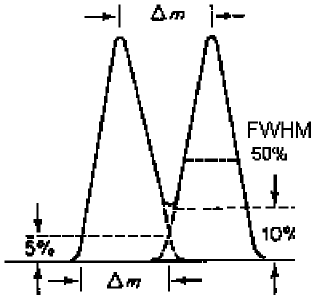
Resolution:

The resolution of a mass analyser is defined in terms of the ability to separate ions of differing mass. The resolution R necessary to separate two peaks of mass M and $M+\Delta M$ is

$$R = M / \Delta M$$

This value may be expressed in parts per million: $R(ppm) = 10^6 \Delta M / M$



According to the '10% valley' definition of resolution, two peaks of equal height are said to be separated if the valley between them is 10% of the height of the peaks. The value of ΔM is then the difference in the mass of the two peaks. This value is the same as the width of either peak at the 5% level.

An alternative definition is to use as ΔM the width of the peak at half the height of the peak. This is known as the FWHM (Full Width Half Maximum) definition of resolution.

Mass Analysers

Magnetic sector analyser:

Ions are extracted from the source and accelerated by a voltage (typically 8kV). They pass through a variable-width slit (the **source slit**).

The ions then pass into a magnetic field perpendicular to the direction of travel. The ions are deflected by the magnetic field.

The equation describing the deflection of an ion in the magnetic field is:

$$m / z = B^2 r^2 e / 2V$$

where m is the mass of the ion
z is the charge state
B is the magnetic field strength
r is the radius of the flight path
e is the charge on an electron
V is the accelerating voltage

or, for a singly charged ion of mass M,

$$M = 4.83 \times 10^3 (B^2 r^2 / V)$$

where B is in Tesla
r is in cm
V is in volts

The magnetic field also has a focusing effect on angularly diverging ions in the beam.

A mass spectrometer consisting only of a magnetic sector is called a single focusing mass spectrometer.

Because the magnetic sector is a momentum analyser, ions with the same mass but different velocities are not all brought to a focus at the same point. This limits the **resolution** of the magnetic sector by broadening of the peaks.. This can be overcome by the use of an electrostatic sector (the electrostatic analyser or **ESA**). This consists of two very accurately positioned parallel curved plates with a voltage applied between them.

The motion of ions in the field of the ESA is given by:

$R = 2V / E$ where R is the radius of the flight path
V is the accelerating voltage
E is the voltage between ESA plates

Thus the path taken by an ion through the ESA is energy- not mass- dependent. Thus the ESA may be used to filter the energy of the ion beam, resulting in much greater resolution.

The ESA is combined with the magnetic sector to provide a 'double focusing' spectrometer. If the ESA is placed before the magnetic sector, this is known as 'forward' or 'Nier-Johnson' geometry; if it is placed after the magnetic sector, it is known as 'reverse' geometry.

Magnetic sector instruments can have maximum resolutions of up to 150,000. Normal operation is carried out with resolutions in the range 1000 - 10,000. For these instruments, resolution is constant throughout the mass range.

Quadrupole analyser:

A quadrupole analyser consists of 4 rods of hyperbolic or circular cross-section arranged symmetrically.

A voltage consisting of a DC component U and an RF (Radio Frequency) component $V_0 Cos\omega t$ is applied between adjacent rods. Opposite rods are connected. Ions entering the rod assembly at one end with an energy of 10eV-20eV oscillate in the x and y directions.

For certain values of U and V_0, ions of a certain mass perform stable oscillations, and travel down the space between the rods to the detector. Other ions go into unstable oscillations, the amplitude of which rapidly tend to infinity. With no DC voltage applied $(U = 0)$, the analyser is in 'RF only' mode, and ions of all masses reach the detector. A mass is selected by varying U and V_0. The mass range is scanned by varying U and V_0, keeping the ratio U / V_0 constant.

The resolution is selected by changing the value of U. High values of U give high resolution. This reduces the region of stable oscillation, and thus the sensitivity.

Quadrupole instruments have a constant value of ΔM throughout the mass range, so might have a resolution of 300 at mass 300, and 1000 at mass 1000.

Time-of-flight analyser:

If an ion is accelerated with a voltage, its resulting velocity is a function of its mass/charge ratio. In a TOF analyser, separation is by velocity, and the mass of an ion may be determined by the time taken for it to travel a fixed distance.

This time is given by: $t = L\sqrt{m/(2zeV)}$ where L = length of flight path
V = accelerating voltage

In a TOF analyser, the ion source is pulsed, and the time taken from this pulse of ions to travel to the detector is measured.

Ion trap analyser:

In the ion trap, a ring of hyperbolic internal cross-section is enclosed by two end caps. The end caps are at earth potential, and an RF voltage is applied to the ring. For a particular RF amplitude, ions above a threshold mass are "trapped" in stable orbits within the assembly.

Scanning is accomplished by trapping all ions above a low threshold, and turning off the ion source. The RF amplitude is then increased, and ions escape the trap into the detector in order of increasing mass.

Fourier Transform / Ion Cyclotron Resonance analyser (FT/ICR):

In the ICR mass analyser, ions are produced and stored inside a cell. The cell is within the field of a superconducting magnet, and consists of transmitter and receiver plates parallel to the magnetic field, and trapping plates normal to it. Ions within the cell are constrained to rotate in the magnetic field with a frequency dependent on their mass, where the frequency, w is given by:

$$\omega = 1.537 \times 10^{7} \left(\frac{zB}{M} \right)$$

A small DC voltage across the trapping plates prevents the ions from escaping axially. Ions rotating at a given frequency may be excited to larger orbital radii by application of an r.f. voltage of the appropriate frequency applied to the transmitter plates.

A frequency sweep of the r.f. voltage causes all ions to be thus excited, and to produce an 'image current' in the receiver plates.

This signal is a time-domain signal which may be converted to a frequency domain signal by application of a Fourier transform. The frequency-domain signal may then be converted to a mass spectrum, from the relationship between frequency and mass.