Mass Analysers

- Scanning analysers transmit ions of different masses successively along a time scale.
  - magnetic sector instruments with a flight tube in the magnetic field
  - quadrupole intruments

- Some analysers allow the simultaneous transmission of all ions.
  - dispersive magnetic analysers
  - time of flight mass analysers
  - ion traps
  - ion cyclotron resonance instruments

- Instruments combining several analysers in sequence
  - tandem mass spectrometers

Main characteristics of a mass analyser

- the upper mass limit
  highest value of the m/z ratio that can be measured (1000 for GC-MS).

- the ion yield and transmission
  ratio between the number of ions reaching the detector and the number of ions produced in the source.

- the resolution
  ability to yield distinct signals for two ions with a small mass difference.

- the scan rate
  time it takes to record a spectrum.

Empirical formula

Relative / nominal atomic mass

Accurate atomic mass

Relative / nominal molecular weight

Accurate molecular weight

Mass Analyser

Resolution

Valley definition:

- Two peaks are considered to be resolved if the valley between the two peaks is equal to 10% of the weaker peak intensity when using magnetic or ion cyclotron resonance instruments and 50% when using quadrupoles.

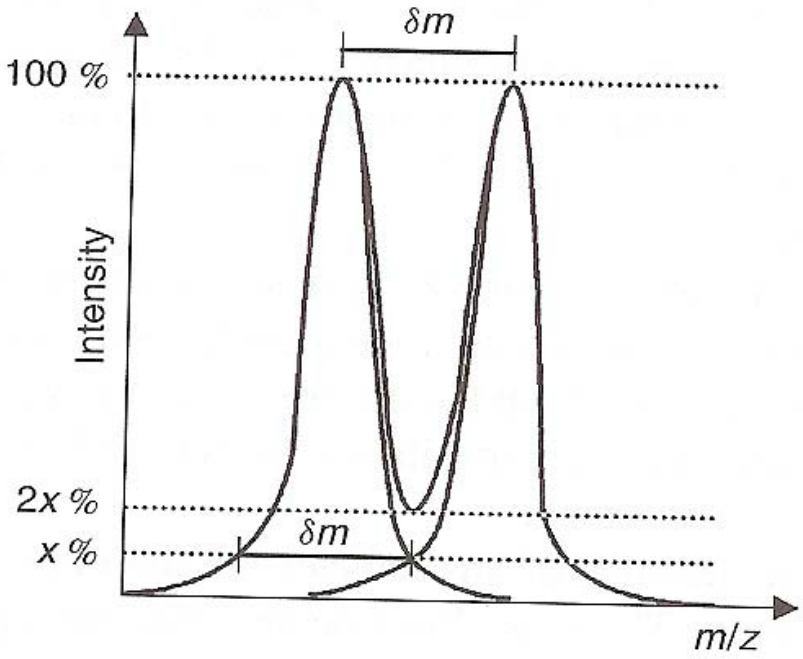
δm-definition:

- If δm is the smallest mass difference for which two peaks with masses m and m + δm are resolved:

$$R = \frac{m}{\delta m} = \frac{4000\,amu}{1\,amu} = 4000$$

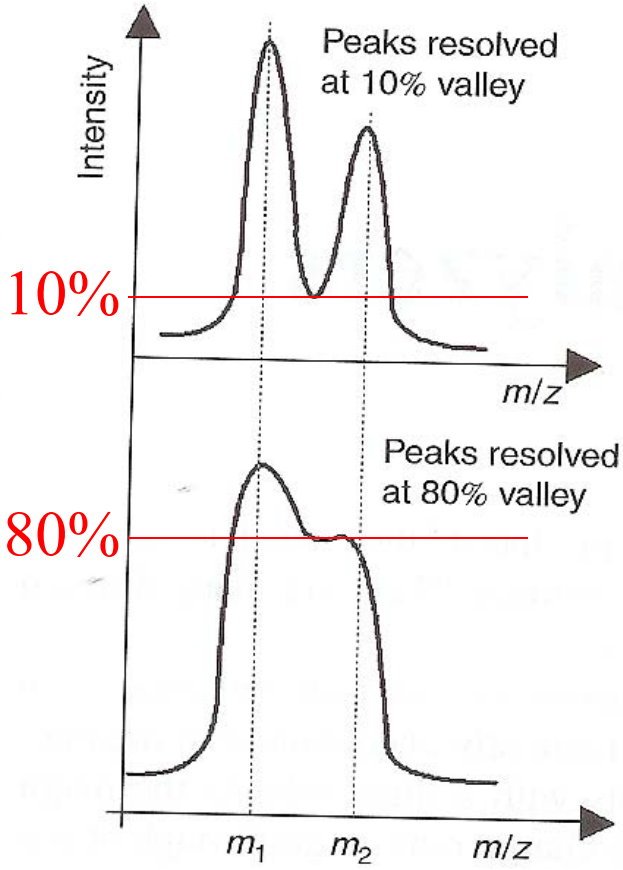
δm-definition of a single peak:

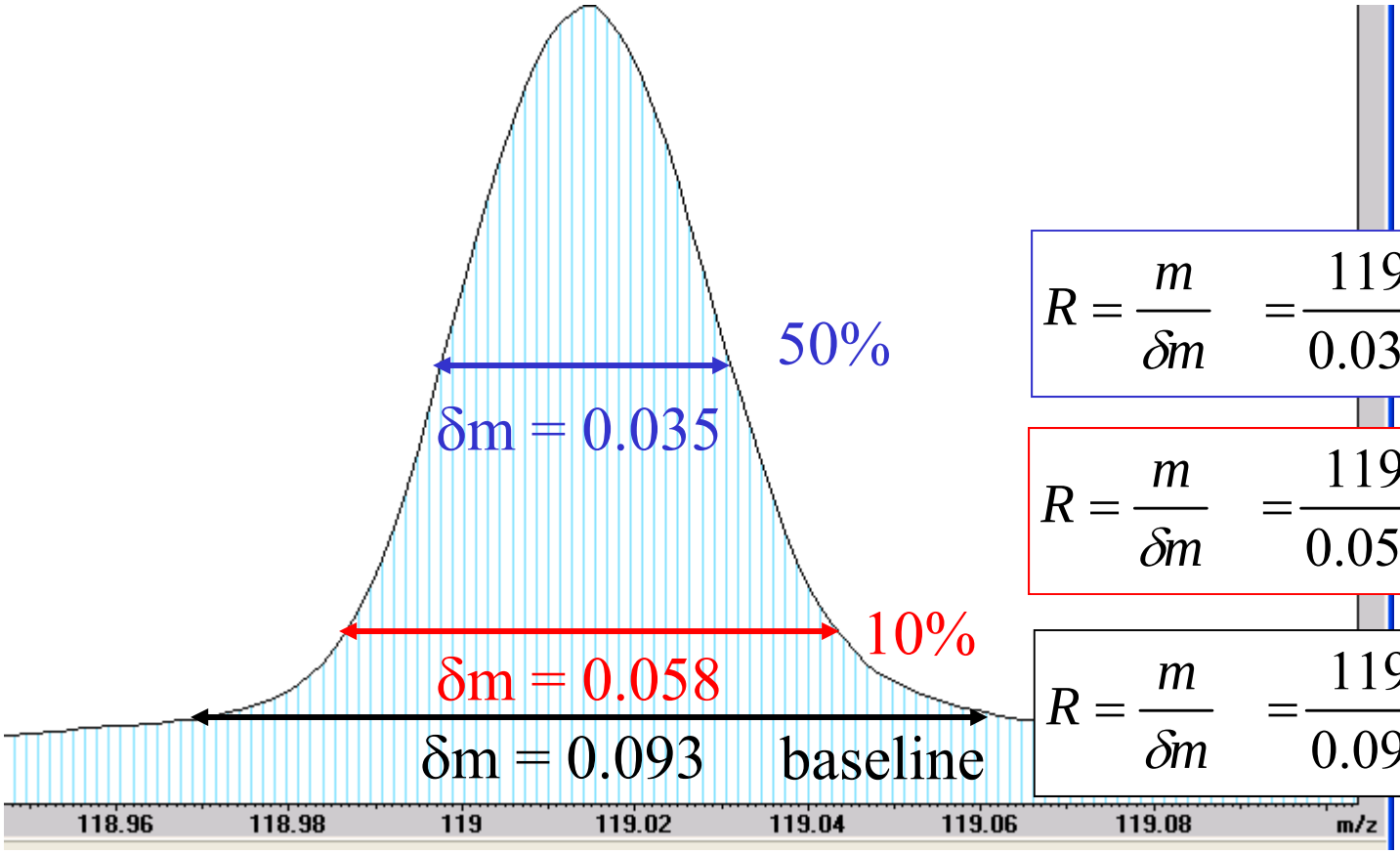
- R can be defined as being the peak width δm at X% of the peak height. Often X is taken to be 50% and δm is designated as the **f**ull **w**idth at **h**alf-**m**aximum, FWHM.



Relationship between the two δm definitions of resolution

Concept of peak resolution and valley





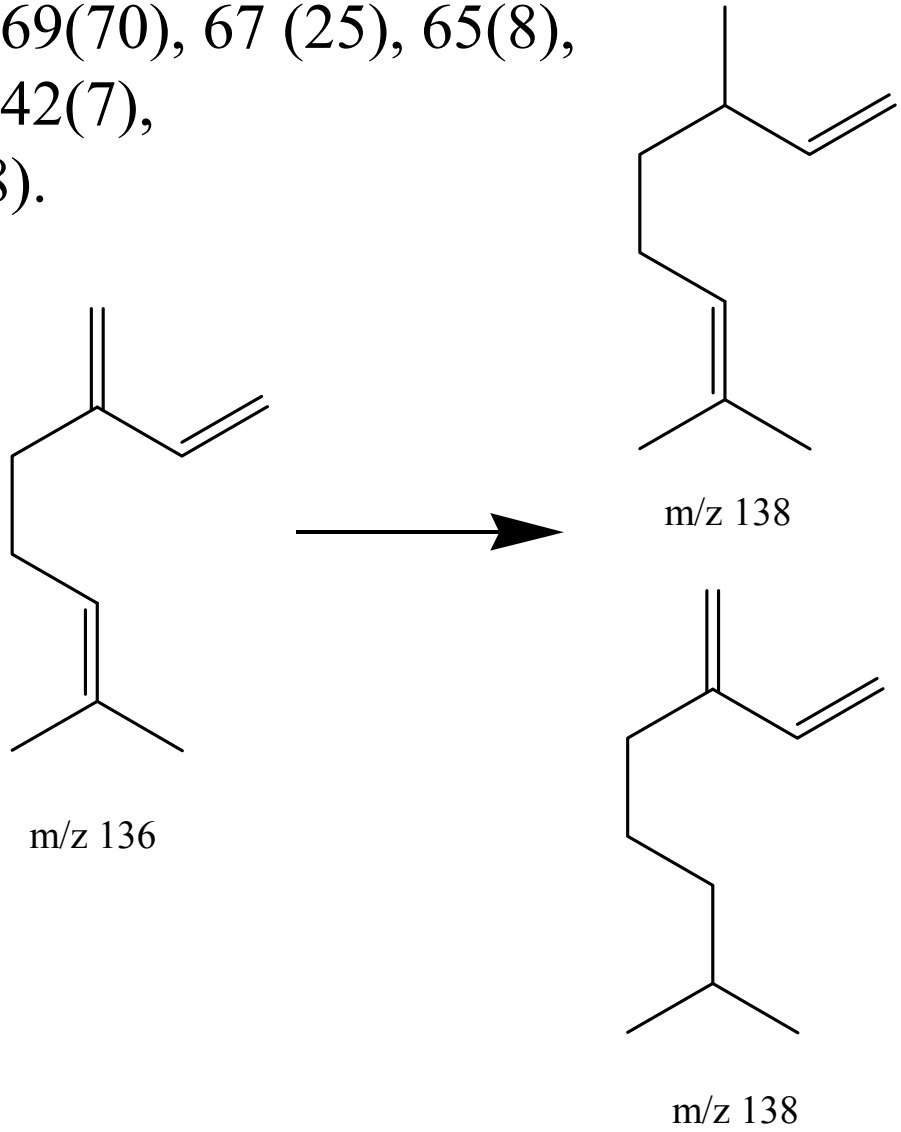
$$R = \frac{m}{\delta m} = \frac{119\,amu}{0.035\,amu} = 3400$$

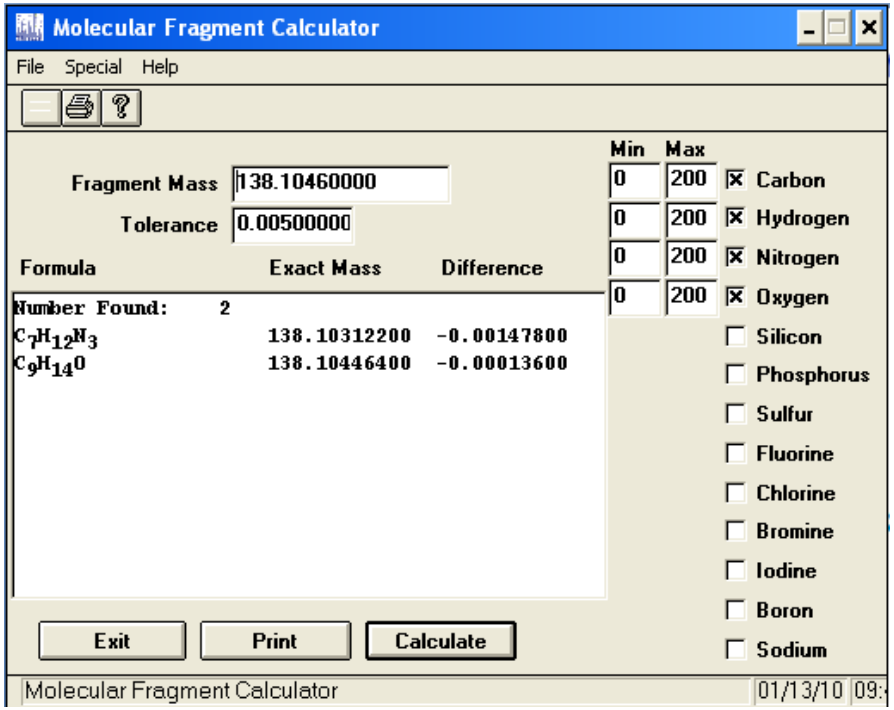
$$R = \frac{m}{\delta m} = \frac{119\,amu}{0.058\,amu} = 2000$$

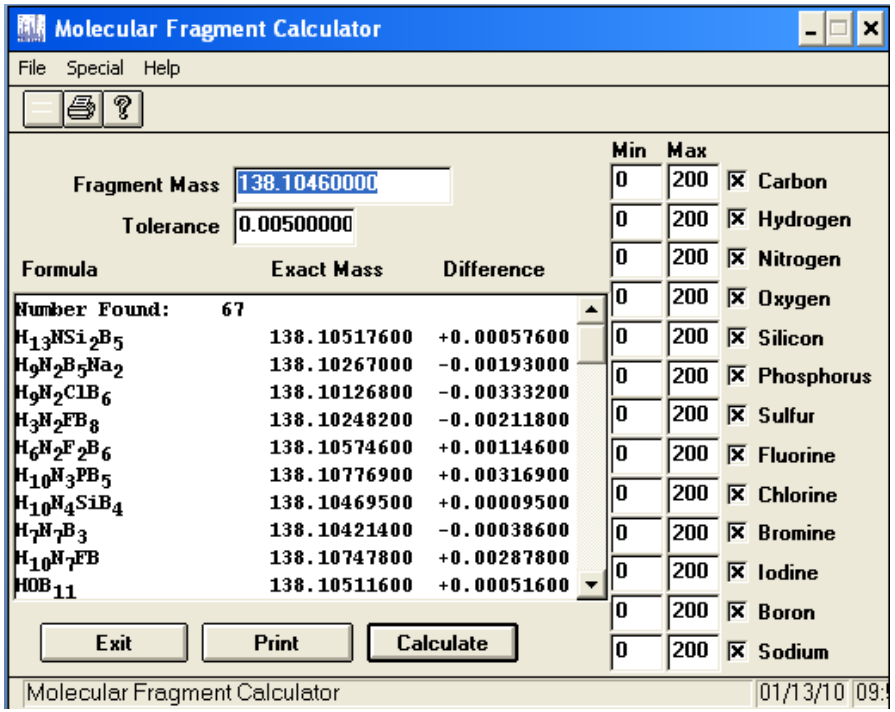
$$R = \frac{m}{\delta m} = \frac{119\,amu}{0.093\,amu} = 1280$$

Mass resolution using different δm-definitions

MS[m/z(%)]: 138, M+(2), 123(2), **120 (2)**,
109(4), 95(19), 79(6), 77(6), 69(70), 67 (25), 65(8),
55(9), 53(23), 51(12), 50(7), 42(7),
41(100), 40(21), 39(88), 38(8).







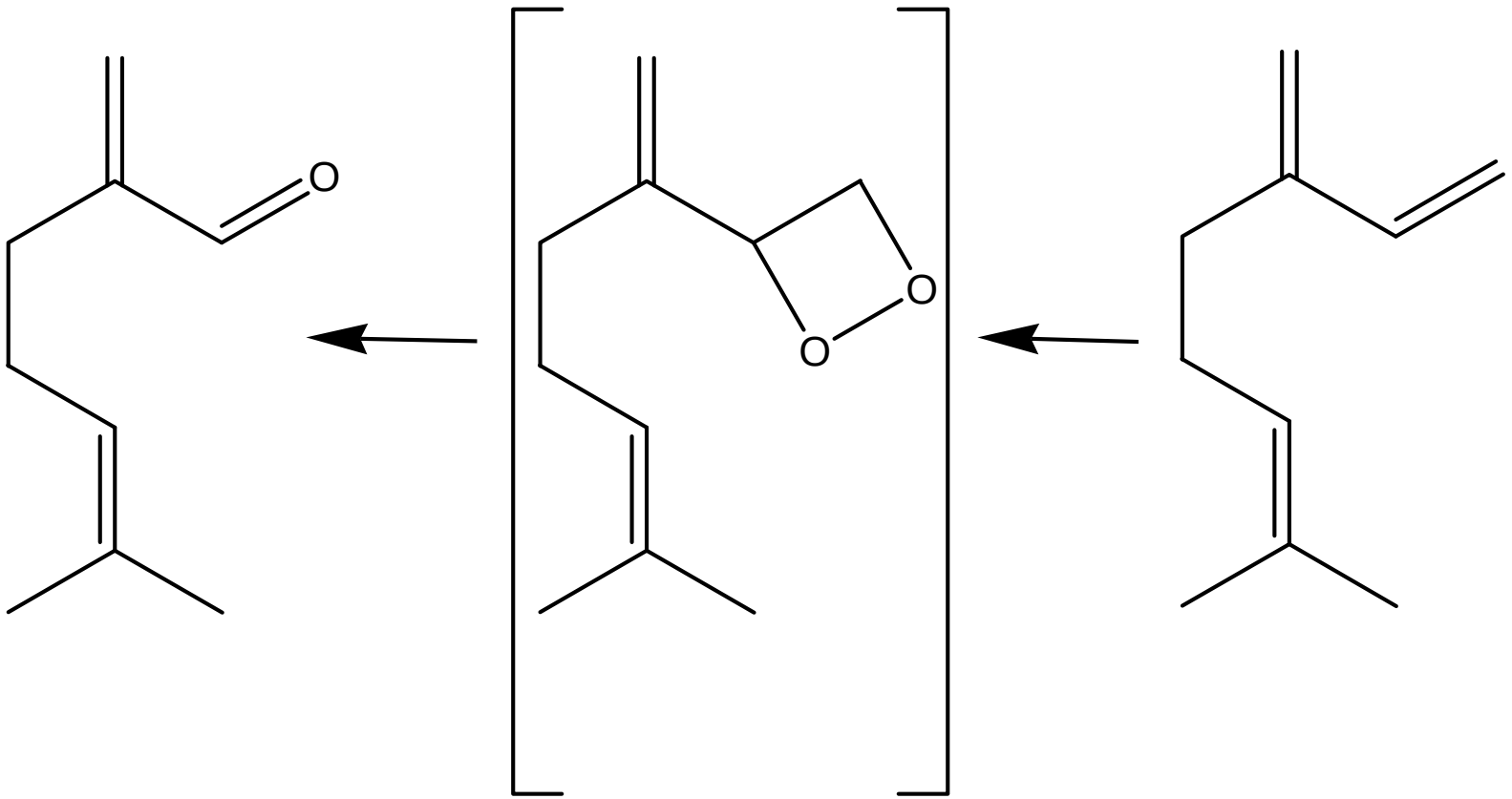
HR-EIMS m/z 138.1046

(calcd for $C_9H_{14}O$ 138.10446; $C_{10}H_{18}$ 138.14085)

Δm = -0.00014, ≅ 1 ppm; Δm = +0.026, ≅ 262 ppm

⇒ 6-Methyl-2-methylene-hept-5-enal

Mass Analyser



Mass Analyser

Tab.: Comparison of some features of various mass analysers

Feature	Double-focusing sector	Linear quadrupole	Ion trap	TOF
Scanning	Low (B-Scan)	Fast	Fast	Super fast
Vacuum	Critical	Required	Required	Required
Mass range	10000	4000	2000	No limits
Aquisition	Full-scan, SIM	Full-scan, SIM	Full-scan, SIM	Full-scan
Resolution	High	Unit-mass	Unit-mass	High
Mass accuracy	Accurate (1 ppm)	Nominal	Nominal	Accurate 5 ppm

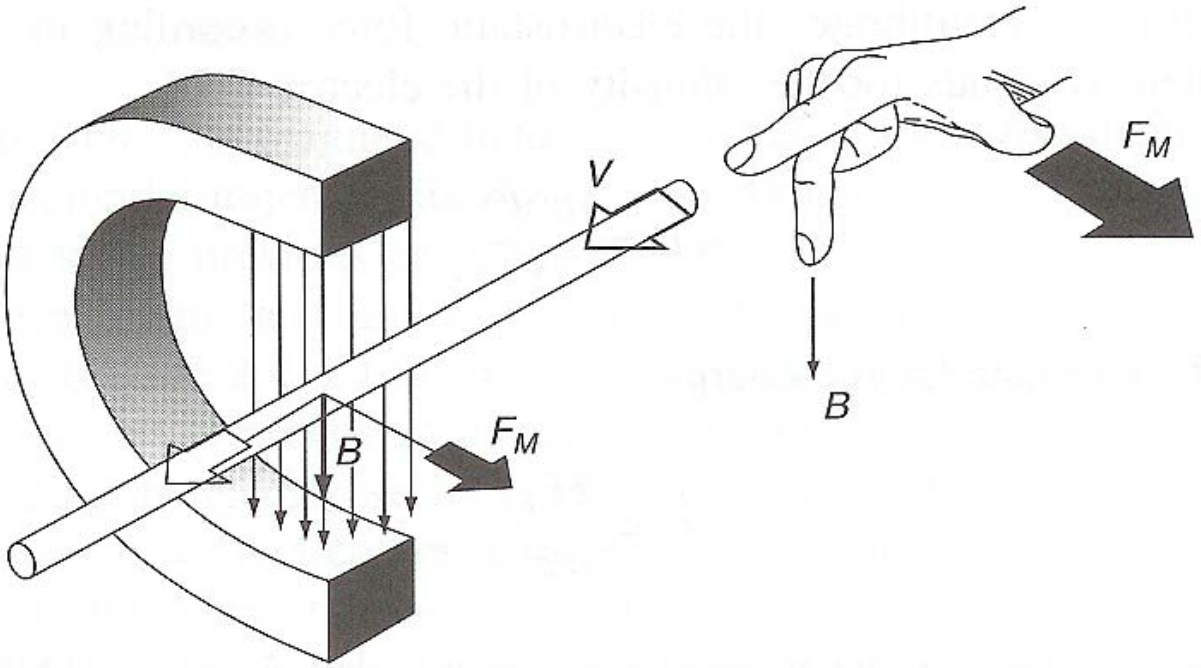
$$ppm = \frac{\delta m}{m} = \frac{0.005 \quad u}{1000 \quad u} = 0.000005 = 5 \text{ ppm}$$

$$ppm = \frac{\delta m}{m} = \frac{0.0005 \quad u}{100 \quad u} = 0.000005 = 5 \text{ ppm}$$

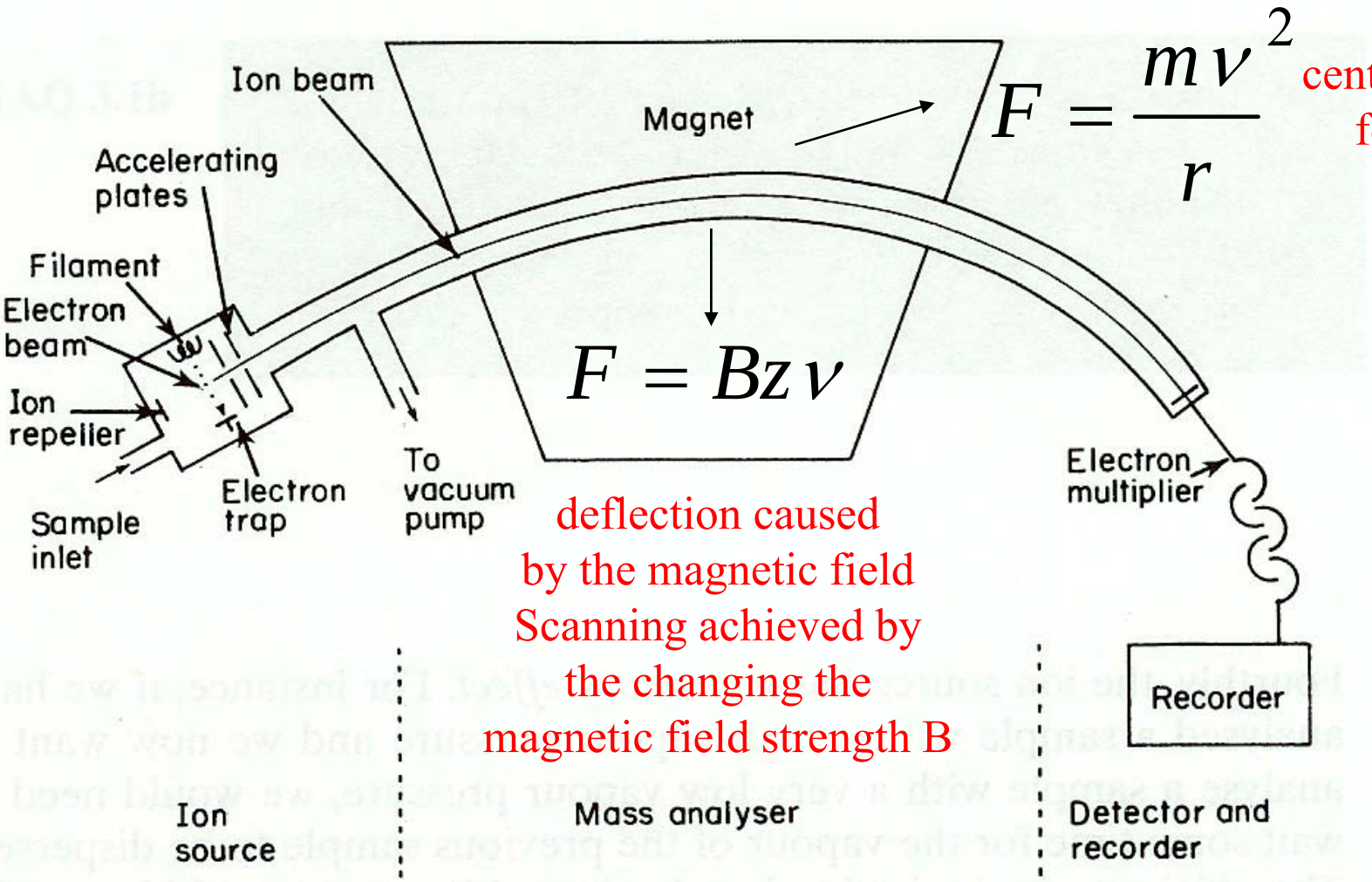
Magnetic-Sector Instruments

- Analysis is obtained *via* the use of a magnetic field.
- When an electrical current is passed through a magnetic field, it follows a path that is curved.
- The beam of ions (from a source) can be thought of as an electrical current.
- The magnet is often constructed so that the ion beam traverses the circumference of a circle whose sector angle is 60° to 90°.

  $\Rightarrow$ referred to as magnetic-sector instruments



Orientation of the magnetic force B upon a moving ion



Schematic diagram of a single-focusing mass spectrometer

Mass Analyser

Forces that affect an ion of mass m and charge z as it passes through a magnetic field of strength B:

Centrifugal force, F:

$$F = \frac{m v^2}{r}$$

v = velocity
r = radius of the circle
m = mass of the ion

The counterbalancing force is achieved by applying a magnetic field:

$$F = Bz v$$

v = velocity
B = magnetic field strength
z = charge

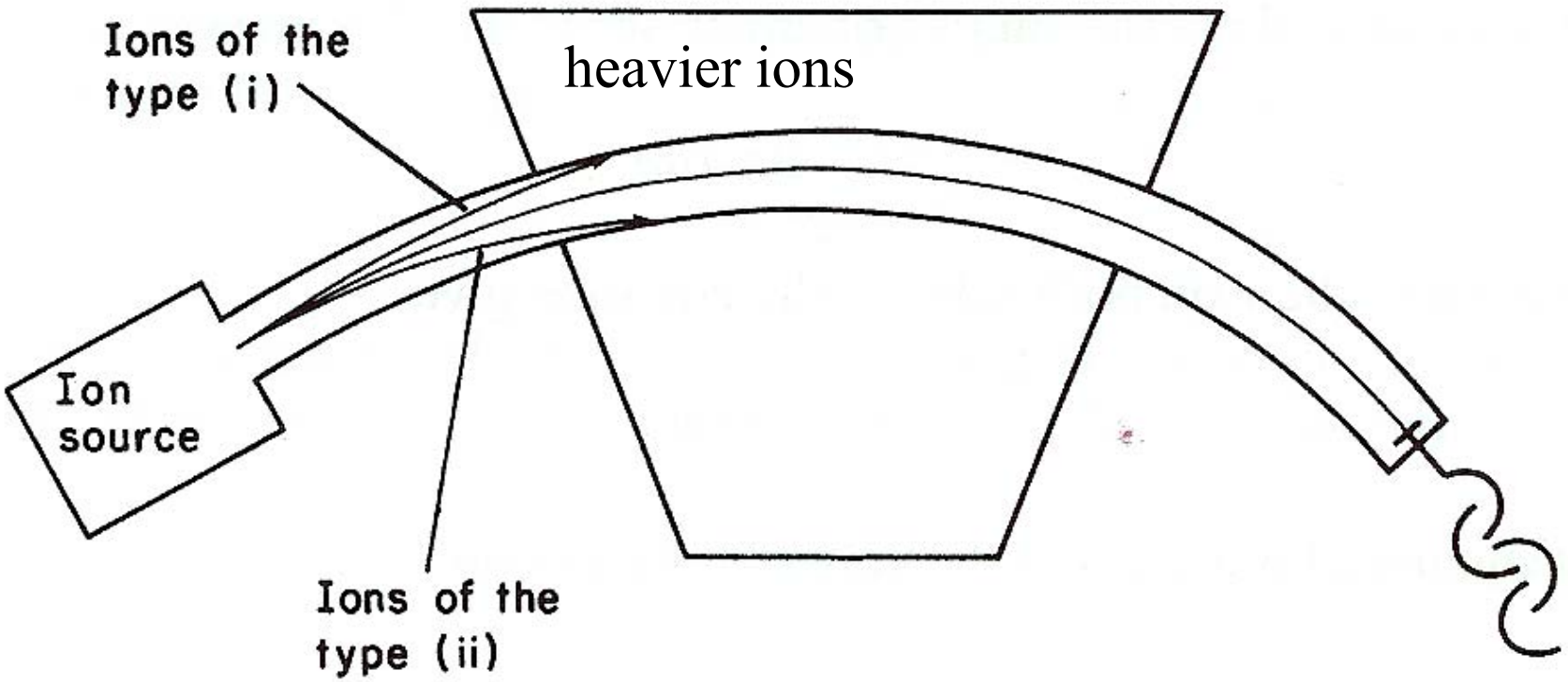
The forces are equal and in opposite directions:

$$Bz\nu = \frac{m\nu^2}{r} \qquad \frac{1}{2}m\nu^2 = zV$$

by eliminating v and making m/z the subject we gain

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

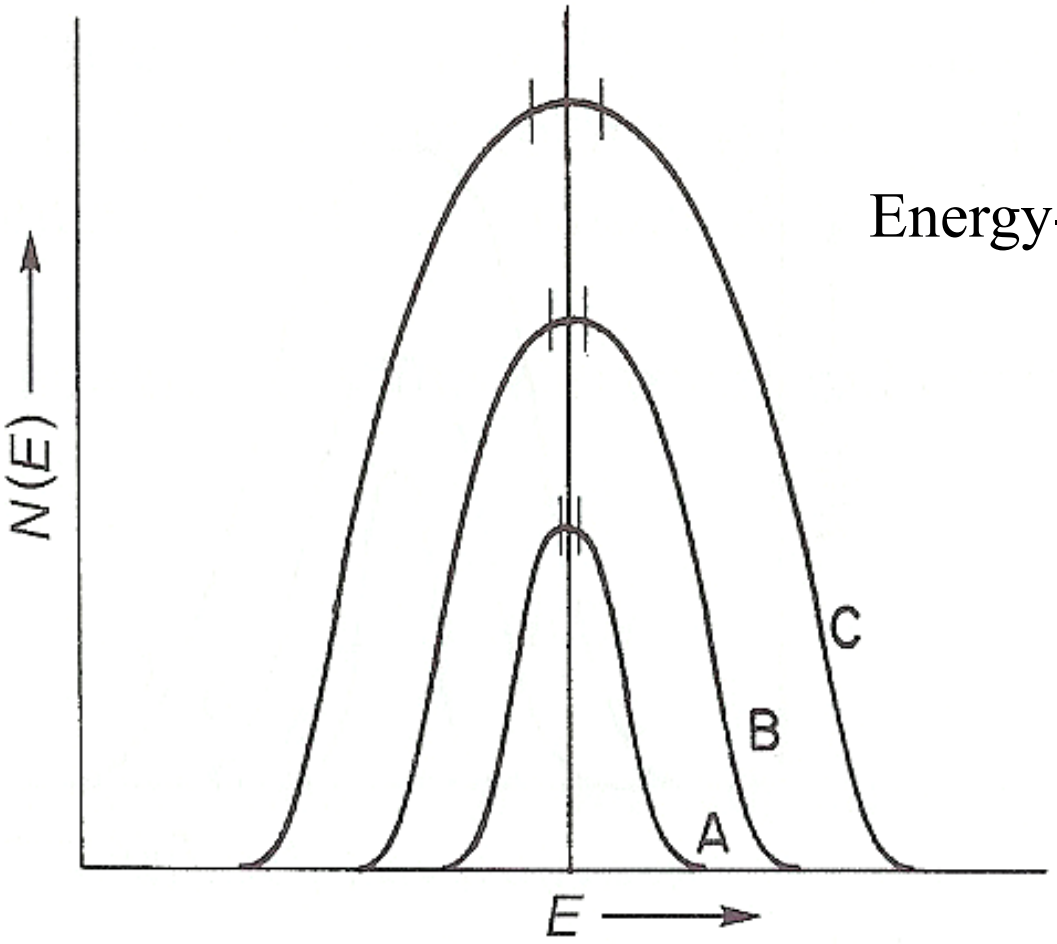
- vary V and keep B constant ⇒ voltage scanning spectrometer
- vary B and keep V constant ⇒ magnetic scanning spectrometer



- vary V and keep B constant ⇒ voltage scanning spectrometer
- vary B and keep V constant ⇒ magnetic scanning spectrometer

Flight path of ions in a single focusing mass spectrometer

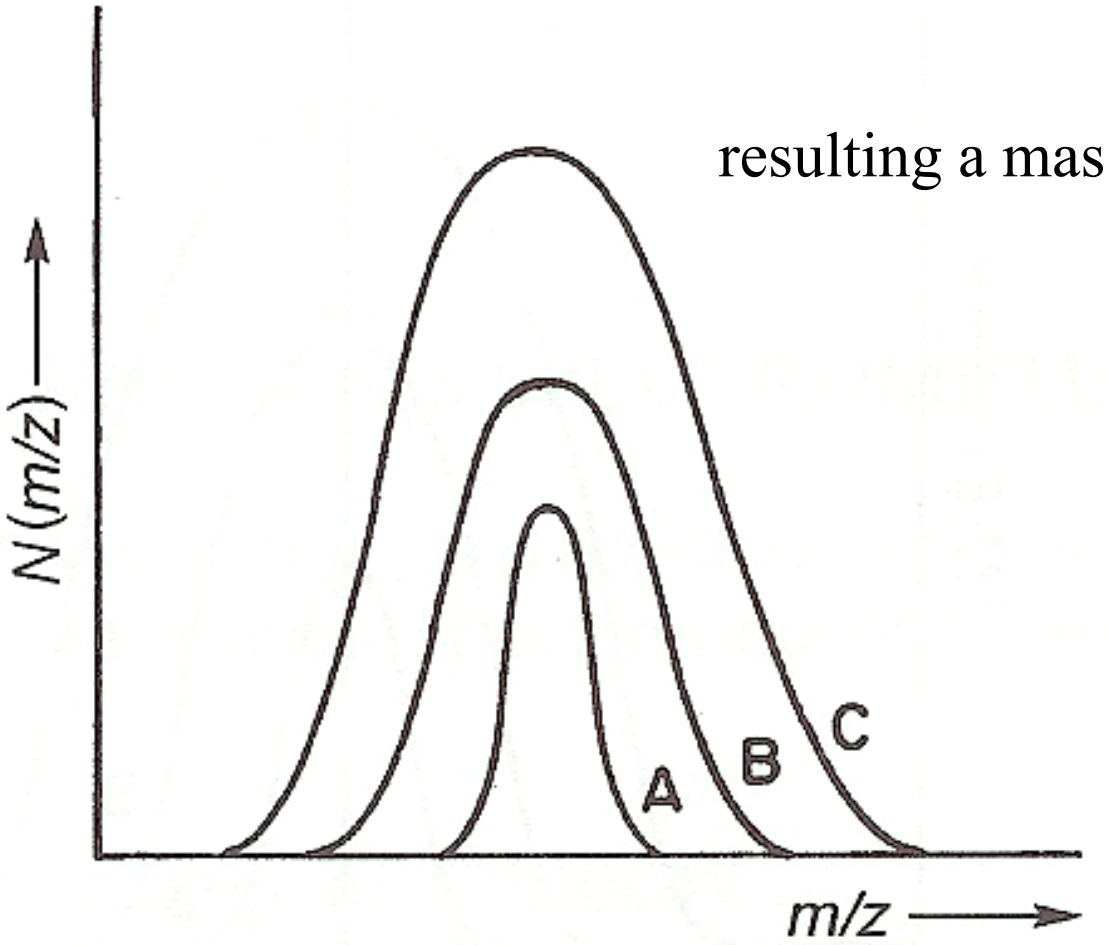
Energy-dispersion



Plots of the number of ions of energy E [N(E)] against E

Mass Analyser

resulting a mass-dispersion



Plots of the number of ions of m/z ratio [N(m/z)] against m/z

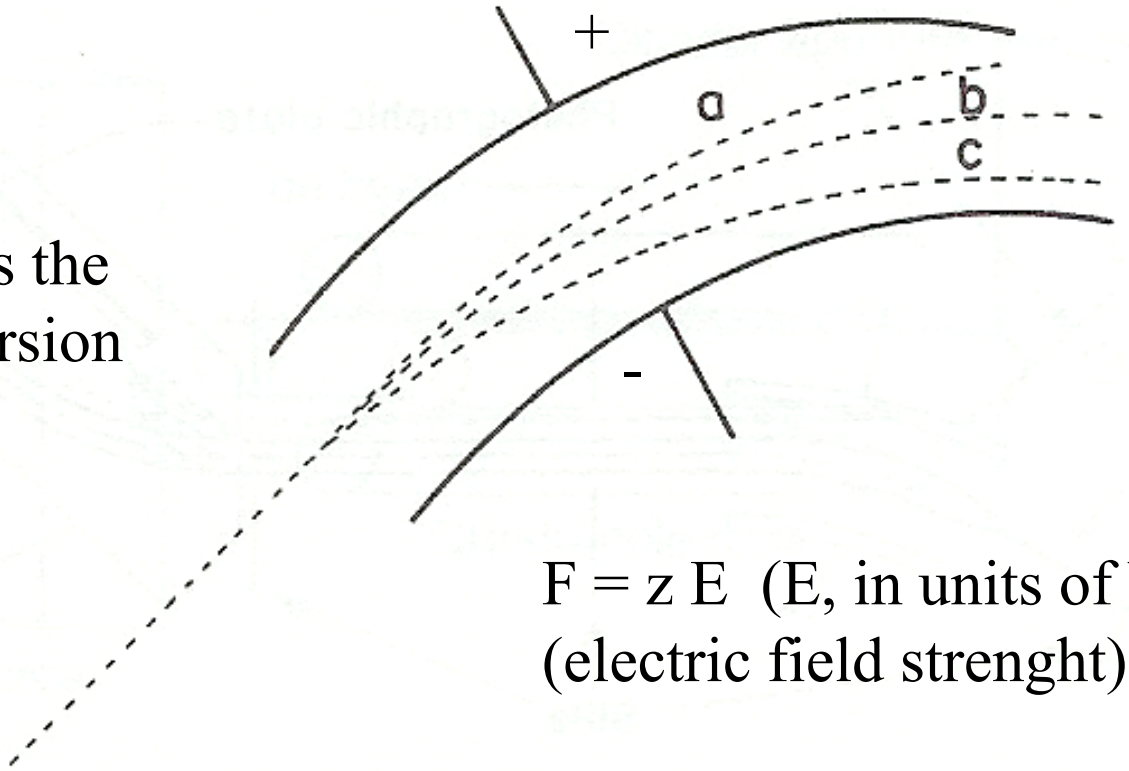
Mass Analyser

centrifugal force = mv^2/R

$zE = mv^2/R$

$R = 2V/E$

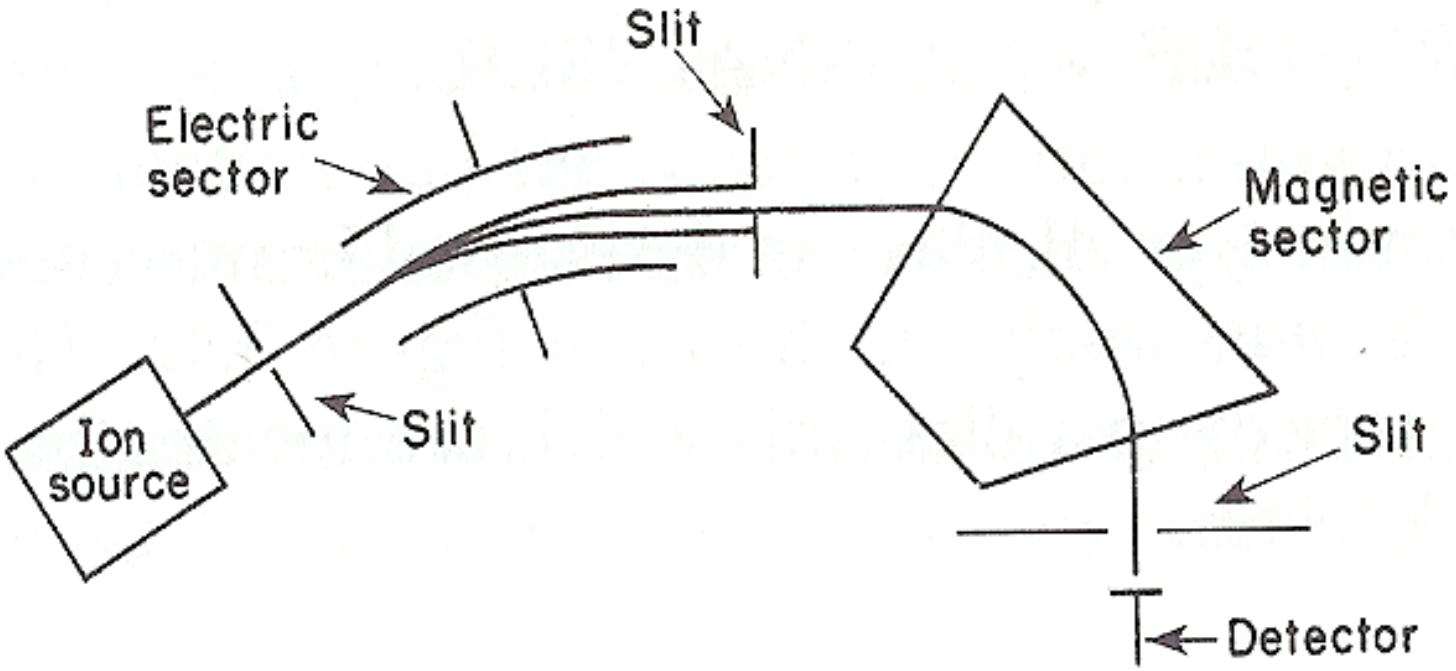
ESA: reduces the energy-dispersion



$F = z\,E$ (E, in units of Vm^{-1})
(electric field strenght)

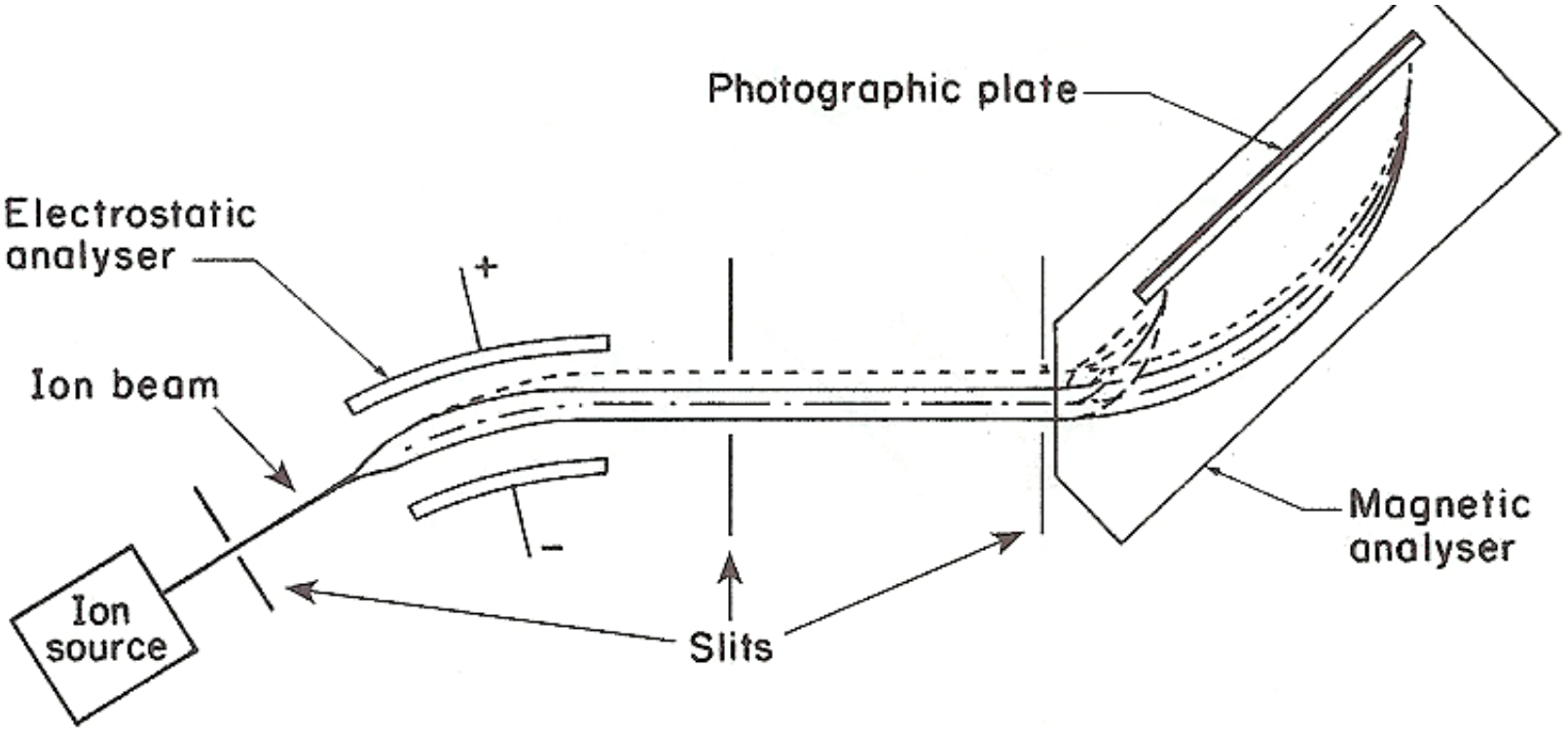
Flight paths of ions of different kinetic energies in an electrostatic analyser, ESA

Mass Analyser



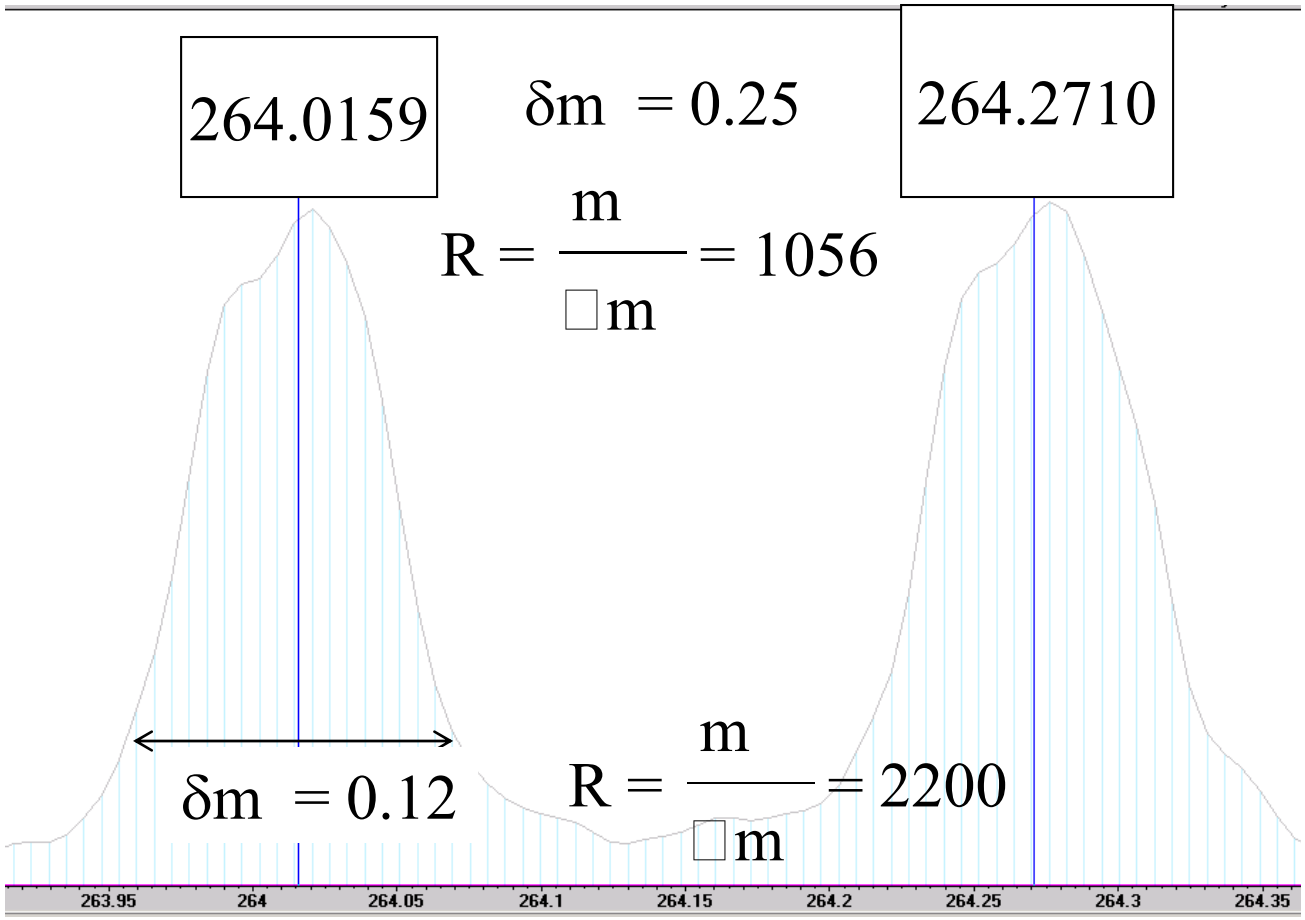
Schematic diagram of a double-focusing mass spectrometer using both electrostatic and magnetic focusing

Mass Analyser



Schematic diagram of a double-focusing mass spectrometer employing Mattauch-Herzog geometry

Mass Analyser



Resolution of two peaks with equal nominal masses

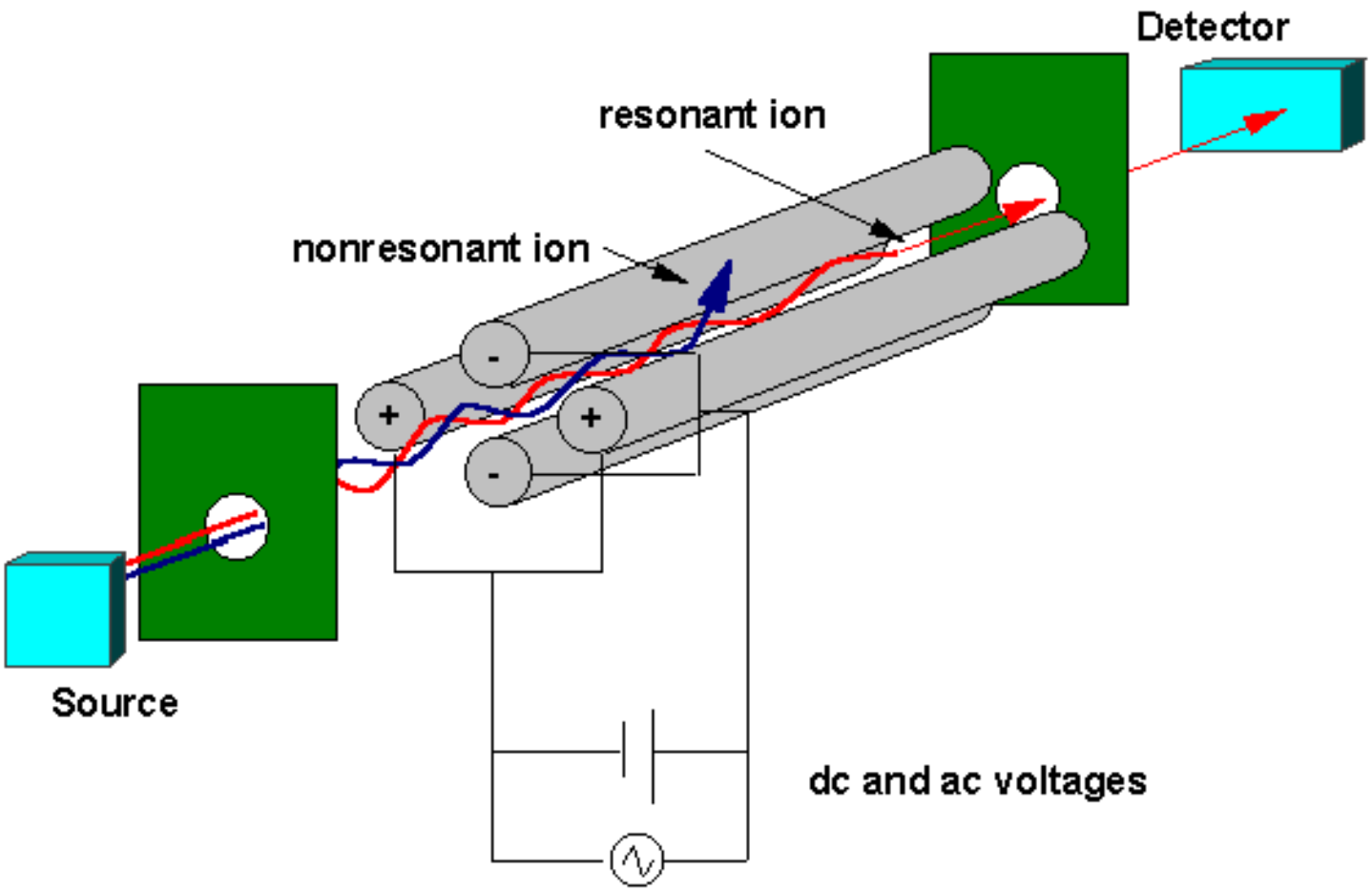
Some aspects and features of a double-focusing sector instrument:

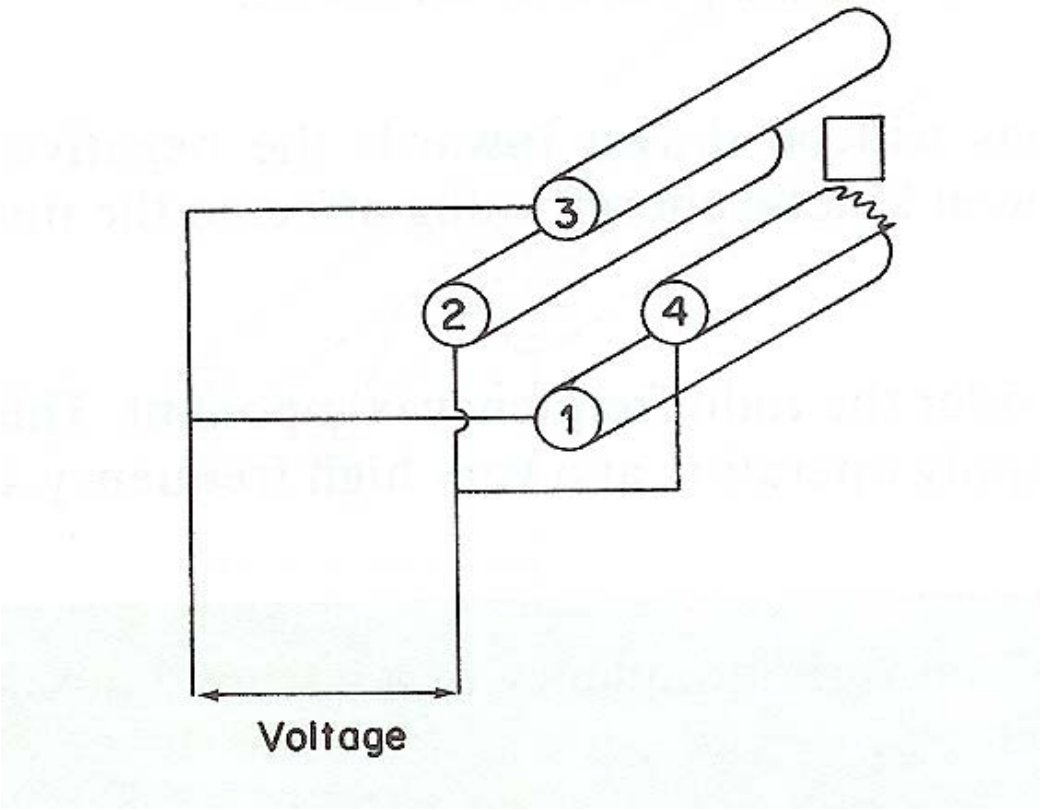
- Ions from the ion source enter the magnetic sector or ESA from a slit rather than a point. This affects resolution, which in principle can be increased by narrowing the slits (source or detector side). Obviously, narrowing the slit has an adverse effect on the transmission.

- A double-focusing sector instrument allows collision-activated ion dissociation (CID) for tandem mass spectrometry (MS-MS) in the field free regions. Special linked scanning procedures of the instrument, such B/E linked scans, allow the acquisition of product-ion mass spectra.

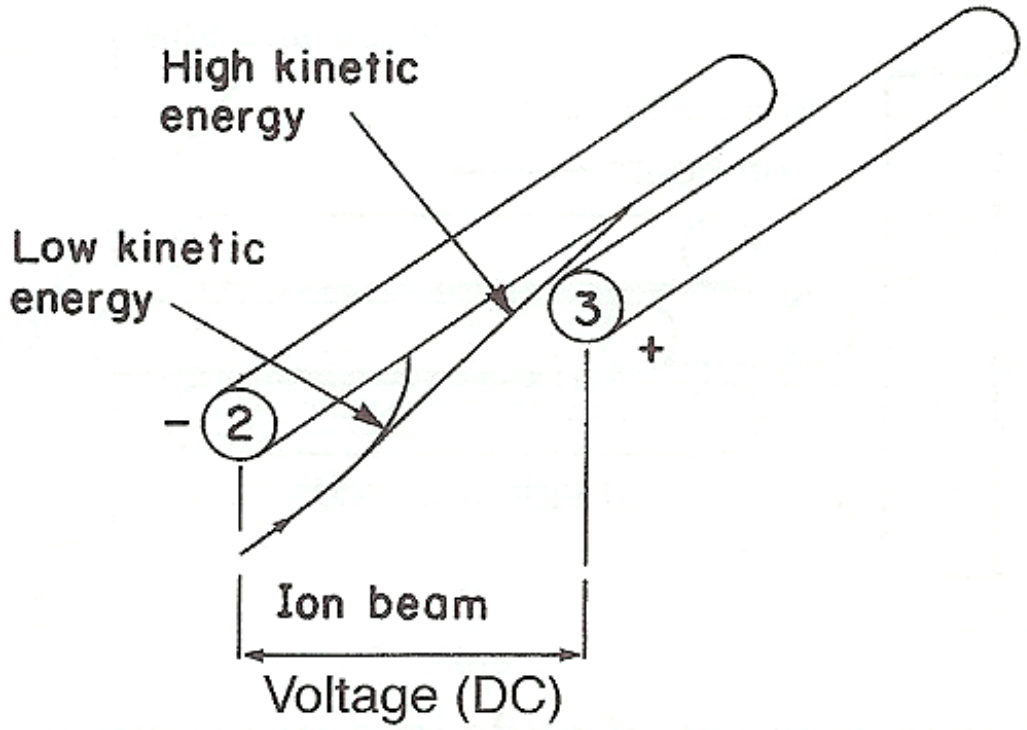
- A double-focusing sector instrument allows high-resolution measurements, enabling
  (1) determination of accurate m/z of ions (at 1 ppm or better) and
  (2) improvement of selectivity in the analysis of compounds in complex matrices.

Quadrupole-Instruments



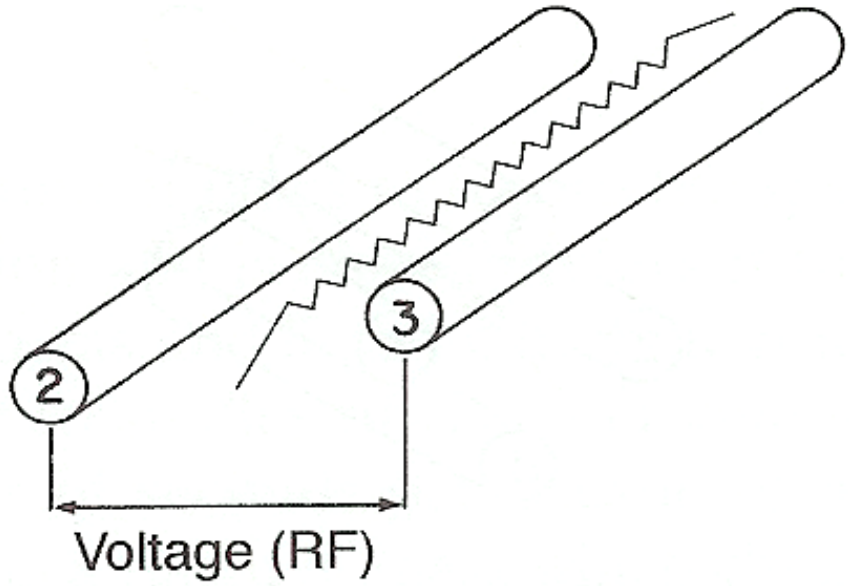


Electrical connections between the rods of a quadrupole mass analyser

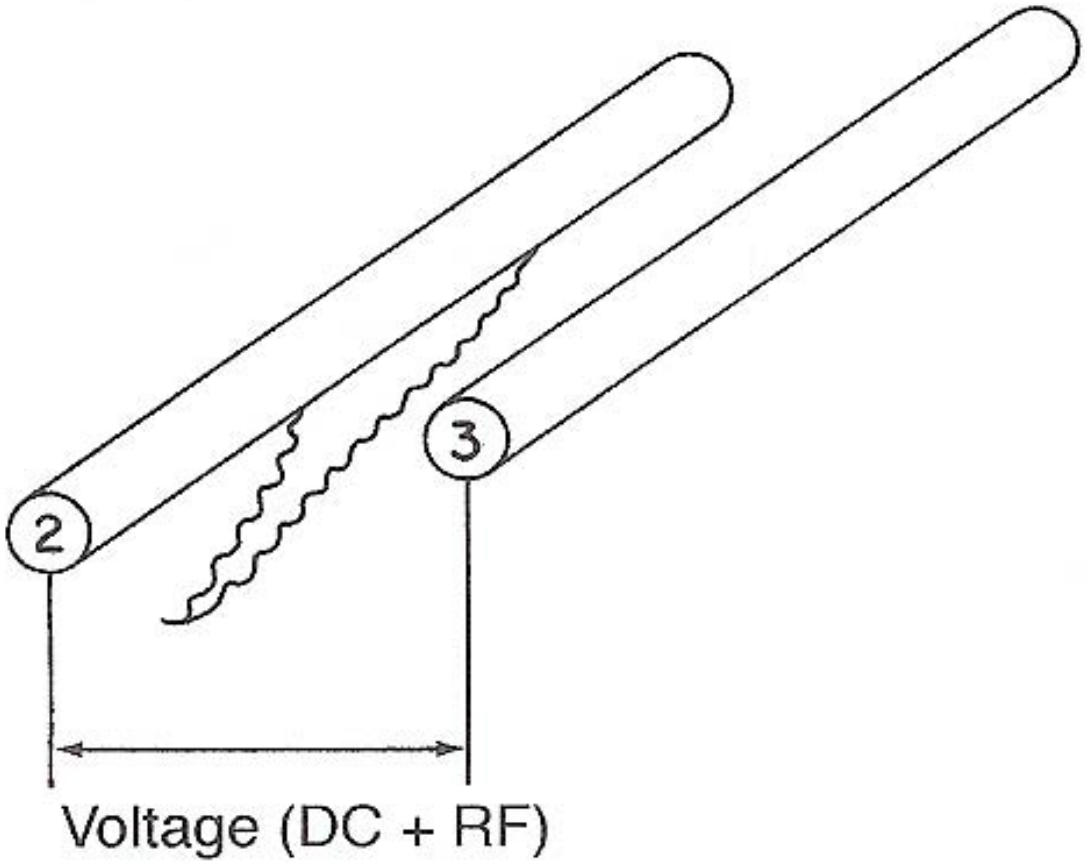


Deflection of positive ions between two rods set at a fixed potential difference

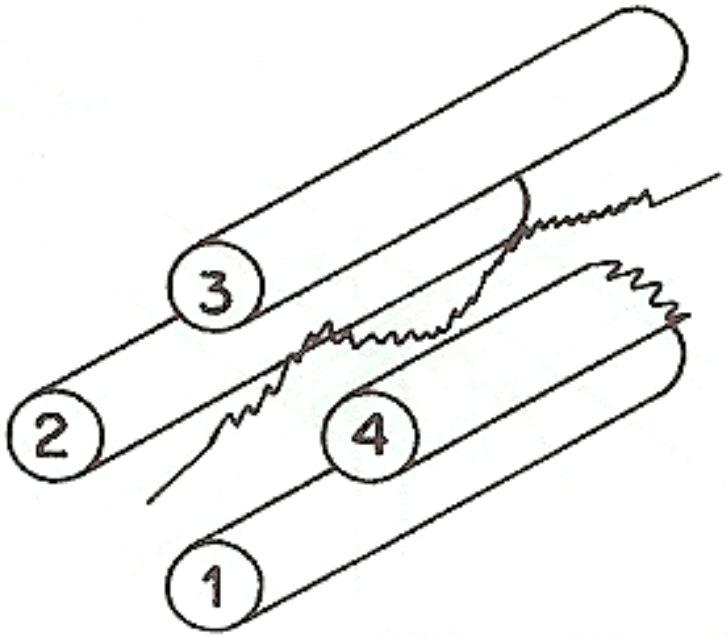
Mass Analyser



Deflection of ions between two rods at an RF potential difference

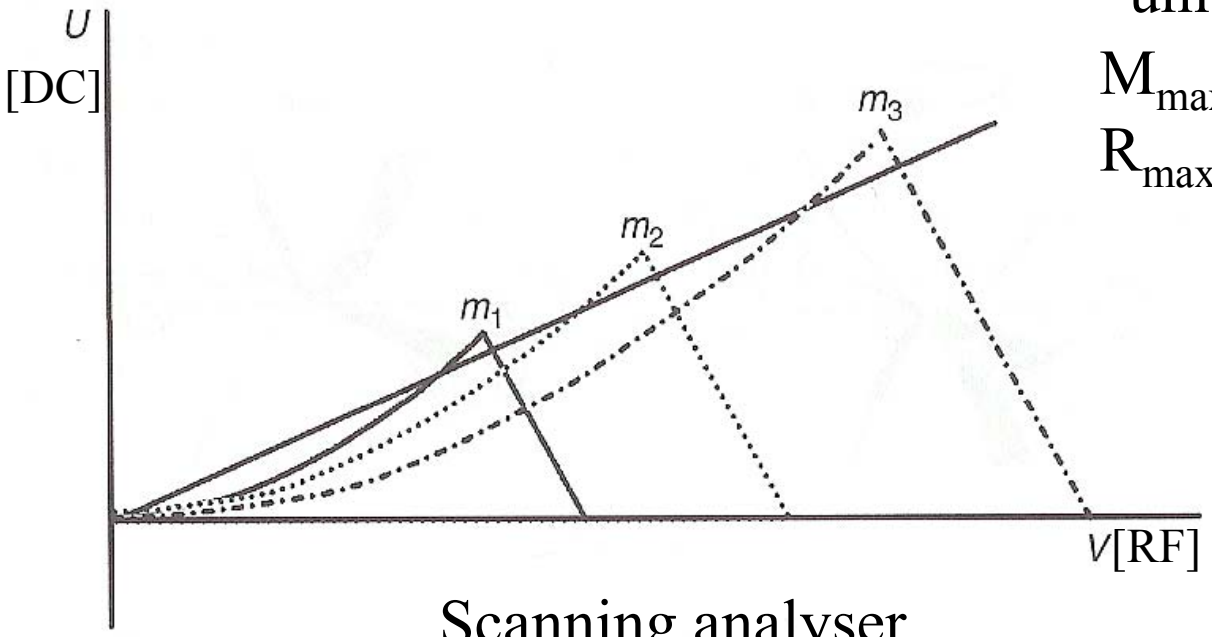


Deflection of ions between two rods at a variable (DC + RF) potential difference



Deflection of positive ions in a quadrupole mass analyser

Mass Analyser



"unit resolution"

M_{max} = 4000 amu

R_{max} = 4000

Scanning analyser

Stability areas as a function of U and V for ions with different masses ($m_1 < m_2 < m_3$)

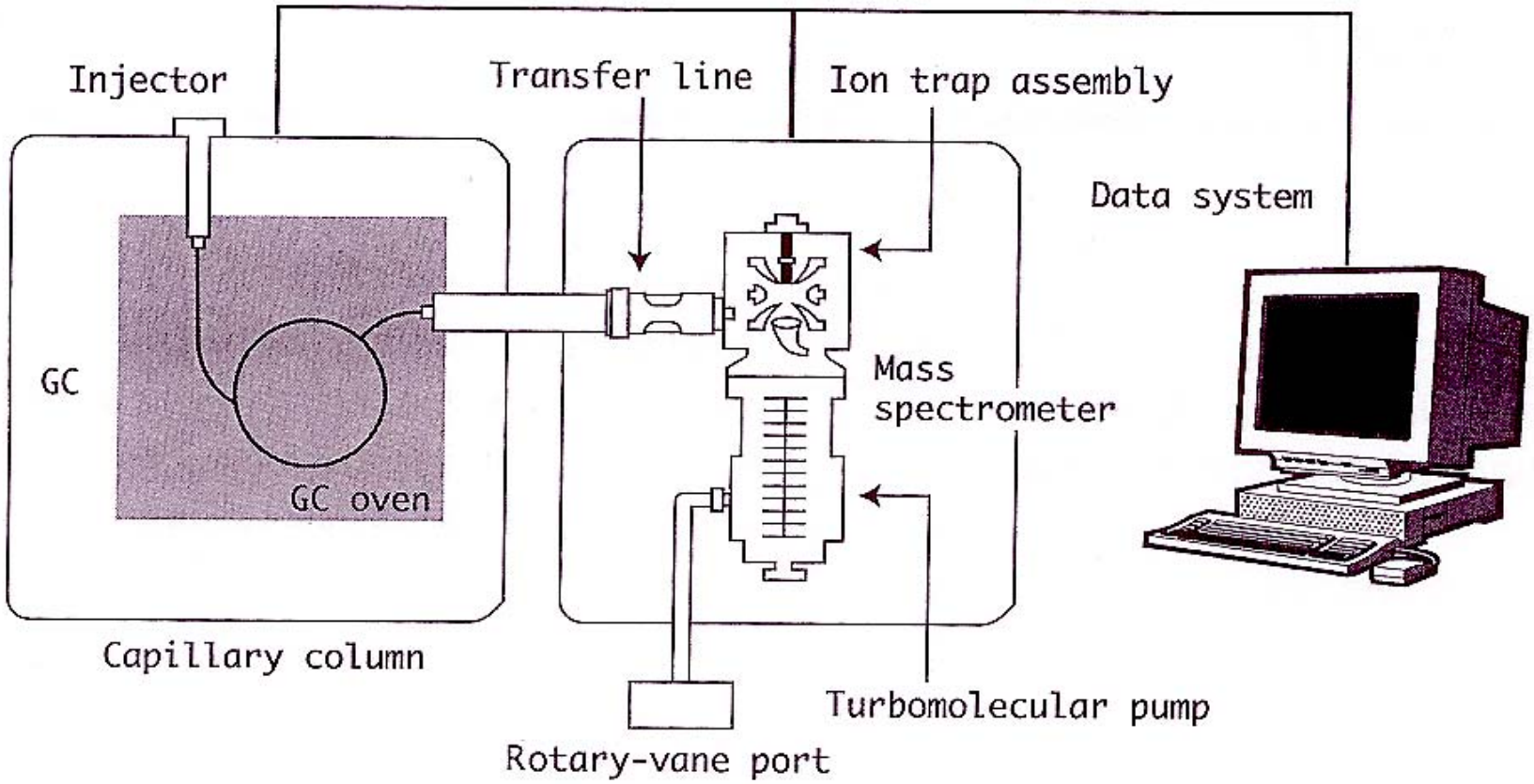


Figure 12.1 Ion trap GC/MS system.

Mass Analyser

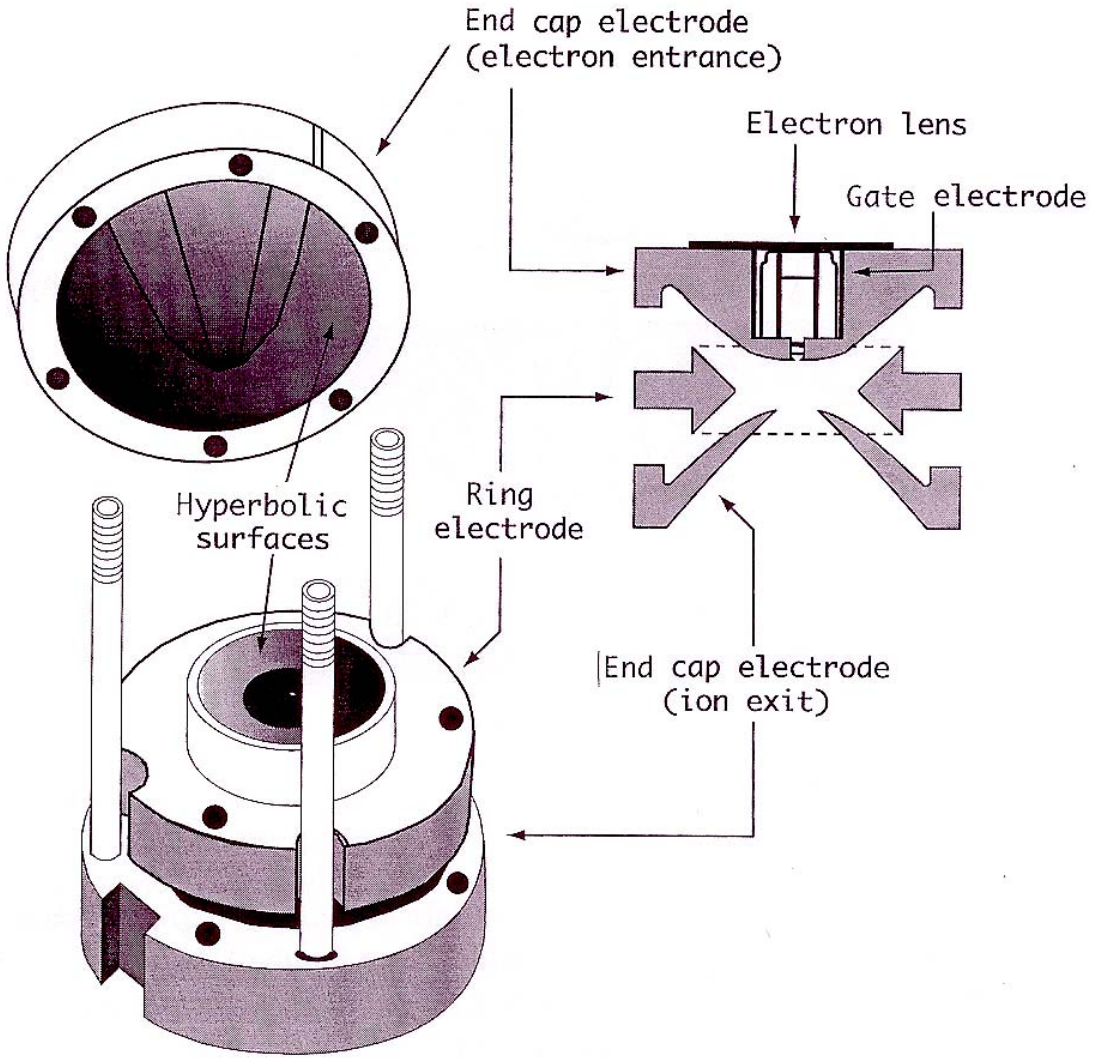
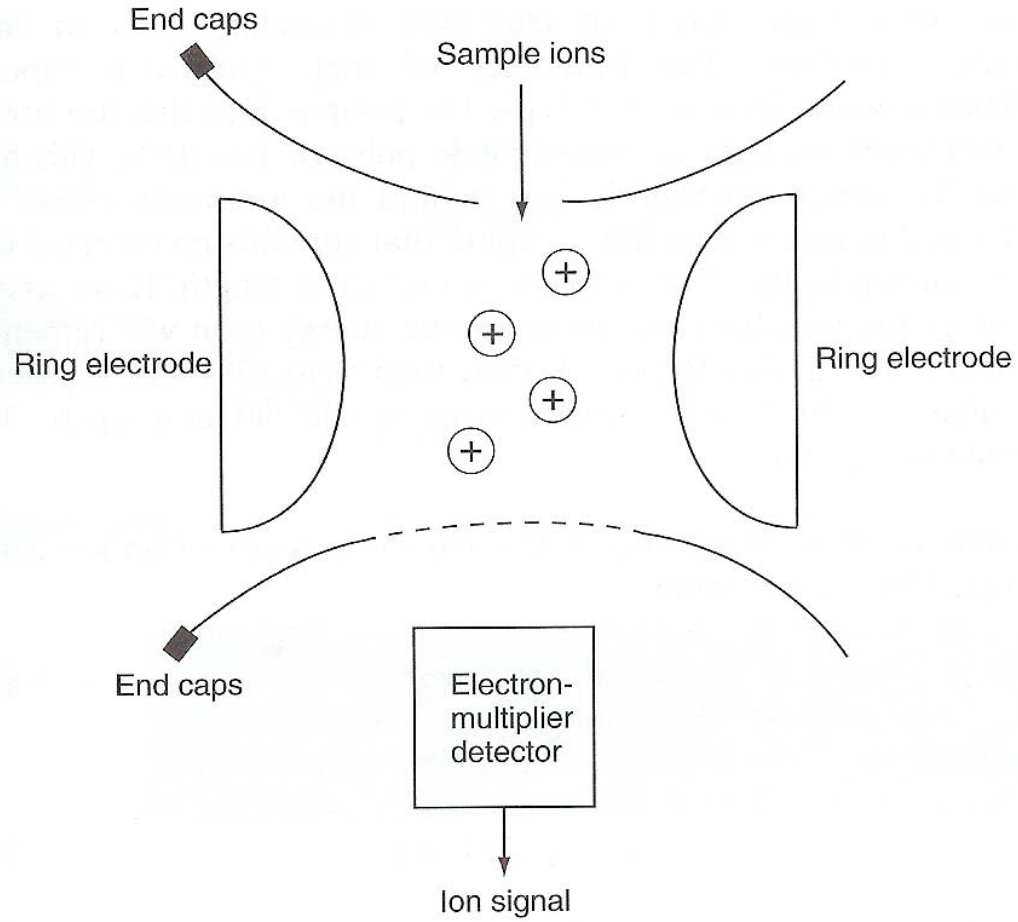


Figure 12.2 Ion trap electrode configuration.

Mass Analyser



Schematic diagram of an ion-trap mass analyser

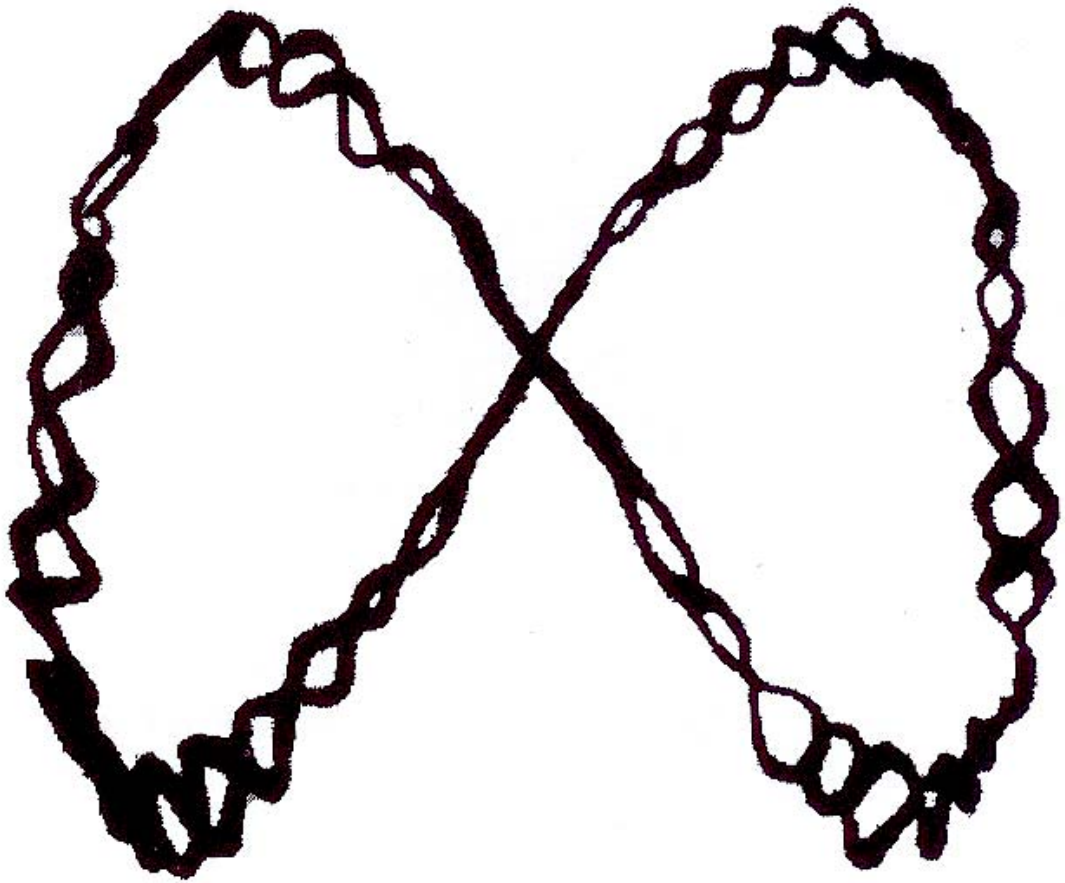
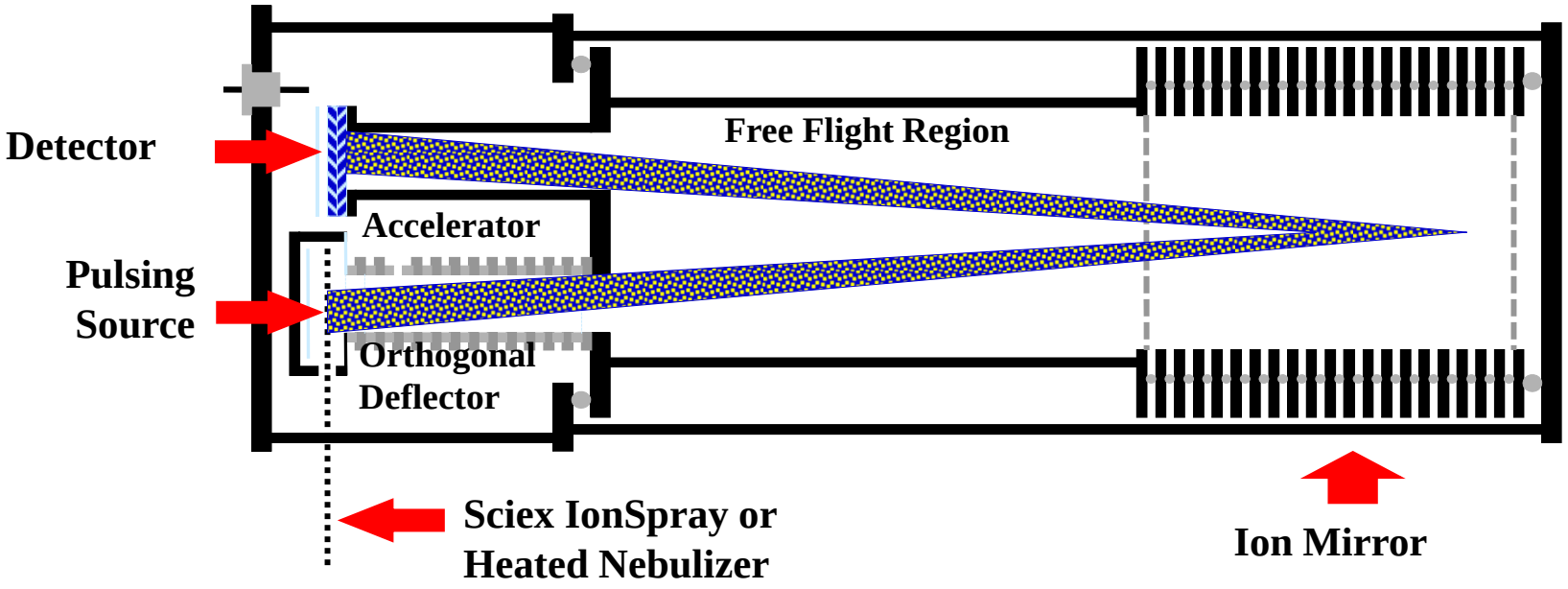


Figure 12.4 Ion trajectory schematic.

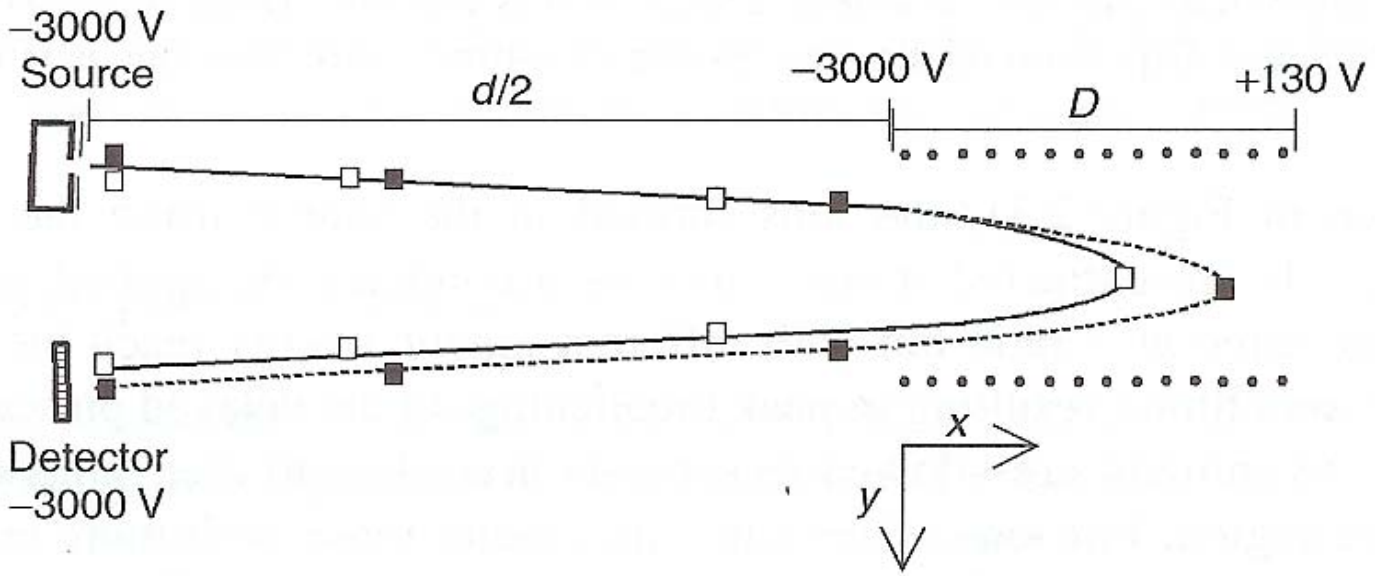
Mass Analyser

Principle of TOF-MS



- continous extraction
- delayed pulsed extraction from a field-free region

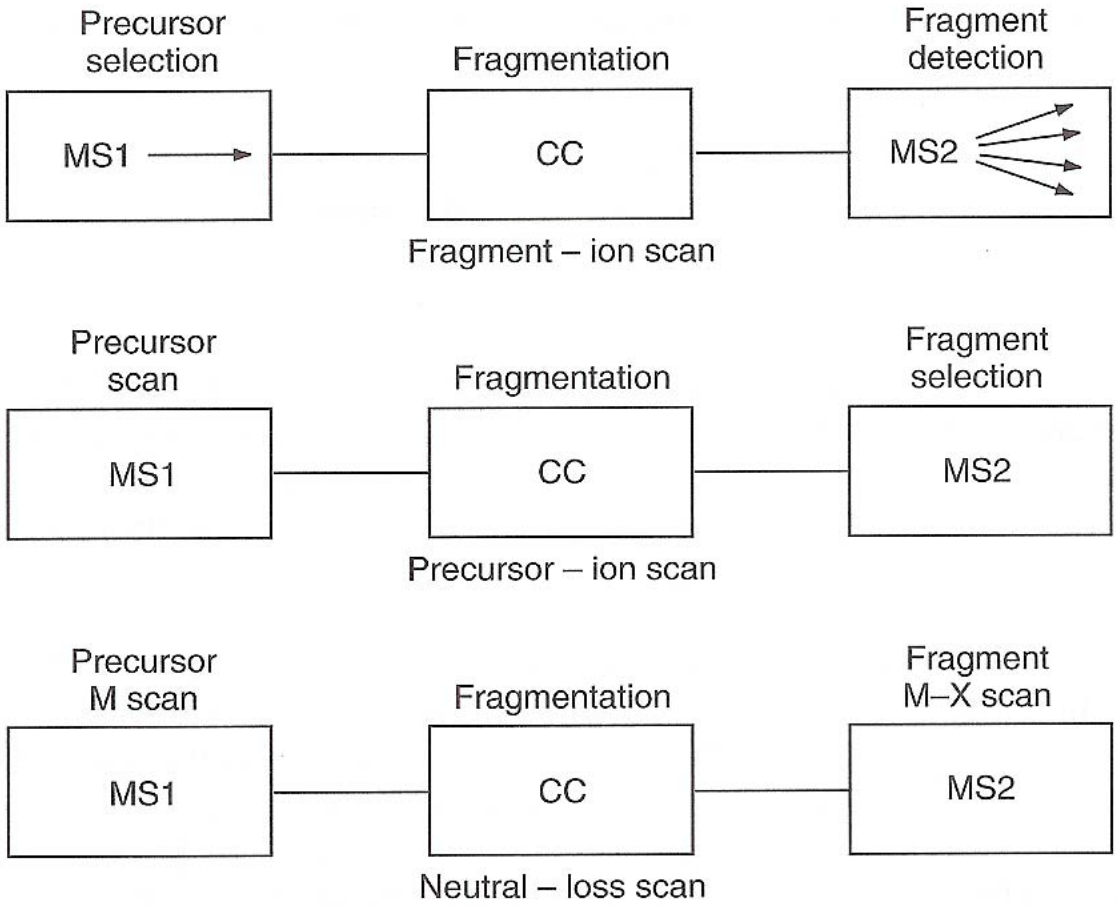
Mass Analyser



■ ions of given mass with a correct kinetic energy

□ ions of the same mass with a kinetic energy that is to low

Schematic description of a TOF instrument equipped with a reflectron



Which are the daughter ions to a selected fragment ion? (Fragment-ion scan, daughter-ion scan, parent mode)

Which are the parent ions to a selected fragment ion? (precursor-scan, parent-ion scan, daughter mode)

Which are the ions (fragment or molecular ion) derived by the loss of a neutral fragment?

Examples of possible scan modes for a tandem mass spectrometer

13.1. SEQUENTIAL MASS SPECTROMETRY (TRIPLE-QUADRUPOLE OR TANDEM GC/MS) 129

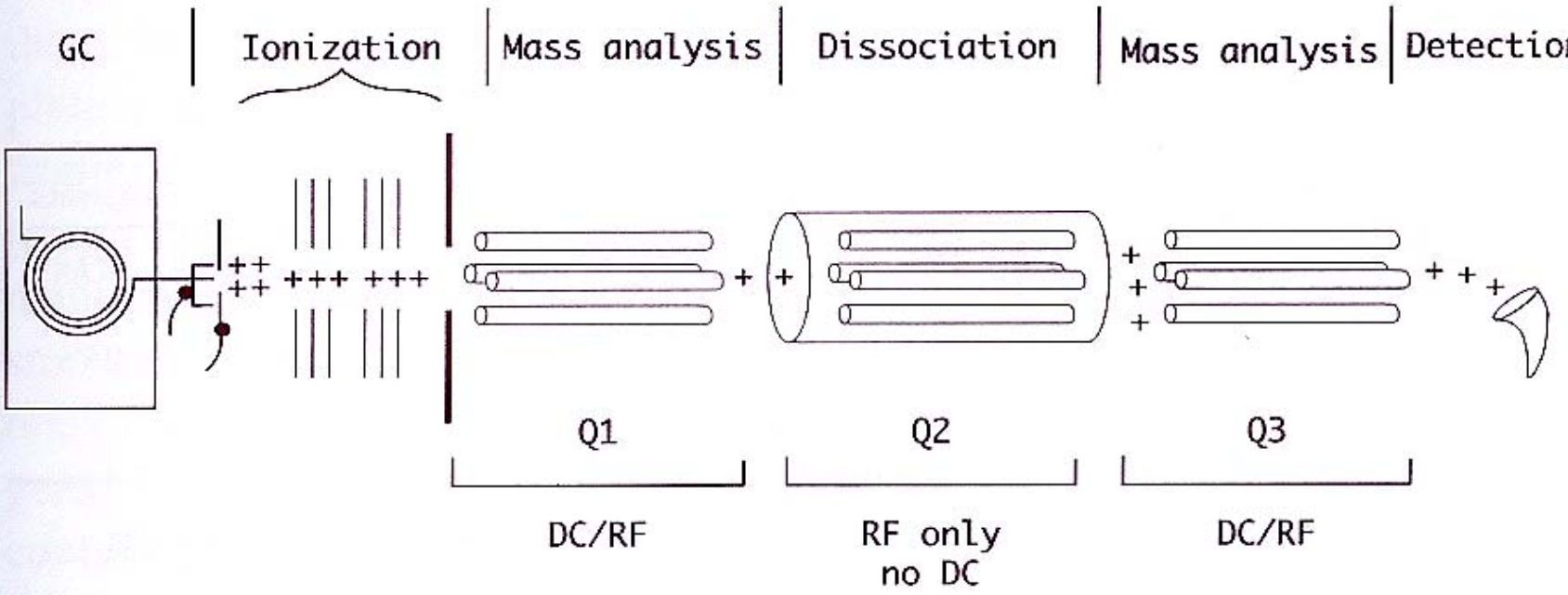


Figure 13.1 Triple-quad GC/MS system.

Mass Analyser

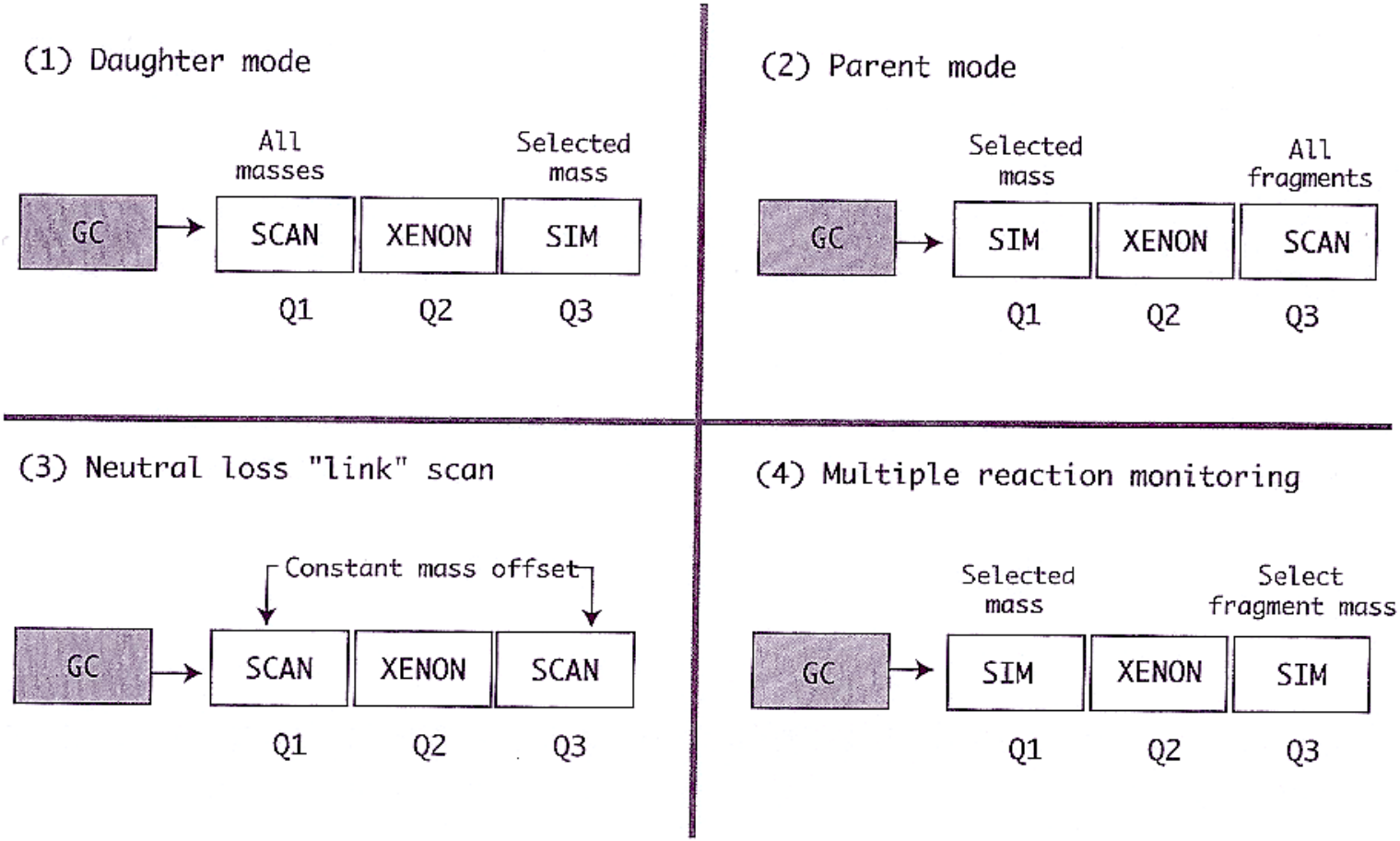


Figure 13.2 Triple-quad operational modes.

Examples of possible operation modes for a tripple-quad MS

Mass Analyser