

Mass spectroscopy

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1 Definitions

Mass spectroscopy Mass spectroscopy or mass spectrometry is an analytic method that employs ionization and mass analysis of compounds 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.

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

- Quadrupole Mass Analyzer
- Time of Flight Mass Analyzer
- Magnetic Sector Mass Analyzer
- Electrostatic Sector Mass Analyzer
- Quadrupole Ion Trap Mass Analyzers
- Ion Cyclotron Resonance

Quadrupole Mass Analyzer: The DC bias will cause all the charged molecules to accelerate and move away from the center line, the rate being proportional to their charge to mass ratio. If their course goes off too far they will hit the metal rods or the sides of the container and be absorbed. So the DC bias acts like the magnetic field B of the mass spec and can be tuned to specific charge to mass ratios hitting the detector.

The two sinusoidal electric fields at 90 orientation and 90 degrees degrees phase shift will cause an electric field which oscillates as a circle over time. So as the charged particles fly down toward the detector, they will be traveling in a spiral, the diameter of the spiral being determined by the charge to mass ratio of the molecule and the frequency and strength of the electric field. The combination of the DC bias and the circularly rotating electric

field will be the charge particles will travel in a spiral which is curved. So by timing the peak of the curved spiral to coincide with the position of the detector at the end of the quadrupole, a great deal of selectivity to molecules charge to mass ratio can be obtained.

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:

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

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

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

Magnetic Sector Mass Analyzer: Similar to time of flight (TOF) 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.

$$F_b = zvB = F_c = \frac{mv^2}{r}$$

or:

$$v = \frac{Bzr}{m}$$

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.

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 two 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.

$$KE = z V = \frac{mv^2}{2}$$

$$F_e = F_c = \frac{mv^2}{r}$$

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.

$$zevB = \frac{mv^2}{r}$$

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

$$zeB = mw_c$$

$$w_c = \frac{zeB}{m}$$

2 References:

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