Chem Factsheet

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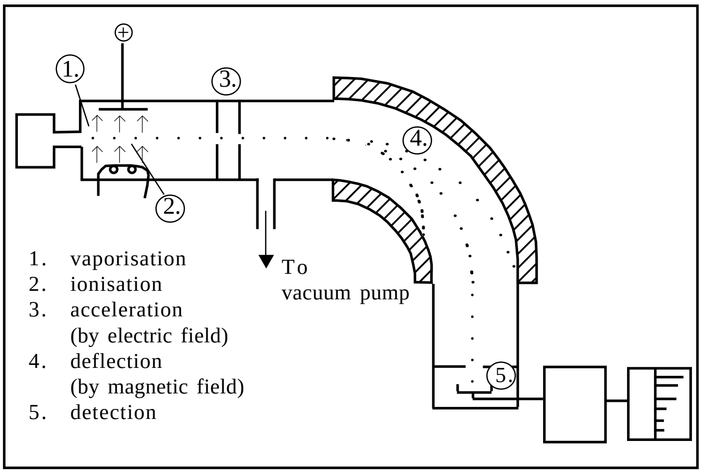
Organic Analysis II- Mass Spectroscopy

Before reading through this Factsheet you should:
- Have a good understanding of Atomic Structure (Factsheet 01);
- Have a basic understanding of the way in which a mass spectrometer works;
- Have a good knowledge of the Organic Chemistry covered at AS and A2 level;
- Understand covalent bonding and molecular structure (Factsheets 05 and 06).

After working through this Factsheet you will be able to:
- Interpret simple mass spectra;
- Recognise mass spectra as useful tools in organic analysis.

Before we discuss the role of mass spectra in organic analysis, candidates should remind themselves of the simplified appearance of a mass spectrometer (as shown below) and how the machine works.

Fig 1. Mass Spectrometer



The five stages listed on the above diagram are discussed in more detail in Factsheet 01 – Atomic Structure.

Mass spectrometer traces (Fig 2) are used to identify atomic masses of any isotopes present and to provide the information to calculate relative atomic mass.

Note the axis labels:
- Relative abundance
- Mass/Charge ratio (or m/e)

The relative abundance is self explanatory – the more common a particular mass of particle, the higher the peak. Usually the highest peak (**base peak**) is given a value of 100, with the other peaks scaled accordingly.

An understanding of the mass/charge ratio is important. After electron bombardment, the majority of the ions formed have a +1 charge as just one electron is removed.

If the ion has a +1 charge then the mass/charge ratio is the same as the mass.

e.g. $^{23}Na^{+}$ *m/e = 23/1 = 23*

If a higher number of electrons are removed from a species, a different peak will be generated on the spectrum.

e.g. $^{23}Na^{2+}$ *m/e = 23/2 = 11.5*

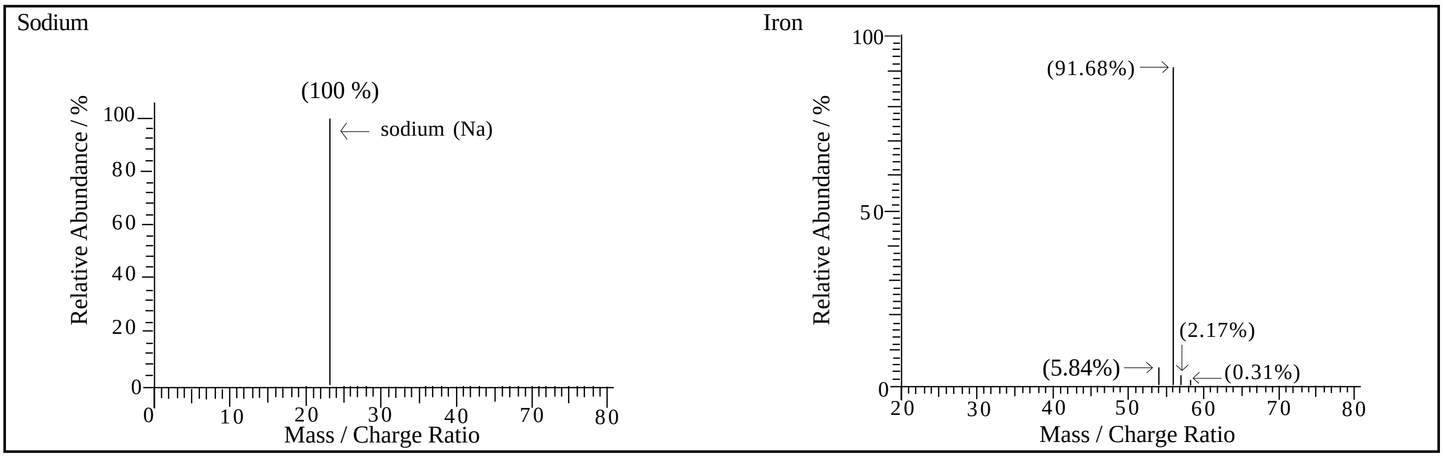
However, it is worth reinforcing that the vast majority of ions formed have a +1 charge.

Mass Spectra in Organic Analysis.

Mass spectra, like infrared spectra (Factsheet 54 Organic analysis I- Infrared Spectroscopy), are a useful tool in identifying organic molecules. The aim of this Factsheet is to give candidates the necessary experience in interpreting mass spectra to be able to extract the relevant information from them. This information is likely to be used in conjunction with other data to identify chemicals. In exam questions the mass spectrum of an unknown organic compound is often supplied with the IR spectrum and results from chemical tests. The skill of the analytical chemist is to piece together all of the information.

Exam Hint: *Candidates should be aware that exam questions at A2 level may test knowledge and understanding of how mass spectra are generated.*
Examples of mass spectra observed at AS level will include those of simple elements.

Fig 2. Mass spectrometer traces

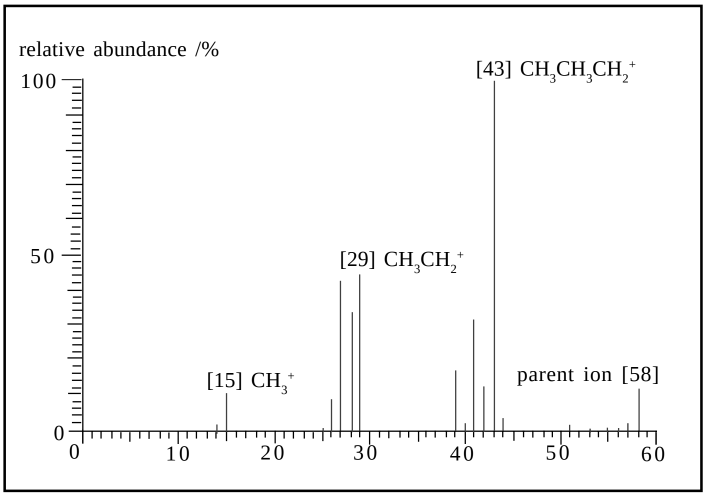


When an organic compound is placed into the mass spectrometer for analysis, the initial reaction is for an electron to be removed – ionisation.

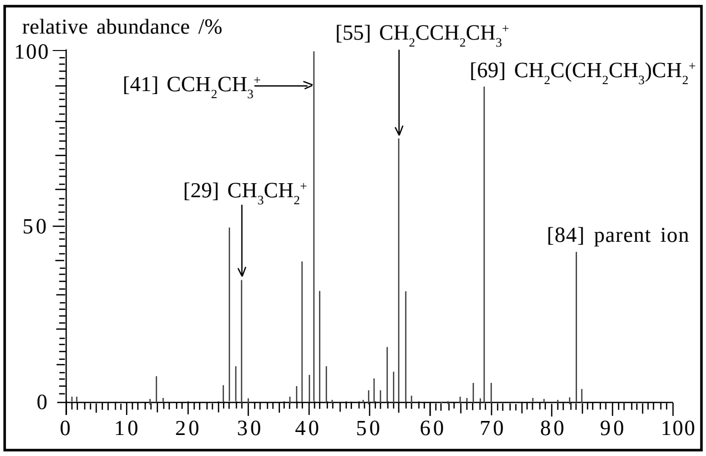
$$M \xrightarrow{\text{electron bombardment}} M^+ + e^-$$

M^+ can be described as the molecular ion or the parent ion. It is rare that the molecular ion is undetectable on a mass spectrum.

***Exam Hint**: - When a candidate is presented with a mass spectrum, the first task should be to locate the peak associated with the molecular ion. This will be the peak of significant relative abundance which has the largest mass/charge ratio. From this the relative molecular mass of the compound can be deduced.*



The RMM of the compound is 58



The RMM of the compound is 84

Candidates should be aware that there is the possibility of small, low relative abundance peaks further up the spectrum than the peak for the molecular ion. These peaks are due to the occasional presence of heavy isotopes of elements (e.g. ^{14}C, ^{18}O, ^{2}H) which can occur in organic molecules. These peaks can be ignored.

When an organic compound is ionised by electron bombardment in the mass spectrometer, not all of the molecular ions survive. Often the molecular ions are broken up into smaller pieces by a process called **fragmentation**.

e.g. $$CH_3CH_3^+ \xrightarrow{\text{electron bombardment}} \underset{\text{fragment ion}}{CH_3^+} + \underset{\text{radical by-product}}{CH_3^\bullet}$$

The fragment ions are detected and are responsible for all of the other peaks on a mass spectrum.

There will be a variety of fragments formed from an organic compound, as each molecule can be fragmented in a variety of ways.
e.g. Some possible fragments of methane, CH_4

Fragment	m/e
CH_4^+	16
CH_3^+	15
CH_2^+	14
CH^+	13
C^+	12
H^+	1

Some fragments will be more stable and therefore more likely to occur than others, hence different heights of relative abundance peaks are observed.

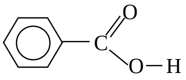
By assigning fragments to peaks on a spectrum, valuable information about the structure of a molecule can be gained.

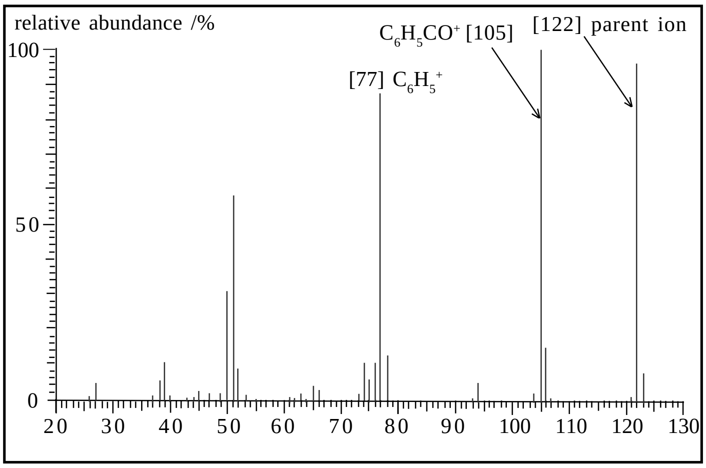
The assigning of peaks can be something of a 'numbers game' using relative atomic masses, but bearing in mind that mass spectra are usually supplied with other analysis data this is not a difficult task.

The following data may be useful when assigning fragments to peaks on a mass spectrum; these are examples of commonly occurring fragments:

Fragment	m/e
CH_3^+	15
$CH_3CH_2^+$ or CHO^+	29
$CH_2NH_2^+$	30
CH_2OH^+	31
CH_3CO^+ or $CH_3CHCH_3^+$ or $CH_3CH_2CH_2^+$	43
$CONH_2^+$	44
$COOH^+$ or CH_3CHOH^+	45
$C_6H_5^+$	77
$C_6H_5CH_2^+$	91
$C_6H_5CO^+$	105

The reason that these fragments are more common is that they are relatively stable. This is well illustrated if we look at the mass spectrum and structure of benzenecarboxylic acid:





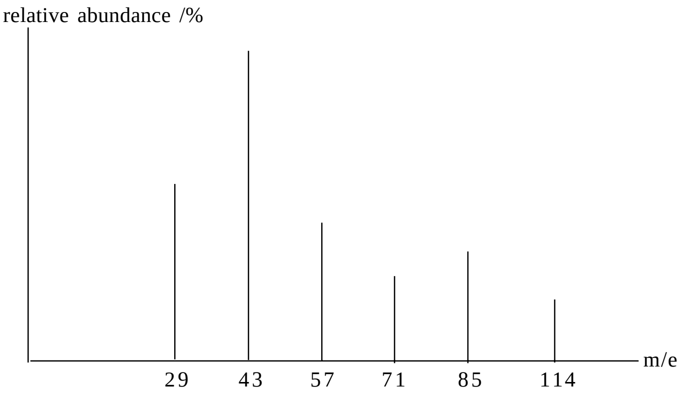
Note the large peaks at 77 ($C_6H_5^+$) and 105 ($C_6H_5CO^+$). The benzene ring is especially stable due to the delocalised system of electrons, so it is unlikely to be fragmented. Consequently, if an analytical chemist observes a peak at 77, the presence of a benzene ring is strongly suggested.

For the worked examples and questions in this Factsheet, use the following data to help you.

Fragment	m/e
CH_3^+	15
$CH_3CH_2^+$ or CHO^+	29
$CH_2NH_2^+$	30
CH_2OH^+	31
CH_3CO^+ or $CH_3CHCH_3^+$ or $CH_3CH_2CH_2^+$	43
$CONH_2^+$	44
$COOH^+$ or CH_3CHOH^+	45
$C_6H_5^+$	77
$C_6H_5CH_2^+$	91
$C_6H_5CO^+$	105

Worked Example

The following mass spectrum is of a hydrocarbon which does not react with bromine water.



- The first task is to use the molecular ion peak to give the relative molecular mass, 114.
- The fact that the compound is a hydrocarbon which does not react with bromine water suggests an alkane.
- Alkanes general formula is C_nH_{2n+2}, where the atomic masses are C=12 and H=1.
- Hence suggested formula for the compound is: $\mathbf{C_8H_{18}}$

The fragment peaks can be assigned as follows:

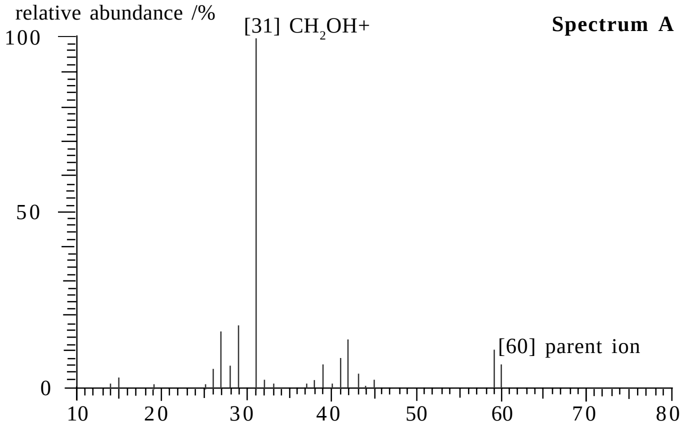
Fragment	m/e
$C_2H_5^+$	29
$C_3H_7^+$	43
$C_4H_9^+$	57
$C_5H_{11}^+$	71
$C_6H_{13}^+$	85

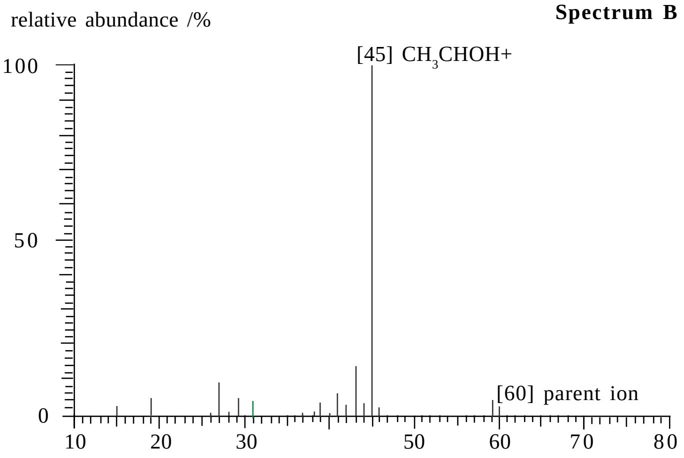
Note that suggesting a name for the compound is not straightforward, as it would be difficult to tell whether this is the mass spectrum of octane or an isomer, for example 3,4-dimethylhexane.

*Every species detected by a mass spectrometer is a positive ion. Ensure that you **always** remember to include the + charge when writing the formula of a molecular ion or fragment.*

Worked Example

The following are mass spectra of simple alcohols.





It can be seen from the spectra that both alcohols have relative molecular masses of 60 (they are isomers).

The formulae of the molecular ions can then be ‘suggested’. Knowing that we are dealing with alcohols, the following elements will be present:

Element	Atomic Mass
C	12
H	1
O	16

Knowledge of the general formula of the homologous series ($C_nH_{2n+1}OH$), chemistry ‘common sense’ and being aware that the RMM is 60 suggests that the formula of each molecular ion will be: $C_3H_8O^+$, as

$(3\times12) + (8\times1) + (1\times16) = 60$.

By now looking at fragments within each spectrum, some structural information can also be gained:

In spectrum A the base peak is at m/e = 31. This could be due to the presence of the CH_2OH^+ fragment. This fragment can only come from a primary alcohol:

e.g. $R\text{-}CH_2\text{-}OH$ fragmenting to give $R^\bullet$ and CH_2OH^+.

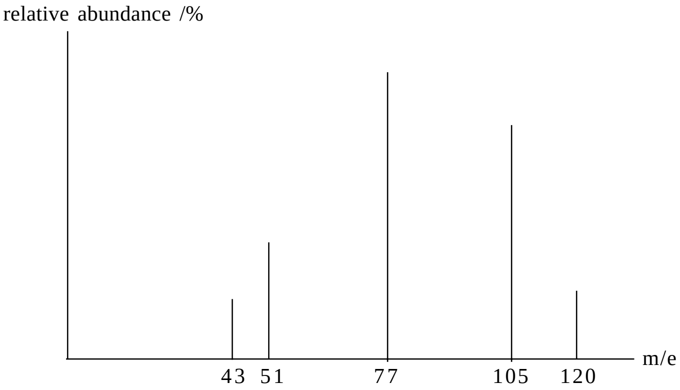
In spectrum B the base peak is at m/e = 45. This could be due to the presence of the CH_3CHOH^+ fragment. This fragment can only come from a secondary alcohol:

e.g. $CH_3\text{-}CHOH\text{-}R$ fragmenting to give $R^\bullet$ and CH_3CHOH^+.

These deductions are correct, as spectrum A is that of propan-1-ol (CH_3CH_2OH) and spectrum B is that of propan-2-ol ($CH_3CHOHCH_3$).

Practice Questions

1. The mass spectrum of a liquid is given. The liquid is known to be an aromatic ketone with percentage composition C 80%, H 6.7%, O 13.3%.

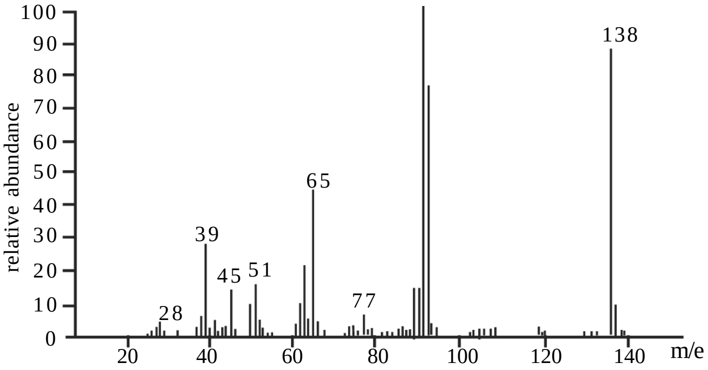


   (a) Use the mass spectrum to determine the relative molecular mass of the compound.
   (b) Combine this information with the percentage composition to deduce the molecular formula.
   (c) Suggest a structure for the molecule.
   (d) What fragment is responsible for the peak at m/e 105?

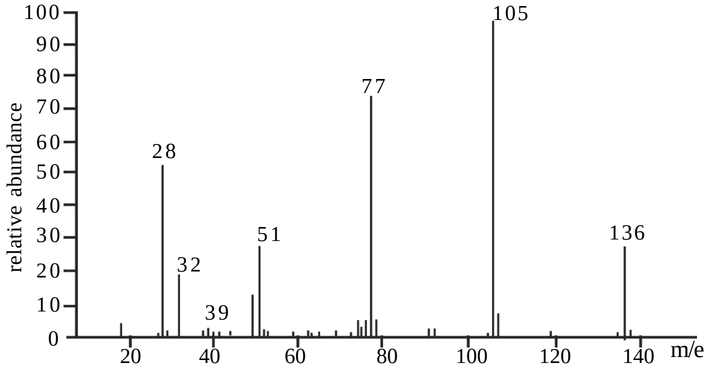
2. Two organic compounds, A and B are isomers with percentage composition C 70.5%, H 5.9%, O 23.6%.
   A is moderately soluble in water, forming a solution of pH 5.
   B is a pleasant smelling liquid.

   (a) What is the empirical formula of A and B?

mass spectrum of compound A



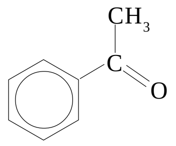
mass spectrum of compound B



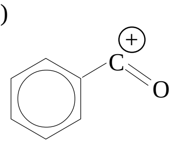
   (b) What is the molecular formula of A and B?
   (c) Give the formulae of the molecular fragments corresponding to the following peaks: m/e: 136; 105; 91; 77.
   (d) Suggest structural formulae for A and B.

Answers

1. (a) 120
   (b) C_8H_8O
   (c) Use information given from fragment peaks, e.g. peak at 77 suggests presence of benzene ring, peak at 43 could be due to CH_3CO^+.



   Suggested formula (with RMM=120):
   (d)

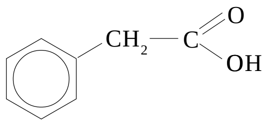


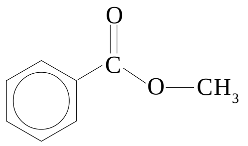
   or $C_6H_5CO^+$

2. (a) C_4H_4O
   (b) $C_8H_8O_2$ (as RMM = 136, deduced from spectra).
   (c)

m/e	Fragment formula
136	$C_8H_8O_2^+$
105	$C_7H_5O^+$
91	$C_7H_7^+$
77	$C_6H_5^+$

   (d)





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