Updated: 10 December 2014

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CEE 772: Instrumental Methods in Environmental Analysis

Lecture #21

Mass Spectrometry: Mass Filters & Spectrometers

(Skoog, Chapt. 20, pp.511-524)

(Harris, Chapt. 24&25)
(699-706; 742-749)

MS Mass Analyzers

- Mass analyzers are analogous to optical monochromator
- Two main properties of mass analyzers
  - Able to distinguish between very small mass difference
  - Allow a sufficient number of ions to pass through to give readily measurable ion currents
- These two properties are not entirely compatible
  - There is no ideal mass analyzer

Parameters to Describe Mass Analyzers

- ***Resolution*** **describe the ability of a mass analyzer to separate adjacent ions.**
- ***Mass accuracy*** **is the ability of a mass analyzer to assign the mass of an ion close to its true mass.**
- ***Mass range*** **is usually defined by the lower and upper m/z value observed by a mass analyzer.**
- ***Sensitivity*** **is the ability a particular instrument to respond to a given amount of analyte.**
- ***Scan speed*** **is the rate at which we can acquire a mass spectrum, generally given in mass units per unit time.**
- ***Tandem mass spectrometry*** **(MS/MS; or MS^n, n=1,2,3…)provides the ability to mass-analyze sample components sequentially in time or space to improve selectivity of the analyzer or promote fragmentation and facilitate structural elucidation.**

Types of MS

- 4 Types commonly used in environmental analysis
  - Magnetic Sector MS
  - Quadrupole MS
  - Ion-trap MS
  - Time of Flight MS
- Others
  - Fourier Transform Ion Cyclotron Resonance MS (FT-ICR)

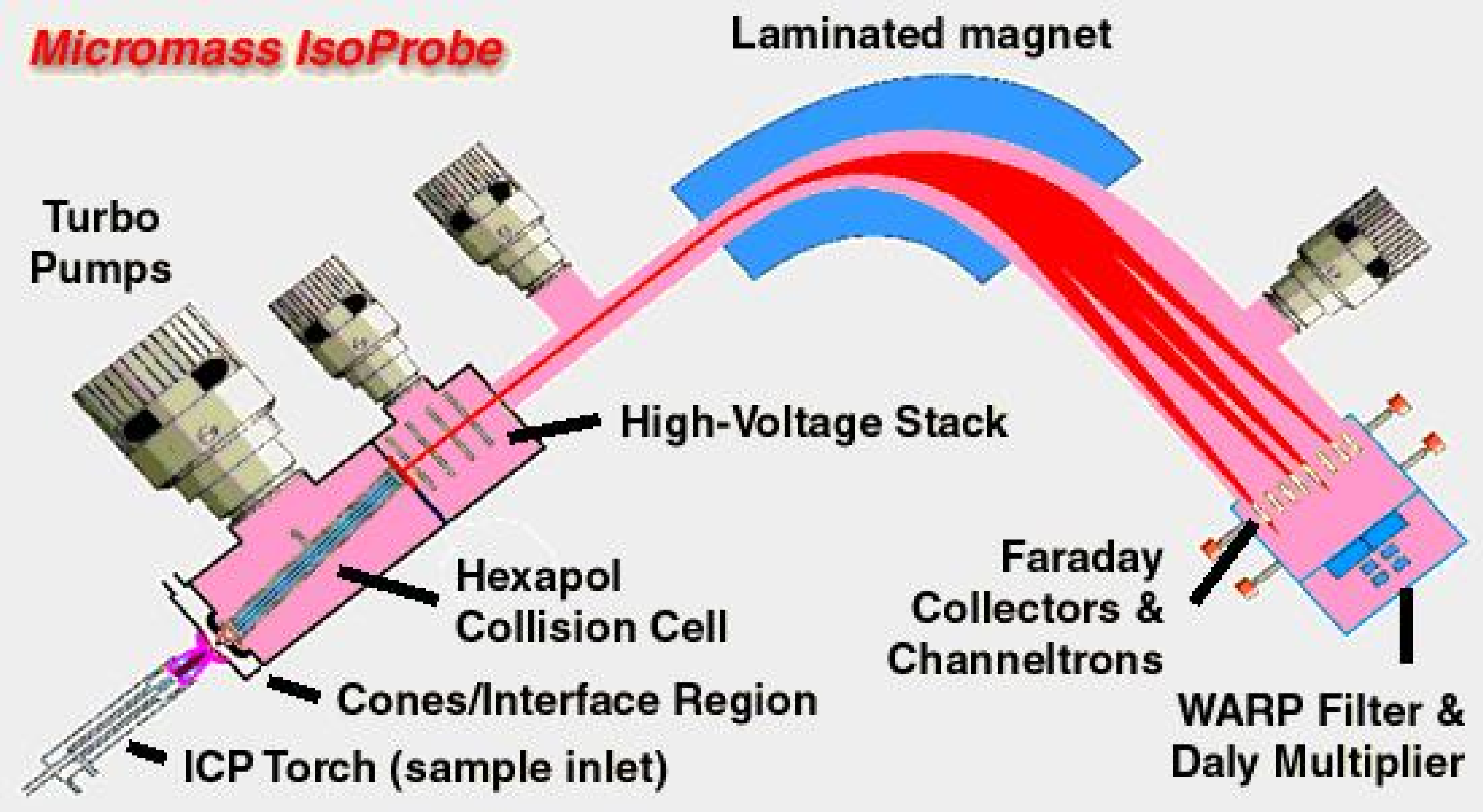
Summary of Mass analyzers

	Quadrupole	Ion trap	Time-of-Flight	Magnetic Sector	Fourier Transform
Resolution	Low	Low, can operate higher	Moderate - high	Moderate-High	High (up to 500,000)
Mass Range	50-2,000 u	2,000 u	Unlimited	20,000u	>15,000u
Scan Speed	4,000 u/sec max	4,000 u/sec	Very Fast	Slow	Fast (1 millisecond)
Vacuum Require-ment	Minimal: 10^{-4} 10^{-5}	Low: 10^{-3} torr	High: 10^{-7} torr or higher	High: 10^{-7} torr	High
Common LC/MS interfaces	ES, APCI, PB, TS	ES, APCI	ES, APCI	ES, APCI, PB, TS, CFFAB	ES, APCI

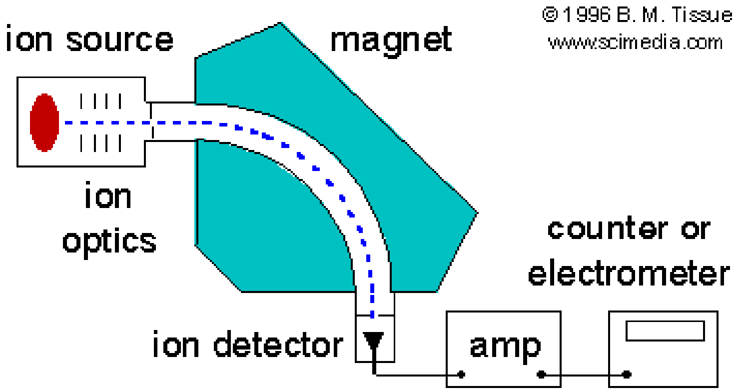
MS Magnetic Sector

- The cations from the ion source are passed through a magnet that is located outside the tube
- The magnetic force deflects the ions toward the detector at the end of the tube
- Lighter ions are deflected too much and heavier ions are deflected too little
- Only ions that match the small mass range reach the detector
- A 10^{-7} vacuum is applied to the metal analyzer tube

Inside a Mass Spectrometer



Magnetic-Sector Mass Spectrometry



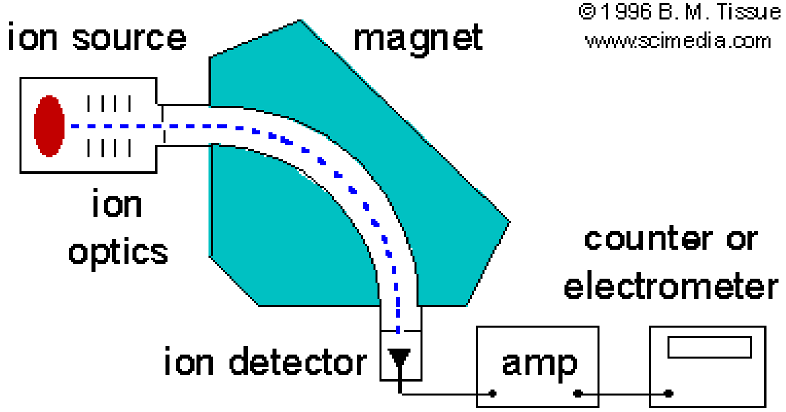
THEORY:

The ion source and repeller plate accelerates ions to a kinetic energy given by:

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

Where m is the mass of the ion, v is its velocity, z is the charge on the ion, and V is the applied voltage of the ion optics.

Magnetic-Sector Mass Spectrometry



•The ions enter the flight tube and are deflected by the magnetic field, B.

•Only ions of mass-to-charge ratio that have equal *centripetal* and *centrifugal* forces pass through the flight tube:

$$mv^2 /r = BzV, \text{ where r is the radius of curvature}$$

Magnetic-Sector Mass Spectrometry

$$mv^2 /r = BzV$$

- By rearranging the equation and eliminating the velocity term using the previous equations, $r = mv/zB = 1/B(2Vm/z)^{1/2}$
- Therefore, $m/z = B^2r^2/(2V)$
- This equation shows that the m/z ratio of the ions that reach the detector can be varied by changing either the magnetic field (B) or the applied voltage of the ion optics (V).

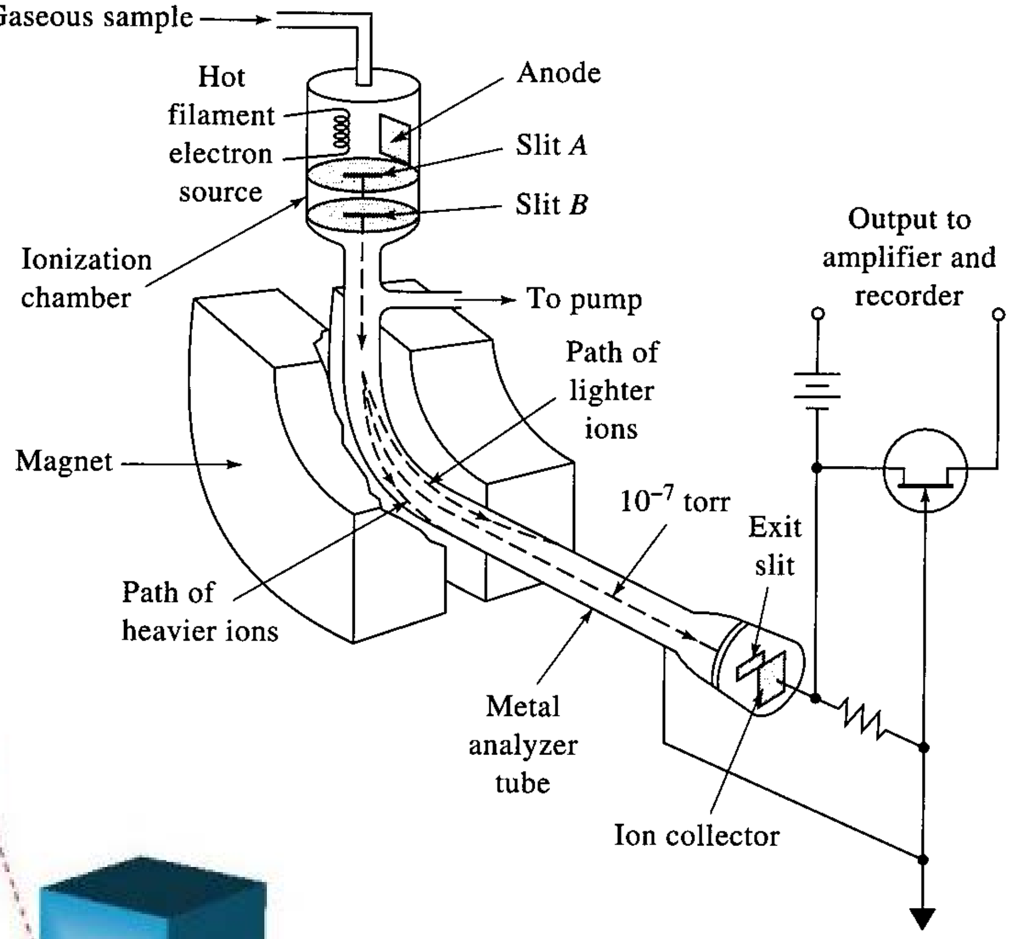
Magnetic-Sector Mass Spectrometry

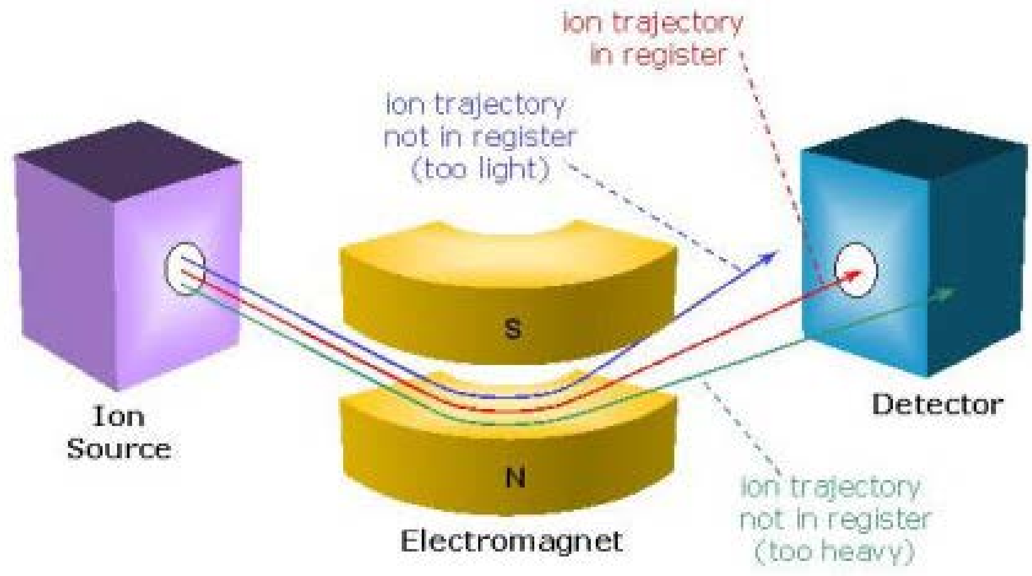
In summary, by varying the voltage or magnetic field of the magnetic-sector analyzer, the individual ion beams are separated spatially and each has a unique radius of curvature according to its mass/charge ratio.

$$\frac{m}{z} = \frac{B^2 r^2}{2V}$$

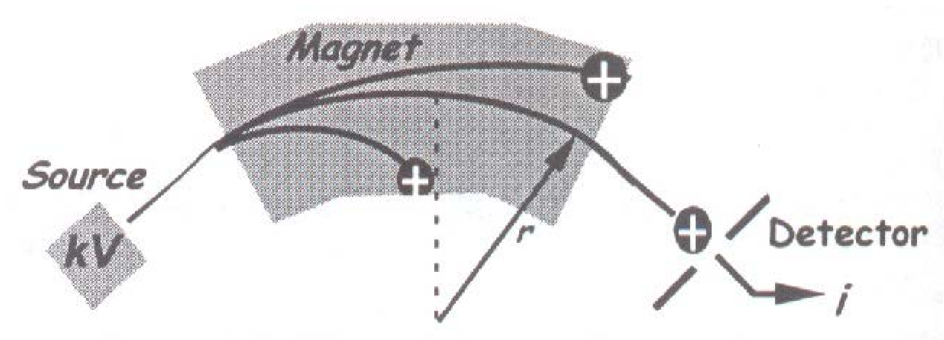
M = mass of ion
z = charge of ion
V = voltage
B = magnetic field
r = radius of circle

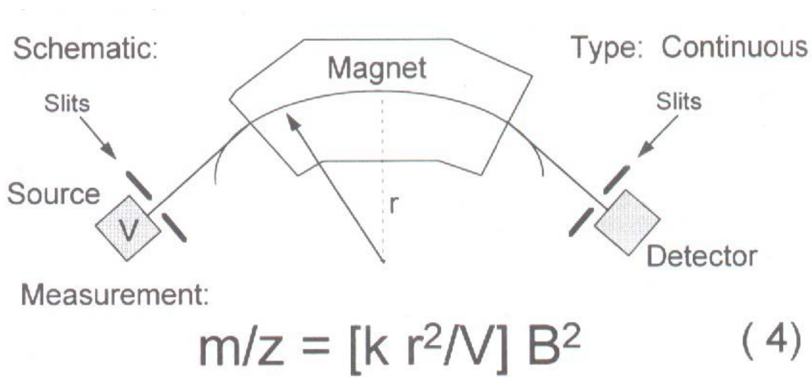
Magnetic Sector Analyzer





Sector Mass Analyzers

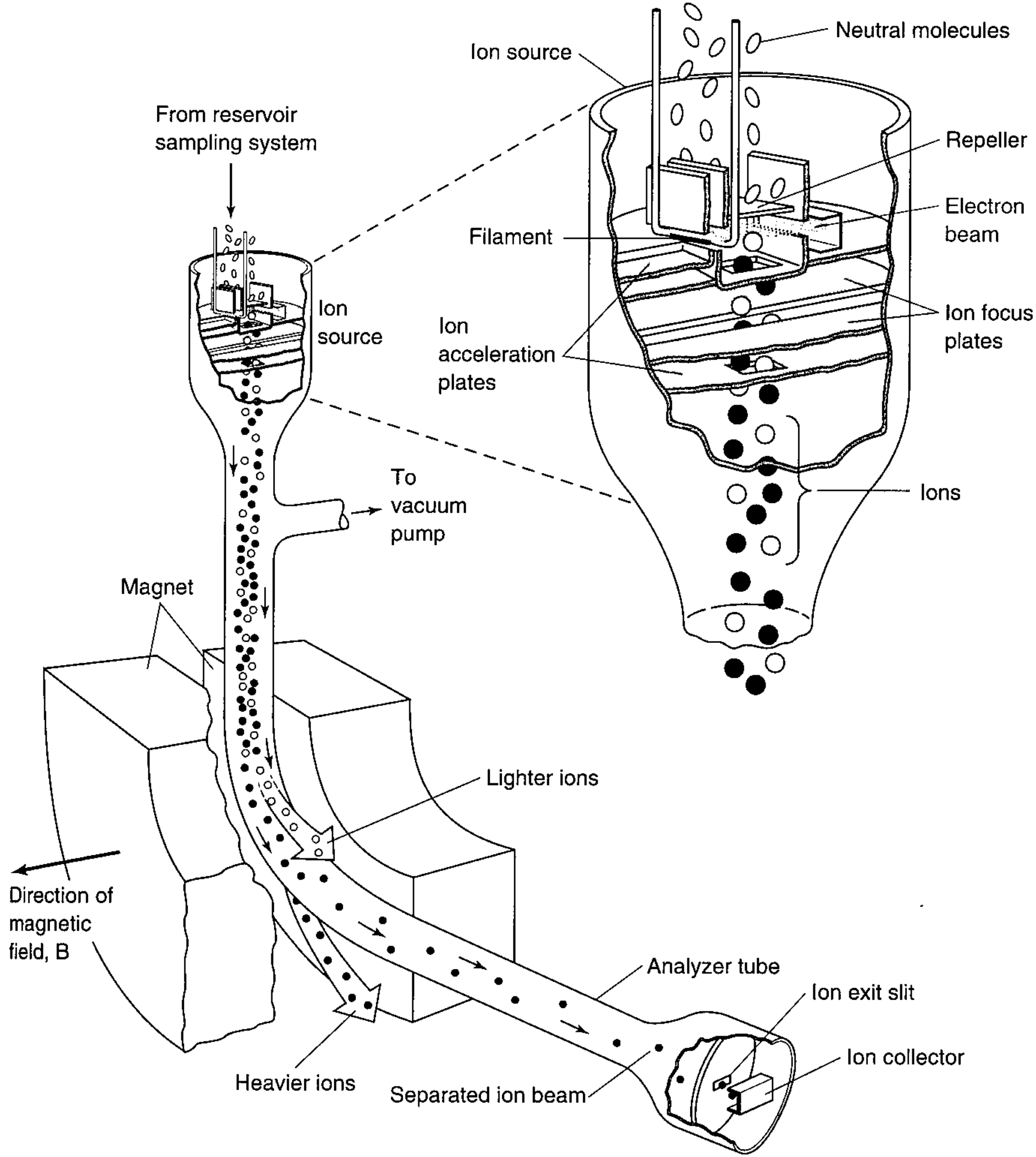




B: magnetic field strength

- **Ions created in the ion source are accelerated with voltages of 4-8kV into the analyzer magnetic field.**
- **The radius of curvature in a given magnetic field of the sector is a function of m/z.**
- **By varying either the magnetic field(B) or the accelerating voltage(V), ions of different m/z are separated.**

- Magnetic Sector MS



From: Harris, 2000

MS Quadrupole

- Most common mass analyzer
  - in use since the 1950s
- Quadrupole MS are smaller, cheaper and more rugged than magnetic sectors
- Low scan times (<100 ms) – ideal for GC or LC inlets
- Called mass filters rather than mass analyzers
  - ions of only a single mass to charge (m/q) ratio pass through the apparatus
  - separate ions based on oscillations in an electric field (the quadrupole field) using AC and DC currents

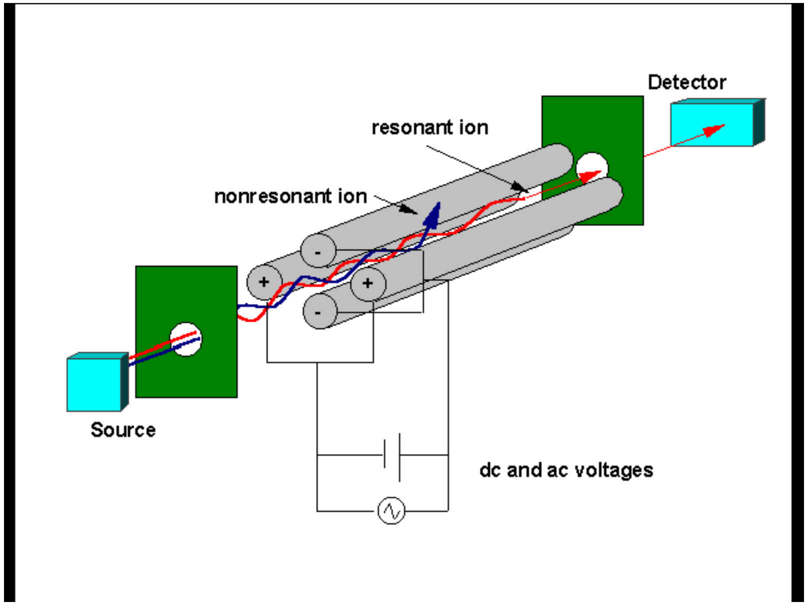
Quads and LC

- tolerant of relatively poor vacuums (~5 x 10-5torr)
  - makes them well suited to electrospray ionization (because these ions are produced under atmospheric conditions)
- quadrupoles are now capable of routinely analyzing up to a m/q ratio of 3000
  - useful in electrospray ionization of biomolecules, which commonly produces a charge distribution below m/z 3000

Basis of Quadrupole Mass Filter

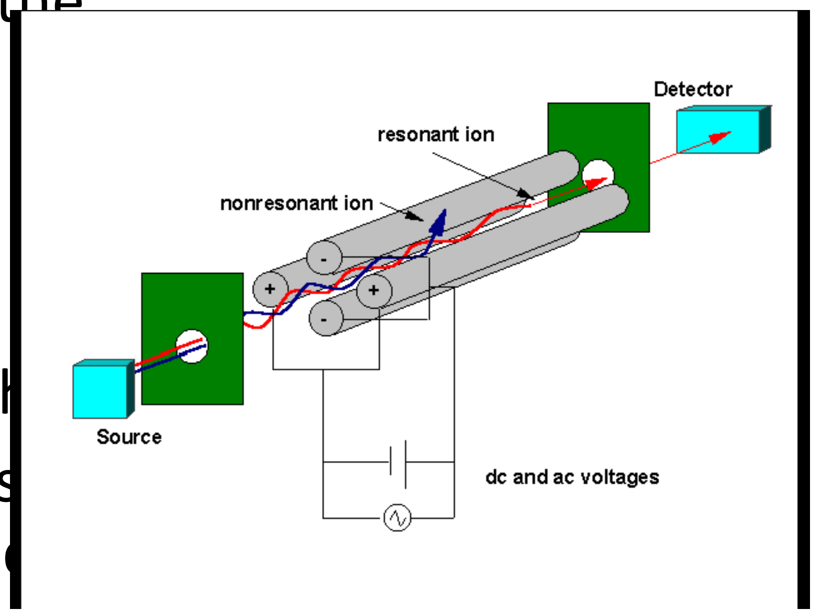
- consists of 4 parallel metal rods, or electrodes
- The ions are accelerated by a potential of 5-15 V and injected into the area between the 4 rods
- opposite electrodes have potentials of the same sign
- one set of opposite electrodes has applied potential of [U+Vcos(ωt)]
- other set has potential of

  \- [U+Vcosωt]
- U= DC voltage, V=AC voltage, ω= angular velocity of alternating voltage

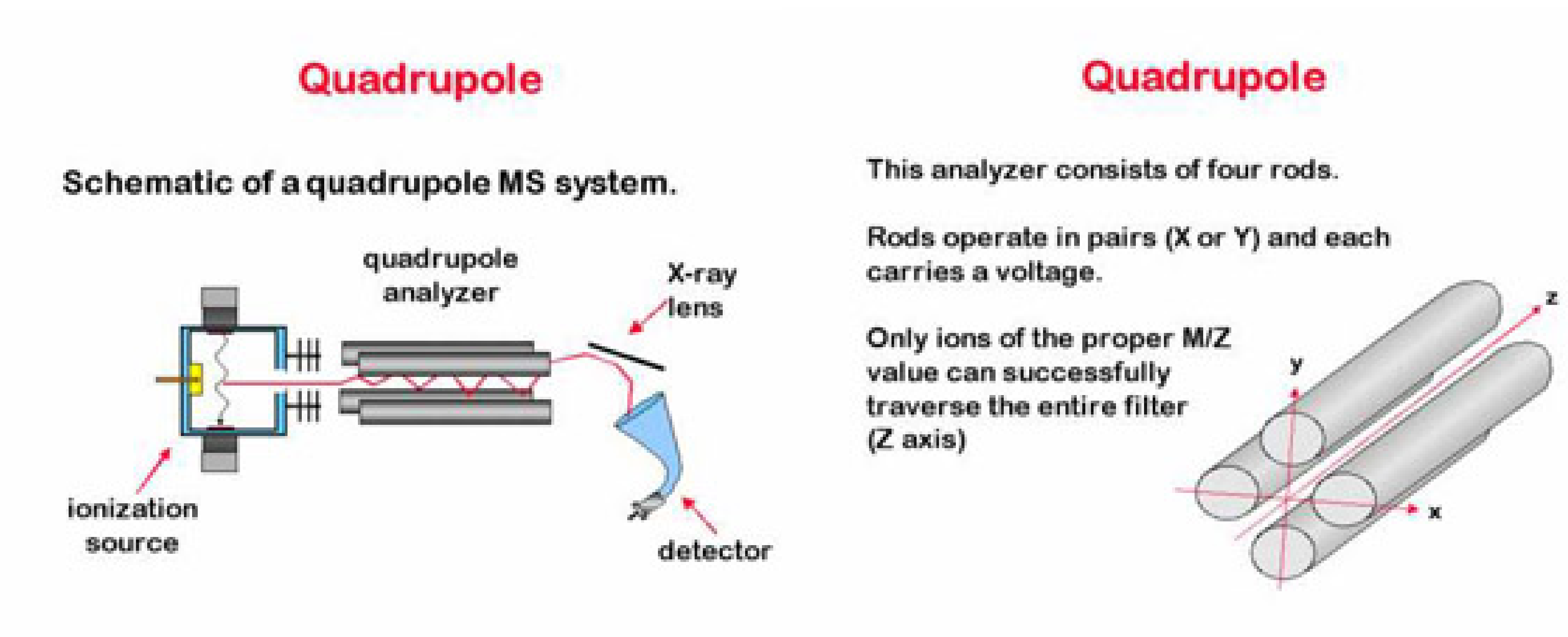


Operation of Quadrupole Mass Filter

- voltages applied to electrodes affect trajectory of ions with the m/q ratio of interest as they travel down the center of the four rods
- these ions pass through the electrode system
- ions with other m/z ratios are thrown out of their original path
- these ions are filtered out or los the walls of the quadrupole, an then ejected as waste by a vacuum system
- in this manner the ions of interest are separated



Schematic of Quadrupole



Hardy, U of Akron

Qua

- schematics

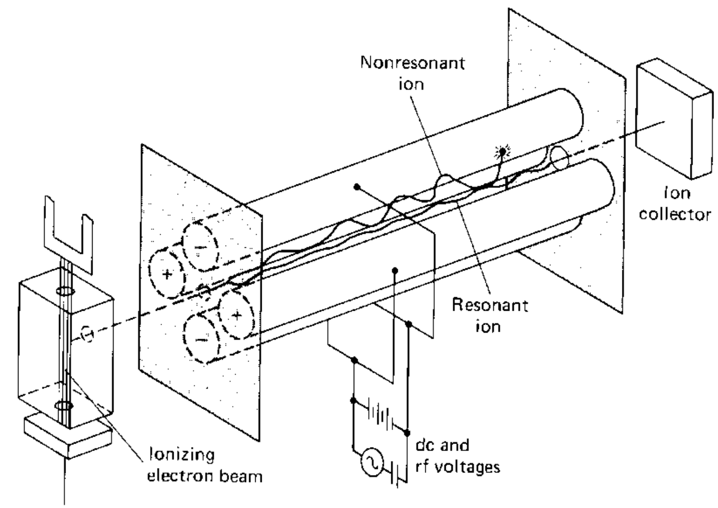
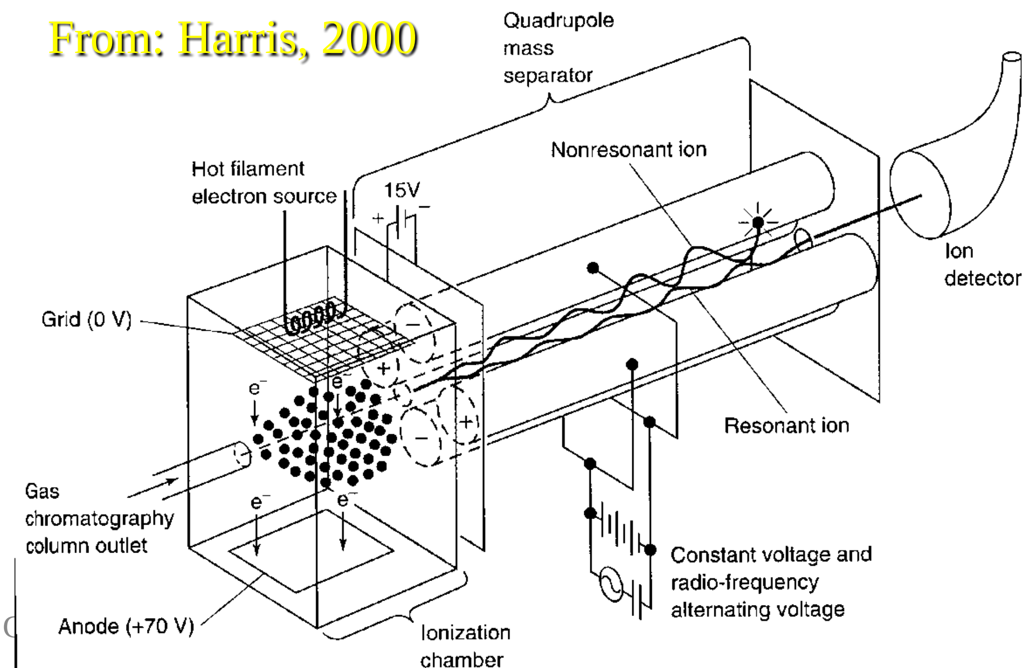
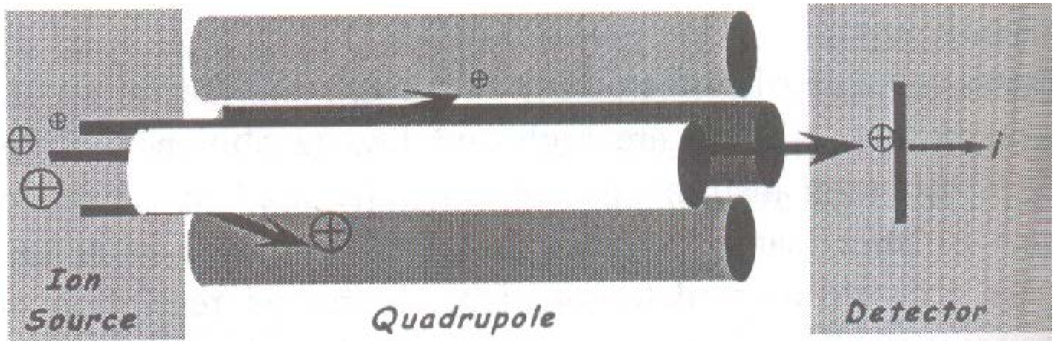


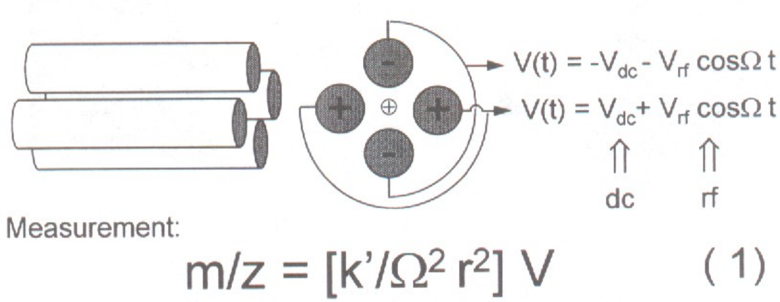
FIGURE 18-8 A spectrometer. (F Res. Dev., 1964, permission.)

From: Harris, 2000



Quadrupole Mass Analyzer (Q)





dc: direct current
ac: alternating current or radio frequency

- **A continuous beam of ions enters one end of of this assembly and exits the opposite end to be detected by a high voltage detector.**
- **Ions are filtered on the basis of their mass-to-charge ratio(see equation 1).**
- **Ions below and above a certain m/z value will be filtered out of the beam depending on the ratio of the dc and ac voltages**
- **By ramping the voltages on each set of poles, a complete range of masses can be passed to the detector.**

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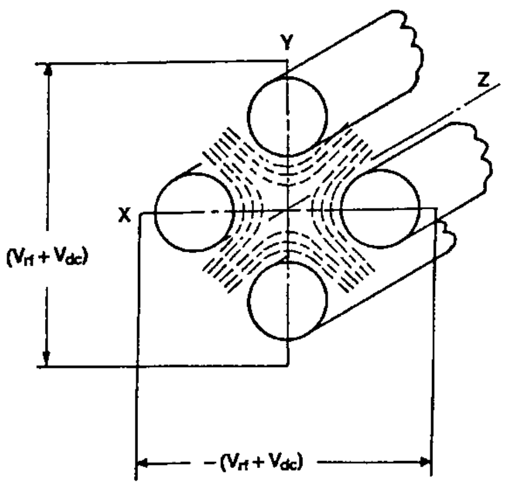


FIGURE 4.38 Schematic showing the radio-frequency tages applied to the diagonally opposite rods.

- Miller & Denton, 198 *J. Chem. Ed.* 63(7)617 622

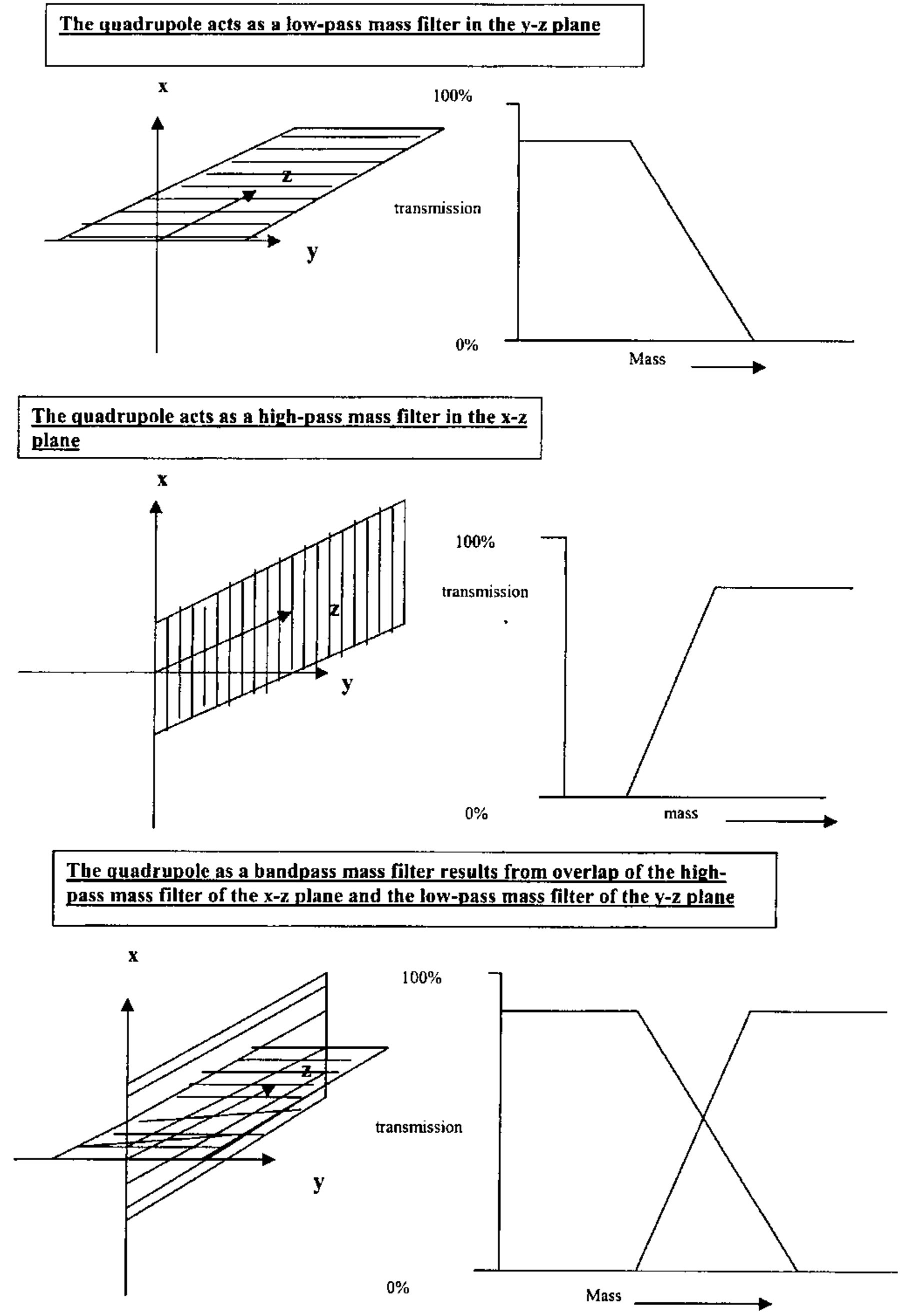
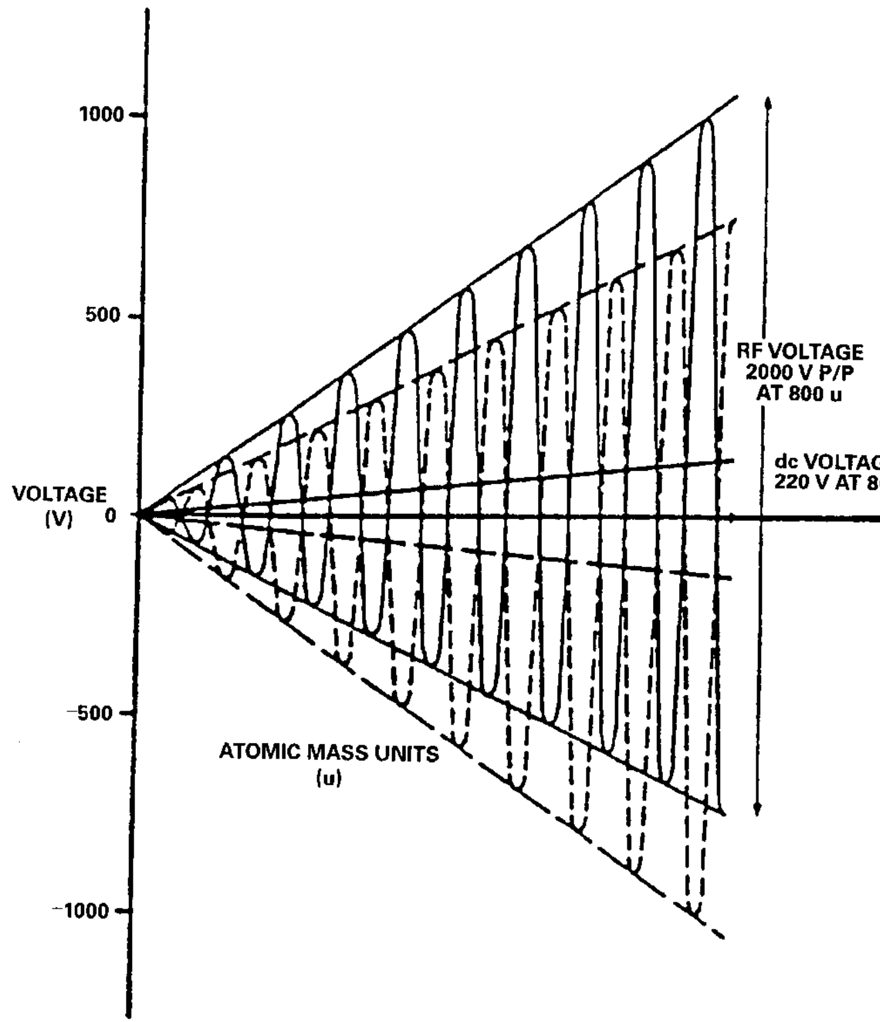
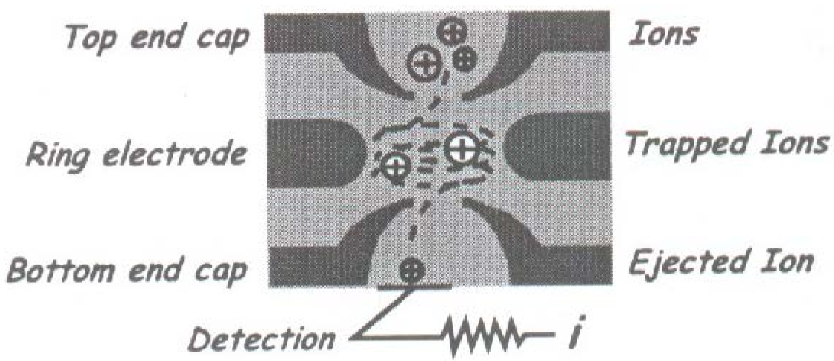


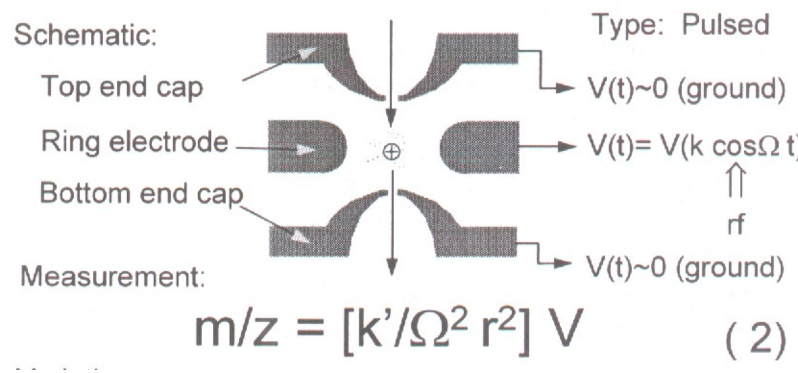
FIGURE 4.39 Conceptual framework to help explain the mass filtering properties of the quadrupole mass spectrometer. (From Ref. 78.)

- Quadrupole operation
  - Plot of DC and RF voltages applied to the rods



Ion Trap Mass Analyzer (IT)





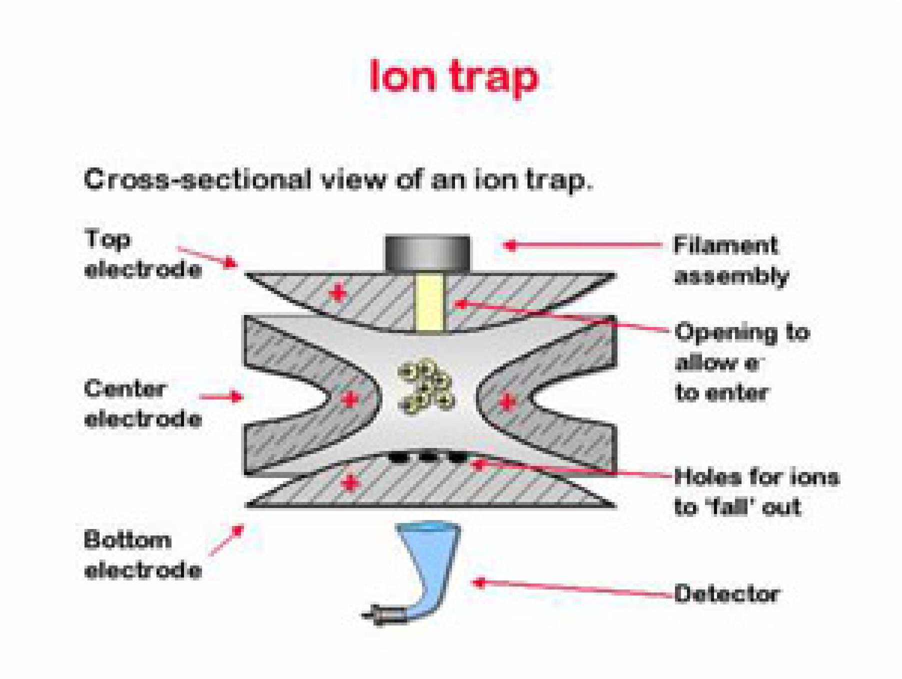
- **The ion trap is a variation of the quadrupole mass filter, and consequently is sometimes refer to as a *Quadrupole Ion Trap*.**
- **The trap contains ions in a 3-dimensional volume rather than along the center axis.**
- **Helium gas is added to the trap causing the ions to migrate toward the center.**
- **After trapping, the ions are detected by placing them in unstable orbits, causing them to leave the trap.**

Ion trap Analyzers

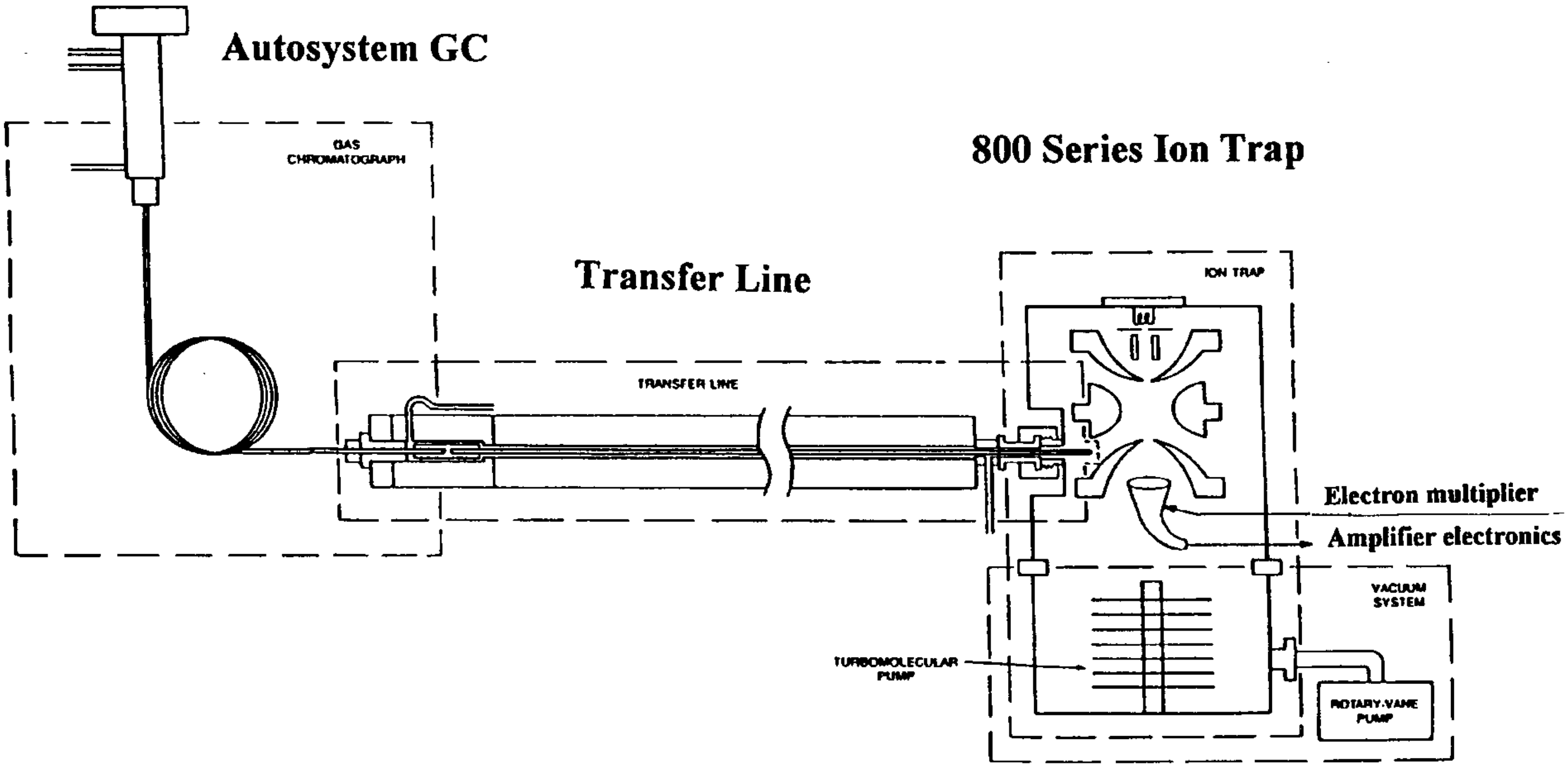
- Ion trap analyzer forms positive or negative ions and holds them for a long period of time by electric and/or magnetic fields.
- It can be used as a detector for GS/MS
- It is cheap, more compact and more rugged then magnetic sector and quadrupole

Ion trap Analyzers

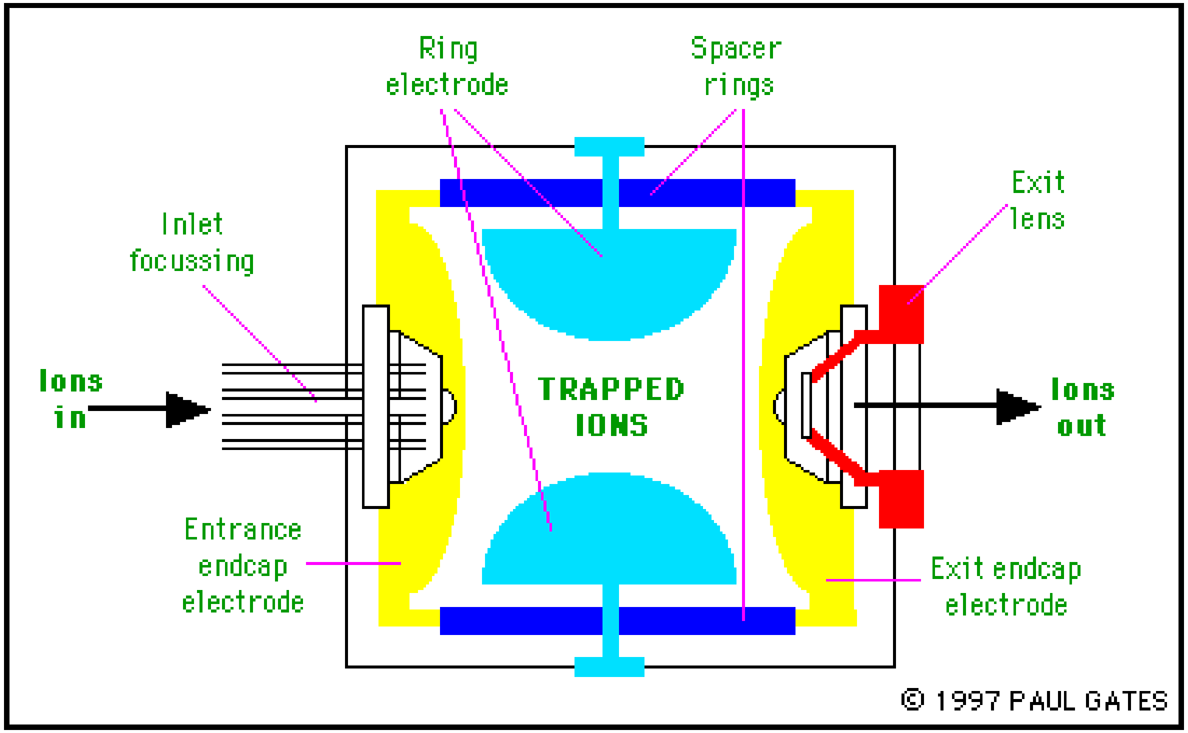
- Consisted of ring electrode and a pair of end-cap electrodes
- Radio-frequency voltage is applied and varied to the ring electrode
- As radio-frequency voltage increases, heavier ions stabilize and lighter ions destabilized and then collide with the ring wall

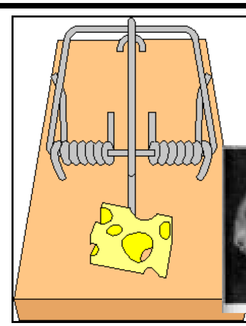


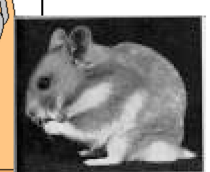
GC/MS Ion Trap



Ion Trap MS/MS

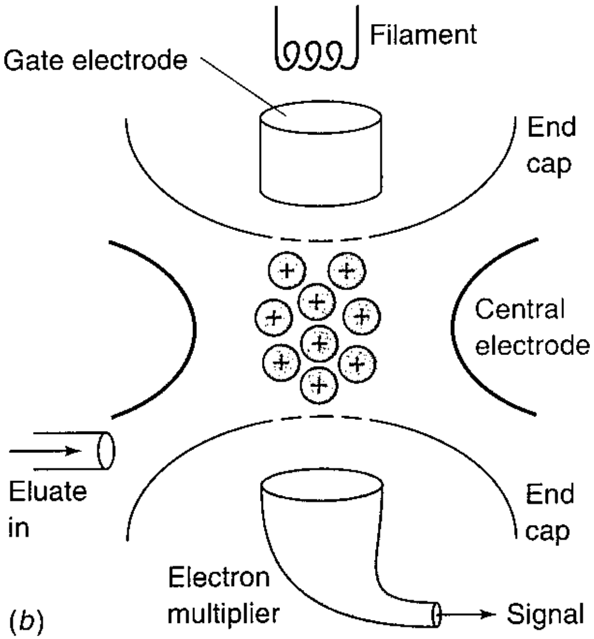




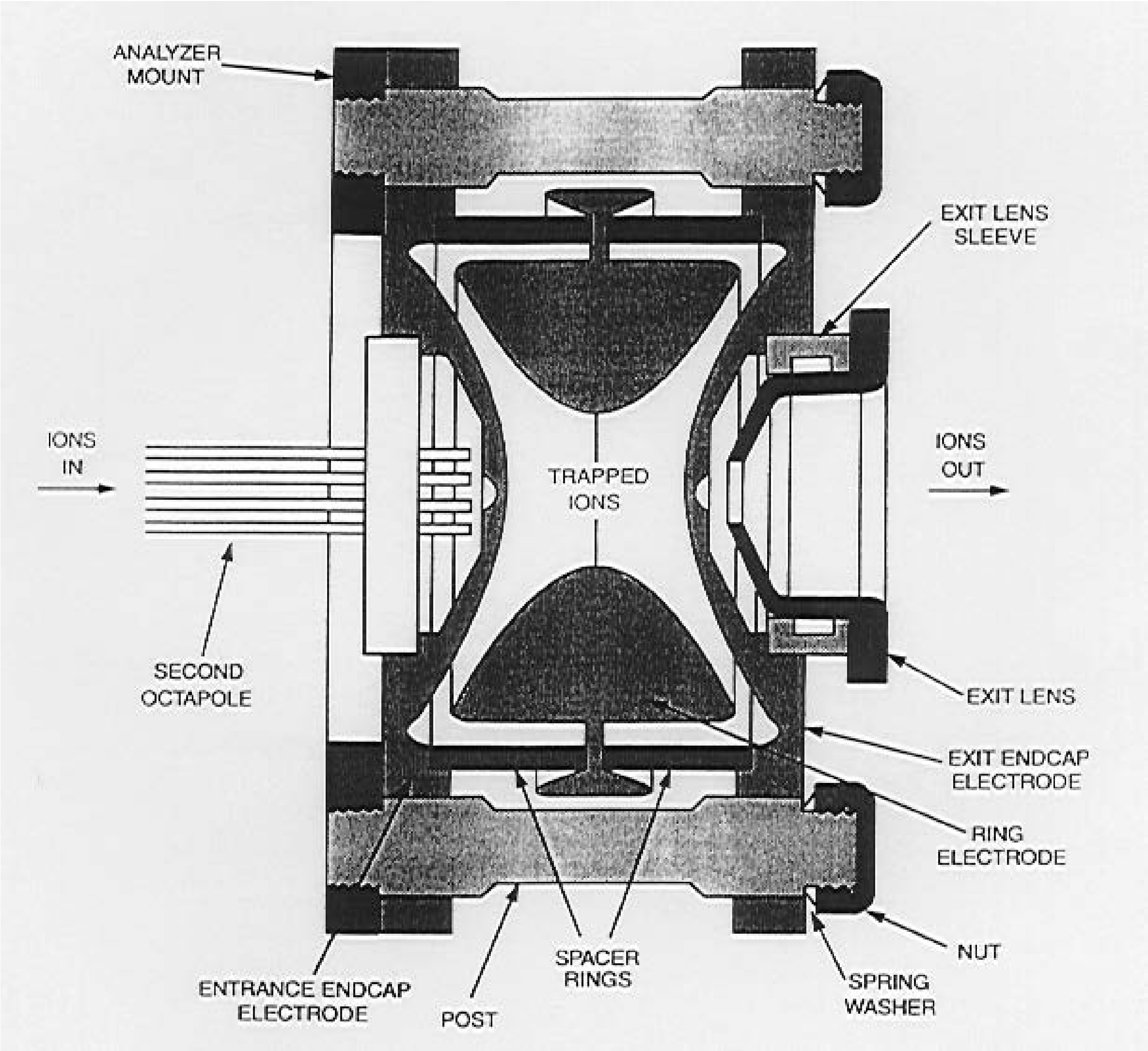


Slide courtesy of Meyer et al., USGS

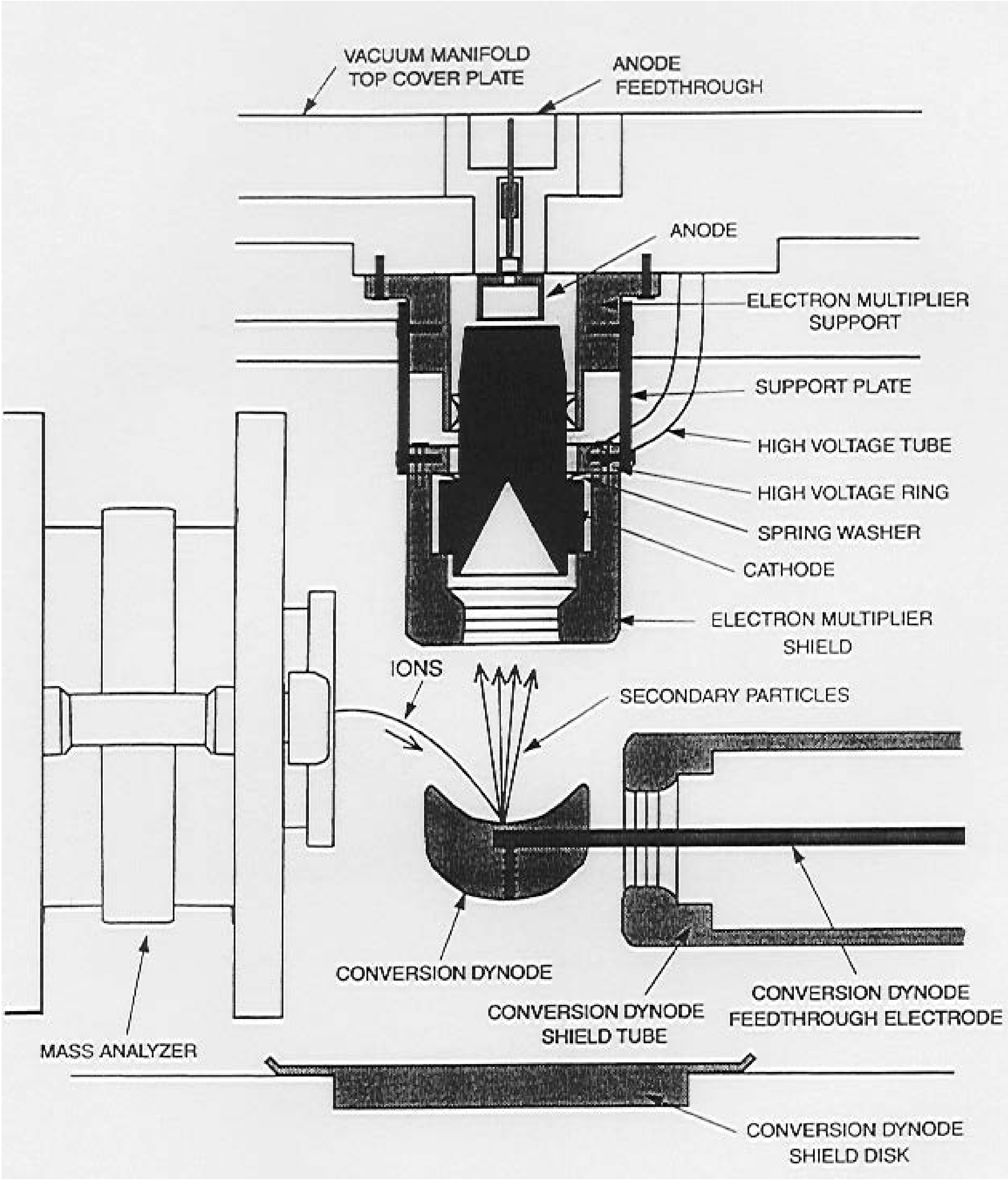
Ion Trap



From: Harris, 2000

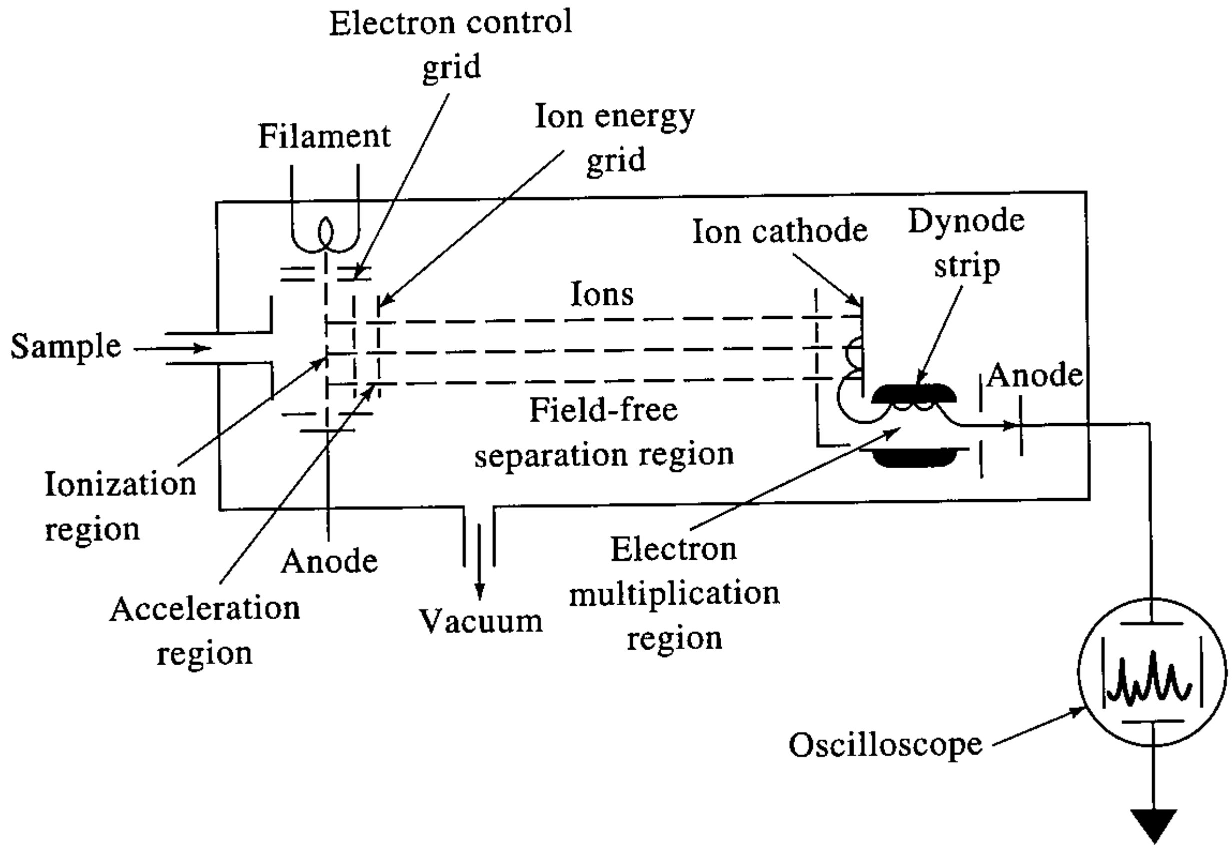


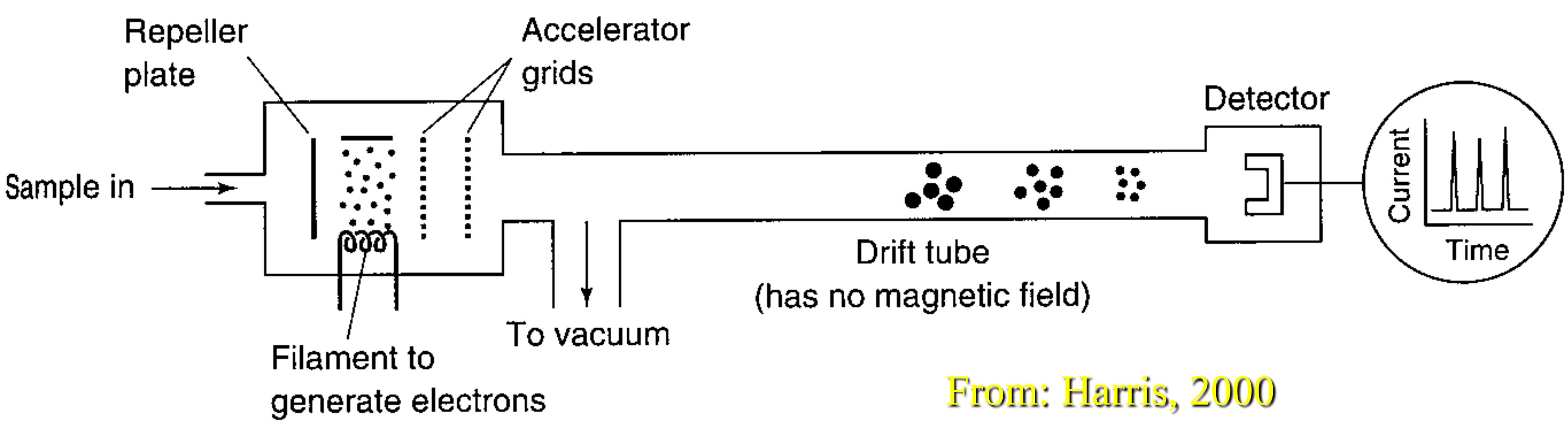
- Ion detection system
  - Conversion dynode
  - Electron multiplier



Tin

- Lighter ions are subject to greater acceleration





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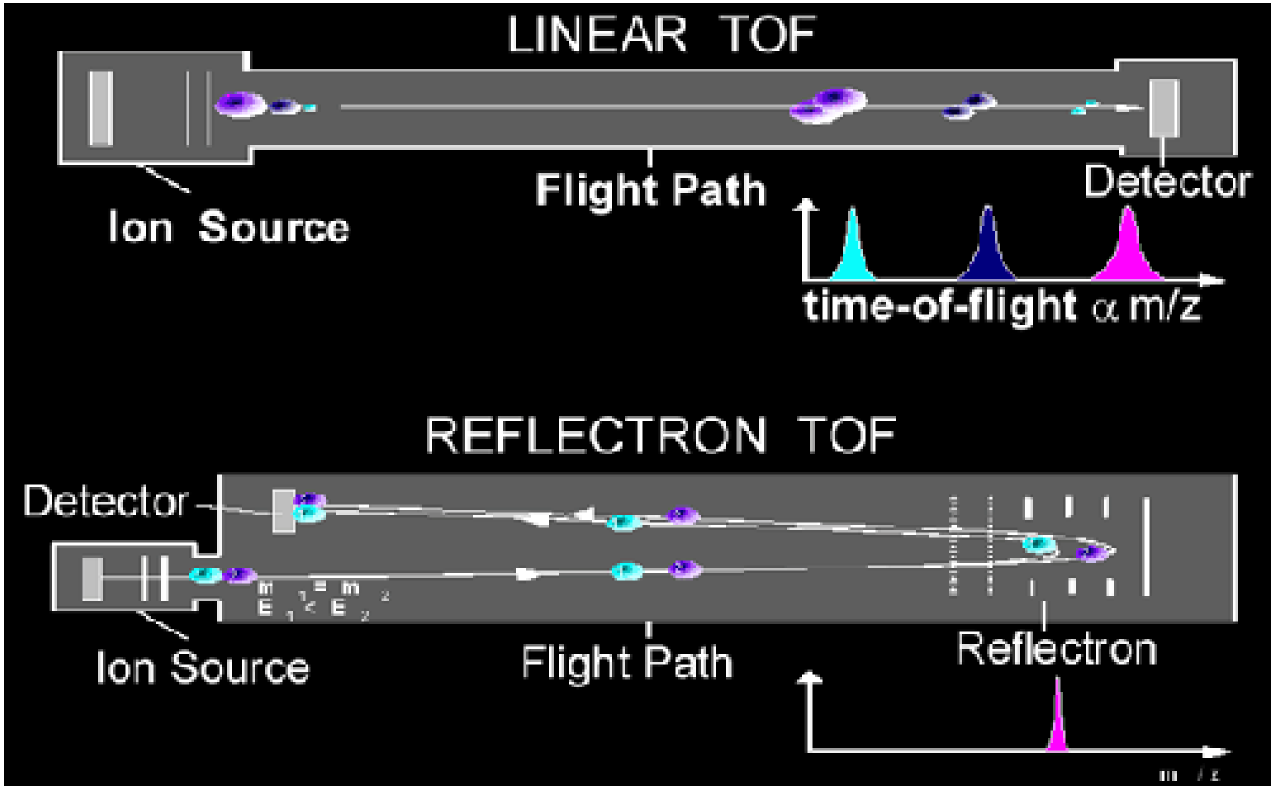
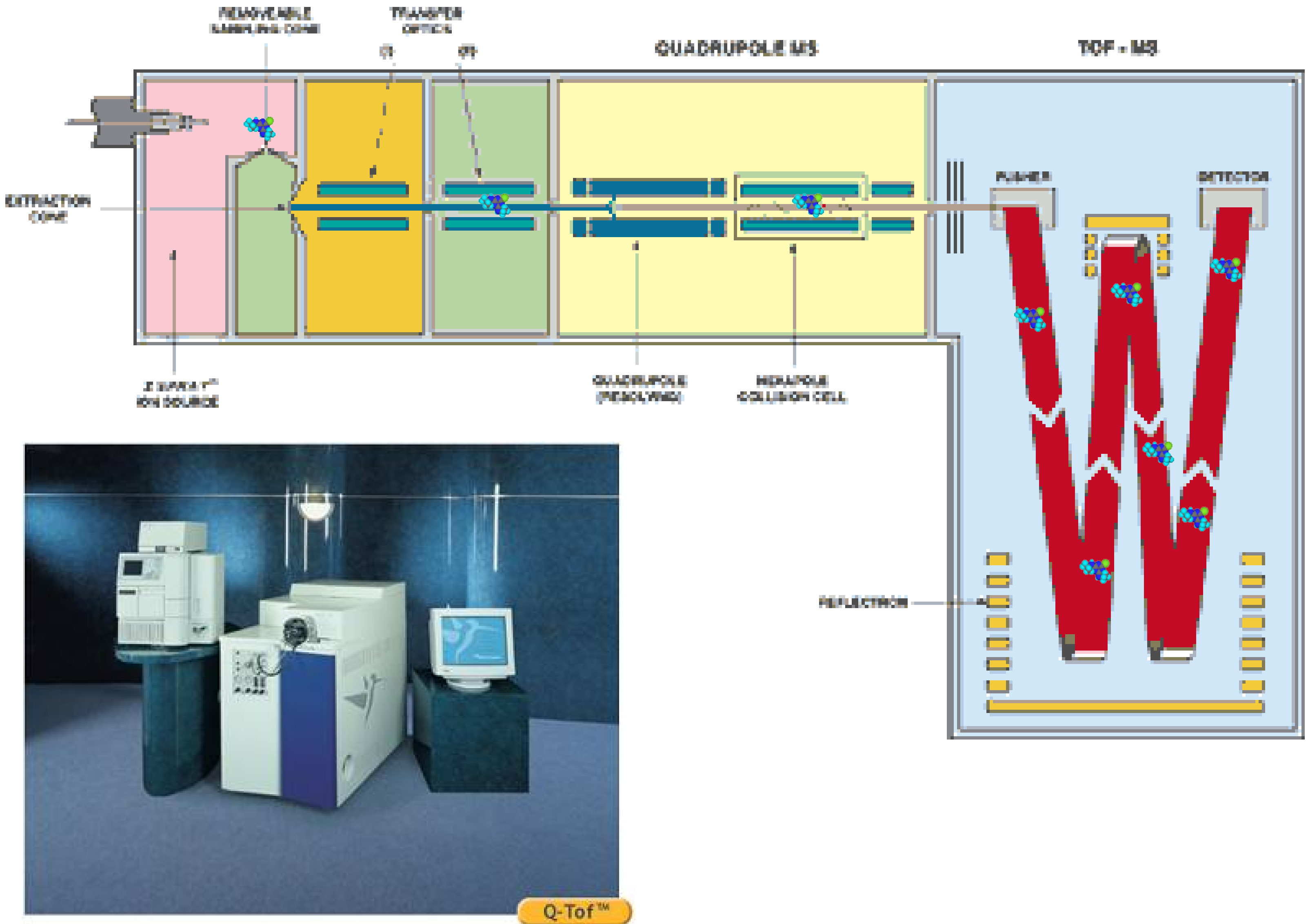
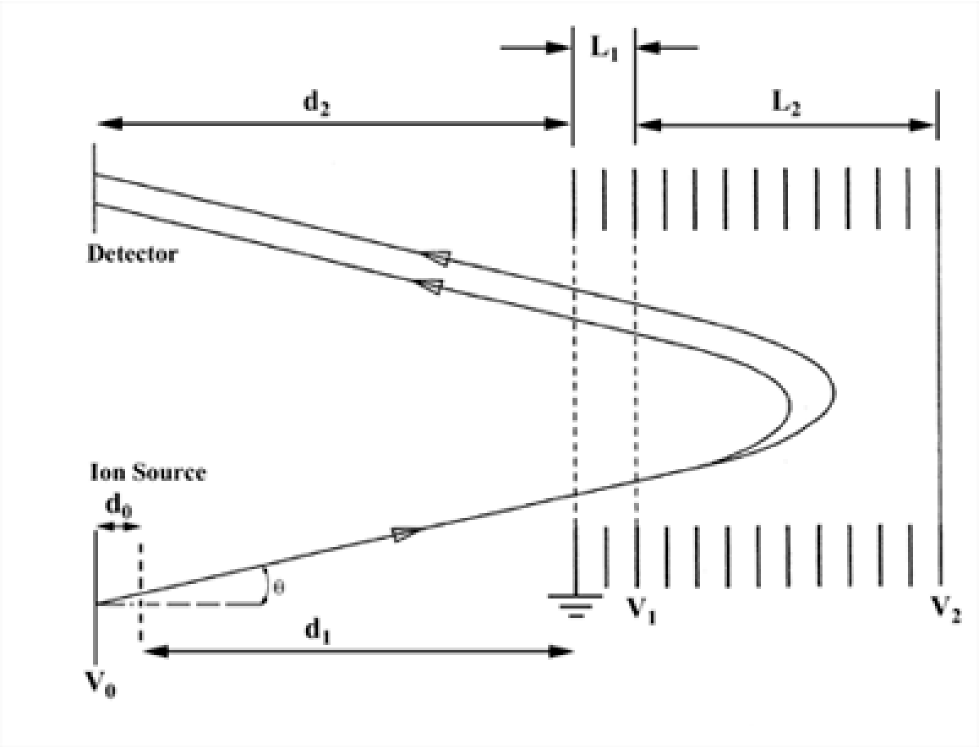

LINEAR TOF
Ion Source
Flight Path
Detector
time-of-flight α m/z
REFLECTRON TOF
Detector
Ion Source
Flight Path
Reflectron

How Q-TOF Works



Slide courtesy of Meyer et al., USGS

- Reflectron



Time-of-Flight Mass Spectrometry

- Ionization: positive ions are produced periodically by bombardment of the sample with brief pulses of electrons, secondary ions, or in cases laser-generated photons.
  - Laser pulses typically have a frequency of 10 to 50 kHz and a lifetime of 0.25 μs.
- Acceleration: The ions are then accelerated by an electric field pulse of 10^3 to 10^4 V (the "pusher") that has the same frequency as, but lags behind, the ionization pulse
  - 33 μs for the GC-TOF, resulting in 30,000 spectra per second (30 kHz)
- Drift: The accelerated particles then pass into a field-free drift tube. The drift tube's length can range from 0.5 - 3.0 meters

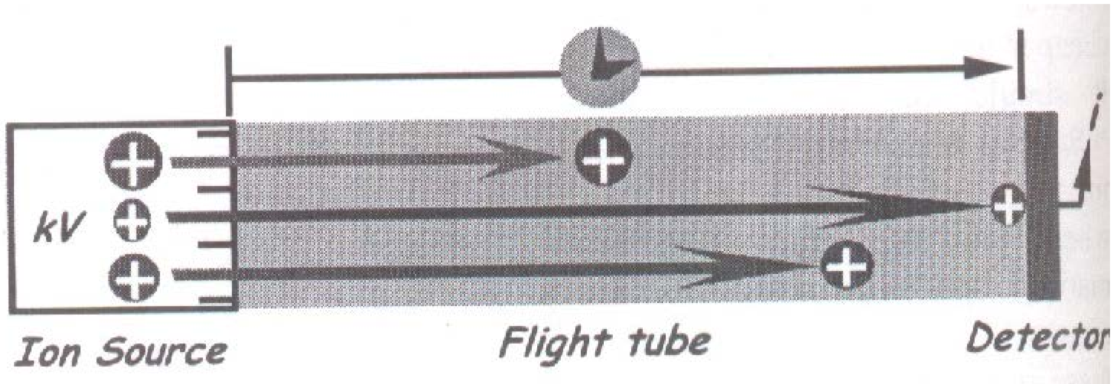
Time-of-Flight Mass Spectrometry

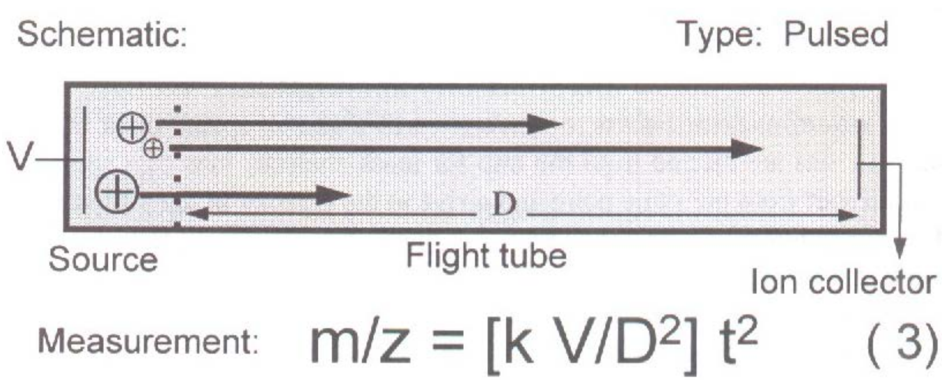
- An electric field accelerates all ions into a field-free drift region with a kinetic energy of zV, where z is the ion charge and V is the applied voltage. Since the ion kinetic energy is $0.5mv^2$, lighter ions have a higher velocity than heavier ions and reach the detector at the end of the drift region sooner
- Kinetic energy
  - $K.E. = zV = 1/2\ mv^2$
- Solving for velocity (v)
  - $v = (2zV/m)^{1/2}$
- The transit time (t) through the drift tube is L/v where L is the length of the drift tube (usually 1-3 meters).
  - $t=L\ /\ (2V/m/z)^{1/2}$

$$t = \left(\frac{m}{z}\right)^{1/2}\left(\frac{1}{2V}\right)^{1/2} L$$

Note that the voltage (V) is sometimes expressed as the product of an extraction pulse potential (E) and the distance over which it is applied (s), giving V=eEs

Time-of-Flight Analyzer (TOF)

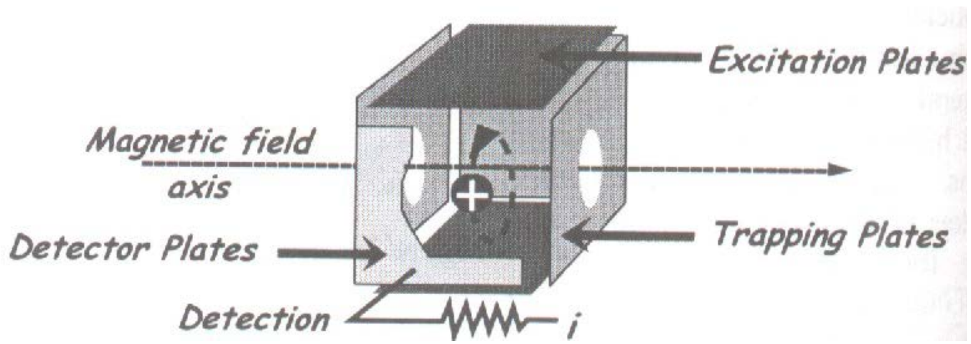


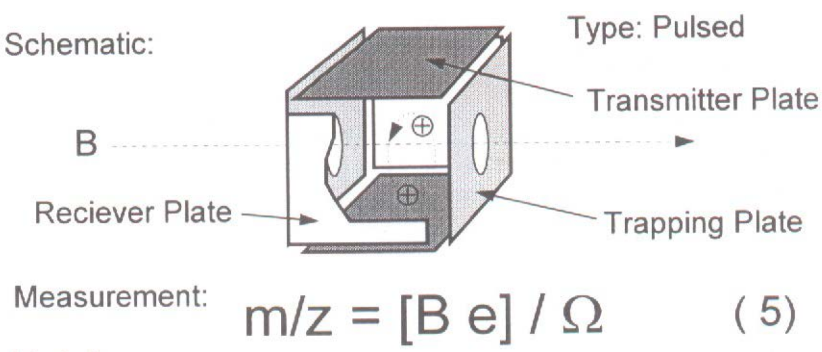


- **Ion velocity is mass dependent.**
- **A bundle of ions from the ion source region are pulsed down the flight tube.**
- **Small mass ions have higher velocity relative to large to large mass ions.**
- **The arrival time is directly related to m/z.**

In this drawing the drift tube length is “D” instead of “L”

Fourier Transform-MS (FTMS)





FTMS consists of a cell contained within a high vacuum chamber centered in a very high magnetic field.

Ions are trapped in the cell by a combination of a magnetic field and electric potentials.

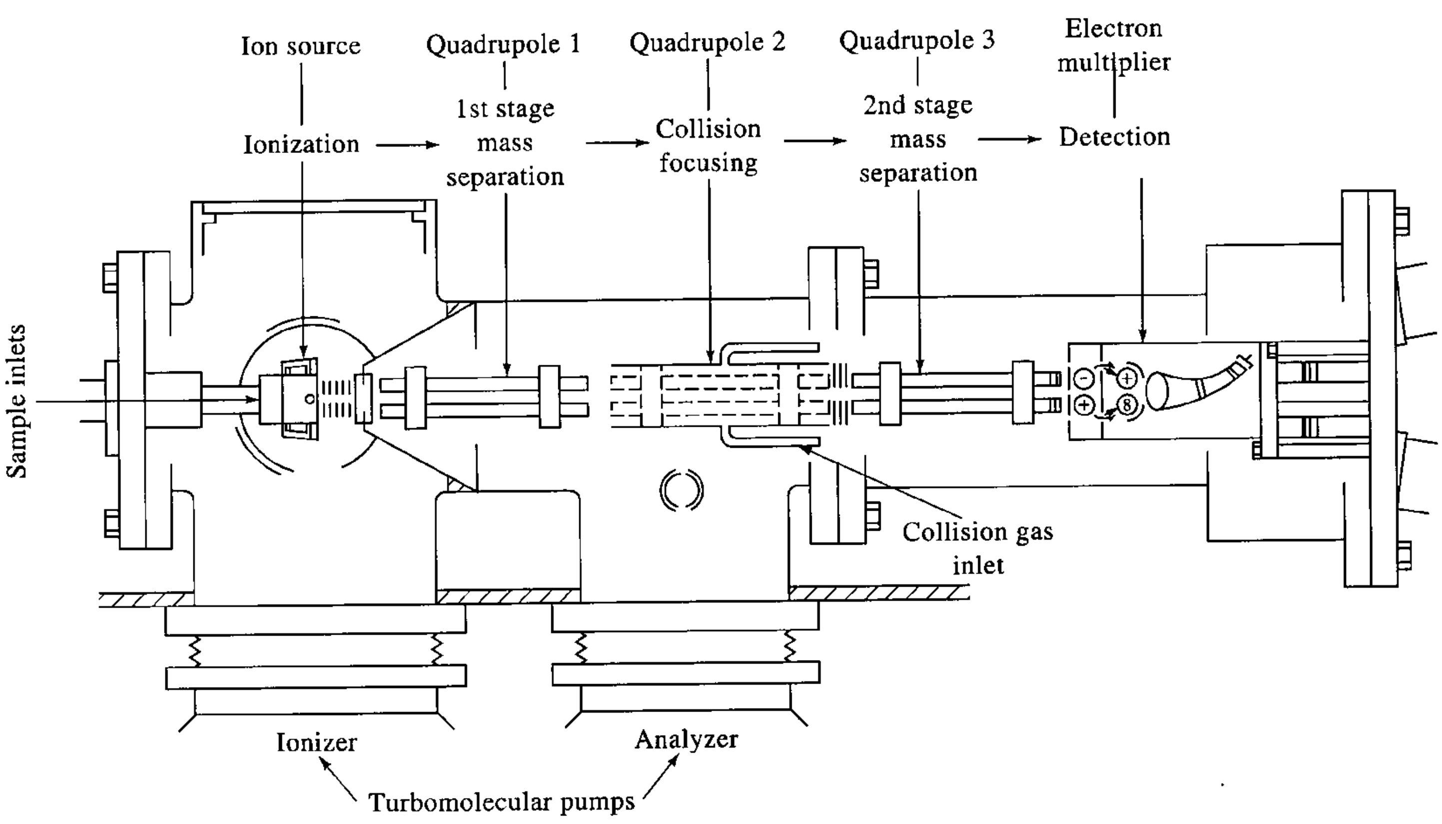
Ions will take on circular trajectories about the axis of the magnetic field. The frequency of rotation of ions is inversely proportional to mass.

The frequency of ion rotation is detected indirectly through induced current on the detector plates as the ions pass near the plates.

The frequency of ion rotation can be converted to mass through a fourier transform.

MS/MS

- Quadrupole



- To next lecture