Anglo-Chinese Junior College
Department of Chemistry

Mass Spectrometry

Prepared by: ACJC Chemistry Department

No.	References
1	K. B. Yeong; Mass Spectrometry Lecture Notes; ACJC; 2008
2	J. McMurry; Organic Chemistry; Brooks/Cole Publishing Company; 3rd Edition; 1992

Learning Outcomes	Section
Candidates should be able to:	
(a) outline the basic pinciples of the mass spectrometry, with reference to	2
(i) ionisation and fragementation	
(ii) mass/charge ratio, m/z	
[Detailed knowledge of instrumentation is **not** required]	3
(b) understand the following features and use them in the interpretation and prediction of mass spectra:	4.1, 4.3
(i) molecular ion peak	
(ii) isotopic abundances including the use of (M+1) peak caused by 13C and (M+2) and (M+4) peaks for the identification of halogen compounds	5
(iii) major fragement ions	4.3
[fragment ions obtained from rearrangements are **not** included]	

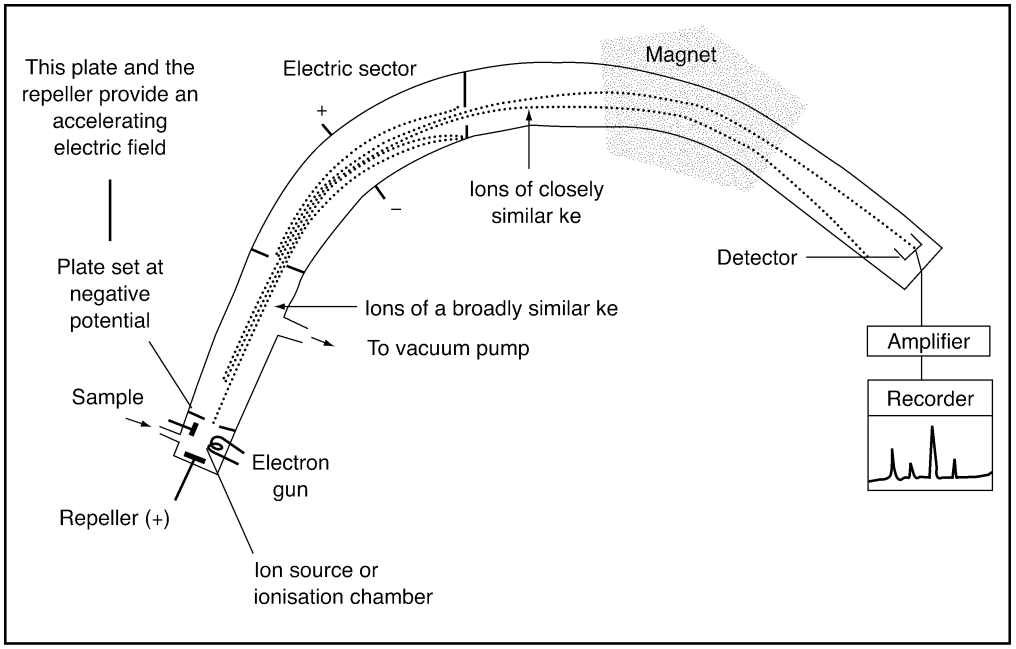
1. **Introduction**

Mass spectrometry is not strictly a branch of spectroscopy as it does not involve the absorption of electromagnetic radiation. Mass spectrometry is one of the most useful and valuable analytical techniques used in Chemistry and Biochemistry to determine the chemical structure and formula of compounds, particularly organic compounds.

The principle of mass spectrometry is very simple, although modern mass spectrometers are very sophisticated, precision-made instruments, capable of determining molecular masses to an accuracy of 1 part in 100,000. In addition, it is often possible to gain information about an unknown structure by measuring and identifying the masses of fragments produced when high-energy molecules fly apart. Structures of large complex unknown organic molecules can thus be elucidated.

2. Basic Features of Mass Spectrometer

(b) outline the basic principles of mass spectrometry, with reference to
  (i) ionisation and fragmentation
  (ii) mass/charge ratio, m/z



The double-focusing mass spectrometer

Figure 1: Double-focusing Mass Spectrometer

Six processes occur in a double-focussing mass spectrometer (see figure 1):

1. The compound is first dissolved in a solvent and injected into the mass spectrometer. Once in the mass spectrometer, the compound is vaporised in an oven. Since the interior of the instrument is kept under a high vacuum, only a small vapour pressure is required. Thus, mass spectrometry can be used even when only a small amount of the compound is available.

2. Low energy electrons (70 eV) from the electron gun are then fired at the gaseous molecules and knock off other electrons from some of the molecules producing **radical cation**. When a molecule loses one electron, it then has a positive charge and one unpaired electron. This ion is called a radical cation:

$$M + e^- \rightarrow M^{+\cdot} + 2\ e^-$$

In addition to ionising a molecule, the impact of an energetic electron may cause the molecule to break apart. This fragmentation process gives a characteristic mixture of ions (**molecular ion and fragment ions**).

3. The gaseous ions are accelerated by passing through an electric field (at a voltage of 5-10 kV).

4. The fast-moving ions now pass through the poles of an electromagnet, where they are deflected. **The deflections are proportional to the ions' charge to mass ratios.** If all ions have a +1 charge (which is usually the case) the extents of deflection will be inversely proportional to their masses.

5. The deflected ions pass through a narrow slit and are collected on a metallic plate connected to an amplifier. For a given strength of magnetic field, only ions of a certain mass pass through the slit and hit the collector plate. As the (positive) ions hit the plate, they cause a current to flow through the amplifier. The more ions there are, the larger the current.

6. A mass spectrum is produced, which plots *relative (or percentage) abundance* against ***mass/charge (m/e) ratio***.

Important Features of Mass Spectrum

Mass spectrum of a compound is usually presented as a vertical bar graph.

(i) Vertical axis
Signal intensity or peak height, measures the **relative abundance** of the ion which gives rise to the peak.

(ii) Horizontal axis (x –axis)
mass/charge or **m/e** ratio. Since e (charge of the ion = +1) the m/e values are, therefore, the masses of ions responsible for the peak.

(iii) Base peak
Tallest peak. It is arbitrarily assigned an intensity of 100%, and all other peaks are reported relative to its intensity. The base peak usually corresponds to a particularly **stable fragment** of the molecules under investigation.

(iv) Parent peak (or molecular ion peak)
The peak that corresponds to the unfragmented cation radical is called the parent peak or the **molecular ion peak**.

3. Relative Atomic Mass of an Element

The following information can be obtained from the mass spectrum of a monoatomic element:

Information	Evidence from mass spectrum
• number of isotopes present in the element	• number of peaks or lines
• relative isotopic mass of each isotope	• m/e value of each peak
• relative abundance of each isotope	• height of each peak

A_r of an element = sum of (relative isotopic mass x relative abundance)
= sum of (m/e value x relative abundance)

$$A_r = \frac{\sum(\text{isotopic mass} \times \text{relative abundance})}{\text{total abundance}}$$

An analysis of the mass spectrum of an element allows us to calculate its relative atomic mass, A_r.

For elements with only one isotope, only one peak is obtained, e.g. Na.

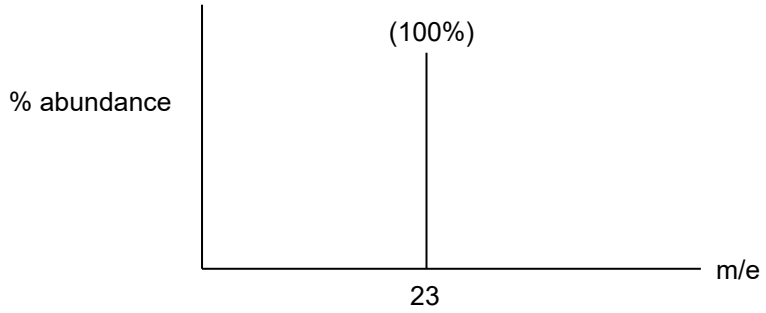


Figure 2: Mass spectrum of Na

For elements with more than one isotope, several peaks corresponding to ions of different isotopes are obtained, e.g. Fe.

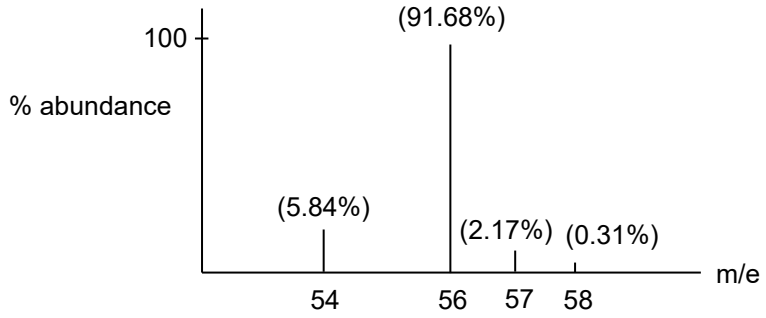
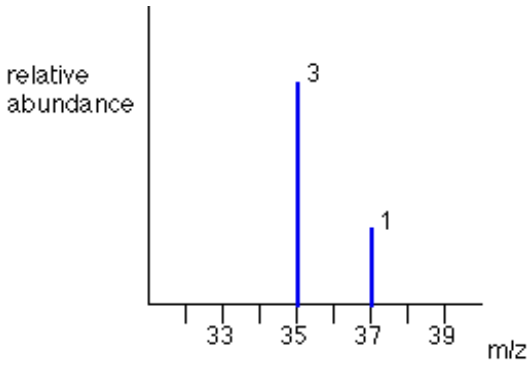


Figure 3: Mass spectrum of Fe

The m/e value of each peak corresponds to the relative isotopic mass of each isotope. The relative intensity (height) of each peak corresponds to the natural relative abundance of that isotope.

Example 3.1
The mass spectrum of chlorine is as shown:



i) How many isotopes of chlorine are there? **2**

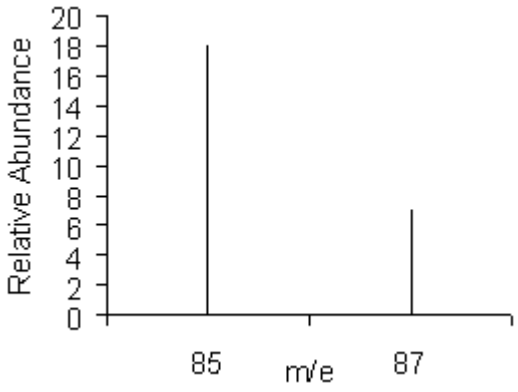
ii) Write down their relative isotopic masses. **35, 37**

iii) Which is the more abundant isotope? **^{35}Cl**

iv) Calculate the relative atomic mass of chlorine.

$$\left(\frac{3}{4}\times 35\right)+\left(\frac{1}{4}\times 37\right) = 35.5$$

Quick Check 1
The figure shows the mass spectrum of elemental rubidium.



i) State the isotopes present in rubidium.

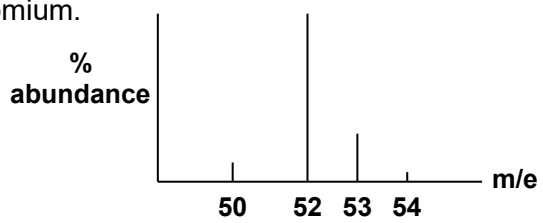
ii) Calculate the respective percentage abundance of each isotope

iii) Calculate the relative atomic mass of rubidium.

Example 3.2
Given

Isotope	% abundance
^{50}Cr	4.31
^{52}Cr	83.76
^{53}Cr	9.55
^{54}Cr	2.38

i) Sketch the mass spectrum that would be obtained from naturally occurring chromium.



ii) Calculate the relative atomic mass of chromium, correct to 3 significant figures.

$$A_r\,(Cr) = \frac{4.31}{100}\times 50 + \frac{83.76}{100}\times 52 + \frac{9.55}{100}\times 53 + \frac{2.38}{100}\times 54 = 52.1$$

4. Relative Molecular Mass of Molecules

(c) Understand the following features and use them in the interpretation and prediction of mass spectra: (ii) Molecular ion peak

The mass spectra of molecules provides the following information:

(a) **identity of molecular ion** (**parent ion**) M^+ and hence the **relative molecular mass** of the molecule
This identity is obtained from the largest m/e value, which corresponds to the M_r.

(b) **identity of charged fragments** of the molecule
These lines are produced when the parent ion breaks up to smaller fragments (*fragmentation*). This identity is obtained from m/e values of other peaks.

The following shows the mass spectrum of methanol, CH_3OH.

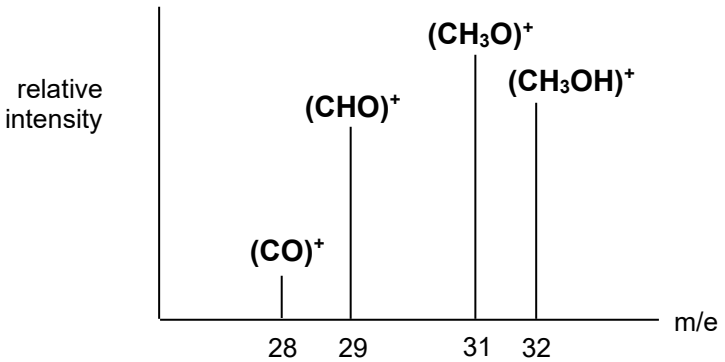


Figure 4: Mass spectrum of CH_3OH

There are three main ways in which mass spectrometry is applied to the determination of the structures of organic compounds:

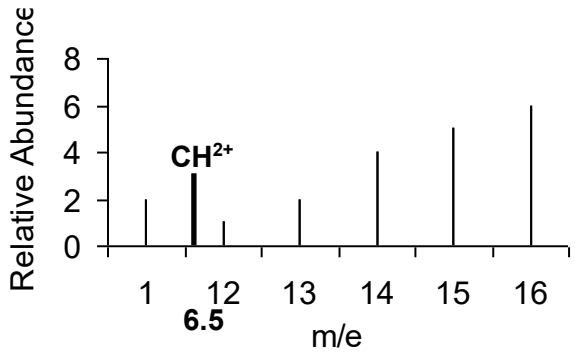
1. By measuring the accurate mass of a molecular ion, we can determine its molecular formula.

2. By identifying the fragments produced when an ion breaks up inside a mass spectrometer, we can often piece together the structure of the parent molecule.

3. By measuring the relative heights of the molecular ion (M) peak and the (M+1) peak, we can determine the number of carbon atoms in a molecule, and by using the (M+2) and (M+4) peaks (if any) we can identify halogen-containing compounds.

4.1 Mass Spectra of Simple Molecules

Example 4.1
The figure shows the mass spectrum of methane, CH_4.



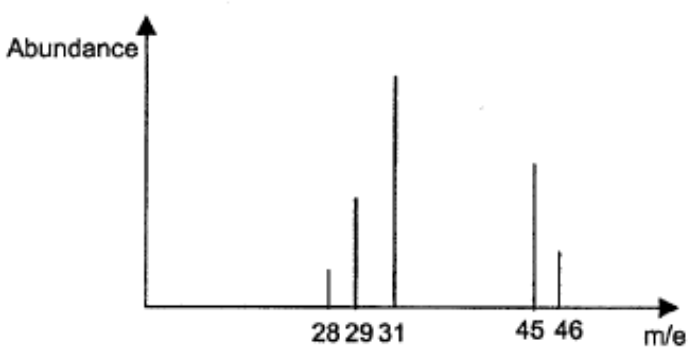
i) What particles are responsible for the peaks at m/e 1, 12, 13, 14, 15 and 16?
1 – H^+, 12 – C^+, 13 – $(CH)^+$, 14 – $(CH_2)^+$, 15 – $(CH_3)^+$, 16 – $(CH_4)^+$

ii) What is the m/e value of the molecular ion? **16**

iii) In the mass spectrum, insert the line caused by the ionic species, CH^{2+}.

$$\textbf{m/e} = \frac{\textbf{13}}{\textbf{2}}$$

Quick Check 2 ACJC Promo 99/B/1 (modified)
Below is the mass spectrum of ethanol.



(i) State the relative molecular mass of ethanol.

(ii) Identify the species responsible for the peaks in this spectrum.

(iii) Suggest a reason why the abundance of peak at m/e value of 31 is the largest.

Quick Check 3 N82/2/2(d)
A sample of carbon monoxide was prepared using carbon and oxygen specially enriched in ^{13}C and ^{17}O. Use the data below to calculate the relative intensities of the lines due to CO^+ when this specially prepared carbon monoxide was analysed in a mass spectrometer.

In summary, the following information can be obtained from the mass spectrum of molecules:

- isotopic composition in a compound
- M_r of a compound
- structure of a compound

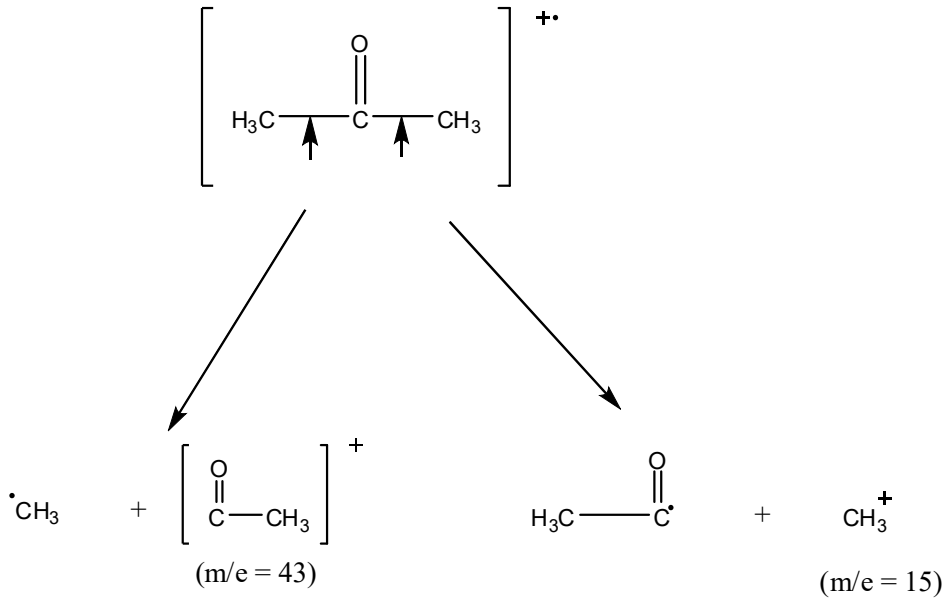
Note: Do not forget the "+" charge on molecular ions and fragments when assigning peaks – this is the most common mistake in exams.

4.2 Fragmentation Patterns

(d) Understand the following features and use them in the interpretation and prediction of mass spectra: (iii) Major fragment ions

Since the ionising electron beam in a mass spectrometer has enough energy (anything from 2000 – 6000 kJ mol^{-1}), the molecular ion formed by the loss of an electron (it is actually a radical-cation as it contains an odd number of electrons) will undergo bond fission, and molecular fragments form. Some of these will carry the positive charge, and therefore appear as further peaks in the mass spectrometer.

Example 4.2 (Propanone)



Note: Both charged and uncharged fragments are formed, but only the positively charged fragments are detected by the mass spectrometer.

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 (see Figure 5).

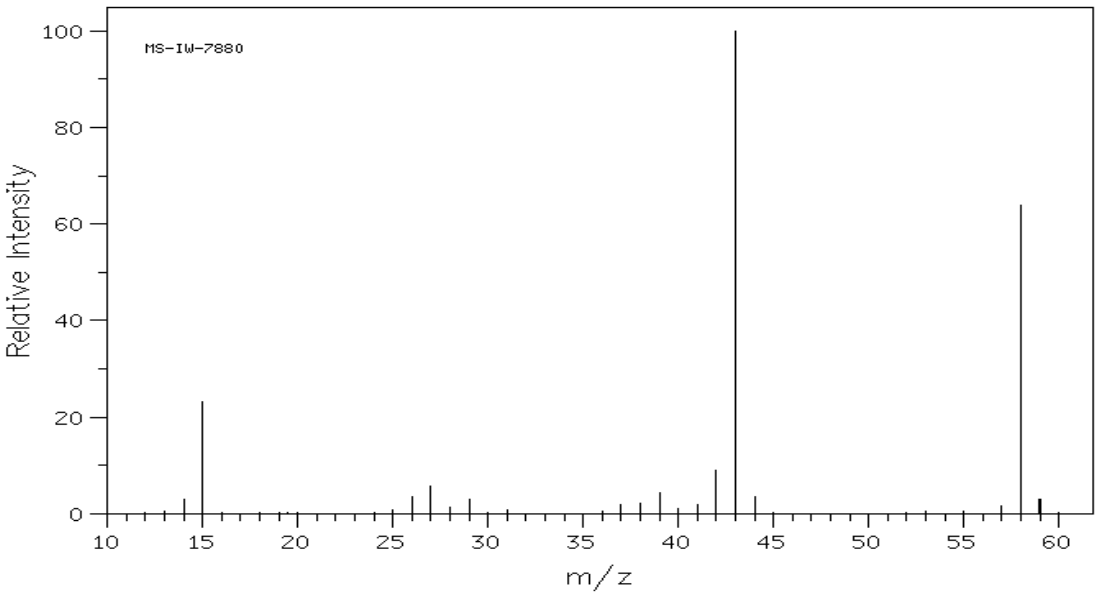


Figure 5: Mass spectrum of propanone

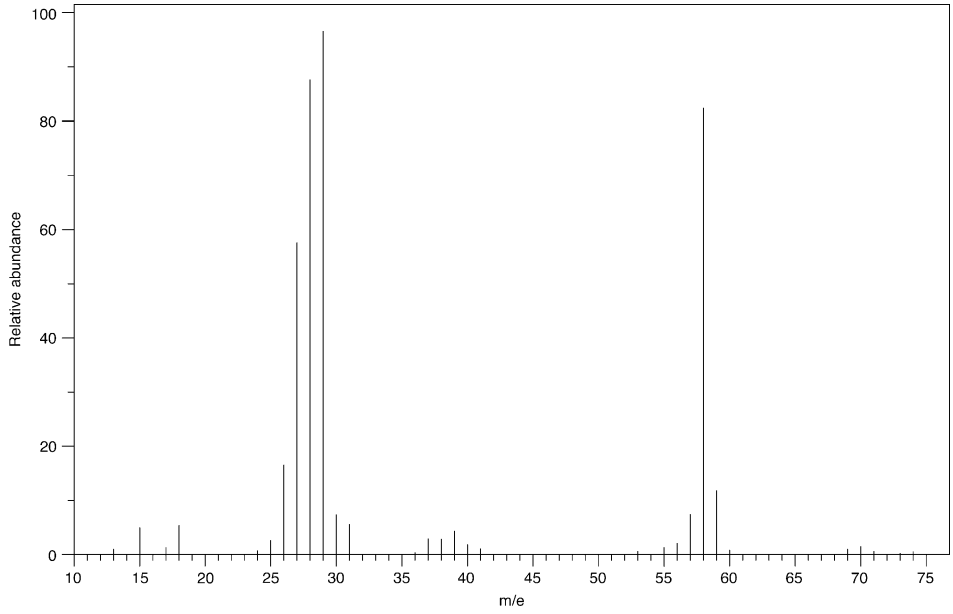


Figure 6: Mass spectrum of propanal

The fragmentation pattern can readily distinguish between isomers. Compare Figure 5 and Figure 6, which shows the mass spectrum of propanal. Here there is no peak at m/e = 15, nor one at m/e = 43. Instead, there are peaks at m/e = 57 and several from m/e = 26 to m/e = 29.

This is readily explained by the following fragmentations:

$[CH_3CH_2CHO]^+ \longrightarrow [CH_3CH_2]^+ + {}^{\bullet}CHO$ m/e = 29 *or* $\longrightarrow CH_3CH_2^{\bullet} + [CHO]^+$ m/e = 29

$[CH_3CH_2CHO]^+ \longrightarrow [CH_3CH_2CO]^+ + H^{\bullet}$ m/e 57 *or* $\longrightarrow CH_3CH_2CO^{\bullet} + H^+$ m/e = 1

Example 4.3

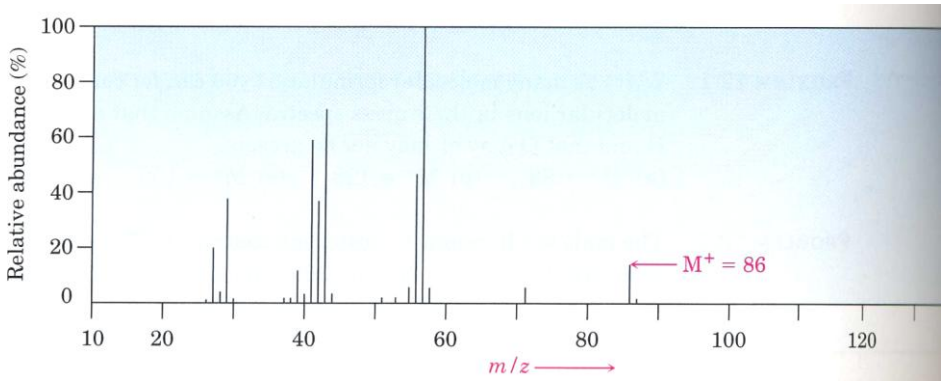
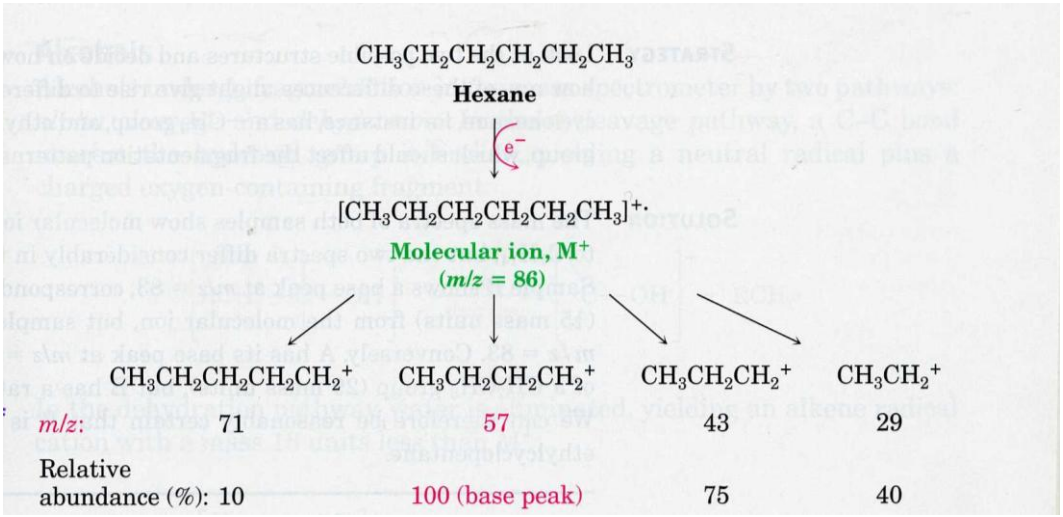


Figure 7: Mass spectrum of hexane



Example 4.4

There are two unlabeled samples, one of methylcyclohexane and the other of ethylcyclopentane. Explain how the two mass spectrums below can be used to tell them apart.

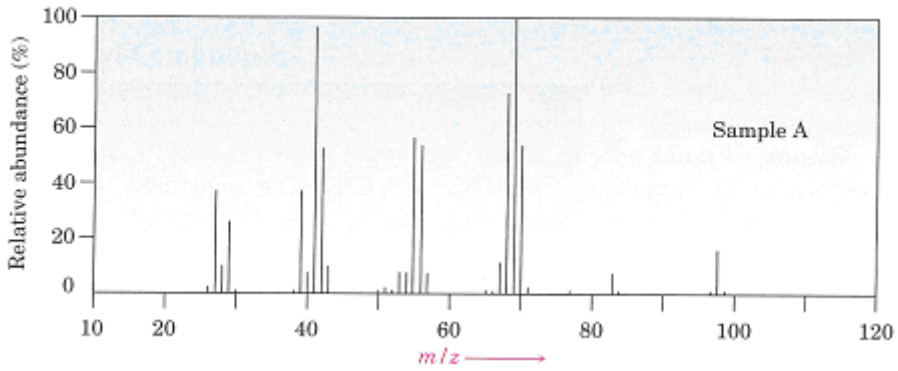


Figure 8: Mass spectrum of Sample A

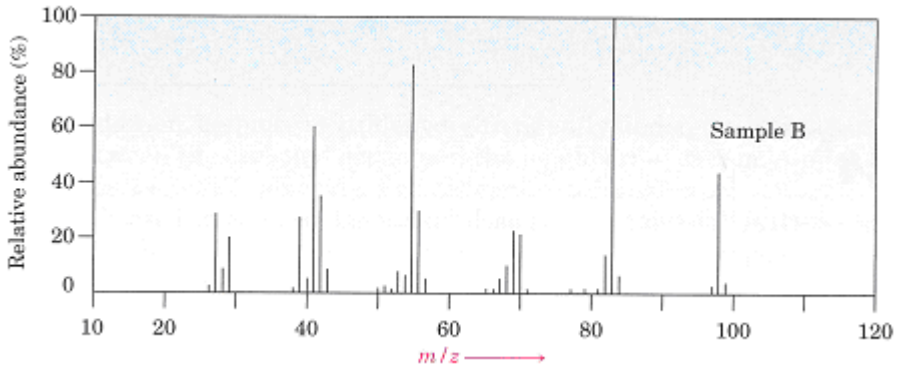


Figure 9: Mass spectrum of Sample B

Mass spectra of both samples show molecular ions at M^+ = 98 ($C_7H_{14}^+$). Sample B shows a base peak at m/e = 83, corresponding to the loss of a CH_3 group (-15). Sample A has only a small peak at m/e = 83. Sample A has its base peak at m/e = 69, corresponding to the loss of a CH_2CH_3 group (-29) but sample B has a rather small peak at m/e = 69.

Hence A is ethylcyclopentane and B is methycyclohexane.

The following table lists the m/e (M_r) values of some common fragment ions, and also the M_r values of some common fragments that are lost from the molecular ion. These will occur at m/e values of (M – X), where M is the molecular mass and X is the mass of the fragment.

common fragments remaining		***common fragments lost***	
M_r	**possible formulae**	**M_r**	**possible formulae**
15	CH_3	15	CH_3
18	H_2O	16	O, NH_2
26	C_2H_2	17	OH
28	C_2H_2, CO, N_2	18	H_2O
29	C_2H_5, CHO	26	C_2H_2
31	CH_2OH	28	CO, C_2H_4
42	C_3H_6, C_2H_2O	29	C_2H_5, CHO
43	C_3H_7, CH_3CO	30	C_2H_6, CH_2O, NO
44	C_3H_8, CO_2, C_2H_6N, $CONH_2$	31	CH_3O
45	CH_2OCH_3, CH_3CHOH	42	C_3H_6, CH_2CO
57	C_4H_9, CH_3CH_2CO	43	C_3H_7, CH_3CO
77	C_6H_5	44	C_3H_8, CO_2
91	$C_6H_5CH_2$	45	CO_2H
105	C_6H_5CO	57	C_4H_9, CH_3CH_2CO

4.3 Determination of Number of Carbon Atoms in Molecules using the ^{12}C:^{13}C Ratio

(b) Understand the following features and use them in the interpretation and prediction of mass spectra:
(ii) Isotopic abundances including the use of (M+1) peak caused by ^{13}C and (M+2) and (M+4) peaks for the identification of halogen compounds

Naturally occurring carbon is composed of 98.9% ^{12}C and 1.109% ^{13}C (along with extremely small, and variable, amounts of ^{14}C). Thus if we had 1000 methane molecules, 11 of them would be $^{13}CH_4$ (m/e = 17) and the rest $^{12}CH_4$ (m/e = 16).

Although the ^{13}C:^{12}C ratio is very small for compounds like methane which contain just one carbon atom, the chance of a molecule containing at least one ^{13}C atom increases in proportion to the number of carbon atoms. In ethane, however, there is twice the chance of a molecule containing a ^{13}C atom (it could be $^{12}CH_3{}^{13}CH_3$ or $^{13}CH_3{}^{12}CH_3$). So if we had 1000 ethane molecules, 2 x 11 = 22 of them would contain one ^{13}C atom, with an m/e = 31. (the chances of an ethane molecule containing two ^{13}C atoms is $(1.1/100)^2$ = 0.00012 which is vanishingly small).

Likewise the chances of a propane molecule containing one ^{13}C atom (m/e = 45) is 3 x 1.1 = 3.3%.

The formula relating the ratio of the abundances of the M+1 and the M peaks to the number of carbon atoms is:

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

where n = number of carbon atoms
A_{M+1} = the abundance of the M+1 peak
A_M = the abundance of the molecular ion, M, peak

Note that this expression stems from a probability distribution of ^{13}C in a generic molecule and is a close approximation of the exact formula. The assumption here being that ^{13}C has an abundance of 1.109 %.

Example 4.5

Compound **A** has a molecular ion at an m/e value of 120, with a relative abundance of 23%, and a peak at m/e 121 with a relative abundance of 2%. How many carbon atoms are in a molecule of A?

n = (100/1.1) x (2/23) = 7.91

The nearest whole number is 8. Therefore compound A is likely to have 8 carbon atoms per molecule.

4.4 Identification of Halogens using the (M+2) and (M+4) peaks

Both chlorine and bromine occur naturally as mixtures of two isotopes, with the relative abundances shown in the table.

element	isotope	relative abundance	approximate ratio
chlorine	^{35}Cl	75.8%	3:1
	^{37}Cl	24.2%	
bromine	^{79}Br	50.5%	1:1
	^{81}Br	49.5%	

Example 4.6

Bromine occurs naturally as two isotopes, ^{79}Br and ^{81}Br, in equal abundance. The mass spectrum for $^{12}C_2{}^{1}H_4Br_2$ is obtained. How would the spectrum for m/z values above 184 appear?

ion	m/z	relative abundance	
$(^{12}C_2{}^{1}H_4{}^{79}Br{}^{79}Br)^+$	186	½ x ½ = ¼	1
$(^{12}C_2{}^{1}H_4{}^{79}Br{}^{81}Br)^+$	188	½ x ½ = ¼	2
$(^{12}C_2{}^{1}H_4{}^{81}Br{}^{79}Br)^+$		½ x ½ = ¼	
$(^{12}C_2{}^{1}H_4{}^{81}Br{}^{81}Br)^+$	190	½ x ½ = ¼	1

*Check that total probability adds up to 1. Note the relative abundances of each m/z peak for M, (M+2) and (M+4).

Quick Check 4

Determine the number of peaks that correspond to the molecular ion, $^{12}C_2{}^{1}H_4C{l_2}^+$, and their relative intensities.

Example 4.7

Determine the number of peaks that correspond to the molecular ion, NCl_3^+, and their relative intensities. Assume nitrogen is mono-isotopic, ^{14}N

ion	m/e	relative intensity	
$(^{14}N^{35}Cl_3)^+$	119	$\frac{3}{4}\times\frac{3}{4}\times\frac{3}{4}=\frac{27}{64}$	27
$(^{14}N^{35}Cl_2{}^{37}Cl)^+$	121	$3\times\frac{3}{4}\times\frac{3}{4}\times\frac{1}{4}=\frac{27}{64}$	27
$(^{14}N^{35}Cl^{37}Cl_2)^+$	123	$3\times\frac{3}{4}\times\frac{1}{4}\times\frac{1}{4}=\frac{9}{64}$	9
$(^{14}N^{37}Cl_3)^+$	125	$\frac{1}{4}\times\frac{1}{4}\times\frac{1}{4}=\frac{1}{64}$	1

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. The ratio of the M:(M+2) peaks should reflect the natural abundances given in the table (i.e. 3:1 for chlorine; 1:1 for bromine).

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. The ratio of M:(M+2):(M+4) peaks should reflect the natural abundances
i.e. 9:6:1 for chlorine; 1:2:1 for bromine

Example 4.8

Determine the structure of an unknown compound B.

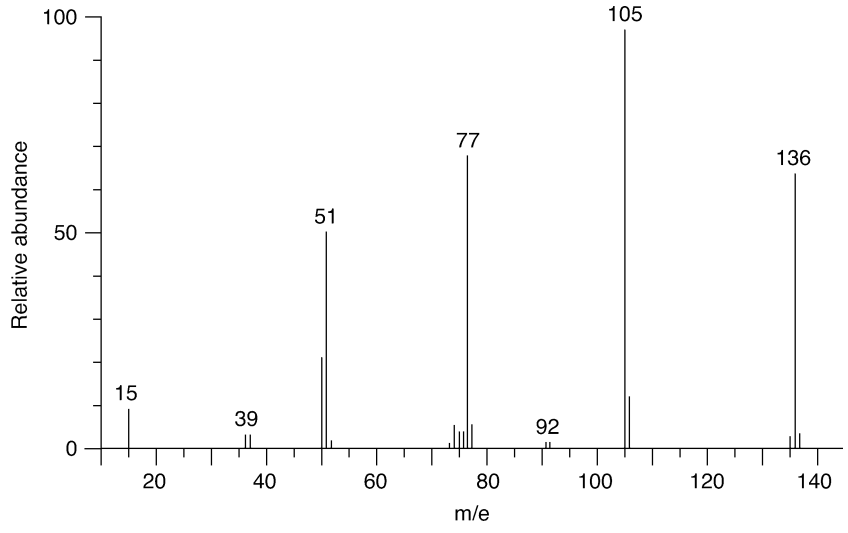


Figure 10: Mass spectrum of Compound B

Step 1: The molecular ion has m/e = 136, and the M:M+1 ratio of 11.5:1 suggests that a molecule of compound B contains 8 carbon atoms, n= (100/1.1) x (1/11.5)

Step 2: An accurate determination of its relative molecular mass suggests its molecular formula is $\mathbf{C_8H_8O_2}$. The high carbon:hydrogen ratio suggests a compound containing an aryl ring. There are, however, many isomers with this formula: phenyl ethanoate, methyl benzoate and methyl benzoic acid are just three examples.

Step 3: The base peak (= most stable fragment) in the spectrum is at m/e = 105. The other significant peaks are at m/e 15, 51 and 77. We can analyse these peaks by either taking their M_r values and guessing at their molecular formulae, or by calculating the molecular formula of the fragment(s) that have been lost from the molecular ion at m/e = 136)

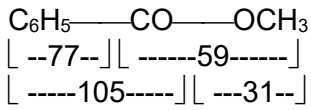
Thus: the peak at m/e = 105 represents the loss of 136-105 = 31

$$\underset{136}{[C_8H_8O_2]^+} - \underset{31}{CH_3O} \longrightarrow \underset{105}{[C_7H_5O]^+}$$

and the peak at m/e = 77 represents the loss of 136-77 = 59

$$\underset{136}{[C_8H_8O_2]^+} - \underset{59}{C_2H_3O_2} \longrightarrow \underset{77}{[C_6H_5]^+}$$

The peak at m/e 105 (28 units higher than C_6H_5 at m/e 77) can be identified with $\mathbf{C_6H_5CO^+}$ **(acyl cations are particularly stable, so are often the base peaks in mass spectra**). This suggests that compound **B** is methyl benzoate:



Just as important as the assigning of structures to the fragments of the molecule is the awareness of the *absence* of fragments that might have been expected in the mass spectrum of alternative structures. Thus, bearing in mind the stability of acyl actions mentioned above, we might have expected **phenyl ethanoate** to have produced a fragment at m/e 43,

$$\underset{\text{m/e = 136}}{[CH_3\text{-}CO\text{-}O\text{-}C_6H_5]^+} - OC_6H_5 \longrightarrow \underset{\text{m/e = 43}}{[CH_3\text{-}CO]^+}$$

and **methylbenzoic acid** to have produced a fragment at m/e 119.

$$\underset{\text{m/e = 136}}{[CH_3\text{-}C_6H_4\text{-}COOH]^+} - OH \longrightarrow \underset{\text{m/e = 119}}{[CH_3\text{-}C_6H_4CO]^+}$$

The absence of both these peaks confirms that **B** cannot be either of these compounds.

Recognisable elements from the molecular ion peak in the spectrum

Br	M+2 as large as M^+
Cl	M+2 a third as large as M^+
I	I^+ at 127
N	odd M^+
S	M+2 larger than usual (4% of M^+)

The following spectra show compounds containing S, Cl and Br.