

## 2.4 Mass Analyzers

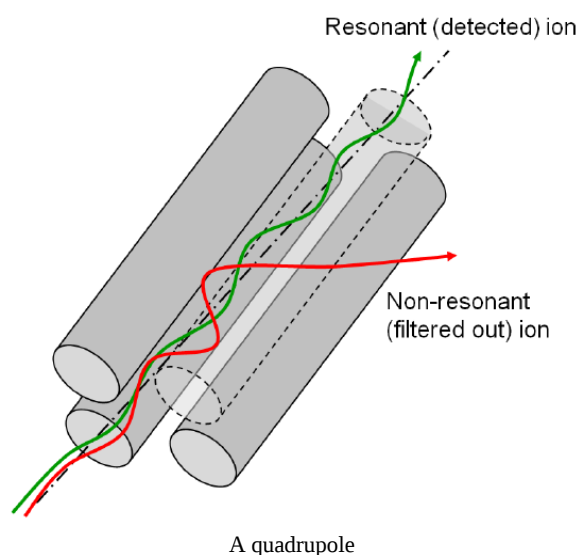
### Learning Objectives

- Describe the function of common mass analyzers

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.

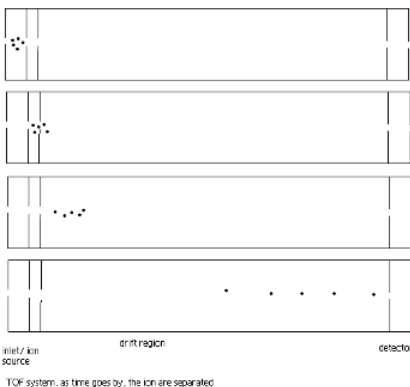
### Quadrupole Mass Analyzer

Ions are passed through four parallel rods which apply a varying voltage and radiofrequency (RF) potential (figure below). As the field changes, ions respond by undergoing complex trajectories. Depending on the applied voltage and RF frequencies, only ions of a certain  $m/z$  ratio will have stable trajectories and pass through the analyzer. If their course goes off too far they will hit the metal rods or the sides of the container and be absorbed. A great deal of selectivity to molecules charge to mass ratio can be obtained because the rods bias can be tuned to specific charge to mass ratios hitting the detector. Quadrupole analyzers are relatively inexpensive, but have limited resolution and low mass range.



### TOF (Time of Flight) Mass Analyzer

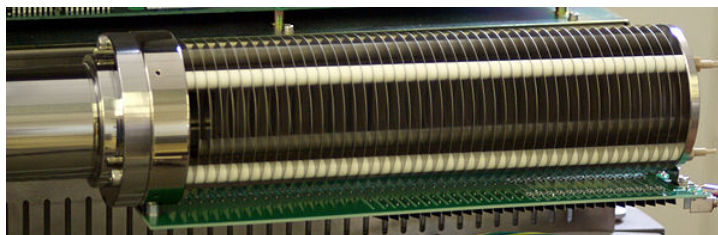
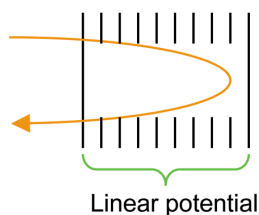
The amount of time required for an ion to travel a known distance is measured. A pulse of ions is accelerated through an electric analyzer such that they have identical kinetic energies. As a result, their velocity is directly dependent on their mass. Extremely high vacuum conditions are required to extend the mean free path of ions and avoid collisions. TOF mass analyzers are fastest, have unlimited mass ranges, and allow simultaneous detection of all species, but are best coupled with pulsed ionization sources. 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.



As time evolves, the ions (formed at the source) are separated.

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.

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.

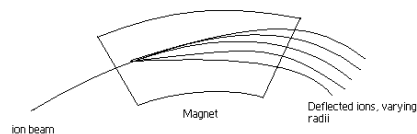


(top) A reflection. from Wikipedia. (bottom) A photo of a reflectron. An ion mirror attached to a flight tube of the reflectron. Voltages applied to a stack of metal plates create the electric field reflecting the ions back to the flight tube. In this particular design, gaps between the mirror electrodes are too large. This can lead to a distortion of the field inside the mirror caused by a proximity of metal surface of the enveloping vacuum tube. from Wikipedia.

## 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.



A magnetic sector separator.

Basically the ions of a certain  $m/z$  value will have a unique path radius which can be determined if both magnetic field magnitude, and voltage difference 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 voltage and magnetic field 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.

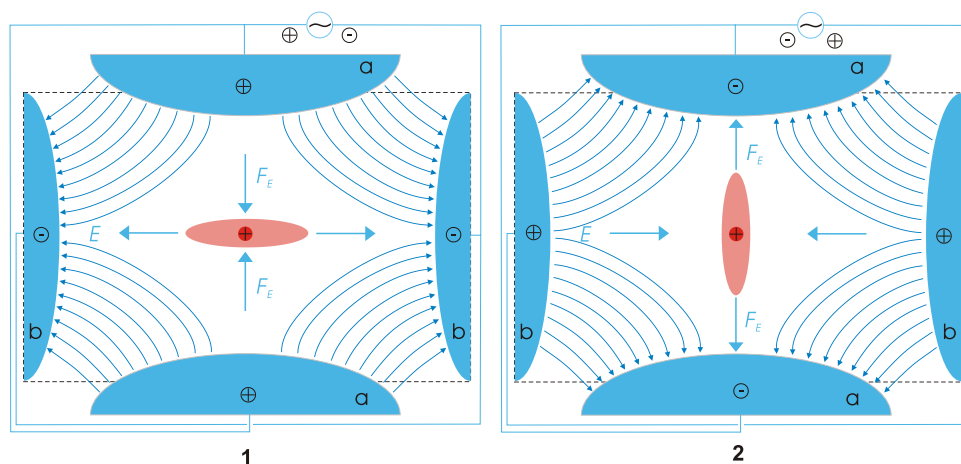
### Electrostatic Sector Mass Analyzer

Again, this 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.

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.



Scheme of a Quadrupole ion trap of classical setup with a particle of positive charge (dark red), surrounded by a cloud of similarly charged particles (light red). The electric field  $E$  (blue) is generated by a quadrupole of endcaps (a, positive) and a ring electrode (b). Picture 1 and 2 show two states during an AC cycle. (CC BY 2.5; Arian Kriesch [Akriesch](#) via [Wikipedia](#)).

Ion traps are uniquely suited for repeated cycles of mass spectrometry because of their ability to retain ions of desired  $m/z$  ratios. Selected fragments can be further fragmented by collision induced dissociation with helium gas. Ion traps are compact, relatively inexpensive, and can be adapted to many hybrid instruments.

## 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.

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. The relationship is that, at high angular velocity, there is low  $m/z$  value, and at low angular velocity, 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.

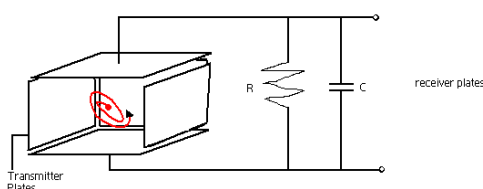


Figure 2.3.4.62.3.4.6: An ICR trap.

### ? Exercise 1

How are ions separated?

#### Answer

By accelerating them through magnetic and electric fields.

## References

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2. Skoog, Holler, Grouch, *Principles of Instrumental Analysis*, Thomson Brooks/Cole 2007, chapter 20
3. C. Herbert, R. Johnstone, *Mass Spectrometry Basics*, CRC Press LLC, 2003 chapter 25, 26, 39
4. E. De Hoffman, V. Stroobant, *Mass Spectrometry: Principles and Applications*, 2<sup>nd</sup> ed.; Wiley: England, 2001, chapter 2

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