MS INSTRUMENTATION II

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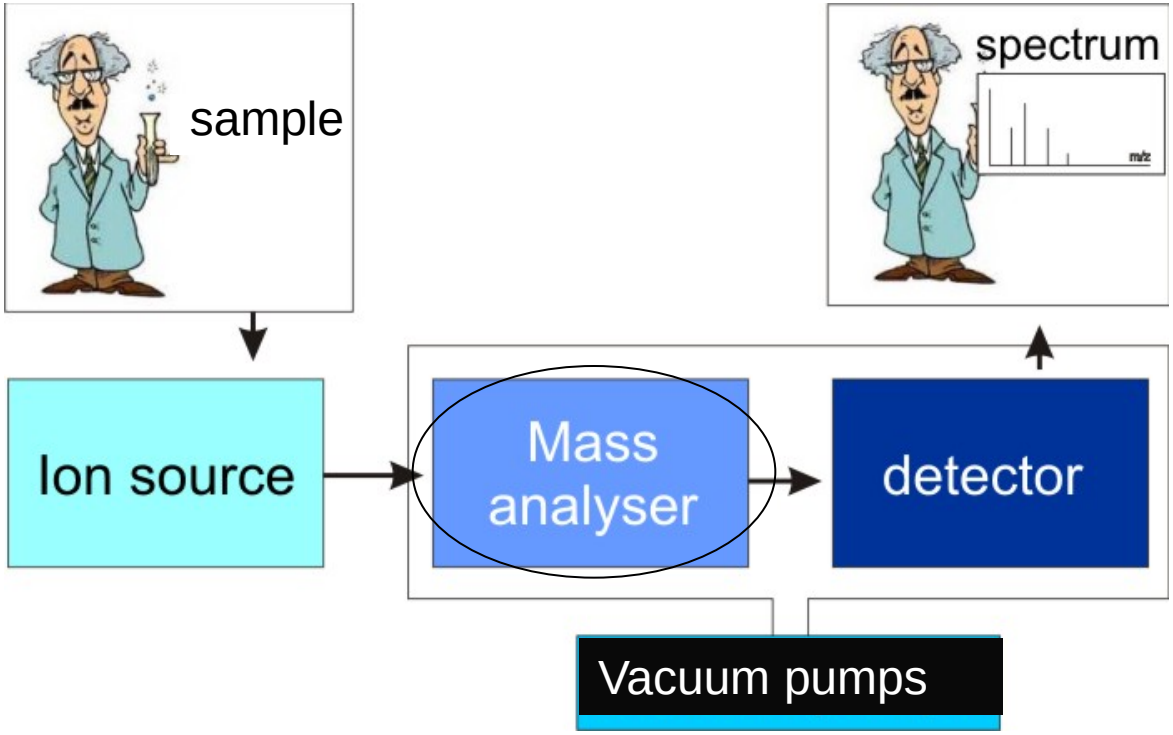
Mass analyser



- Mass analysers - separate the ions according to their mass-to-charge ratio

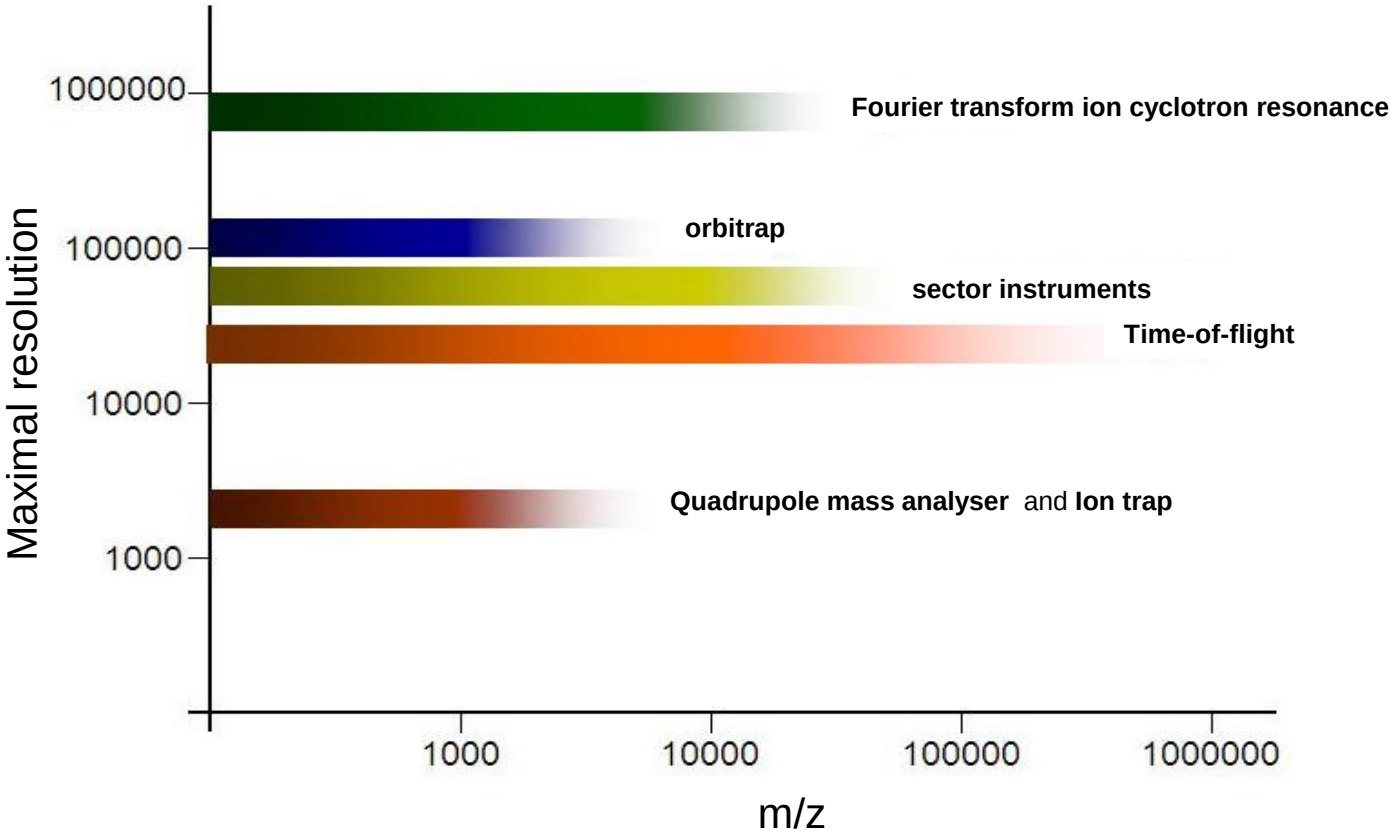
Mass analyser

Separate the ions according to their mass-to-charge ratio in space or time

- Magnetic Sector (MAG)
- Electrostatic Sector (ESA)
- **Time-of-flight** (TOF)
- **Quadrupole mass analyser** (Q)
- **Ion trap (IT)**
  - **Three-dimensional quadrupole ion trap (3D)** (QIT)
  - **Linear ion trap (2D)** (LIT)
- **Fourier transform analzyers**
  - **Fourier transform ion cyclotron resonance** (FT-ICR-MS)
  - **Orbitrap (FT-Orbi)**

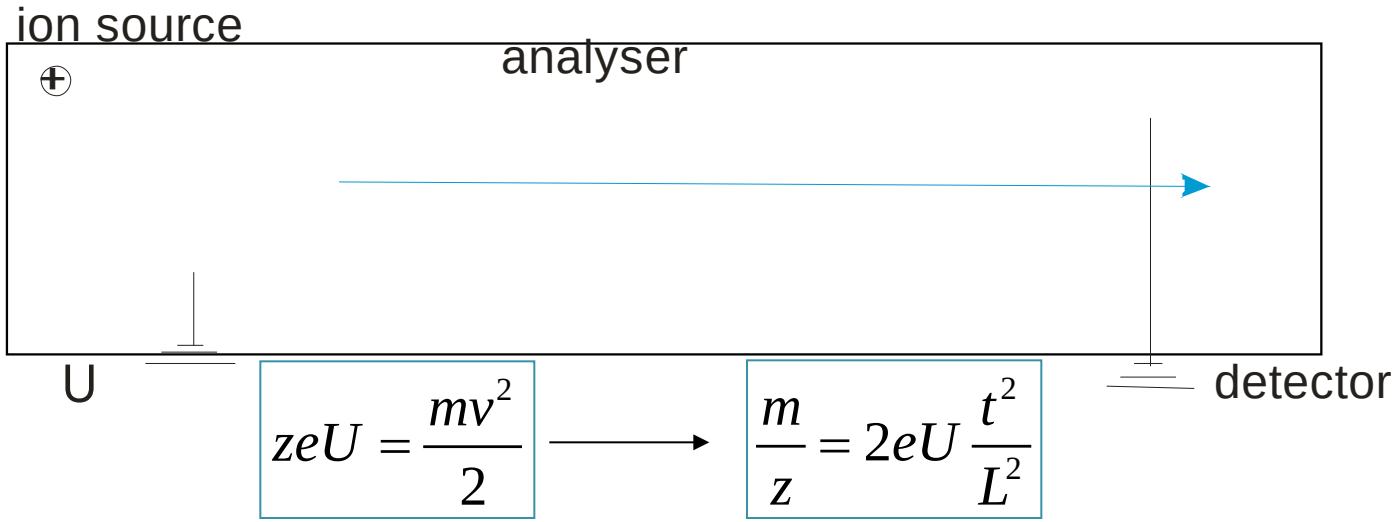
- Tandem mass spectrometry (MS/MS or MS^n)
  - fragmentation of analyte

Mass analysers



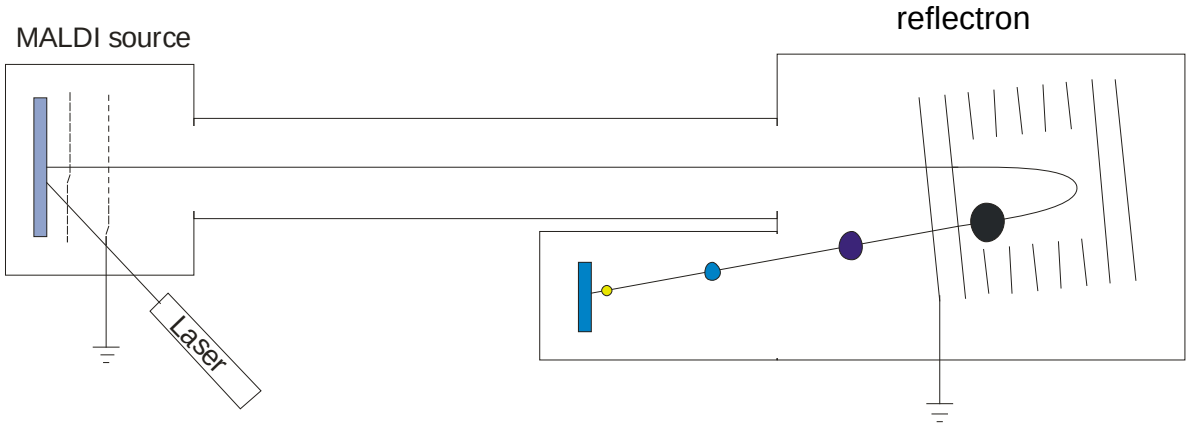
- **Ion mobility –** separate and identify ionized molecules in the gas phase based on their mobility in a carrier buffer gas
  - Based on an ion's **mass, charge, size** and **shape (Jana Dytrtová)**

TIME-OF-FLIGHT (TOF)

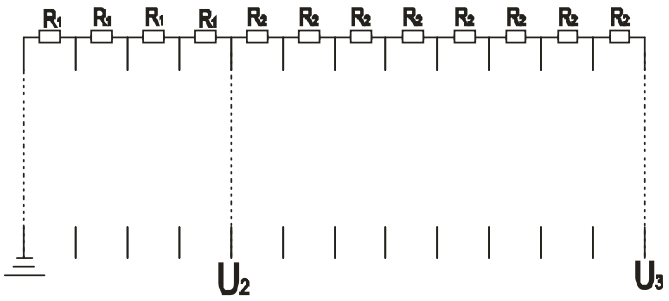


- Ions are accelerated by an electrostatic field - travel over a drift path to the detector
  - Measuring the flight time for each ion allows the determination of its mass
- Resolution depends on the length of the path
- Major advantages are
  - The extremely high transmission
  - The detection of all masses (all spectrum for each puls)
  - The theoretically unlimited mass range
- Suitable for MALDI (MALDI-TOF instruments)
- Can be use for accurate mass spectra

TOF WITH REFLECTRON

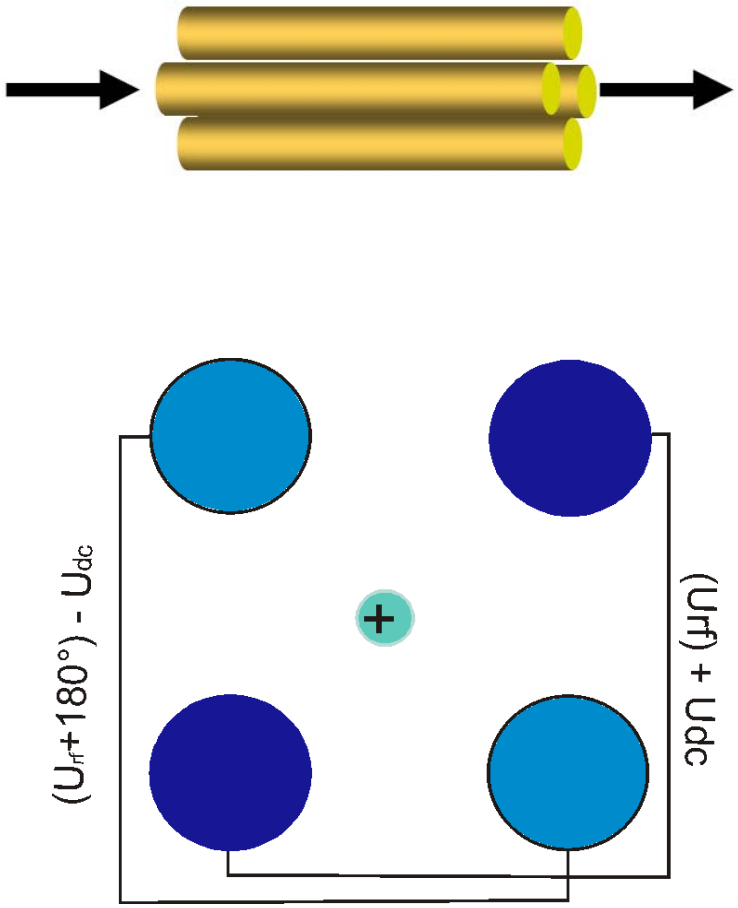


- The reflectron uses an electrostatic field to reflect the ion beam toward the detector.
  - Ring electrodes
- Advantage – better resolution
  - Longer path of ions
  - Focusing of ions in reflectron
- Disadvantage
  - Not suitable for protein – too long pass for large molecules




BRUKER
ultrafleXtreme

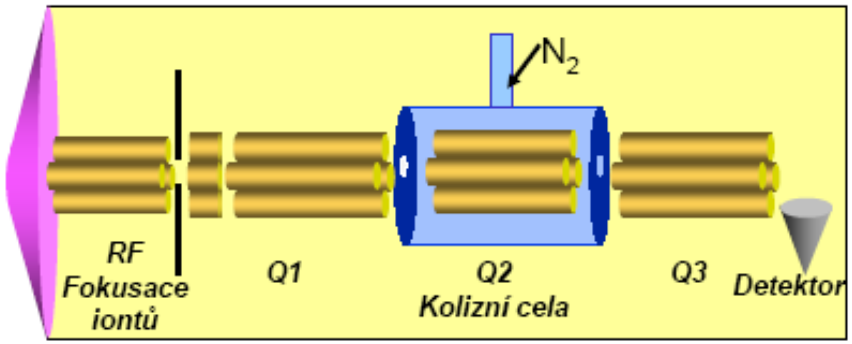
Quadrupole mass analyser (Q)

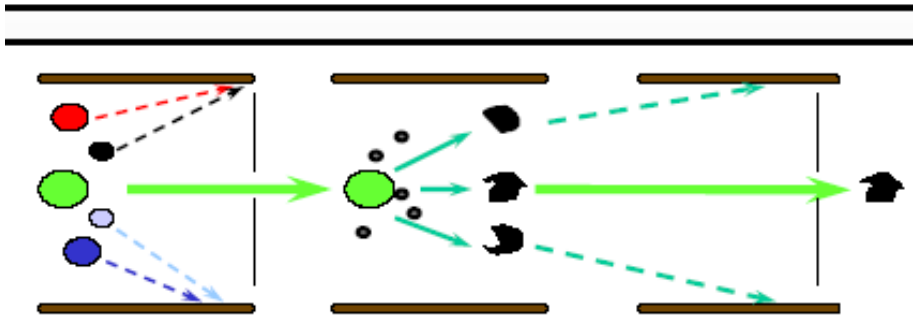


- Use oscillating electrical fields to selectively stabilize or destabilize the paths of ions passing through a radio frequency (U_{RF}) quadrupole field created between 4 parallel rods
  - Only the ions in a certain range of m/z are passed through the system at any time
- Limits m/z 2000 – 4000
- Low resolution spectra (not for accurate mass measurement)
- One Q can not be use for MS/MS

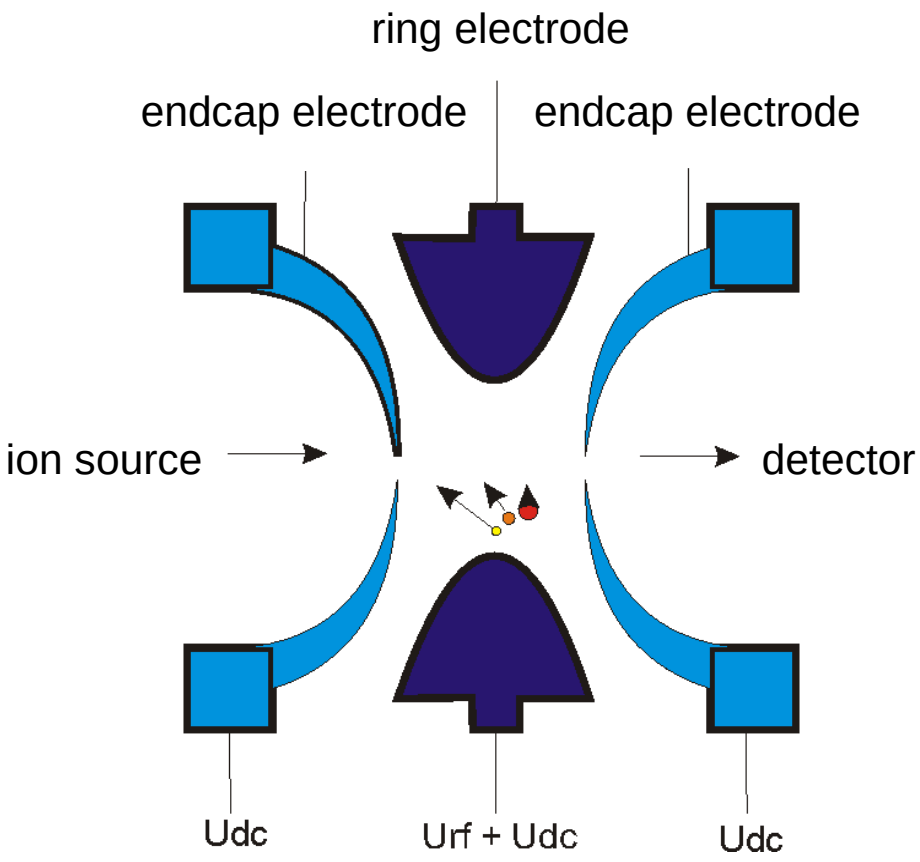
Collision-induced dissociation (CID) in collision cell

- QqQ
  - Q1 mass analyser can isolate one m/z (precursor ion)
  - **Q2 as a collision cell** - they collide with a gas - they are fragmented.
  - Q3
    - Scan all fragment – identification of compound
    - Scan one or a few ions – **quantitative analysis**





Three-dimensional quadrupole ion trap (QIT)



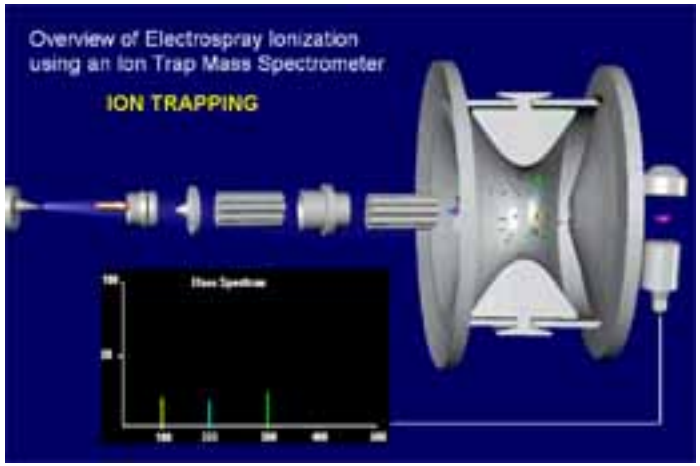
- The ions enter into the trap through the inlet and they are trapped through action of the three hyperbolic electrodes.
- The ions are in a stable oscillating trajectory
- The ions are ejected in order of increasing m/z by a gradual change in the potentials


Thermo
LCQ Fleet

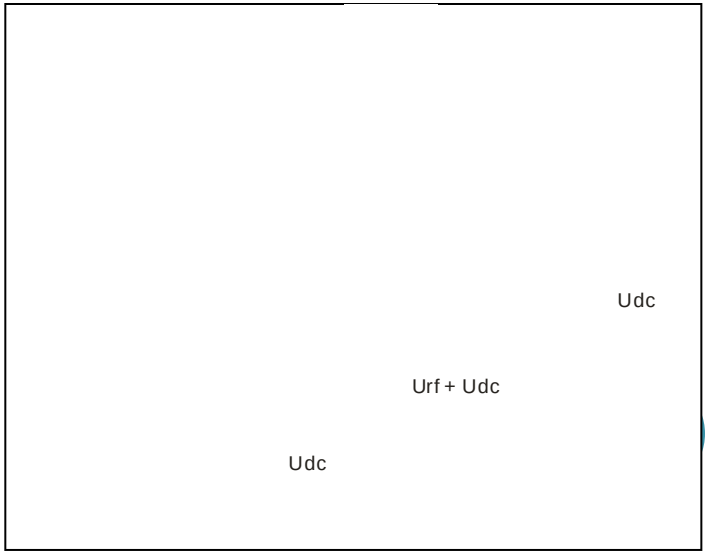
Ion trap (IT)

- Possibility MS/MS (CID) (to MS^{10}, in real life MS^3)
  - Rule 30:70 – ions at low 30% of m/z range are not stabile in ion trap – lose information
- Limits m/z 2000 – 4000
- Low resolution spectra (not for accurate mass measurement)
- Three-dimensional x lineat ion trap
  - **Linear ion trap (2D)** (LIT) better sensitivity, resolution, capacity and scanning faster

3D

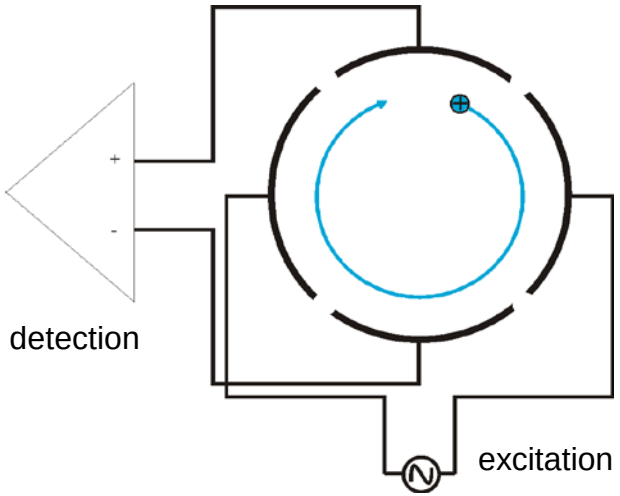


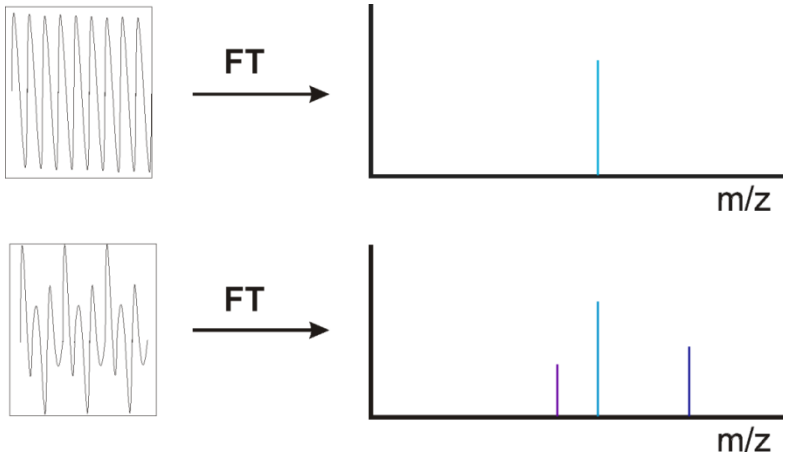
2D



Fourier transform ion cyclotron resonance (FT-ICR -MS)

- Based on the circular movement of charged particles in a strong magnetic field (cyclotron movement)
  - The cyclotron frequency depends directly on the mass-to-charge ratio of the ions





$$\omega = \frac{v}{r} = \frac{Be}{m/z}$$

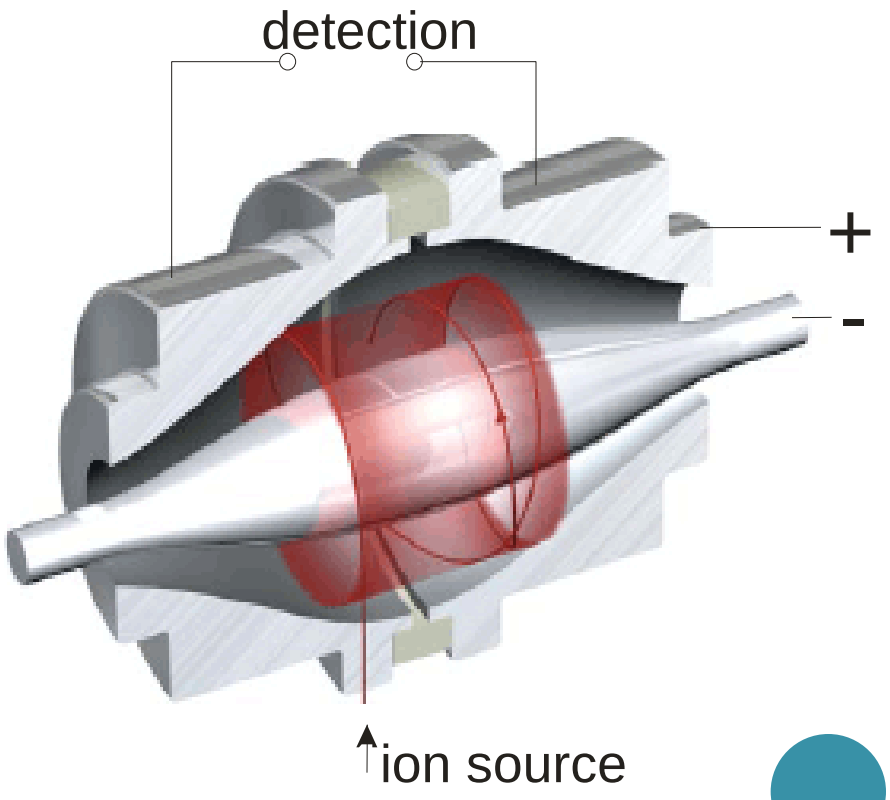
- Detector electrodes measure the electrical signal of ions which pass near them over time, producing a periodic signal

Fourier transform ion cyclotron resonance (FT-ICR-MS)

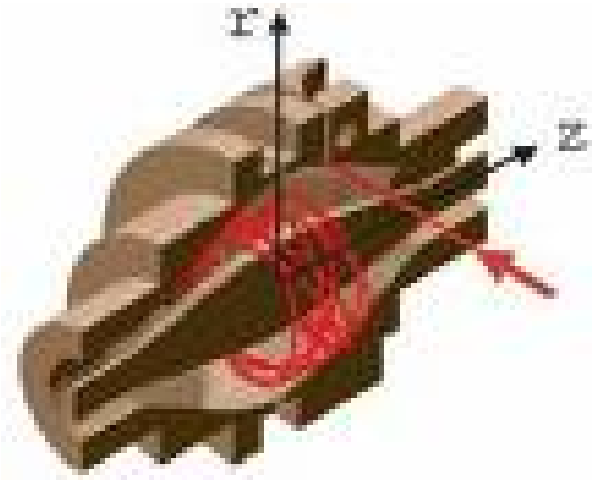
- Advantage
  - High accuracy (about 1 ppm)
  - High resolution (900 000)
  - Possible measured of MS^n
    - CID
      - Proteomic - primarily *b*- and *y*- type of fragment
    - Electron capture dissociation (ECD)- by captruing a thermal electron
      - Proteomic - primarily *c*- and *z*- type of fragments
    - Infrared multiphoton dissociation (IRMPD) - by IR laser

Orbitrap

- Similar principle to FT-ICR-MS
- The Orbitrap is an ion trap – but there are not RF or magnet fields!
- Ions in orbitrap
  - Moving around a central electrode
  - **Moving in *z* axis**
  - Detector electrodes measure the electrical signal of ions

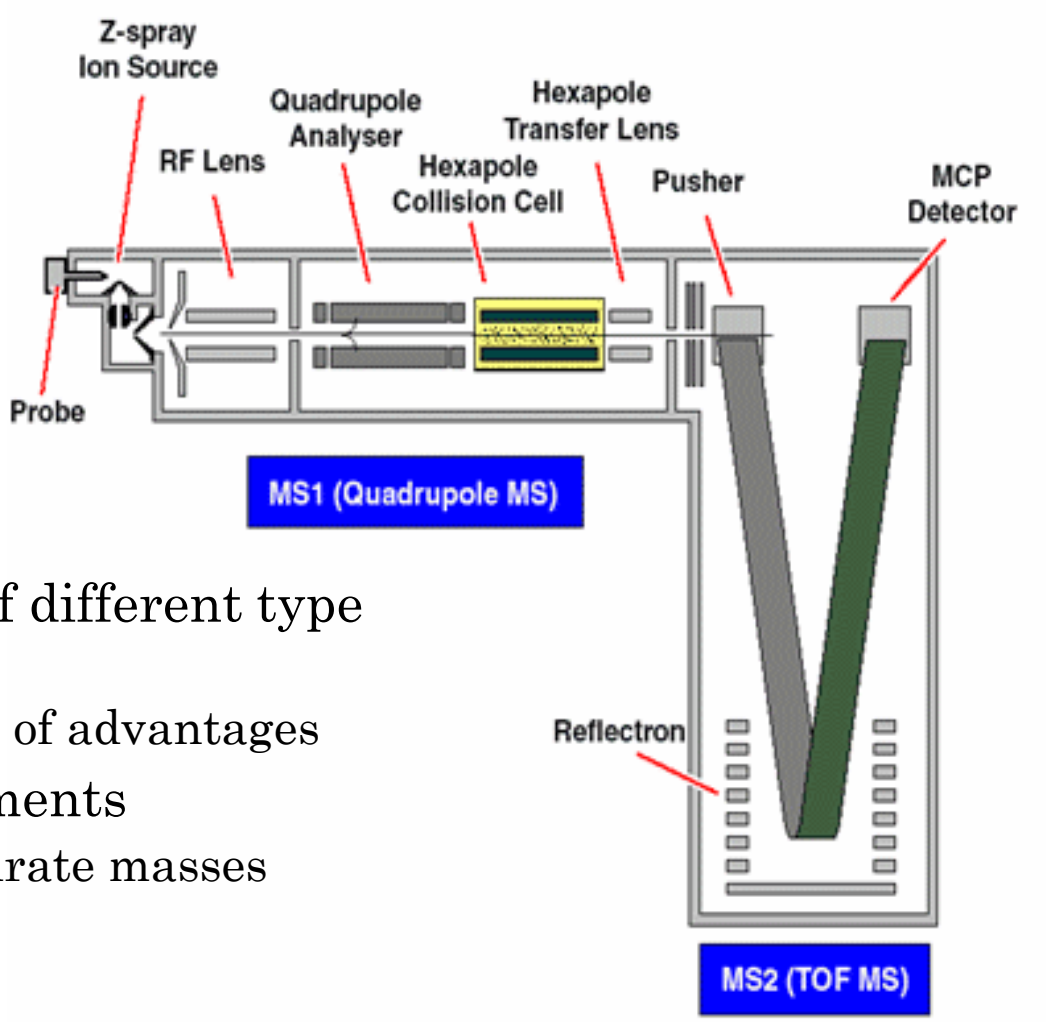


Orbitrap



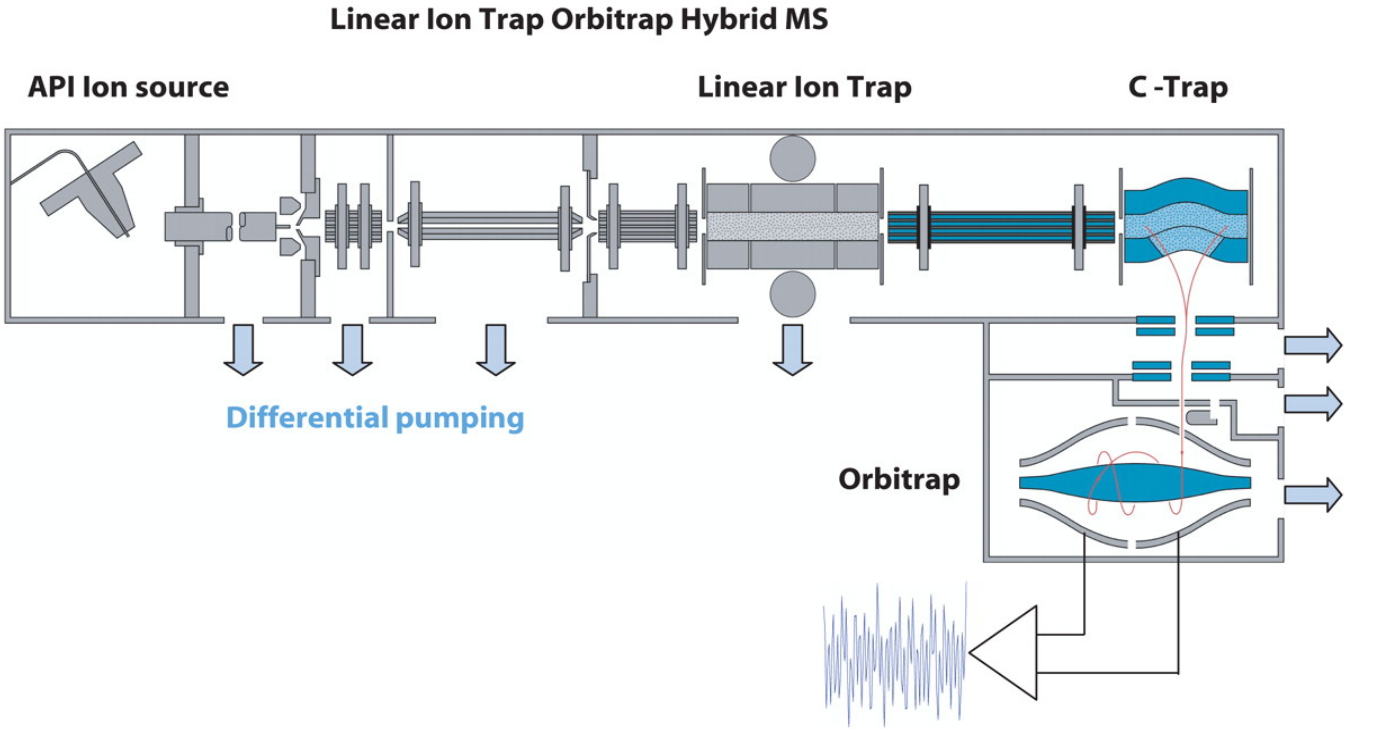
- Advantage
  - High accuracy (about 1 ppm)
  - High resolution (100 000)
    - New generation of instrument 250 000
  - Does not need magnet – the most expensive part of instrument
- Electron-transfer dissociation
    - Proteomic - c- and z-type of fragments (similar to ECD)
      - ETD does not use free electrons but employs radical anions (e.g. anthracene, azobenzene,.....)

Hybrid mass spectrometers

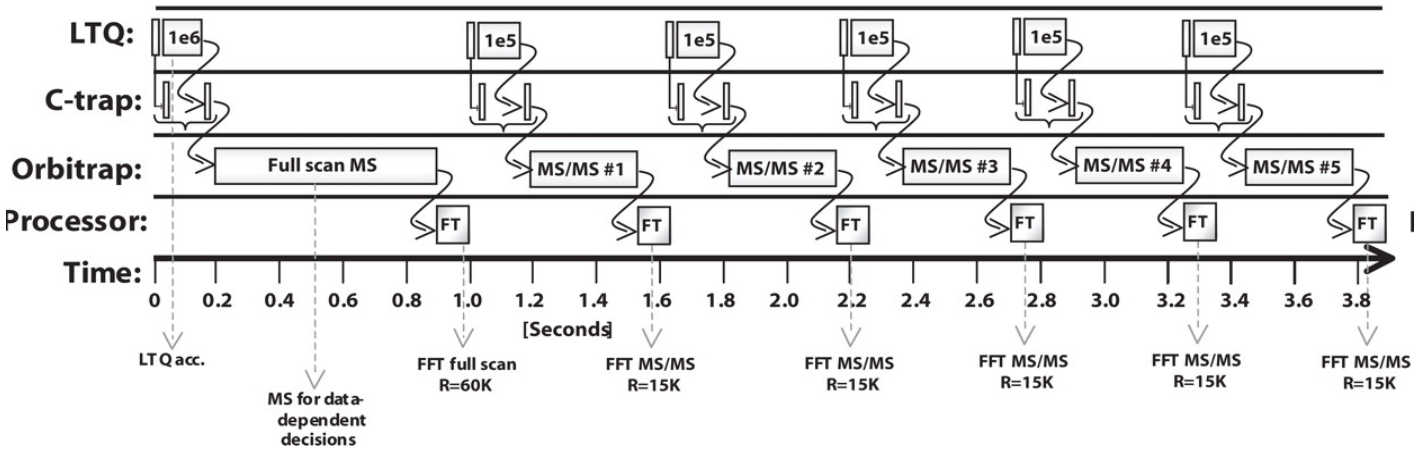


- Combination of different type of analysers
  - Combination of advantages
- Q-TOF instruments
  - MS/MS, accurate masses
- LTQ-Orbitrap
- ……..

(a)


Linear Ion Trap Orbitrap Hybrid MS
API Ion source
Linear Ion Trap
C -Trap
Differential pumping
Orbitrap

(b)


LTQ:
C-trap:
Orbitrap:
Processor:
Time:
1e6
1e5
Full scan MS
MS/MS #1
MS/MS #2
MS/MS #3
MS/MS #4
MS/MS #5
FT
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8
[Seconds]
LTQ acc.
MS for data-dependent decisions
FFT full scan R=60K
FFT MS/MS R=15K


LTQ ORBITRAP XL

Thank you for your attention