

Mass Analyzers

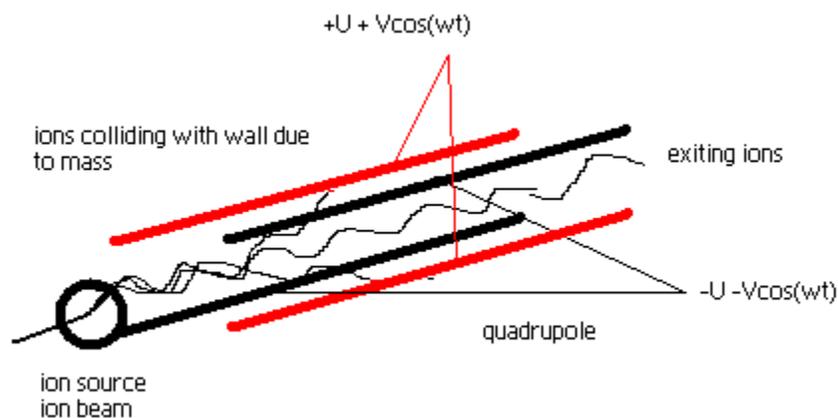
Mass spectrometry is an analytic method that employs ionization and mass analysis of compounds in order to determine the mass, formula and structure of the compound being analyzed. A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output.

Introduction

There are four general types of mass analyzers that can be used for the separation of ions in a mass spectrometry.

Quadrupole Mass Analyzer

A Quadrupole is a mass analyzer that uses an electric field to separate ions. The Quadrupole consists of 4 parallel rods/ poles, where adjacent rods have opposite voltage polarity applied to them. The voltage applied to each rod is the summation of a constant DC voltage (U) and a varying radio frequency ($V_r \cos(\omega t)$), where ω = angular frequency of the radio frequency field. The electric force on the ions causes the ions to oscillate/orbit in the area between the 4 rods, where the radius of the orbit is held constant.

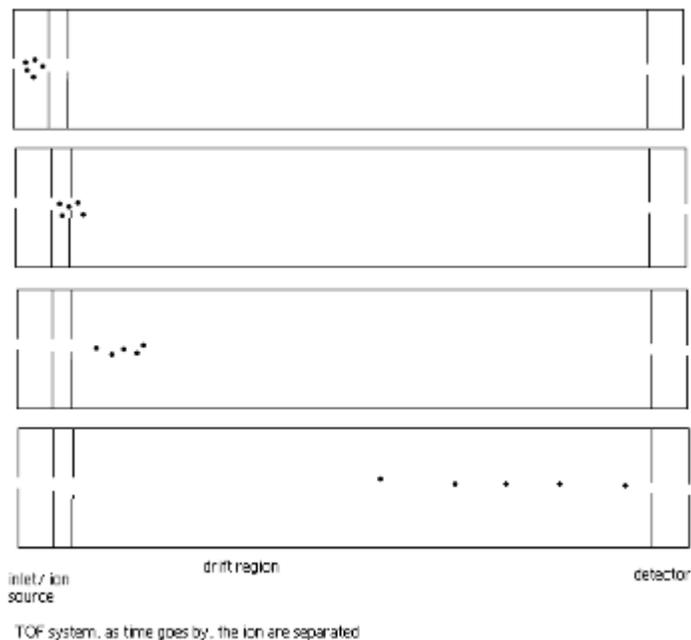


The ion moves in a very complex motion that is directly proportional to the mass of the ion, voltage on the quadrupole, and the radio frequency. The ions will remain orbiting in the area between the poles with no translation along the length of the poles unless the ions have a constant velocity that is created as the ions enter the quadrupole. Before entering the analyzer, the ions travel through a potential of a certain voltage, usually created by ring electrode, in order to give the ions a constant velocity so they can transverse along the center of the quadrupole.

While in the quadrupole, the trajectories of the ions change slightly based on their masses. Ions of specific mass have a certain frequency by which they oscillate. The greater the mass, the greater the frequency. A certain limit is associated with each quadrupole and it selects ions which are within the desirable frequency range.

TOF (Time of Flight) Mass Analyzer

TOF Analyzers separate ions by time without the use of an electric or magnetic field. In a crude sense, TOF is similar to chromatography, except there is no stationary/ mobile phase, instead the separation is based on the kinetic energy and velocity of the ions.



Ions of the same charges have equal kinetic energies; kinetic energy of the ion in the flight tube is equal to the kinetic energy of the ion as it leaves the ion source:

$$KE = mv^2/2 = zV$$

The time of flight, or time it takes for the ion to travel the length of the flight tube is:

$$T_f = L(\text{length of tube})/v(\text{velocity of ion})$$

Substituting the equation for kinetic energy in equation for time of flight:

$$T_f = L(m/z)^{1/2}(1/2V)^{1/2} (\text{Constant})*(m/z)^{1/2}$$

During the analysis, L, length of tube, V, Voltage from the ion source, are all held constant, which can be used to say that time of flight is directly proportional to the root of the mass to charge ratio.

Unfortunately, at higher masses, resolution is difficult because flight time is longer. Also at high masses, not all of the ions of the same m/z values reach their ideal TOF velocities. To fix this problem, often a reflectron is added to the

analyzer. The reflectron consists of a series of ring electrodes of very high voltage placed at the end of the flight tube. When an ion travels into the reflectron, it is reflected in the opposite direction due to the high voltage.

The reflectron increases resolution by narrowing the broadband range of flight times for a single m/z value. Faster ions travel further into the reflectrons, and slower ions travel less into the reflector. This way both slow and fast ions, of the same m/z value, reach the detector at the same time rather than at different times, narrowing the bandwidth for the output signal.

Sector: Magnetic Sector Mass Analyzer

Similar to time of flight analyzer mentioned earlier, in magnetic sector analyzers ions are accelerated through a flight tube, where the ions are separated by charge to mass ratios. The difference between magnetic sector and TOF is that a magnetic field is used to separate the ions. As moving charges enter a magnetic field, the charge is deflected to a circular motion of a unique radius in a direction perpendicular to the applied magnetic field. Ions in the magnetic field experience two equal forces; force due to the magnetic field and centripetal force.

$$F_B = zvB = F_c = mv^2/r$$

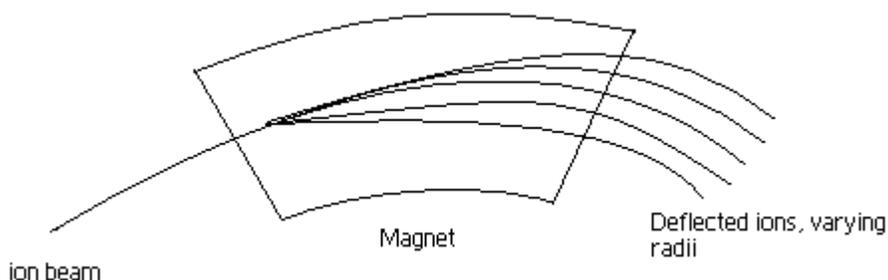
The above equation can then be rearranged to give:

$$v = Bzr/m$$

If this equation is substituted into the kinetic energy equation:

$$KE = zV = mv^2/2$$

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



Basically the ions of a certain m/z value will have a unique path radius which can be determined if both magnetic field magnitude B , and voltage difference V for region of acceleration are held constant. When similar ions pass through the magnetic field, they all will be deflected to the same degree and will all follow the same trajectory path. Those ions which are not selected by V and B values, will collide with either side of the flight tube wall or will not pass through the slit to the detector. Magnetic sector analyzers are used for mass focusing, they focus angular dispersions.

Sector: Electrostatic Sector Mass Analyzer

Is similar to time of flight analyzer in that it separates the ions while in flight, but it separates using an electric field. Electrostatic sector analyzer consists of 2 curved plates of equal and opposite potential. As the ion travels through the electric field, it is deflected and the force on the ion due to the electric field is equal to the centripetal force on the ion. Here the ions of the same kinetic energy are focused, and ions of different kinetic energies are dispersed.

$$KE = zV = mv^2/2$$

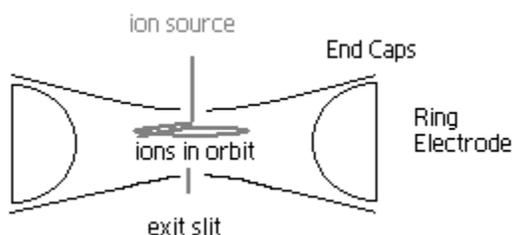
$$F_e = zE = F_c = mv^2/R$$

Electrostatic sector analyzers are energy focusers, where an ion beam is focused for energy.

Electrostatic and magnetic sector analyzers when employed individually are single focusing instruments. However when both techniques are used together, it is called a double focusing instrument., because in this instrument both the energies and the angular dispersions are focused.

Quadrupole Ion Trap Mass Analyzers

This analyzer employs similar principles as the quadrupole analyzer mentioned above, it uses an electric field for the separation of the ions by mass to charge ratios. The analyzer is made with a ring electrode of a specific voltage and grounded end cap electrodes. The ions enter the area between the electrodes through one of the end caps. After entry, the electric field in the cavity due to the electrodes causes the ions of certain m/z values to orbit in the space. As the radio frequency voltage increases, heavier mass ion orbits become more stabilized and the light mass ions become less stabilized, causing them to collide with the wall, and eliminating the possibility of traveling to and being detected by the detector.



The quadrupole ion trap usually runs a mass selective ejection, where selectively it ejects the trapped ions in order of increasing mass by gradually increasing the applied radio frequency voltage.

Ion Cyclotron Resonance (ICR)

ICR is an ion trap that uses a magnetic field in order to trap ions into an orbit inside of it. In this analyzer there is no separation that occurs rather all the ions of a particular range are trapped inside, and an applied external electric field helps to generate a signal. As mentioned earlier, when a moving charge enters a magnetic field, it experiences a centripetal force making the ion orbit. Again the force on the ion due to the magnetic field is equal to the centripetal force on the ion.

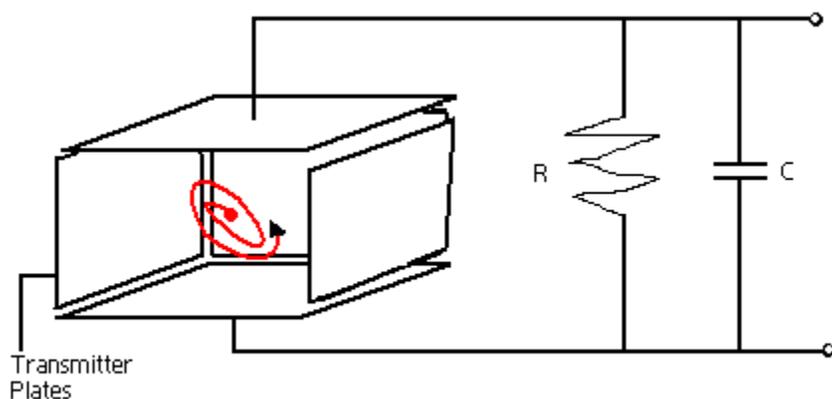
$$z v B = m v^2 / r$$

Angular velocity of the ion perpendicular to the magnetic field can be substituted here $\omega_c = v/r$

$$z B = m \omega_c$$

$$\omega_c = z B / m$$

Frequency of the orbit depends on the charge and mass of the ions, not the velocity. If the magnetic field is held constant, the charge to mass ratio of each ion can be determined by measuring the angular velocity ω_c . The relationship is that, at high ω_c , there is low m/z value, and at low ω_c , there is a high m/z value. Charges of opposite signs have the same angular velocity, the only difference is that they orbit in the opposite direction.



In order to generate an electric signal from the trapped ions, a vary electric field is applied to the ion trap $E = E_0 \cos(\omega_c t)$.

When the ω_c in the electric field matches the ω_c of a certain ion, the ion absorbs energy making the velocity and orbiting radius of the ion increase. In this high energy orbit, as the ion oscillates between two plates, electrons accumulate at one of the plates over the other inducing an oscillating current, or current image. The current is directly proportional to the number of ions in the cell at a certain frequency.

In a Fourier Transform ICR, all of the ions within the cell are excited simultaneously so that the current image is coupled with the image of all of the individual ion frequencies. A Fourier transform is used to differential the summed signals to produce the desired results.

Source : [http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Mass_Spectrometry/Mass_Spectrometers_\(Instrumentation\)/Mass_Analyzers_\(Mass_Spectrometry\)](http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Mass_Spectrometry/Mass_Spectrometers_(Instrumentation)/Mass_Analyzers_(Mass_Spectrometry))