

Teaching notes: Time of flight mass spectrometry

These teaching notes relate to section 3.1.1.2 Mass numbers and isotopes of our AS and A-level Chemistry specifications (7404, 7405).

This resource aims to provide background material for teachers preparing students for AS and A-level Chemistry. It is provided as an additional resource to cover specification topics with which teachers may not be familiar. This information goes beyond the requirements of the specifications. It may well be of interest to students but the specifications indicate the limits of the knowledge and understanding of this topic that will be examined.

Specification overview

Content	Opportunities for skills development
<p>Mass number (A) and atomic (proton) number (Z).</p> <p>Students should be able to:</p> <ul style="list-style-type: none"> determine the number of fundamental particles in atoms and ions using mass number, atomic number and charge explain the existence of isotopes. <p>The principles of a simple time of flight (TOF) mass spectrometer, limited to ionisation, acceleration to give all ions constant kinetic energy, ion drift, ion detection, data analysis.</p> <p>The mass spectrometer gives accurate information about relative isotopic mass and also about the relative abundance of isotopes.</p> <p>Mass spectrometry can be used to identify elements.</p> <p>Mass spectrometry can be used to determine relative molecular mass.</p>	<p>MS 1.1</p> <p>Students report calculations to an appropriate number of significant figures, given raw data quoted to varying numbers of significant figures.</p> <p>MS 1.2</p> <p>Students calculate weighted means eg calculation of an atomic mass based on supplied isotopic abundances.</p> <p>MS 3.1</p> <p>Students interpret and analyse spectra.</p>

<p>Students should be able to:</p> <ul style="list-style-type: none">• interpret simple mass spectra of elements• calculate relative atomic mass from isotopic abundance, limited to mononuclear ions.	
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Mass spectrometry

Traditional mass spectrometers that use magnetic fields to separate moving ions are being replaced by time of flight (TOF) mass spectrometers that are able to separate ions without the need for a strong magnetic field. TOF mass spectrometers are therefore smaller and lighter than the traditional machines.

In both types of mass spectrometer, there are three stages involved in the analysis of a sample:

1. Ionisation.
2. Separation of charged species.
3. Detection.

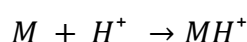
Ionisation

There are several different ways in which a sample can be ionised. The traditional method involves bombardment of a gaseous sample with a beam of high-energy electrons, fired from an electron gun. This technique is still in use with TOF mass spectrometers for obtaining the mass spectra of small molecules and atoms.

New methods of ionisation have been developed that are particularly suited to large organic molecules because they overcome the destructive effects of an electron gun that could lead to complete fragmentation of a molecule and therefore no molecular ion. These new 'soft' methods of ionisation are electrospray ionisation and matrix assisted laser desorption ionisation (MALDI), which uses a laser to ionise the sample. One of these new ionisation techniques, electrospray ionisation, is explained below.

Electrospray ionisation

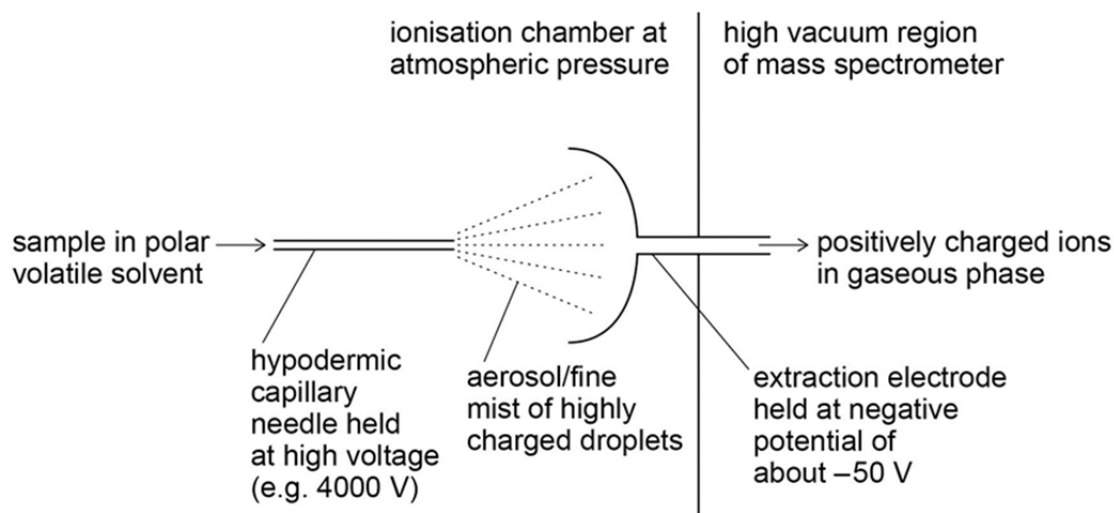
The sample is dissolved in a polar, volatile solvent such as water or methanol or a mixture of the two. The solvent can act as a source of protons to facilitate the ionisation process.



where M represents a large molecule.

The solution is pumped through a hypodermic capillary needle, where the sample is converted into a fine mist (nebulized). A very high voltage (typically 4,000 volts) is applied to the tip of the capillary and the sample emerges dispersed in an aerosol of highly charged droplets. The solvent evaporates (desolvation) and we are only interested in the singly charged $MH^+(g)$ ions produced.

Figure 1: the electrospray ionisation process.



Electrospray ionisation is considered a 'soft' technique as generally no fragmentation occurs upon ionisation and is commonly used to determine the relative molecular masses of polar molecules and biological macromolecules such as proteins. In the absence of fragmentation little structural information is obtained. For large biomolecules, molecular masses can be measured to an accuracy of 0.01%. For small organic molecules, the molecular mass enables the molecular formula of a compound to be identified.

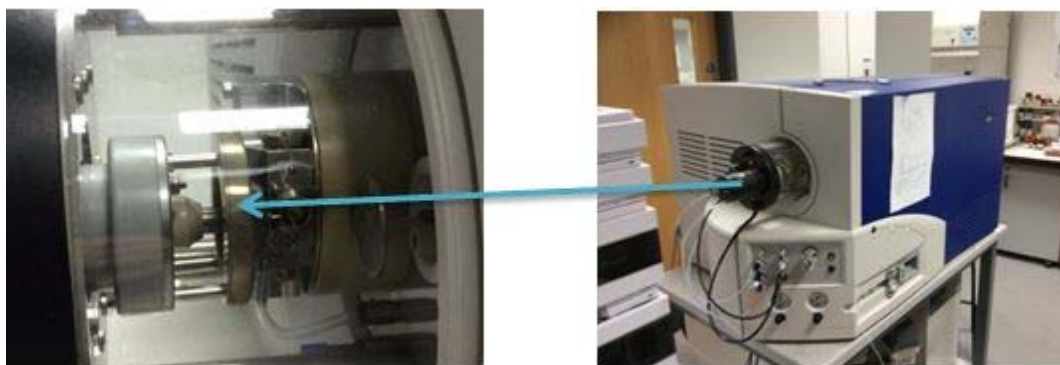
The mass-to-charge ratio for a protonated molecule will be:

$$m/z = M_r + 1$$

It is possible for some molecules to form positive ions by combining not with a proton but with another different positive ion, eg Na^+

Some machines are set up to investigate negative ions, usually created by loss of a proton from the parent molecule. A solvent can be chosen that acts as a base and therefore facilitates the loss of a proton. Negative ions are extracted into the mass spectrometer by changing the polarity of the extraction electrode from a negative to a positive potential.

Figure 2: photographs (one enlarged) of a hypodermic capillary needle where electrospray ionisation occurs in a TOF mass spectrometer.



Separation of charged species

Traditional mass spectrometers

For more than 50 years, electromagnets and then quadrupoles have been used to separate ions. A quadrupole consists of four parallel metal rods. Each opposing rod pair is connected together electrically, and a radio frequency voltage is applied between one pair of rods and the other. Ions are separated using differences in their mass-to-charge ratio.

TOF mass spectrometers

TOF mass spectrometers separate ions by time without the use of a magnetic field. In a crude sense, TOF is similar to chromatography, except there is no stationary or mobile phase, instead the separation is based on the different velocity of ions that are each given the same kinetic energy.

Separation process

All forms of mass spectrometry require the molecule to carry some charge. Molecules are ionised and the ions are then separated and sorted according to their mass-to-charge ratio (m/z values) by the speed they travel before passing into a detector, where their concentration is measured and displayed on a mass spectrum chart.

All ions are accelerated by an electric field into a 'field-free' drift region (ie free of electrical fields) with the same kinetic energy.

Ions are accelerated away from the ion source by applying an electric field. The potential energy of a charged particle is given by:

$$PE = qV$$

where PE is the potential energy, q is the charge on the particle, and V the electrical potential difference (or voltage).

The potential energy is converted into kinetic energy, which is given by:

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

where KE is the kinetic energy, m the mass and v the velocity.

The velocity can be expressed in terms of s , which is the distance travelled or length of the flight tube, and time, t :

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

If we substitute this into the equation for kinetic energy:

$$KE = \frac{1}{2}m \left(\frac{s}{t}\right)^2$$

So if we rearrange this:

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

ie

$$t \propto \sqrt{m}$$

Time is proportional to the square root of mass. Lighter species arrive at the detectors earlier than heavier species.

If we now replace KE by qV , where q is the charge and V the applied electrical potential difference, as above, the equation becomes:

$$t = s \sqrt{\frac{m}{2qV}}$$

So

$$t \propto \sqrt{\frac{m}{q}}$$

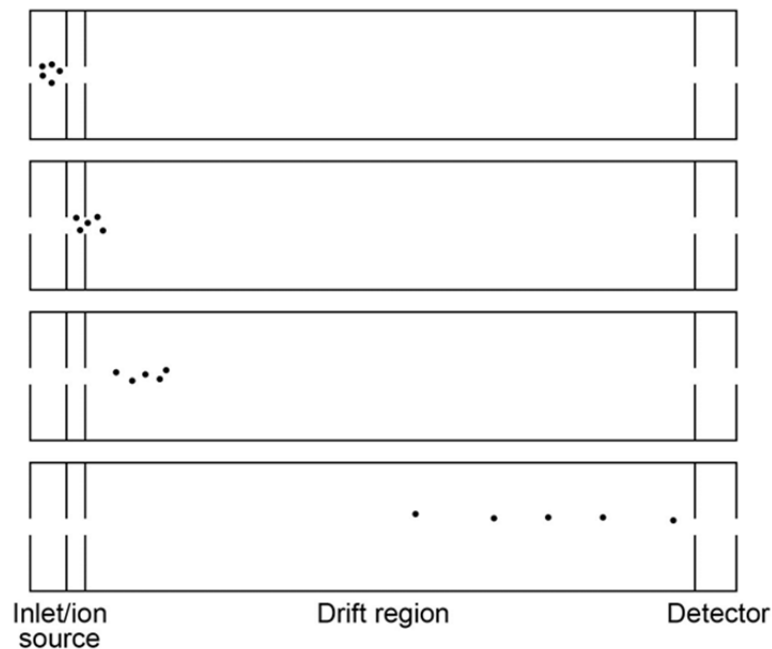
Time is proportional to the square root of the mass-to-charge ratio. So for a given mass, species with a higher charge arrive at the detectors before those with a lower charge.

For example, $^{40}\text{Ar}^{2+}$ would be detected before $^{40}\text{Ar}^+$ and $^{40}\text{Ar}^{2+}$ would be expected to arrive at the detectors at the same time as $^{20}\text{Ne}^+$ - although Ar is twice as heavy as Ne, these two species have the same mass-to-charge ratio (Ar is 40/2, Ne is 20/1). This is something which can cause problems in mass spec, when different species arrive at the detectors at the same time.

For TOF mass spectrometry to work, all the ions have to start accelerating at a well-defined time - typically ionisation events will occur at approximately kHz frequency. One way of doing this is to create the ions in a static electric field in a well-defined event (a pulsed laser can do this). To integrate a continuous ion source (like electrospray) with a TOF instrument, a linear region can be filled with ions from the source before an electric field is imposed perpendicular to the direction in which the ions from the source are travelling. This is called 'orthogonal time of flight mass spectrometry'.

Since all ions have the same kinetic energy, separation is achieved because the 'lighter' ions move with a higher velocity and reach the detector first.

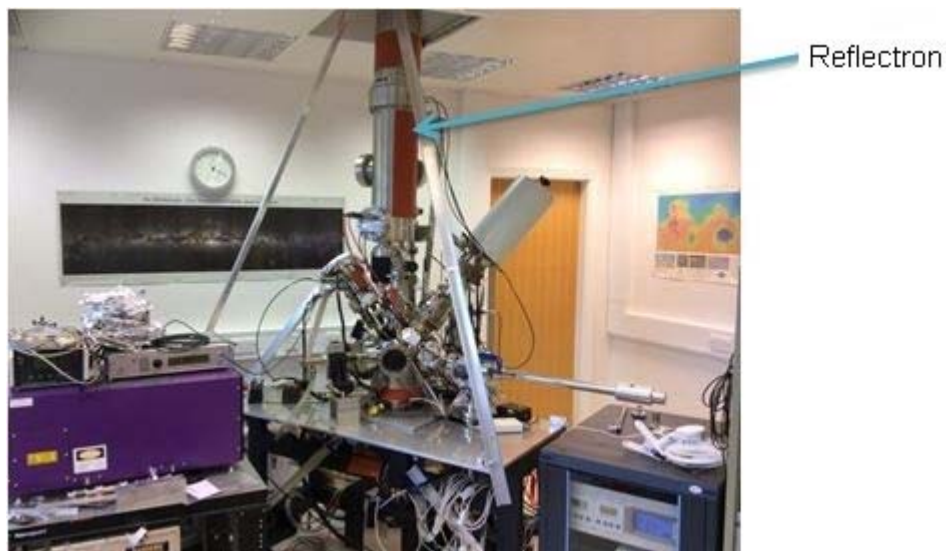
Figure 3: separation of ions with passing time (ion drift).



Reflectron

A reflectron is a type of TOF mass spectrometer that enhances the resolution of the mass spectrometer. This is achieved by using a long time of flight tube in which the ions move in one direction, are reflected back and then focused by electrostatic lenses before reaching the detector.

Figure 4: a reflectron mass spectrometer at the University of Manchester research department.



They had to make a hole in the ceiling to accommodate the instrument! The reflectron is the vertically-mounted red cylinder.

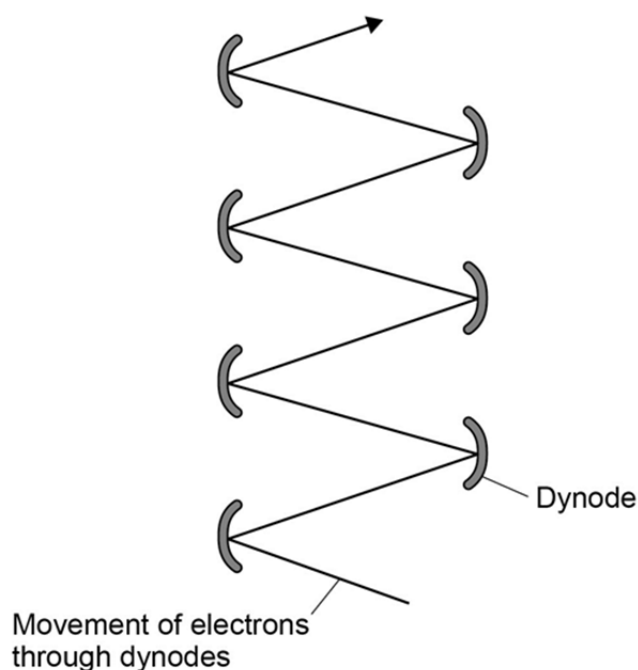
Detection

After the ions are separated according to their mass/charge (m/z) ratio, they are detected. The detection apparatus needs to be highly sensitive.

The ions are directed to the analyser by electrostatic lenses under low pressure. Here each ion is discharged and the resulting current is measured. As technology has developed, the mass resolution and the sensitivity of the detection have continued to improve.

In mass spectrometry, ion currents are typically low. This requires a significant multiplication of the current generated per ion upon arrival at the detector. Dynodes have been used to multiply the electron signal generated by each ion. Each dynode is held at a more positive voltage than the preceding one. An ion moves toward the first dynode because it is accelerated by an electric field. Upon striking the first dynode, more low energy electrons are emitted, and these electrons are in turn accelerated toward the second dynode. The arrangement of the dynodes is such that a cascade occurs with an ever-increasing number of electrons being produced at each stage. Up to 1,000,000 electrons per ion reaching the anode results in a sharp current pulse that is easily detectable, signaling the arrival of the ion about 50 nanoseconds earlier.

Figure 5: a representation of a dynode array that acts as an electron multiplier.



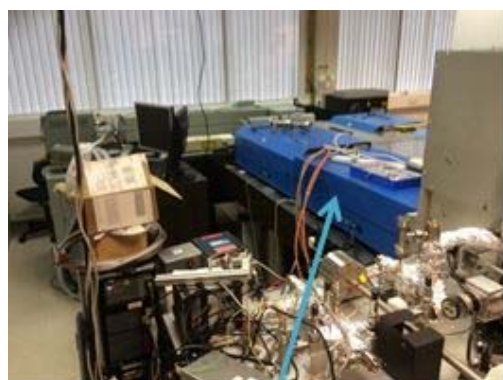
Ions are directed to a micro-channel plate (MCP). Ions arrive at the face of the MCP and generate an electron, which accelerates down a silica microtube. The walls of the microtube behave like an array of dynodes. Each collision with the walls of the microtube multiplies the number of electrons, giving rise to 1,000 electrons at the other end of the tube. A second MCP can be used, which can generate multiplications by a factor of 10^7 .

Modern detectors can accurately represent a very fast ion arrival event. This is crucial, particularly for modern time of flight analysers. Ion optics designers have invested a lot of effort to time-focus ions of the same mass to arrive at the detector within very short amounts of time, sometimes less than 1 ns.

TOF mass spectrometers uses

NASA missions have collected individual grains from meteorites and stardust from space. Lasers are used to ionise specific elements or molecules released when these samples are heated, which may only consist of just a few thousand atoms of the species of interest.

Figure 6: TOF mass spectrometer used to analyse these samples, developed at the University of Manchester, School of Earth, Atmospheric and Environmental Sciences.



A laser



Time-of-flight tube: The ion source is at the right-hand end and the detector at the left. This image is a closer view of the bottom right of the previous image

TOF mass spectrometers can be made to be very small and light, suitable for space exploration.

The Philae lander was carried during the Rosetta spacecraft's 10-year journey, and achieved the first-ever soft landing on a comet nucleus in November 2014. The Philae carried a number of scientific instruments. This included the Cometary Sampling and Composition instrument (COSAC), which is a combined gas chromatograph (see Teaching notes: Chromatography) and TOF mass spectrometer. It was used to perform analysis of soil samples and determine the content of volatile components. Preliminary results reveal organic compounds are present on the comet's surface, and also hint at a dense, icy interior. Philae touched down in an icy hollow without enough sunlight to recharge its batteries. Scientists hope that Philae will be able to power up again when the comet moves closer to the Sun and the lander's solar panels are illuminated.

References

[COSAC - Cometary Sampling and Composition Experiment](#)

Education in Chemistry, January 2015, p.3 (available free to schools through Royal Society of Chemistry - [RSC](#))

Acknowledgement

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