoms, n, in a compound using the M +1 peak

and the formula

n =100 × abundance of M+1 ion/(1.1 × abundance of M^+ ion)

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 $^{13}CH_4$. 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. 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 formula relating the (M+1)/M ratio
to the number of carbon atoms is:

$$n = \frac{100}{1.1} \times \frac{(A_{M+1})}{A_M}$$

where, number of carbon atoms
the abundance of the M+1 peak, and
the abundance of the molecular ion peak.

The abundances of the M and M+1 peaks are sometimes quoted as percentages, and sometimes as the actual heights of the two peaks on a printout of the mass spectrum, in arbitrary units. The units do not matter, however, as it is only the ratio that is important.

Deduce the presence of bromine and chlorine atoms in a compound using the M +2 peak

We can tell whether there is chlorine or bromine in an organic compound by comparing the relative heights of the M and $[M + 2]$ peaks. **If the peak heights are equal, there is one atom of bromine per molecule. If the peak heights are in the ratio 3 [M] to 1 [$M + 2$], there is one atom of chlorine per molecule.**

The M+2 and M+4 peaks

Although fluorine and iodine each have only one stable isotope, chlorine and bromine have two. Their natural percentage abundances are shown in Table 20.3.

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	

Any compound containing one chlorine atom will therefore have two 'molecular ion' peaks, one due to molecules containing ^{35}Cl and the other due to molecules containing ^{37}Cl. For example, the mass spectrum of chloromethane, CH_3Cl, will have peaks at m/e 50 (12 + 3 + 35 = 50) and at m/e 52 (12 + 3 + 37 = 52), corresponding to the species $CH_3{}^{35}Cl^+$ and $CH_3{}^{37}Cl^+$. The relative abundances of the two peaks will be in the ratio
3:1, which is the ratio of the two Cl isotopes.
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.
Mass spectra are slightly more complicated when the molecule contains more than one halogen. The simplest situation is that for two bromine atoms. 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 possibilities in Table 20.4, each of which is equally likely.

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.

.....