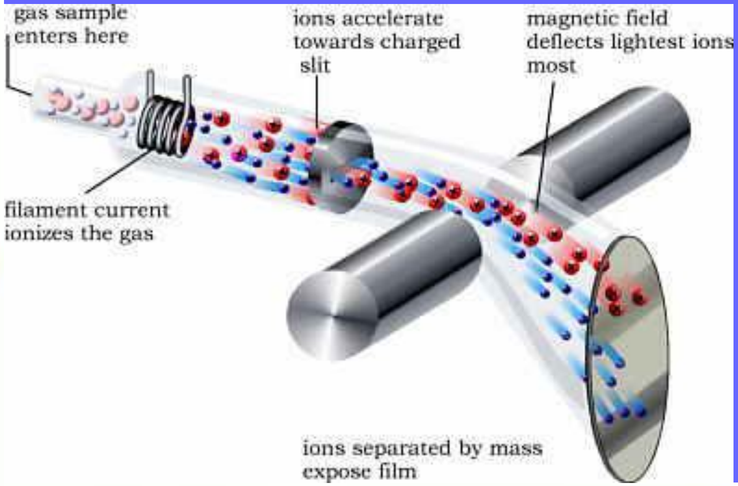
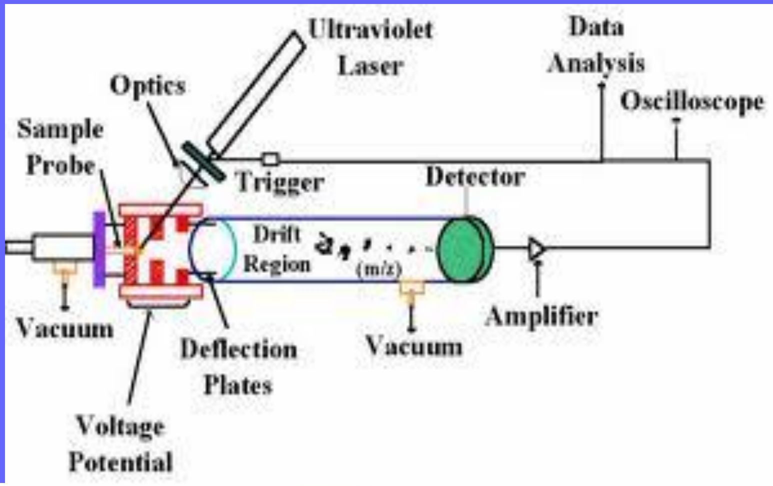
Chemistry 4631

Instrumental Analysis

Lecture 33





Mass Spectrometry (MS)

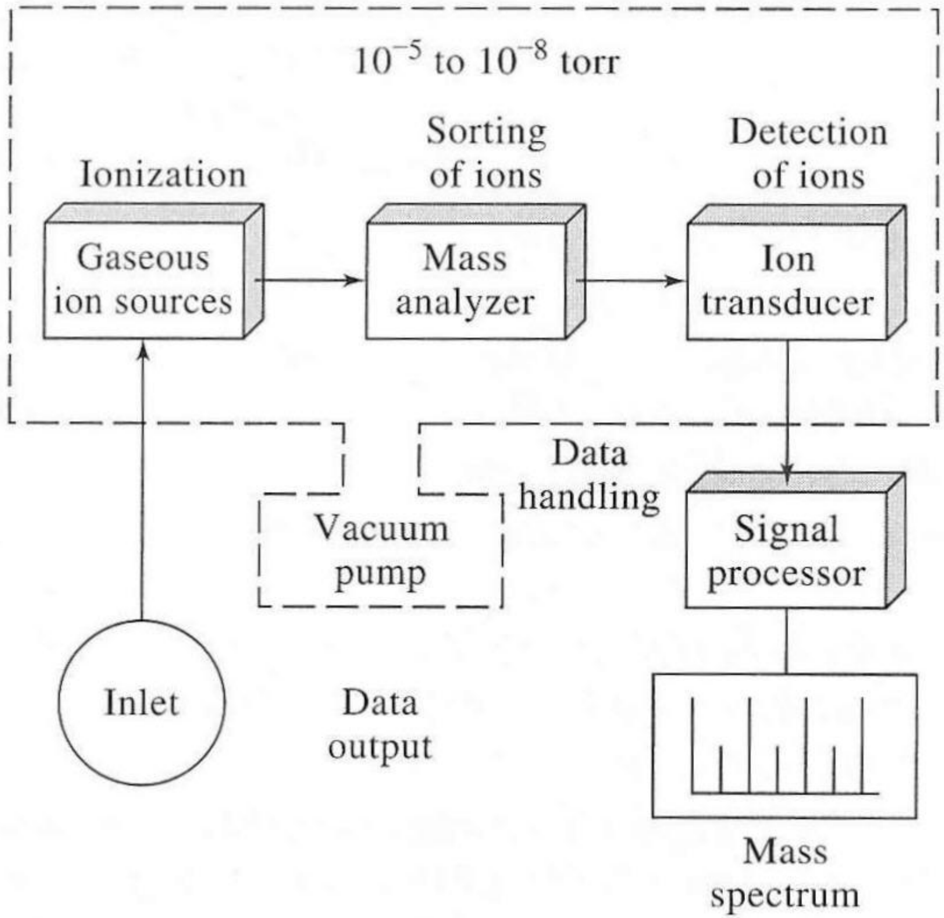


Figure 11-1 Components of a mass spectrometer.

Mass Spectrometry (MS)

Instrumentation

Principle components:

- Inlet
- Ion source
- Mass analyzer
- Ion transducer
- Pumps
- Signal processor

Mass Spectrometry (MS)

Instrumentation

Mass analyzers

– Quadrupole
– Time of Flight
– Double Focusing
– Ion Trap

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers

- Most common type of MS
- Compact less expensive
- Rugged
- High scan rates (entire spectrum in 100 ms)

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers

Contains 4 parallel cylindrical rods that serve as electrodes.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers

Opposite rods are connected electrically. Both direct current (DC) and fixed radio frequency (RF) potentials are applied to opposite poles.

- One pair to positive side of variable dc source.
- Other pair to negative terminal.
- Also variable radio frequency ac potentials, that are 180 degrees out of phase are applied to each pair.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers

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Ions passing through the analyzer are alternately deflected by and attracted to the poles.

For any specific ratio of RF amplitude and DC voltage only ions with a single mass (m/z) will reach the detector.

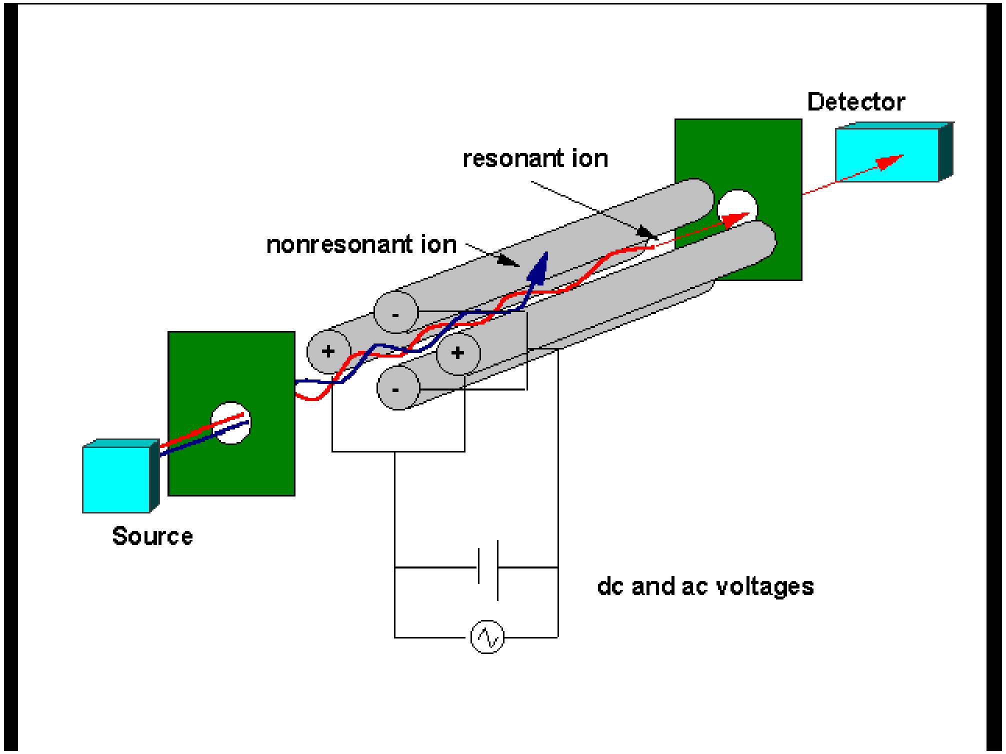
The entire range of masses is scanned by systematically changing the RF amplitude and DC voltages while keeping the ratio constant.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers



Mass Spectrometry (MS)

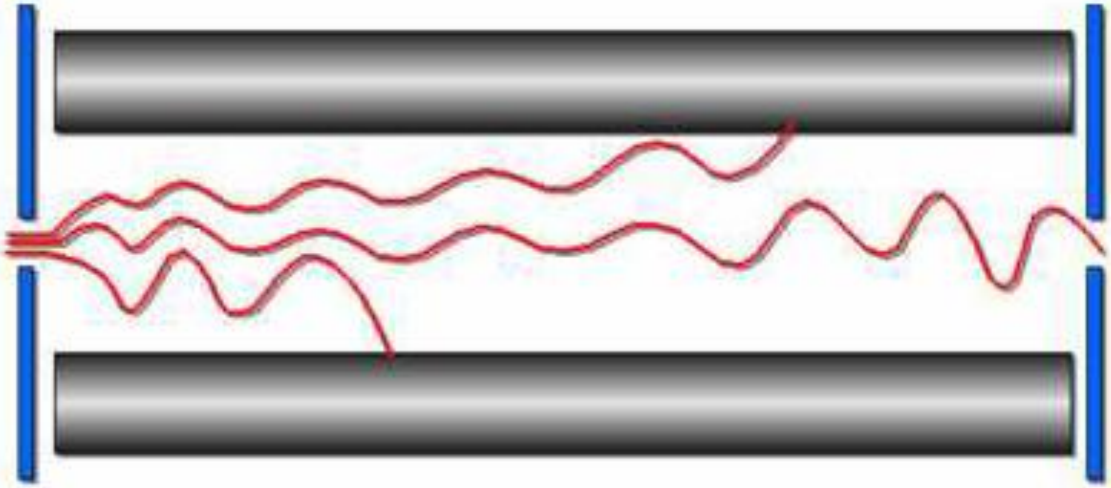
Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers

At any set of conditions, only ions of a specific M/Z can successfully travel through the entire filter.

Others are drawn into the rods.

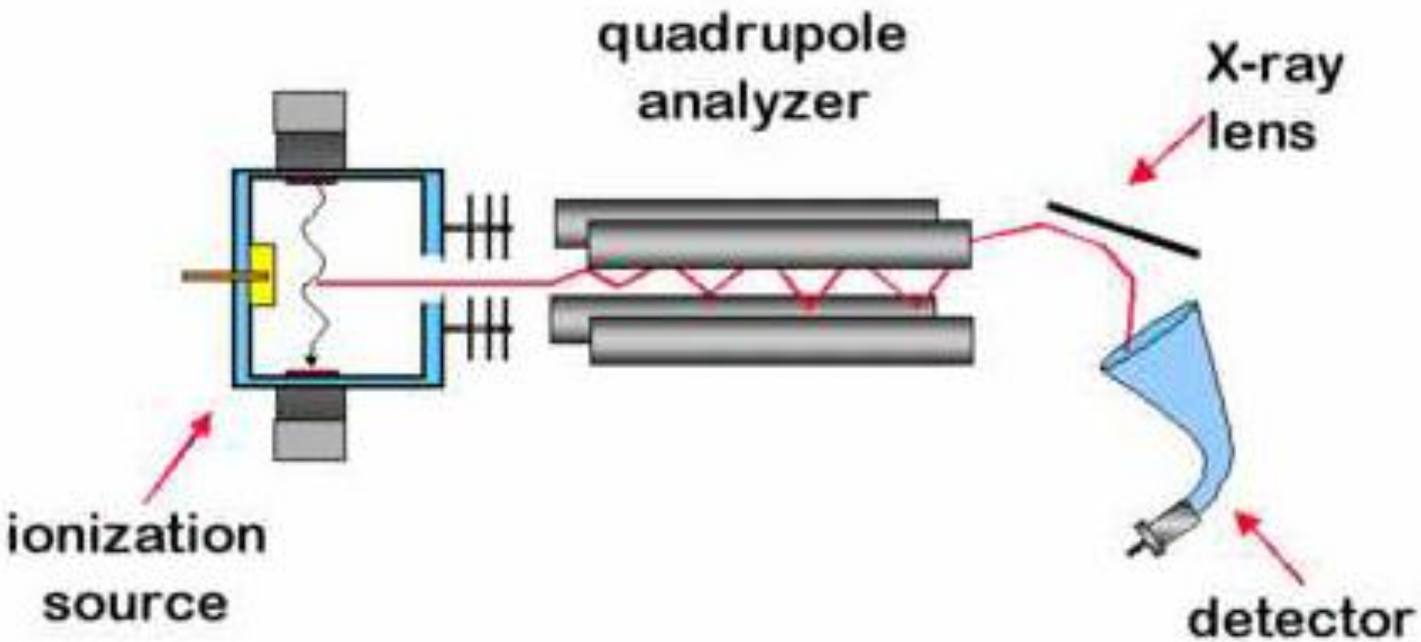


Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole Mass Analyzers



Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Quadrupole

Advantage

- Simple
- Rugged
- Low cost
- High scan rate

Disadvantage

- Must be periodically cleaned
- Range is 0-500 m/z

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Time of Flight Mass Analyzers

Positive ions are produced periodically by bombardment of the sample with brief pulses of electrons, secondary ions, or laser-generated photons.

The pulses have a frequency of 10-50 kHz and lifetimes of 0.25 μs.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Time of Flight Mass Analyzers

The ions produced are accelerated by an electric field of 10^3 to 10^4 V with the same frequency.

The accelerated particles pass into a field-free drift tube (linear or reflectron) about a meter in length.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Time of Flight Mass Analyzers

The ions entering the tube have the same kinetic energy but the velocities vary inversely with the ions masses.

Lighter particles arrive at detector first.

Flight times are 1-30 μs.

Mass Spectrometry (MS)

Time of Flight Mass Analyzers

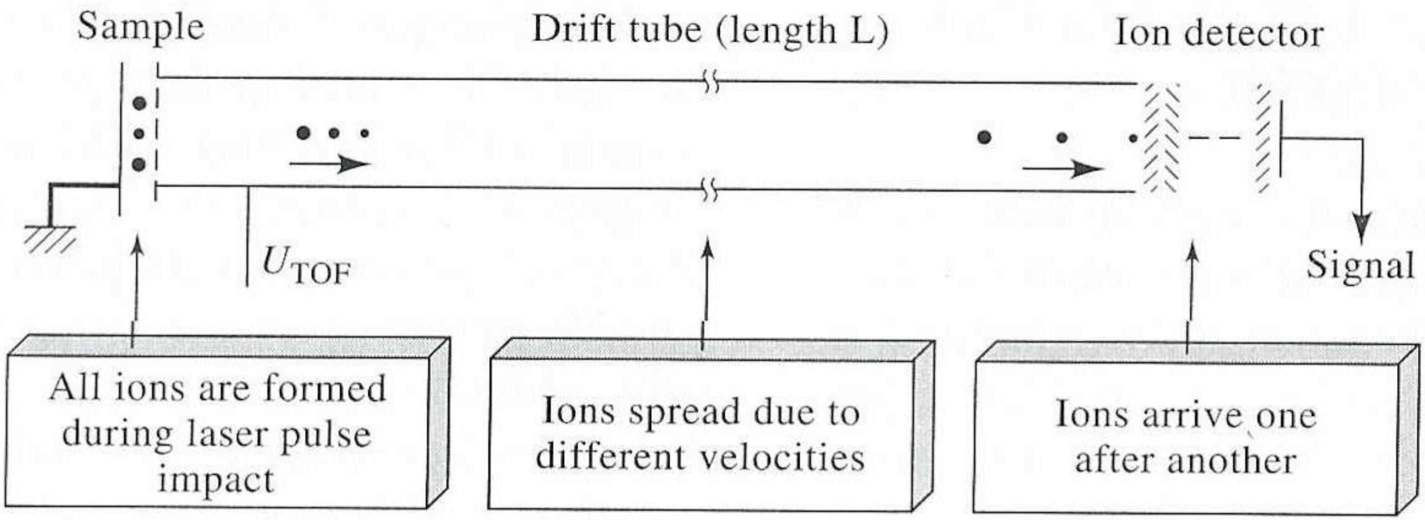


Figure 11-8 Principle of a time-of-flight mass spectrometer. A bunch of ions produced by a laser probe is accelerated into the drift tube where separation occurs. *(From A. H. Verbueken, F. J. Bruynseels, R. Van Grieken, and F. Adams, in* Inorganic Mass Spectrometry, *p. 186. F. Adams, R. Gijbels, and R. Van Grieken, Eds. New York: Wiley, 1988. With permission.)*

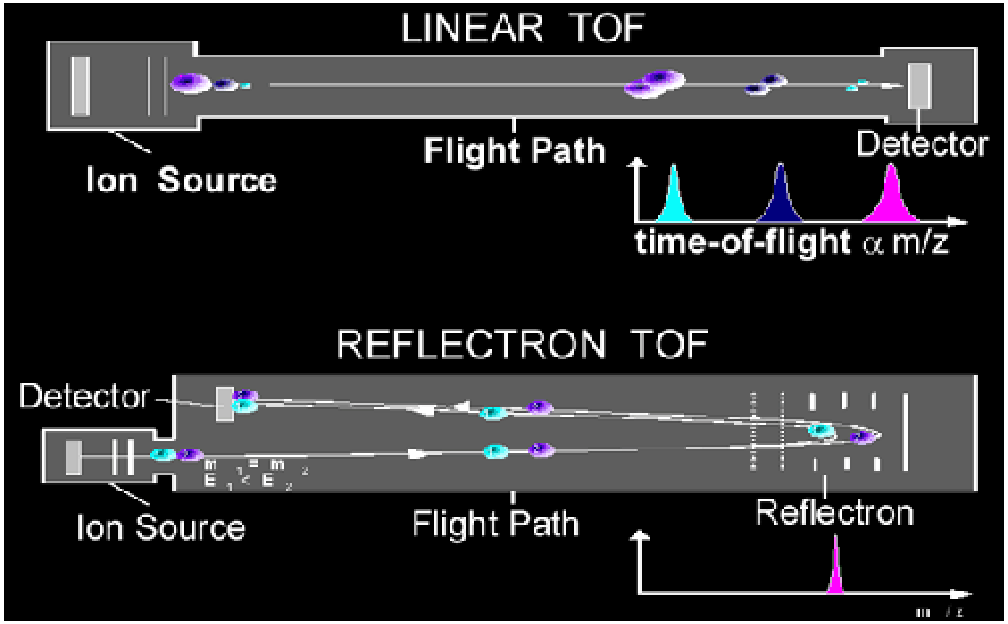
Mass Spectrometry (MS)

Instrumentation

<u>Mass Analyzers</u>

Time of Flight Mass Analyzers

Linear or Reflectron.



Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Time of Flight Mass Analyzers

Advantage

- Simple
- Rugged
- Unlimited mass range
- Rapid data acquisition

Disadvantage

- Poorer resolution
- Less reproducible

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

Focuses a beam of ions using an electrostatic analyzer and a magnetic sector analyzer.

Use an electric field to select ions with a single kinetic energy and a magnetic field to select ions with a single mass-to-charge ratio.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

Ions from a source are accelerated through a slit into a curves electrostatic field (electrostatic analyzer).

The field focuses the beam of ions through a slit leading into a curved magnetic field according to kinetic energy.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

In the magnetic field, the lightest ions are deflected most and heaviest ions the least.

The dispersed ions fall on a detector and are recorded.

Mass Spectrometry (MS)

Double-Focusing Analyzers

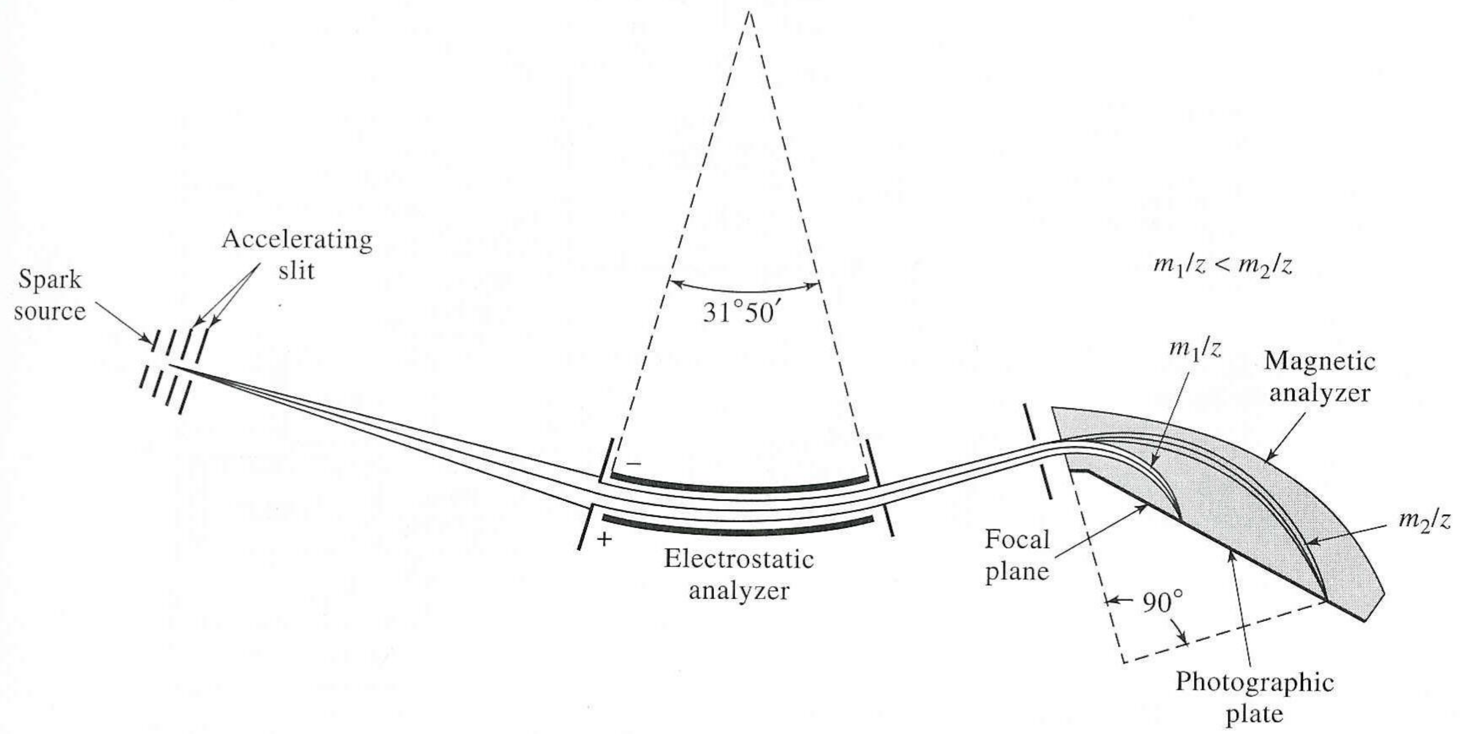


Figure 11-9 Mattacuh-Herzog–type double-focusing mass spectrometer. Resolution > 10^5 has been achieved with instruments based on this design.

Mass Spectrometry (MS)

Double-Focusing Analyzers

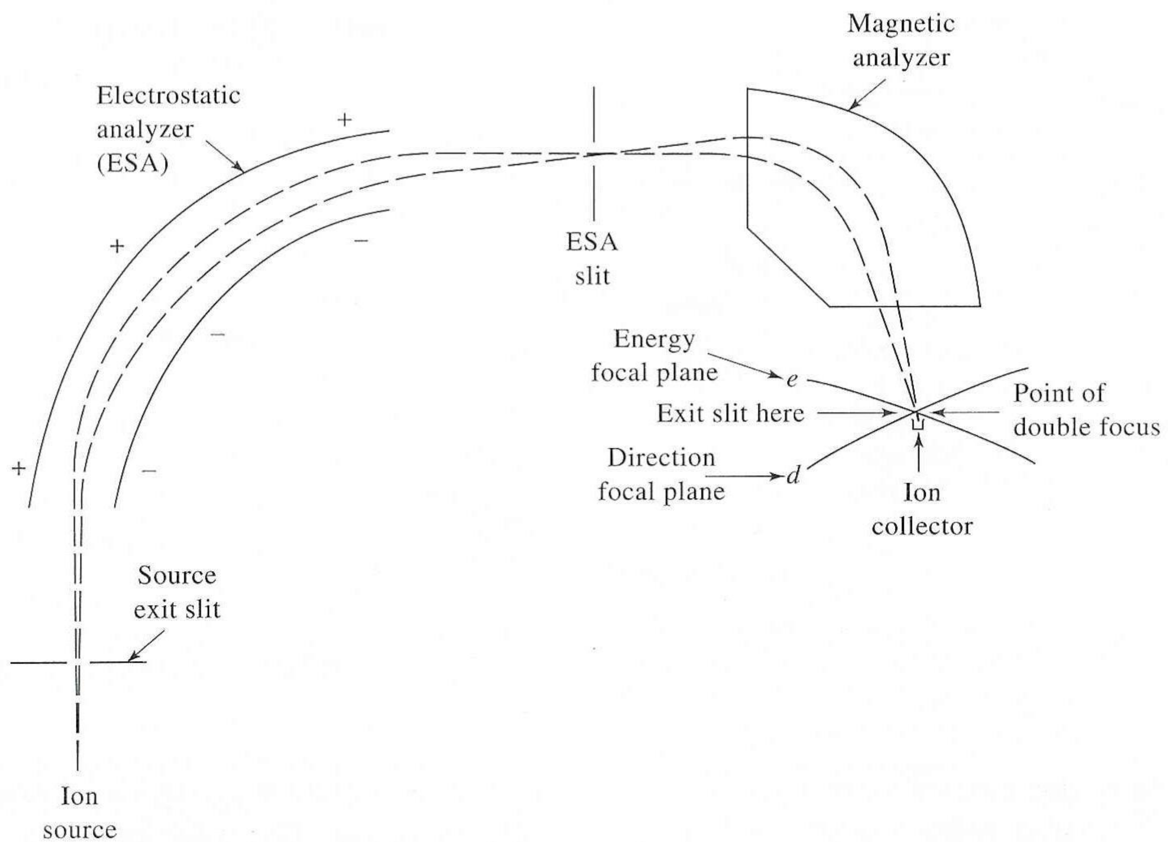


Figure 20-13 Nier-Johnson design of a double-focusing mass spectrometer.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

Kinetic energy of an ion is given by:

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

m – mass

z – charge

V – voltage

v – velocity

e – electronic charge ($e = 1.60 \times 10^{-19}$ C)

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

Magnetic force, F_m, given by:

$$F_m = BzeV$$

B – magnetic field strength

Centripetal Force, F_c

$$F_c = (mv^2)/r$$

r – radius of curvature of magnetic sector

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

F_m and F_c must be equal for ion to travel through sector.

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

The mass spectra can be acquired by varying either B, V, or r, while holding others constant.

Usually V and r are constant and B is varied.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Double-Focusing Analyzers

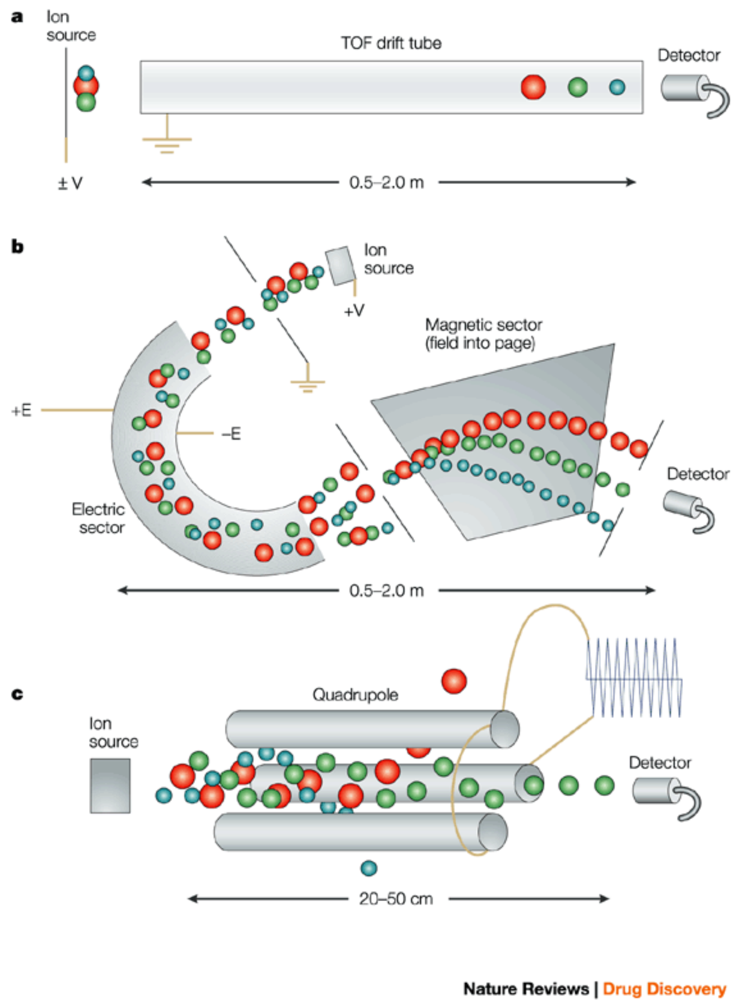
Have very high resolution (5ppm) and mass accuracy (+/- 0.0001 m/z units).

Also capable of measuring ions with a m/z greater than 10,000.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers



Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Ion Trap Analyzers

A common type is a quadrupole or simple ion trap.

Consist of a central doughnut shaped ring electrode and a pair of end capped electrodes.

A variable radio-frequency voltage is applied to the ring electrode while the two end electrodes are grounded.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Ion Trap Analyzers

Ions with correct m/z value circulate in a stable orbit.

The mass spectrum is obtained by destabilizing the orbits for individual masses (m/z) one at a time.

When the orbits are destabilized, some of the ions are ejected into the detector.

Mass Spectrometry (MS)

Ion Trap Analyzer

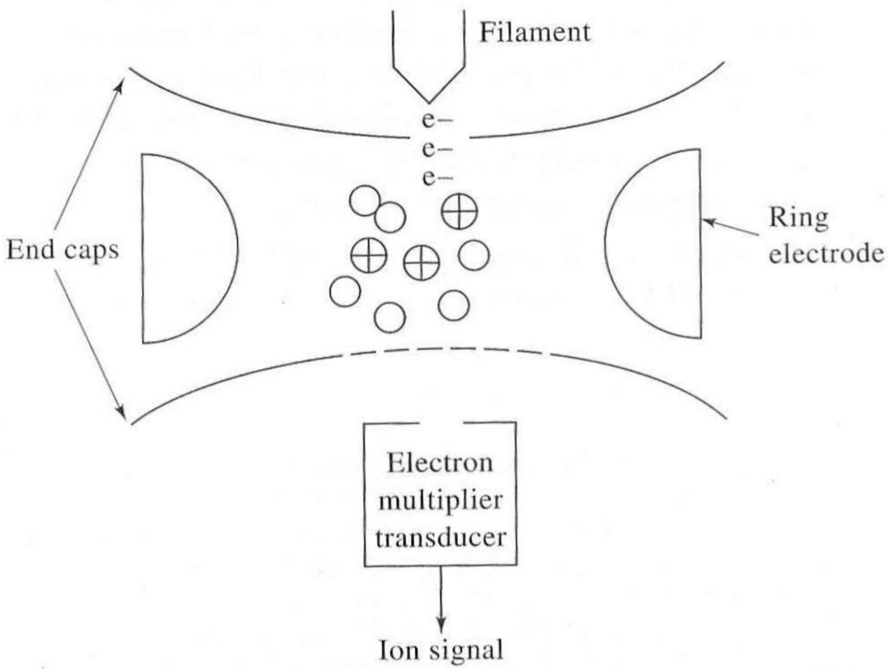
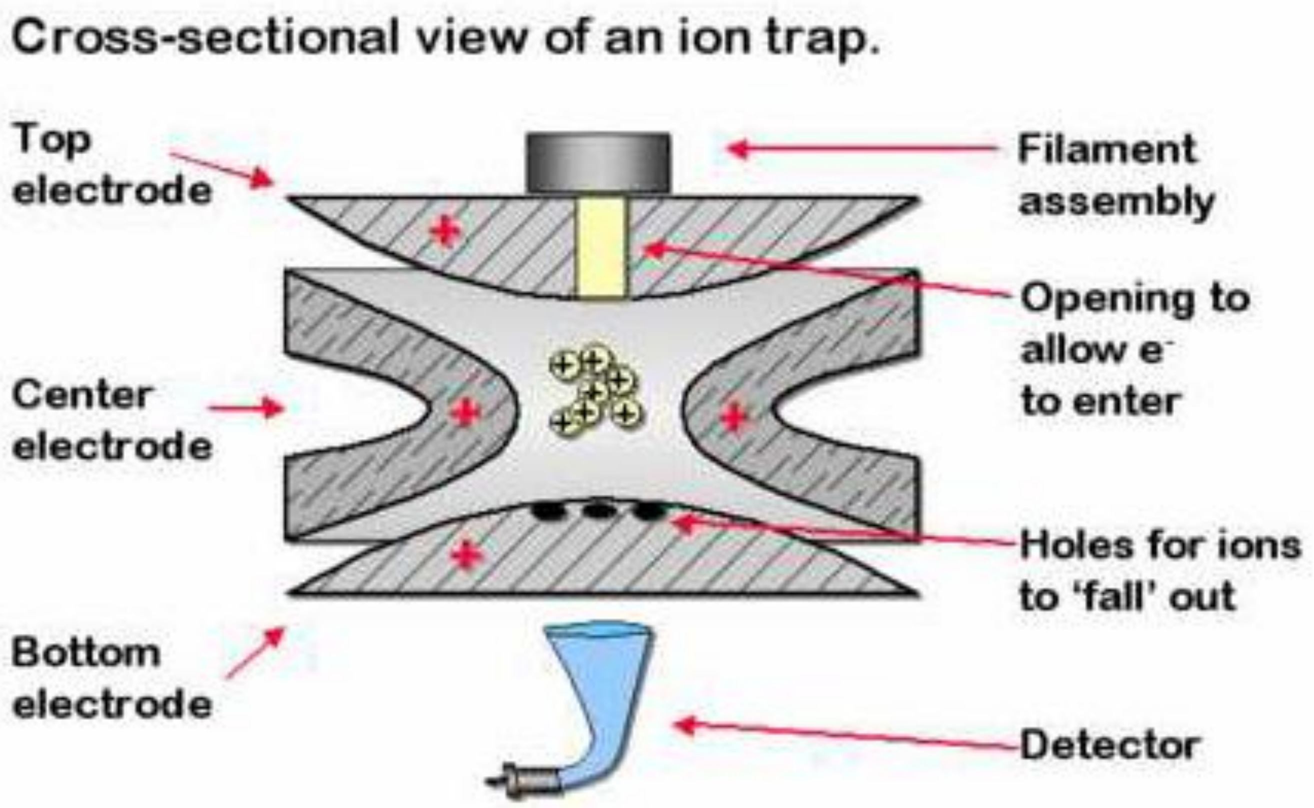


Figure 20-15 Ion trap mass spectrometer. *(Adapted from J. T. Watson,* Introduction to Mass Spectrometry, *p. 89. Philadelphia: Lippincott-Raven Press, 1997. With permission.)*

Mass Spectrometry (MS)

Ion Trap Analyzer



Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Ion Cyclotron Resonance Analyzer (ICR)

Confines gaseous anions or cations by electric and/or magnetic fields.

When gaseous ions drift into a strong magnetic field, the motion becomes circular in a plane that is perpendicular to the direction of the field.

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Ion Trap Analyzer - ICR

The angular frequency of this motion is called the cyclotron frequency, ω_c.

$$\omega_c = v/r = (zeB)/m$$

Mass Spectrometry (MS)

Instrumentation

Mass Analyzers

Ion Trap Analyzer - ICR

The ions trapped in a circular path in a magnetic field can absorb energy from an ac electric field, if the frequencies of the field matches the cyclotron frequency.

The absorbed energy increases the velocity of the ions (and thus the radius).

Only those ions of a matching m/z ratio are set in motion.

Mass Spectrometry (MS)

Ion Trap Analyzer - ICR

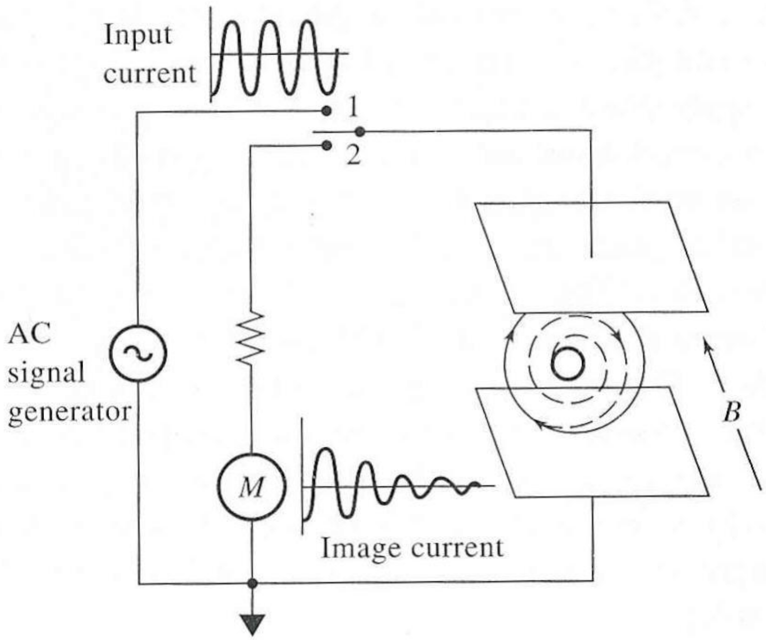
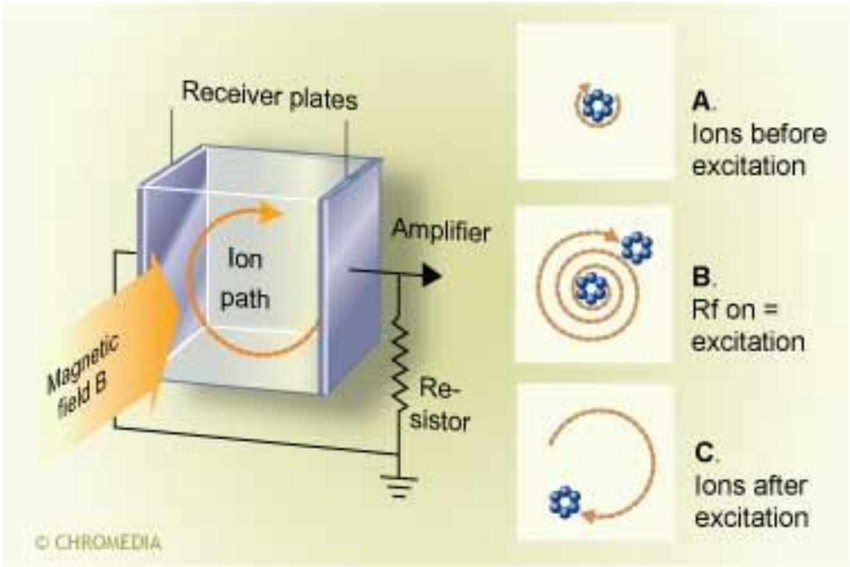


Figure 20-16 Path of an ion in a strong magnetic field. Inner solid line represents the original circular path of the ion. Dashed line shows spiral path when switch is moved briefly to position 1. Outer solid line is new circular path when switch is again opened.



Assignment

- Read Chapter 11
- HW 18 Chapter 11: 2, 4, 5, 7
- HW 18 Due 04/27/26

- Read Chapter 20
- HW 19 Chapter 20: 1-5, 7-11, 17
- HW 19 Due 04/29/26

- Test 4 - Lectures 24-31 Monday April 27th