Analytical Chemistry

Mass Spectrometry

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Instrument

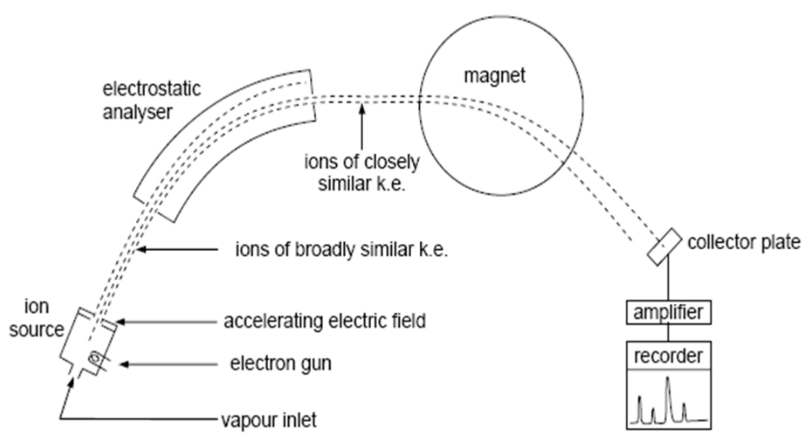


Figure 2.1 – diagram of a mass spectrometer

Mass Spectrometer

- Six processes occur in a mass spectrometer:
- 1. Vapourisation chamber: If not already a gas, the compound is **vaporised in an oven**.
- 2. Ionisation chamber: **Electrons are fired at the gaseous molecules**. These **knock off other electrons from some of the molecules**.

$$M + e^- \longrightarrow M^+ + 2e^-$$

Mass Spectrometer

- 3. Acceleration chamber: The gaseous ions are **accelerated by passing through an electric field**.
- 4. Electrostatic analyser: select ions of kinetic energy within a narrow range by using an electric field.
- 5. Deflection chamber: The fast-moving ions now pass through the poles of an electromagnet, where **they are deflected.**
- 6. The deflected ions **pass through a narrow slit and are collected on a metallic plate connected to an amplifier**.

Determination Using Mass Spectrometry

- Is used to identify unknown or new compounds.
- When a molecule is ionised it forms a **MOLECULAR ION** which can also undergo **FRAGMENTATION** or **RE-ARRANGEMENT** to produce particles of smaller mass.
- Only particles with a positive charge will be deflected and detected.
- The resulting spectrum has many peaks.
- The peak at **highest m/e ratio** is caused by **molecular ion** and indicates the **molecular mass**.
- The rest of the spectrum provides information about the structure.

Mass spectrum

- A mass spectrum is produced, which plots **relative abundance against mass/charge *(m/e)* ratio.**
- ***Most ions that are formed in a mass spectrometer have a charge of +1 ➔ x-axis is a measure of the mass.***
- The ***base peak*** → from ***particularly stable fragment*** **(most abundant)** of the molecule.

Uses of Mass Spectrometry

Determination of the structures of organic compounds:

1. Measuring the relative heights of the molecular ion **(M) peak** and the **(M+1) peak** ⟶ can determine the **number of carbon atoms** in a molecule.
2. Using the **(M+2)** and **(M+4) peaks** → can identify halogen-containing **(*Cl* or Br)**compounds.
3. By measuring the **accurate mass** of a molecular ion ⟶ can determine its **molecular formula**.
4. By identifying the **fragments** produced when an ion breaks up inside a mass spectrometer ⟶ can often piece together the **structure** of the parent molecule.

Use of (M + 1) Peak

- Use to determine number of carbon atoms in molecule.
- Naturally-occurring carbon is composed of 98.9% ^{12}C and 1.1% ^{13}C (along with extremely small, and variable, amount of ^{14}C).
- The formula relating the (M+1)/(M) ratio 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.

Example 1(pg 58)

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

SAQ 1. pg 58

- *Compound B contains carbon, hydrogen and oxygen only. Its mass spectrum contains a molecular ion peak at m/e = 102 (relative abundance 35%) and an M+1 peak at m/e 103 (1.5%).*

Calculate the number of carbon atoms in the molecule, and hence deduce the number of oxygen atoms it contains, and its molecular formula.

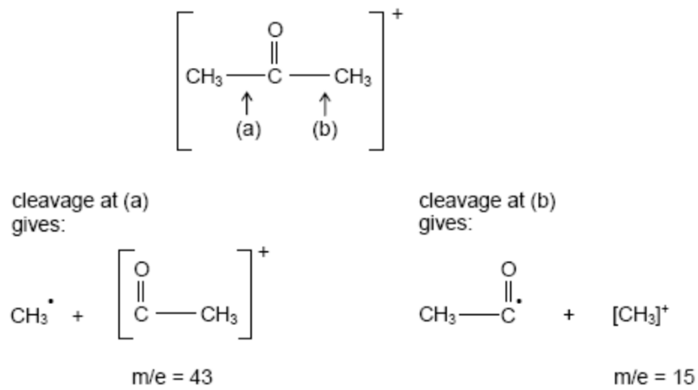
Fragmentation patterns

- In ionisation chamber, bombardment by high speed *electrons* produces positive ions.
- The molecular ions formed undergo bond (homolytic) fission to produce molecular fragments:
  - **1 fragment is positive** ,
  - **1 is a radical.**
- $M \rightarrow M^+ \rightarrow B\bullet + A^+$

A^+ appear as further peaks.

$B\bullet$ does not appear as peaks in the spectrum.

e.g. Propanone



Fragmentation patterns

- Can be used to identify the structural formulae of compounds especially those with the same molecular formula.
- E.g. Propanone CH_3COCH_3 and
  Propanal CH_3CH_2CHO
- Molecular of C_3H_6O with m/e = 58

Mass Spectrum of propanone (pg 60)

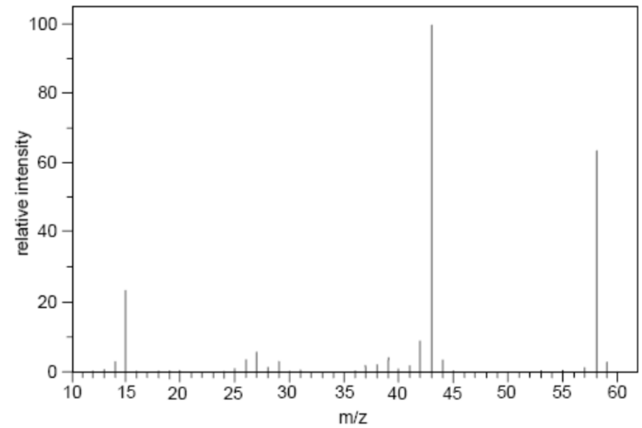


Figure 2.2 – mass spectrum of propanone

Mass Spectrum of propanal (pg 60)

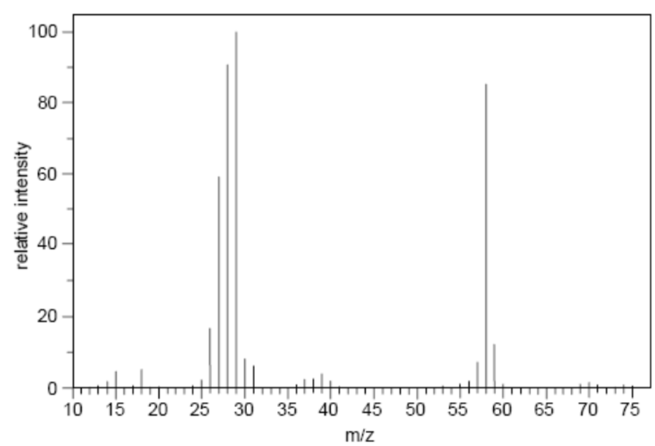


Figure 2.3 – mass spectrum of propanal

Mass Spectrum of propanone

- Highest m/e = 58
  due to $CH_3COCH_3^+$(whole molecule)

- m/e = 43 (base peak)
  due to ($M - 15 = M - CH_3$)
  i.e. CH_3CO^+

- m/e = 15 due to CH_3^+

(M), (M+2) and (M+4) peaks

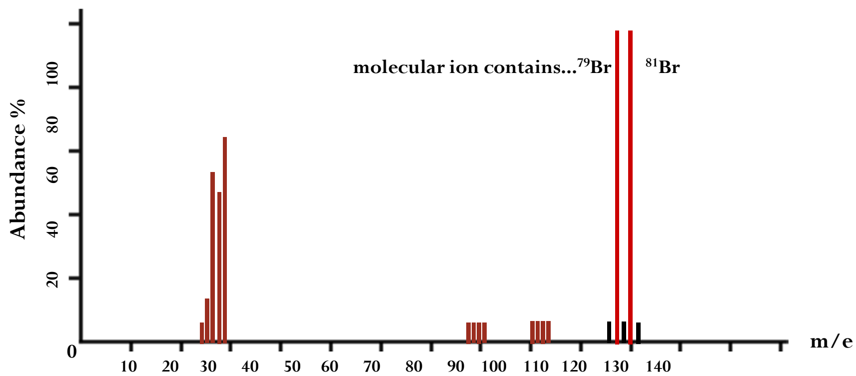
- (M+2) and (M+4) peak occurs when compound contains Cl or Br atom.
- Both Cl & Br naturally occur as mixtures of 2 isotopes, with the relative abundances shown below:

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%	

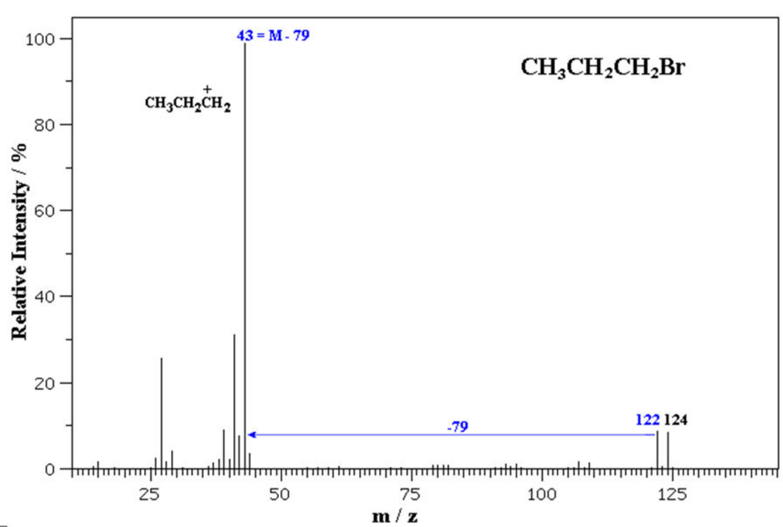
(M+2) Peak

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)

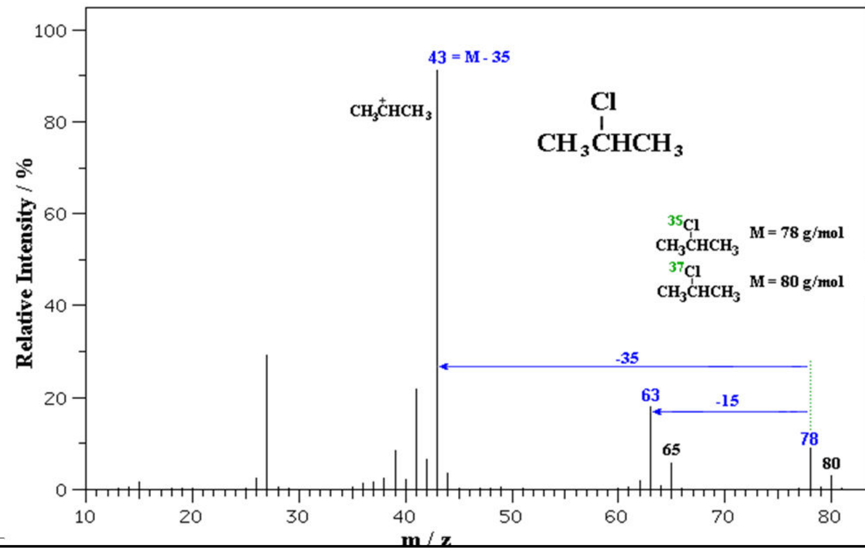
Because the two isotopes are of similar abundance, the peaks are of similar height.



- *Example: mass spectrum of 1-bromopropane*
- Note the isotope pattern at 122 and 124 that represent the M and M+2 in a 1:1 ratio.
- Loss of ^{79}Br from 122 or ^{81}Br from 124 gives the base peak a m/z = 43, corresponding to the propyl cation.
- Note that other peaks, such as those at m/z = 107 and 109 still contain Br and therefore also show the 1:1 isotope pattern.



- The first MS is of 2-chloropropane.
- Note the isotope pattern at 78 and 80 that represent the M and M+2 in a 3:1 ratio.
- Loss of ^{35}Cl from 78 or ^{37}Cl from 80 gives the base peak a m/z = 43, corresponding to the secondary propyl cation.
- Note that the peaks at m/z = 63 and 65 still contain Cl and therefore also show the 3:1 isotope pattern.



M+4 peaks

- 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**.
- *E.g.* M ($^{79}Br_2^+$), M+2 ($^{79}Br^{81}Br^+$) and M+4 ($^{81}Br_2^+$).
- The abundance ratio of Br_2 is 1:2:1
- The abundance ratio of Cl_2 is 9:6:1

Example (pg 58)

- dibromomethane, CH_2Br_2,
- three molecular ion peaks at m/e 172, 174 and 176 in the ratio 1:2:1,

Example (pg 58)

- dichloromethane, CH_2Cl_2,
- ratio 9:6:1,
- due to the greater natural abundance of the ^{35}Cl isotope.

SAQ 2 (pg 58)

- *Calculate the M : M+2 : M+4 ratio for CH_2BrCl*

High resolution mass spectra

- Can distinguish between ions that have same mass on low-resolution mass spectrum.

E.g :

name	structure	molecular formula
pentene	$CH_3CH_2CH_2CH{=}CH_2$	C_5H_{10}
aminopropanonitrile	$CH_3CH(NH_2)CN$	$C_3H_6N_2$
but-1-ene-3-one	CH_2-$CHCOCH_3$	C_4H_6O

- All have an approximate *M*r of 70:

Molecular formulae from accurate masses

element	accurate relative atomic mass
H	1.0078
C	12.000
N	14.003
O	15.995

- These accurate isotopic mass can accurately measure the mass of molecular ion → only correspond to one molecula formula.

Accurate Masses

- C_5H_{10} = 5 x 12.000 + 10 x 1.0078 = **70.078**
- $C_3H_6N_2$ = 3 x 12.000 + 6 x 1.0078 + 2 x 14.003 = **70.053**
- C_4H_6O = 4 x 12.000 + 6 x 1.0078 + 15.995 = **70.042**
- The last two differ by about 0.13%. This is well within the capabilities of a high-resolution mass spectrometer.

SAQ3 (pg 59)

- *Explain whether a molecule having an accurate mass of 60.0574 is 1,2-diaminoethane, $C_2H_8N_2$, or propan-1-ol, C_3H_8O.*

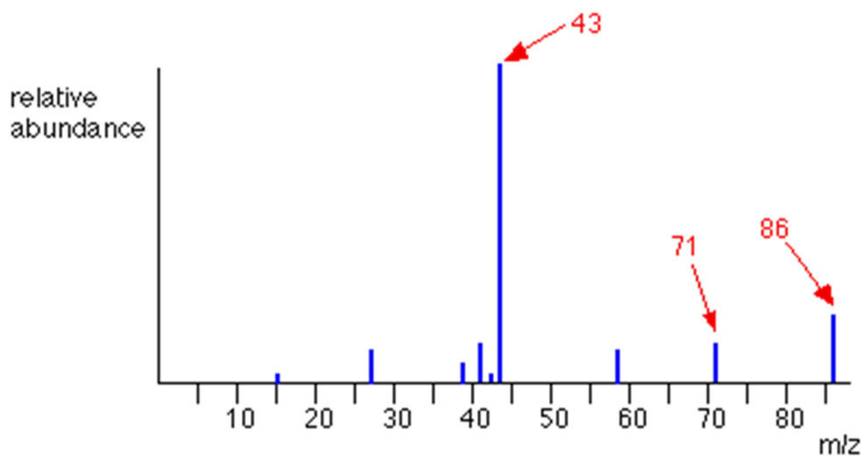
SAQ 4 (pg 61)

- Use the values of accurate relative atomic masses in the table to see whether it would be possible to decide whether the peak at m/e = 29 is due to $CH_3CH_2^+$ or CHO^+.

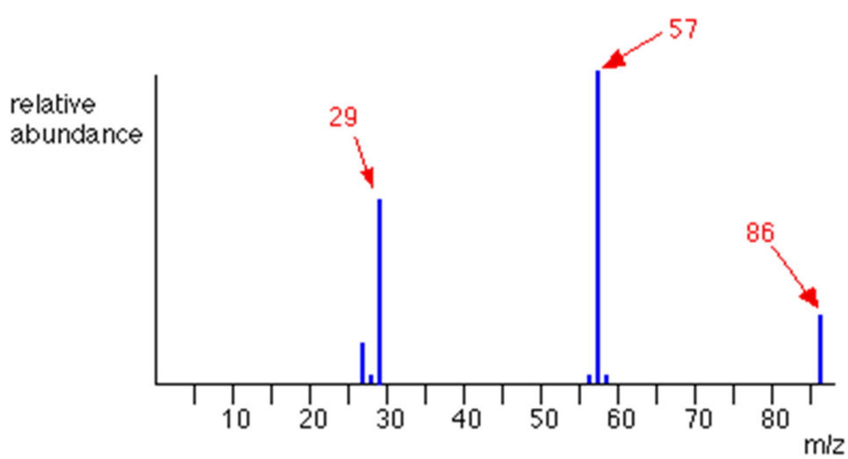
- $CH_3CH_2^+$ = (2x12.000) + (5x1.0078) = 29.039
- CHO^+ = 12.000 + 1.0078 + 15.995 = 29.003

Molecules with same molecular formula but different structure

simplified mass spectrum of pentan-2-one - $CH_3COCH_2CH_2CH_3$



simplified mass spectrum of pentan-3-one - $CH_3CH_2COCH_2CH_3$



The molecular formula of B is $C_8H_8O_2$

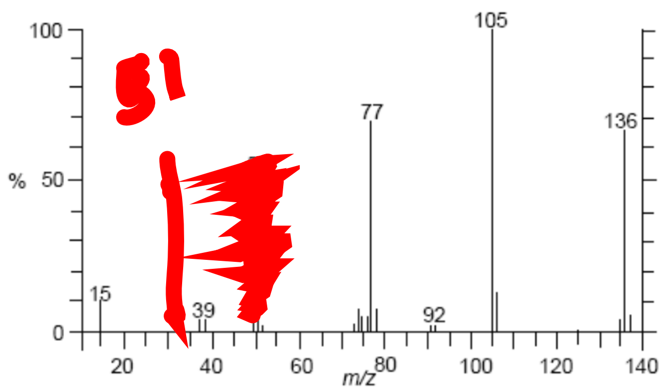


Figure 2.4 – mass spectrum of compound B

Compound B

- **M:M+1** ratio of **11.5 : 1** suggests that it contains **8 carbon atoms**,
- **Accurate determination of its relative atomic mass** suggests its molecular formula is $\mathbf{C_8H_8O_2}$.
- B could be *phenyl ethanoate, methyl benzoate or methyl benzoic acid*

Compound B

- phenyl ethanoate

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

- methyl benzoate

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C6H5——CO——OCH3
└ --77--┘ └ ------59------┘
└ -----105-----┘ └ ---31--┘
```

- methyl benzoic

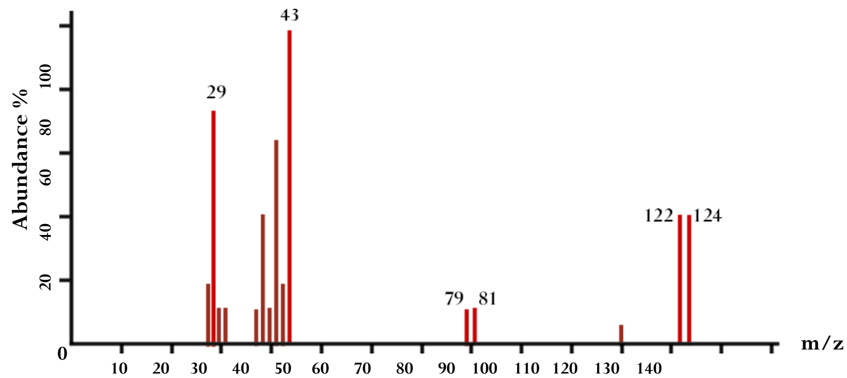
$$\underset{m/e\,=\,136}{CH_3\text{-}C_6H_4\text{-}COOH]^+} \;-\; OH \longrightarrow \underset{m/e\,=\,119}{CH_3\text{-}C_6H_4CO]^+}$$

Ease of formation of carbonium ion fragments

- $CH_3^+ < RCH_2^+ < R_2CH^+ < R_3C^+$

$CH_2\text{=}CH\text{-}CH_2^+ < C_6H_5 - CH_2^+$

IDENTIFY THE COMPOUND



C_3H_7Br

Common Small Ions	
m/z	composition
15 amu	CH_3
17	OH
18	H_2O
19	H_3O, F
26	C_2H_2, CN
27	C_2H_3
28	C_2H_4, CO, H_2CN
29	C_2H_5, CHO
30	CH_2NH_2
31	CH_3O
33	SH, CH_2F
34	H_2S
35(37)	Cl
36(38)	HCl
39	C_3H_3
41	C_3H_5, C_2H_3N
42	C_3H_6, C_2H_2O, C_2H_4N
43	C_3H_7, CH_3CO
44	C_2H_4O
46	NO_2
56	C_4H_8
57	C_4H_9
60	CH_4CO_2
79(81)	Br
80(82)	HBr
91	C_7H_7
127	I
128	HI

Common Neutral Fragments	
mass loss	composition
1 amu	H
15	CH_3
17	OH
18	H_2O
19	F
20	HF
27	C_2H_3, HCN
28	C_2H_4, CO
30	CH_2O
31	CH_3O
32	CH_4O, S
33	CH_3 + H_2O, HS
33	H_2S
35(37)	Cl
36(38)	HCl
42	C_3H_6, C_2H_2O, C_2H_4N
43	C_3H_7, CH_3CO
44	CO_2O, $CONH_2$
45	C_2H_5O
55	C_4H_7
57	C_4H_9
59	$C_2H_3O_2$
60	$C_2H_4O_2$
64	SO_2
79(81)	Br
80(82)	HBr
127	I
128	HI

APPLICATIONS

- By coupling a GLC in conjunction with a mass spectrometer, **rapid analysis of complex mixtures** is possible.
- This is particularly useful for **determining the products and relative yields from organic reactions** and for **monitoring industrial processes**.

- Mass spec. are **suitable for analyzing volatile compounds.**
- It can also be used to **analyze proteins and polypeptides**. This is achieved by methylating the –N-H groups which disrupts the HB, hence more volatile.
- This allows a very rapid method of **determining the a. a sequence in the molecules**.
- This technique is usually computer-linked and has the advantage that very small quantities are required and sequences of amino acids may be rapidly established.