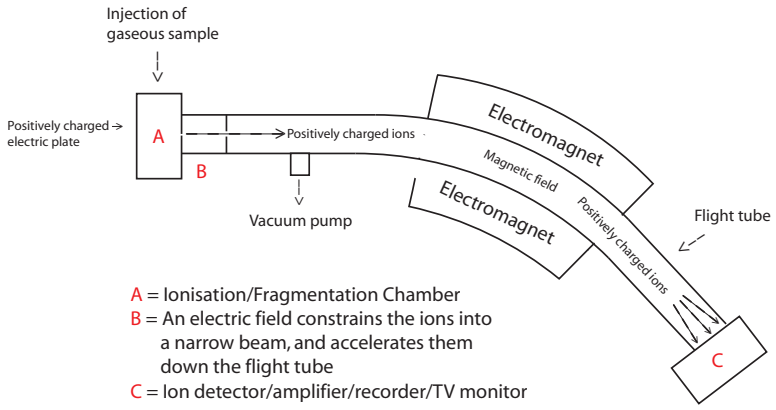
First Year blog on Mass Spectrometry: 20th April 2019

(This is a **revision** blog. It is merely a *summary* of some of the things that you need to know. Everything in this blog can be found in the relevant Chapters of the two books.)

If I had just one molecule of a substance and I wanted to know what the substance was, then one of the things that I could do to identify it would be to calculate its mass, and that is where **Mass Spectroscopy** comes in. However, please note that a Mass Spectrometer does not "weigh" things. A mass spectrometer is **not** a weighing machine. Weight is a function of mass and gravity, and a Mass Spectrometer measures the **Mass** of an object.

A Mass Spectrometer is capable of calculating the mass of as little as one billionth of a gram of a substance. It is an extremely sensitive instrument. If therefore a forensic scientist had only a miniscule amount of something and wished to identify that thing, then one of the analyses that she/he could do would be to find out the mass of that substance (and in your Second Year you will learn that Mass Spectroscopy can be teamed up with say Gas Chromatography to perform a more complete/sophisticated analysis)[1]. The following is a diagram that I have drawn using Adobe Illustrator.

Simplified Diagrammatic Representation of a Mass Spectrometer



A vacuum must first be created in the flight tube, and then the successive activities involved are

Injection	of gaseous sample
Ionisation	whereupon fragmentation will also occur
Acceleration	the ions that are created are constrained into a narrow beam and then accelerated forward down the flight tube
Deflection	in a magnetic field
Detection	where a computer then projects a chart of the abundance of the detected ions of different masses, and
Display	on a computer monitor/screen which can be connected to a printer and the spectrograph printed out.

Deflection is not the only means of separation, and bombardment with a stream of electrons is not the only method of **ionisation** in Mass Spectroscopy.

[1] Pioneered by Fred MacLafferty who is famous for the MacLafferty rearrangement in Infra-red spectroscopy.

Let us say that I had a small amount (Amount, N, is measured in moles) of a Halogen (for a First Year student, but a Second Year student would be confronted with something more complex e.g. a small amount of Butanoic Acid, $CH_3CH_2CH_2COOH$), and I wanted to identify the Halogen, then if I knew its mass I would know what type of Halogen it was.

A Mass Spectrometer is an instrument that measures the MASS of the individual ions of the atoms or the molecules of a substance, and it simultaneously measures the Mass of the individual species into which that substance will fragment.

The Workings of a *Deflection* Mass Spectrometer (NOT a Time-of-Flight machine)

A Mass Spectrometer cannot analyse the mass of solids or liquids – it can analyse only **gaseous** substances, therefore liquids or solid substances must first be converted into their gaseous form (either inside the mass spectrometer or elsewhere).

In order for the mass of an atom or a molecule to be ascertained, a mass spectrometer must first convert that species into a positively charged species, and if an atom or a molecule is bombarded with high speed electrons then one (and sometimes more than one) electron will be knocked off the atom or the molecule, and the atom or molecule then becomes a positively charged ion.

On top of that, a molecule will be broken up/it will become fragmented, *and these fragments will also have an electron knocked off them and thus they also will become positively charged ions*.

A positively charged ion will be repulsed by a positive electrode and attracted to a negatively charged electrode, therefore electrodes are placed in the Mass Spectrometer in such a way as to cause positively charged ions to be repelled and to fly down the "flight tube" towards the detector located at the other end of the flight tube. (NB In order for the path of the flying ions not to be impeded by anything, the flight tube in a Mass Spectrometer must be emptied by vacuum suction *before the injection of the gas sample*.)

Half way down the flight tube, the ions pass through a magnetic field created by a magnet or an electromagnet, and **each ion will be deflected from its original path according to its mass.** *[Imagine if you will, that you are standing on the edge of the pavement on Gerrards Cross High Street or Rangoon High Street (or wherever) and that you are grabbing at passers-by. I think that you will agree that you will be able to deflect a little six year old girl from the path that she was on much more easily than you will deflect a great big hulking 20 stone (280 pound/127 kilo) bloke from his course. Well, the same is true of ionised particles in an electromagnetic deflection field!]* **The greater the mass of the ion, the less will it be deflected from its original path down the flight tube**.

The mass of a particle will determine the amount of deflection that it suffers in an electromagnetic field, therefore an electromagnetic field is placed around the flight tube ***so as to separate the ions according to their masses***, and **it is the amount of deflection suffered by an ion that enables the Mass Spectrometer to ascertain the mass of any particular ion**.

At the end of the flight tube there is a device that records the impact of all the ions on the detector, and this allows the machine to analyse both the **Mass** and the **Abundance** of the positively charged ions that impact upon the detector. Both the **Mass** and the **Abundance** of all the impacting ions is shown in the form of a bar chart on a TV screen/monitor. Some of these ions will be the ionised atoms or molecules of the original substance itself, while other ions will be ionised ***fragments***.

The y-axis of the graph on the monitor will be Abundance or Relative Abundance, and the x-axis will be either the Mass/Charge ratio (i.e. M/e^-) where the divisor is "1" (cf. graph on page 4), or the M/z ratio (where the divisor is the size of the charge on the ion).

In First Year 'A' Level Chemistry, fragments with more than a single positive charge are ignored, therefore if the charge "e^-" = 1, then M÷1 = M = Mass.

Many students are confused when they start to look at Relative Abundance, because the Relative Abundances of all the ionised particles analysed by a Mass Spectrometer can often add up to more than 100% – and quite clearly it is NOT possible to have more than 100% of anything! Some textbooks are remiss in that they do not point out that in Mass Spectrometry, "**Relative Abundance**" tends to be measured against the largest abundance (i.e. the abundance of the fragment that impacts on the detector most), and this abundance is called the "**base peak**". The base peak is determined by the abundance of the most stable of all the fragments that are created. The abundance of the base peak is arbitrarily set at 100% (and *this is the reason why the sum of the relative abundances* ***adds up to more than 100%***).

The identity of every ionised species that impacts on the detector must correlate to its mass e.g. the Mass of CH_2^+ must = 14.

The heaviest particle recorded by the detector will by definition be the 'ionised parent molecule' or the "molecular ion" itself. (It is also known as the "radical cation", and I will explain why later.)

Relative Atomic Mass is the arithmetically weighted average mass of one atom of the commonly occurring isotopes of a given element *relative to 1/12th of the mass of an atom of Carbon-12*, and **Relative Molecular Mass** is the mass of one molecule of a given substance *relative to 1/12th of the mass of an atom of Carbon-12*.

The concept of fragmentation

It is possible to put a whole family on a big weighing machine and find out the weight of the whole family put together ; but equally, it would be possible to put each member of the family on a scale and weigh each one of them individually. That is exactly what a Mass Spectrometer does – it ascertains the total mass of the "*ionised molecule*" of a substance, and it can also ascertain the mass of all the different ionised fragments into which a substance can be broken down.

An ioniser ionises a molecule and its fragments usually by bombarding it/them with electrons and thereby (a) breaks a molecule into smaller pieces, and (b) ionises the molecule and its fragments by knocking electrons off it/them.

Different substances can have exactly the same mass e.g. isomers have the same mass (but with different spatial configurations), but ISOTOPES DO NOT HAVE THE SAME MASS (because they have differing numbers of neutrons) – but, by examining the different fragments that are shown in the analysis generated by a Mass Spectrometer, it is possible to decipher EXACTLY what substance the machine is analysing.

A Mass Spectrometer does two things simultaneously. It

- reveals the Mass of the basic molecule (or ionic unit) of the substance that is being analysed, and also the Mass of each individual different fragment into which the molecule (or ionic unit) can be broken, and it
- reveals the "*abundance*" (i.e. how much there is) of each of these fragments.

"**Abundance**" here means "how much" of each particle there is, e.g. a mass spectrometral analysis of a sample of naturally occurring Chlorine will reveal a relative "abundance" of 75.53% of Chlorine-35 atoms and a relative "abundance" of 24.47% of Chlorine-37 atoms (i.e. for every 10,000 atoms of Chlorine, 7553 will be Cl-35 and 2447 will be Cl-37 atoms). This gives an abundance ratio $\approx$ 3 : 1 .

However, the ionisation is done by impacting/smashing the species with electrons that then knock electrons off the species, but the impact can also

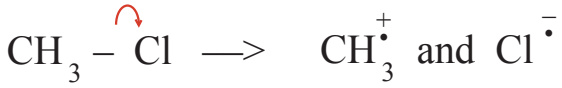
i) break the species into fragments (as already described)
ii) knock more than one electron off the species, and
iii) break molecules into their constituent (ionised) atoms i.e. **ions** e.g. a molecule of Chlorine could be broken into first two free radical atoms of Chlorine, and then into two free radical ions of Chlorine

Cl—Cl would break homolytically into $(Cl^{\bullet})^{+}$ + $(Cl^{\bullet})^{+}$

Free Radical fragments

In the illustration above I have assumed that the molecule will break **homolytically** and, since the two constituent atoms are equi-electronegative, then that is what will happen – but if the two fragments are **not** equi-electronegative, then the bond will break heterolytically and not homolytically.

If, for example, the molecule CH_3–Cl were to break at the bond that I have drawn in, then it will break **heterolytically**. CH_3 will have then lost an electron and become a **positively charged fragment** (and will thus be repelled down the flight tube and be detected at the detector), but **the free radical "$(Cl^{\bullet})^{-}$" fragment is negatively charged because during the heterolytic fission it got back its own electron from the pair of bonding electrons, AND it stole an electron from the C atom in CH_3. It is only *positively charged particles* that are repelled down the flight tube, and therefore the "$(Cl^{\bullet})^{-}$" fragment cannot and will not fly down the flight tube, and it will thus NEVER appear on the detector screen.** It might immediately pair up with a positively charged fragment and form a neutrally charged particle, but again it would not be repelled down the flight tube and never appear on the detector screen. **It is only positively charged particles that ever get registered on the detector screen.**



The "$(Cl^{\bullet})^{-}$" and "$(Cl^{\bullet})^{+}$" fragments are free radicals because they have lone /unpaired electrons.

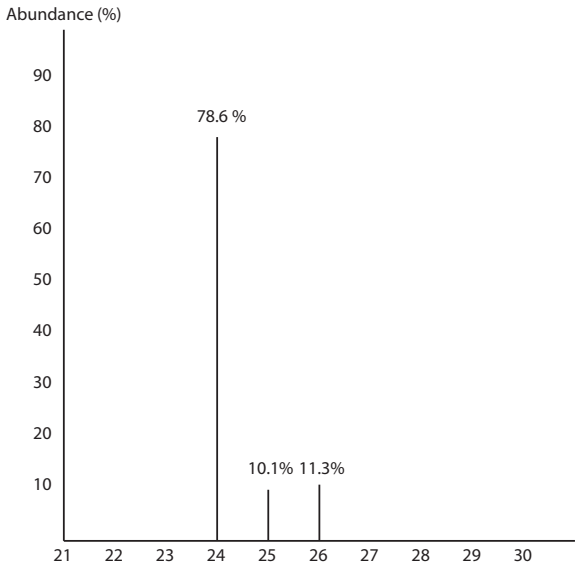
If a molecule of the substance that is being analysed (let's say Propane, CH_3-CH_2-CH_3, has an electron knocked off it in the Ioniser, then it will now have an unpaired electron (therefore it will be a "free radical") and it will now have a positive charge (cf. below), therefore it will be called the **radical cation** of the substance – but its more common name is the **molecular ion** of the substance.

(CH_3-CH_2-CH_3 – e^{-}) becomes **$(CH_3$-CH_2-$CH_3)^{\bullet +}$**

Mass Charge Ratio

ALL mass spectrometers measure a ratio of Mass (m) to Charge (z). When the spectrometer states that it is measuring the mass divided by the charge on one electron i.e. "M/e^{-}", then the divisor is "1"; but, **where the spectrometer measures the mass divided by "z"**, then the divisor is whatever happens to be the charge on the ion. It is fairly common to get a "M/2" ratio, but it would be *most unusual* to get a ratio larger than that (i.e. M/3 and M/4 etc).

Chart from the recording device that forms part of the Detector/Amplifier in a Mass Spectrometer
For example a bar chart on a TV screen would show the RAM/RMM/RFM of the substance and also of all the different fragments involved. The following is the chart for Magnesium.



Mass/Charge Ratio (M/e^-)

NB In an exam, sometimes the percentages above are not supplied but the graph is drawn on graph paper – and in that case, the percentages can easily be measured with a 'ruler'.

RAM of Magnesium $= \frac{78.6}{100} \times 24.0) + \frac{10.1}{100} \times 25.0) + \frac{11.3}{100} \times 26.0)$

$= (18.864 + 2.525 + 2.938)$

$\approx$ 24.3 (to 3 sig figs).

Please note that I have used Relative Abundances that add up to 100%. Had I used the most frequent abundance as the "base peak", and if 78.6 = 100%, then 10.1 = 12.85%, and 11.3 = 14.38%, and the total of these three numbers is 127.23%, then the calculation becomes

RAM of Magnesium $= \frac{100}{127.23} \times 24.0) + \frac{12.85}{127.23} \times 25.0) + \frac{14.38}{127.23} \times 26.0)$

$= 18.86 + 2.525 + 2.939 \approx 24.3$ (to 3 sig figs)

In other words, the calculation gives EXACTLY the same answer!

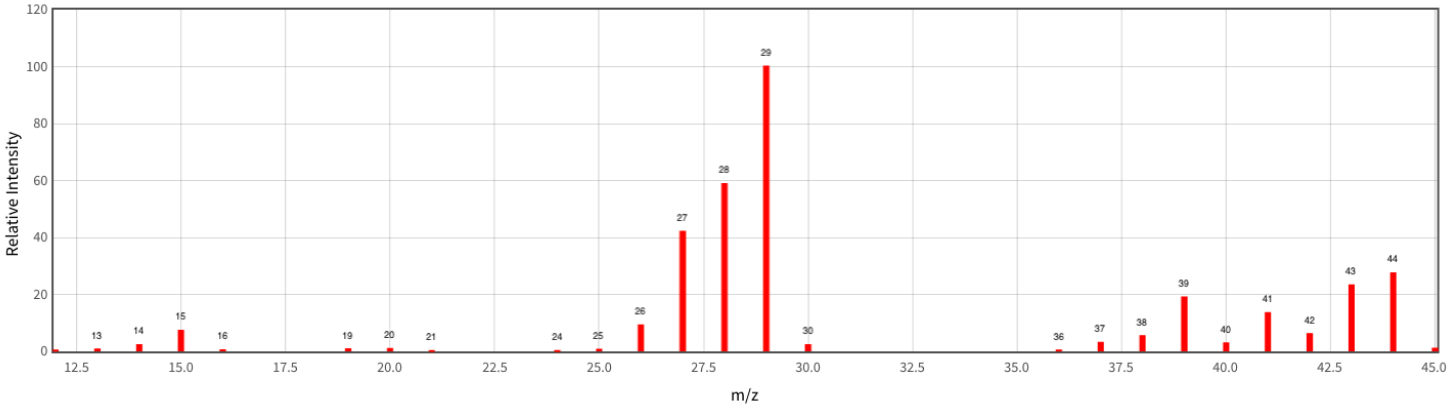
This is the sort of question that you will be asked to do in your First Year 'A' Level Chemistry exams – but please do lots of calculations from your own textbook, and you will see that these calculations are **very** easy to do *(and this is true even of more complicated Second Year calculations)*.

Mass/Charge ratios of (M+1)

Carbon has two common isotopes ^{12}C and ^{13}C with relative abundances of 98.9% and 1.1% (and I trust that you remember the difference between **isotopes** and isomers). ^{14}C also exists and it is of enormous importance in radio-carbon dating, but its relative abundance is only 1 part per trillion and therefore it is not relevant for the purposes of 'A' Level Chemistry Mass Spectroscopy.

Let us therefore pretend that Carbon exists as ^{12}C and ^{13}C with relative abundances of 98.9% and 1.1%. A Mass Spectrometer measures the masses of different entities, therefore the detector will register the mass of C^+ at two different places on the detector screen viz at the mass/charge ratio of 12 and at 13.

Equally, the Spectrograph of Propane would register the masses of both sorts of C atoms below (Source: NIST). The (non-sophisticated) RMM (or M_r) of Propane is 44 g mol^{-1}, but you will notice the little red almost-a-dot registering at 45, and that is for Propane with one ^{13}C atom in it. I do not want to get into the complexities of this topic because that is all that you need to know at 'A' Level.



Mass/Charge ratios of (M+2)

When an element has two or more isotopes e.g. Chlorine has two isotopes i.e. ^{35}Cl and ^{37}Cl, then since a Mass Spectrometer measures the masses of different entities, the detector will register the mass of Cl^+ at two different places on the detector screen viz at the mass/charge ratio of 35 and at 37. However, since the abundance of ^{35}Cl is three times as much as the abundance of ^{37}Cl, then the histogram representation for the abundance or relative intensity for ^{35}Cl should be three times as large as that for ^{37}Cl (but other factors with regard to abundance will also come into play).

This then explains registration at the mass/charge ratio (M+2).

(M+3) and (M+4) registration are possible but you are **not** going to be asked about them.

Masses with many decimal places

Where an element has isotopes, then the arithmetically weighted RAM could have numbers such as 14.0031 g mol^{-1} for Nitrogen (^{14}N and ^{15}N) and 15.9949 g mol^{-1} for Oxygen (^{16}O, ^{17}O and ^{18}O).

Time of Flight Mass Spectrometers

I do not intend to say anything about "Time-of-Flight" machines other than to say that they sperate fragments according to how long they take to travel a specific distance (with objects with less mass travelling faster than objects with more mass). This is in contrast to "Separation-by-Deflection" machines where the trajectory in the flight tube is determined by the mass of the object (with objects that have less mass being deflected more than objects with more mass).

OK, that's enough for First Year students.