MASS SPECTROMETRY

Mass spectrometry is used widely in science. It is used to determine the relative atomic mass of elements, the molecular mass of chemical compounds and the structure of these compounds. It is also used to identify the components of mixtures such as gases from a waste dump and organic pollutants in water. Mass spectrometers are widely used in forensic science, and in the detection of illegal substances in the blood of athletes.

Mass spectrometry is commonly used in association with other analytical techniques such as Gas Chromatography (GC-MS) or High Performance Liquid Chromatography (HPLC-MS).

The chromatographic techniques allow the components of a mixture to be separated before each one is analysed by a mass spectrometer.

Unlike other spectroscopic techniques, mass spectrometry does not measure the interaction of molecules with energies from the electromagnetic spectrum.

As the name implies, mass spectrometry is basically a sophisticated weighing device, which has the objective of measuring the masses of atoms or molecules. A mass spectrum is obtained by converting the test sample into positively charged ions and separating these on the basis of their mass to charge ratios.

A mass spectrum gives the masses and relative abundance of each ion reaching the detector.
ANALYSIS OF COMPOUNDS:
The information given by a mass spectrum of a compound can be used to determine the mass and the structure of the molecules of the compound.

Before a mass spectrum of any substance can be obtained it must first be ionised. This is done by bombarding the sample with high-energy electrons, which have the effect of knocking electrons out of sample molecules (M).

\[
M - e^- \rightarrow M^+ 
\]

The line or ‘peak’ in the mass spectrum corresponding to the ion (M⁺) gives the relative molecular mass of the compound.

*In the mass spectrum of butane the molecular ion has a mass of 58, thus the relative molecular mass of butane is 58.*

The energy required to ionise the molecules not only produces molecular ions but also causes the molecules to break up into charged fragments. These fragments are represented on the mass spectrum as a series of lines.

<table>
<thead>
<tr>
<th>Sample Molecule</th>
<th>Possible Fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH_3CH_2CH_2CH_3)</td>
<td>(CH_3^+)</td>
</tr>
<tr>
<td></td>
<td>(CH_2CH_2^+)</td>
</tr>
<tr>
<td></td>
<td>(CH_3CH_2CH_2^+)</td>
</tr>
<tr>
<td></td>
<td>(CH_3CH_2CH_2CH_3^+)</td>
</tr>
</tbody>
</table>
Analysis of the fragmentation pattern, observed in the mass spectrum, can be used to determine the structure of molecules. This can be done by calculating the difference between the molecular ion peak and other major peaks. The difference in mass is the mass of a fragment, which has broken off the molecular ion. It can be used to identify parts of the molecule.

The following table shows some possible fragments:

<table>
<thead>
<tr>
<th>Difference between $M^+$ and other peaks</th>
<th>Possible fragment broken off the molecular ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>$-\text{CH}_3$</td>
</tr>
<tr>
<td>29</td>
<td>$-\text{C}_2\text{H}_5$</td>
</tr>
<tr>
<td>17</td>
<td>$-\text{OH}$</td>
</tr>
</tbody>
</table>

The overall structure of a sample molecule can be determined by piecing together fragments identified from the mass spectrum, just as one assembles the pieces of a jigsaw to create the final picture.

An easier way to identify the compound being tested is to compare the mass spectrum with a library of pre-recorded mass spectra. This library is held in a database that is connected to a computer, which carries out the comparison. A successful match will give the precise name and structure of the compound.

High Resolution Mass Spectrometry can be used to determine the molecular formula of a compound. This method allows for very precise measurement of the molecular mass of the compound being analysed. A computer program calculates all the possible combinations of atoms that would add up to the specific molecular mass. For example, a molecular mass of 122.036776 can only be achieved by combining 7 carbon atoms, 6 hydrogen atoms and 2 oxygen atoms. Thus the molecular formula of the compound of $M_r$ 122.036776 is $\text{C}_7\text{H}_6\text{O}_2$.

Slightly different masses of 122.071819 or 122.060585 would be obtained by compounds of formulae $\text{C}_6\text{H}_5\text{N}_3$ and $\text{C}_7\text{H}_8\text{NO}$ respectively.
ANALYSIS OF ELEMENTS:

An approximate value for the relative atomic mass of an element can be determined from the information given by the mass spectrum of a sample of the element.

![](Mass Spectrum of Neon)

The relative atomic mass ($A_r$) of neon can be calculated from the information contained in the mass spectrum, which shows that neon consists of 90% $^{20}$Ne and 10% $^{22}$Ne.

$$A_r = \frac{(90 \times 20) + (10 \times 22)}{100} = 20.20$$

An exact value of the relative atomic mass can be obtained from the mass spectrum using precise isotopic mass values.

FUNDAMENTAL PROCESSES

(Involved in Mass Spectrometry)

1. A sample of the substance to be analysed is injected into the mass spectrometer.

   The sample is **vaporised**. Volatile substances will vaporise easily in the very low pressure environment used in a mass spectrometer. Other substances may need to be heated in order to vaporise them.
(2) A stream of gaseous molecules enters an ionisation chamber where it is bombarded at right angles by an electron beam. The high-energy electrons knock electrons out of the sample molecules (M) to form ions (M⁺).

\[ M - e^- \rightarrow M^+ \]

The positive ion formed by the removal of one electron (M⁺) is known as the molecular ion. Detection of this ion will give the molecular mass of the compound under analysis.

After their formation, some molecular ions will fragment in a pattern characteristic of each molecule.

(3) The positively charged ion fragments, along with the intact molecular ions, are forced through a series of negatively charged accelerating slits towards the mass analyser where they are separated on the basis of their mass to charge ratio.

(4) Separation of the ions is carried out in a curved metal tube through which the ion beam passes. The ions are deflected in a curved path by a magnetic field. Lighter particles will be deflected more than heavier particles. Thus by varying the strength of the magnetic field, ions of different masses can be focused onto a detector and recorded.

Mass spectra must be recorded under conditions of high vacuum; otherwise collisions between the ions and molecules of atmospheric gases would interfere with the results.

(5) The ions are focused onto an ion collector, where they are detected and amplified by an electron multiplier. A computer records the mass spectrum.
IONISATION OF SAMPLE MOLECULES
The method of ionisation most commonly used is electron ionisation. An electron stream as described previously bombards the sample molecules. This method is known as a hard source and in some cases it cannot be used because all the molecules break up into fragments and no molecular ion is seen. In these cases it is possible to use a soft source of which the most widely used is chemical ionisation (CI). This method will ensure that a molecular ion is recorded. In CI a reagent gas such as methane, methylpropane or ammonia is ionised by electron bombardment and is then allowed to react with a neutral molecule to produce a molecular ion.

Modern mass spectrometers have accessories, which allow the user to employ both hard and soft ion sources. The two types of spectra that result are useful. Soft sources allow the ready determination of MR of the analyte and the more complex spectra from hard sources allow for unambiguous identification of the structure of the compound.

NEW SYLLABUS.
The use of the mass spectrometer is referred to in following parts of the syllabus
Section 1.2 Atomic Structure. Use of the mass spectrometer in determining relative atomic mass. Fundamental processes which occur in a mass spectrometer: vaporisation of substance, production of positive ions, acceleration, separation, detection (mathematical treatment excluded)
Section 3.3 The Mole. Mr determination using a mass spectrometer (simple treatment only – interpretation of mass spectra not required)
Section 7.5 Chromatography and Instrumentation in Organic Chemistry. Instrumental methods of separation and/or analysis: Mass spectrometry (cf. 1.2). Analysis of (i) gases from a waste dump and (ii) trace organic pollutants in water.

REFERENCES:
(a) Leaving Certificate Chemistry, Guidelines for Teachers.
(c) A good website for information on mass spectrometry is http://antoine.fsu.umd.edu/chem/senese/101/atoms/faq/how-does-mass-spec-work.shtml