

Student guide: Time of flight mass spectrometry

This guide relates to section 3.1.1.2 of our AS and A-level Chemistry specifications. We have produced it to supplement the specification and the Teaching Notes that are already available. On a separate document we have given you a range of summary questions on the topic with example marking guidance.

Time of flight mass spectrometry

Mass spectrometry is a powerful instrumental method of analysis. It can be used to:

- find the abundance and mass of each isotope in an element allowing us to determine its relative atomic mass
- find the relative molecular mass of substances made of molecules.

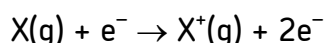
A common form of mass spectrometry is time of flight (ToF) mass spectrometry. In this technique, particles of the substance are ionised to form 1+ ions which are accelerated so that they all have the same kinetic energy. The time taken to travel a fixed distance is then used to find the mass of each ion in the sample.

Stage 1 – Ionisation

The sample can be ionised in a number of ways. Two of these techniques are electron impact and electrospray ionisation (which are simplified here for AS/A level).

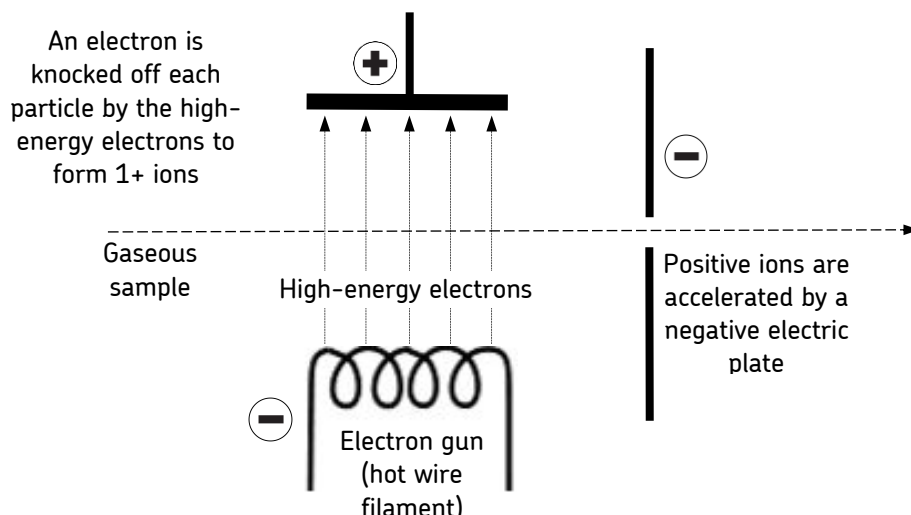
Electron impact (also known as electron ionisation)

The sample being analysed is vaporised and then high energy electrons are fired at it. The high energy electrons come from an 'electron gun' which is a hot wire filament with a current running through it that emits electrons. This usually knocks off one electron from each particle forming a 1+ ion.

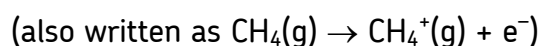
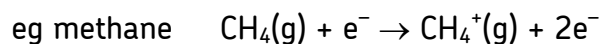


(also written as $X(g) \rightarrow X^{+}(g) + e^{-}$)

The 1+ ions are then attracted towards a negative electric plate where they are accelerated.



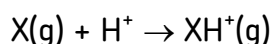
This technique is used for elements and substances with low formula mass (that can be inorganic or organic molecules). When molecules are ionised in this way, the 1+ ion formed is known as a molecular ion.



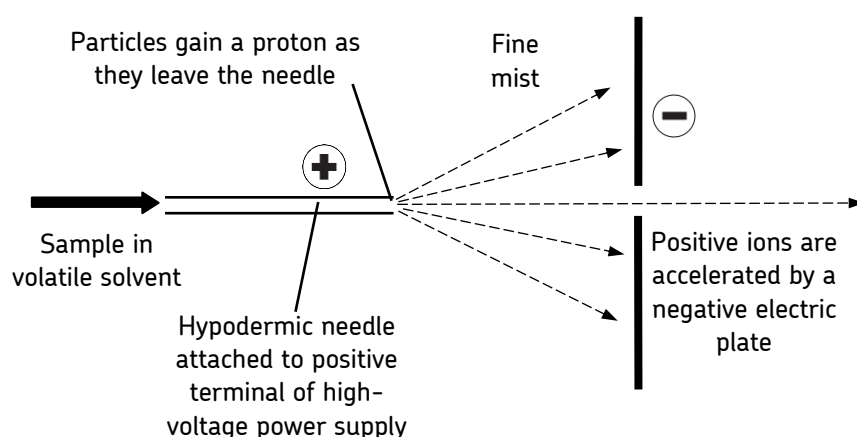
The molecular ion often breaks down into smaller fragments some of which are also detected in the mass spectrum. (Fragmentation of molecular ions is not included on the specification and is only included here as useful background information).

Electrospray ionisation

The sample X is dissolved in a volatile solvent (eg water or methanol) and injected through a fine hypodermic needle to give a fine mist (aerosol). The tip of the needle is attached to the positive terminal of a high-voltage power supply. The particles are ionised by gaining a proton (ie an H^+ ion which is simply one proton) from the solvent as they leave the needle producing XH^+ ions (ions with a single positive charge and a mass of $M_r + 1$).



The solvent evaporates away while the XH^+ ions are attracted towards a negative plate where they are accelerated.



This technique is used for many substances with higher molecular mass including many biological molecules such as proteins. This is known as a 'soft' ionisation technique and fragmentation rarely takes place.

Stage 2 – Acceleration

The positive ions are accelerated using an electric field so that they all have the same kinetic energy.

$$KE = \frac{1}{2}mv^2$$

(students would be given this equation if expected to use it in an exam)

KE = kinetic energy of particle (J)

m = mass of the particle (kg)

v = velocity of the particle ($m\ s^{-1}$)

Therefore, the velocity of each particle is given by: $v = \sqrt{\frac{2KE}{m}}$

Given that all the particles have the same kinetic energy, the velocity of each particle depends on its mass. Lighter particles have a faster velocity, and heavier particles have a slower velocity.

Stage 3 – Flight tube

The positive ions travel through a hole in the negatively charged plate into a tube. The time of flight of each particle through this flight tube depends on its velocity which in turn depends on its mass.

The time of flight along the flight tube is given by the following expression:

$$t = \frac{d}{v}$$

$$t = d\sqrt{\frac{m}{2KE}}$$

(students would be given this equation if expected to use it in an exam)

t = time of flight (s)

d = length of flight tube (m)

v = velocity of the particle (m s^{-1})

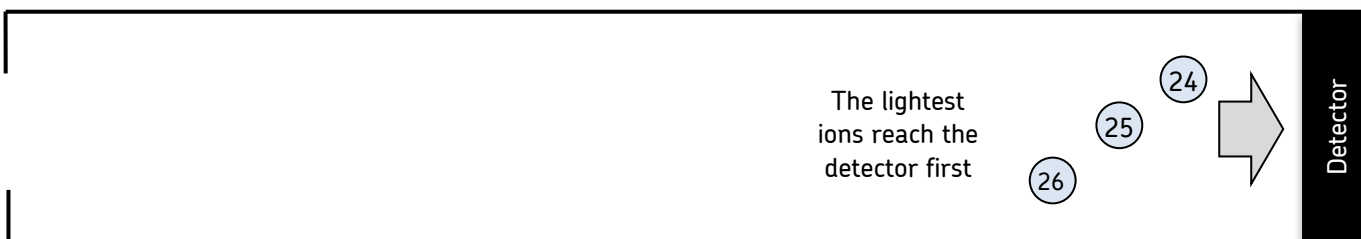
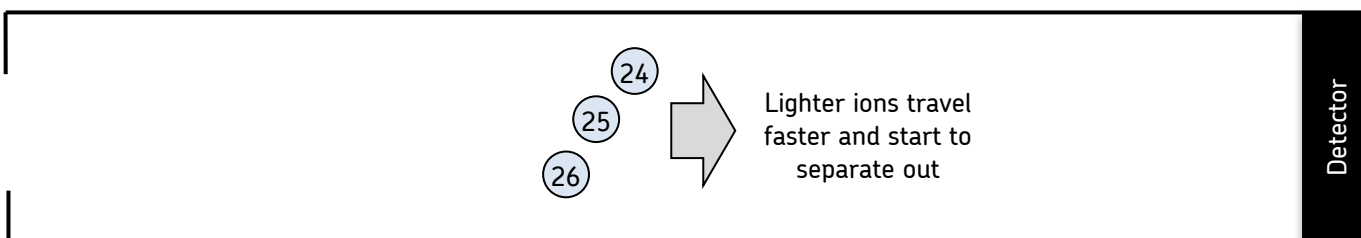
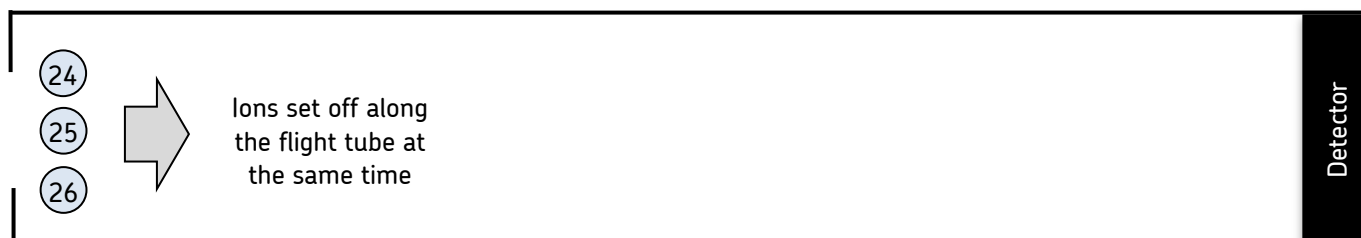
m = mass of the particle (kg)

KE = kinetic energy of particle (J)

This shows that the time of flight is proportional to the square root of the mass of the ions. Therefore lighter ions travel faster and reach the detector in less time than the heavier particles that move slower and take longer to reach the detector.

eg ions of the three isotopes of magnesium ($^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$, $^{26}\text{Mg}^+$) will travel at different speeds through the flight tube and separate, with the lightest ion ($^{24}\text{Mg}^+$) reaching the detector first.

Flight tube



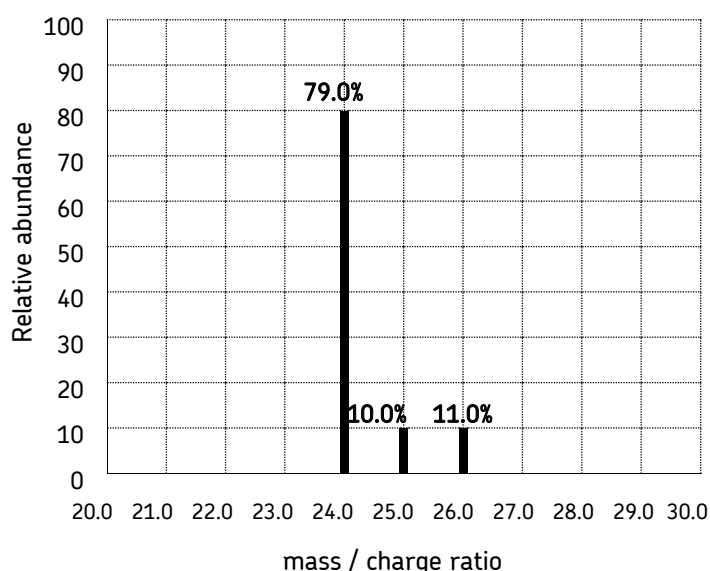
Stage 4 – Detection

The positive ions hit a negatively charged electric plate. When they hit the detector plate, the positive ions are discharged by gaining electrons from the plate. This generates a movement of electrons and hence an electric current that is measured. The size of the current gives a measure of the number of ions hitting the plate.

The mass spectrum

A computer uses the data to produce a mass spectrum. This shows the mass to charge (m/z) ratio and abundance of each ion that reaches the detector. Given that all ions produced by electrospray ionisation and most of the ions by electron ionisation have a 1+ charge, the m/z is effectively the mass of each ion.

In the following example, the mass spectrum of magnesium is shown. Ions with mass to charge ratio 24.0, 25.0 and 26.0 reach the detector. This shows that magnesium is made up of three isotopes: ^{24}Mg , ^{25}Mg and ^{26}Mg .



The relative atomic mass of an element can be found by calculating the mean mass of these isotopes.

$$\text{relative atomic mass } (A_r) = \frac{\text{combined mass of all isotopes}}{\text{combined abundance of all isotopes}}$$

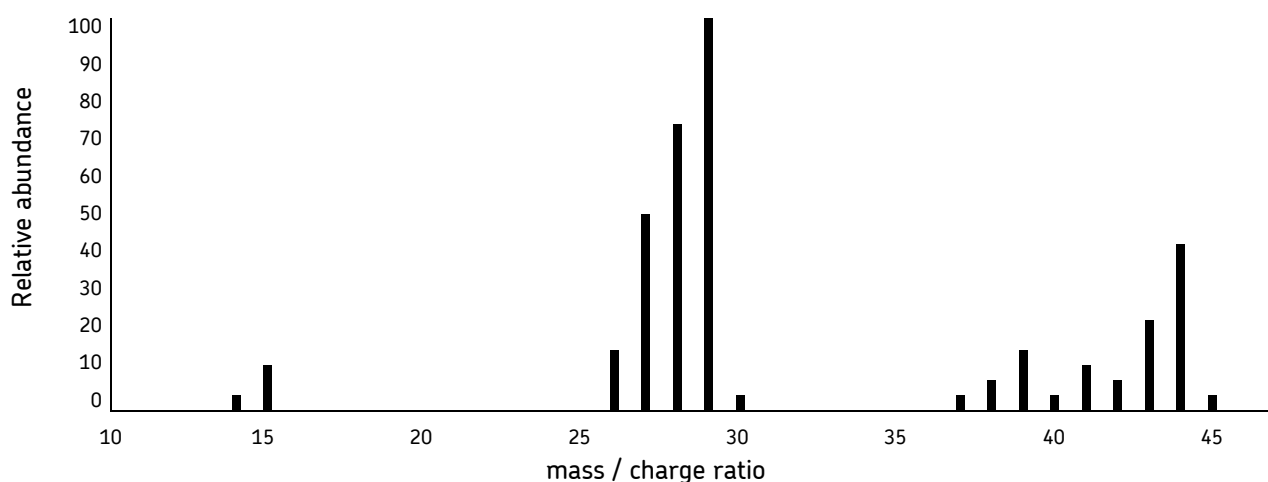
eg for magnesium:

$$\text{relative atomic mass } (A_r) = \frac{(79.0 \times 24.0) + (10.0 \times 25.0) + (11.0 \times 26.0)}{79.0 + 10.0 + 11.0} = 24.3$$

For molecules that are ionised by electron impact, the signal with the greatest m/z value is from the molecular ion and its m/z value gives the relative molecular mass. However, there may be some other small peaks present around the molecular ion peak due to molecular ions that contain different isotopes.

When using electron impact ionisation (but not with electrospray ionisation), there may also be peaks at lower m/z values due to fragments caused by the break up of molecular ion. (Fragmentation of molecular ions is not included on the specification and is only included here as useful background information.)

In the following example, the mass spectrum of propane has been produced following electron impact ionisation. The peak with the greatest m/z is at 44 (apart from a small signal at m/z 45 which is due to molecular ions of propane with one atom of ^2H or ^{13}C). This tells us that the relative molecular mass of propane is 44. Peaks at below m/z 44 are due to the fragmentation of molecular ions.



In this next example, a protein has been analysed by time of flight spectrometry following electrospray ionisation using protonation. The peak at 521.1 is for MH^+ and so the relative molecular mass of the protein is 520.1. The peak at 522.1 is due to MH^+ ions containing one atom of ^{13}C or ^2H .

