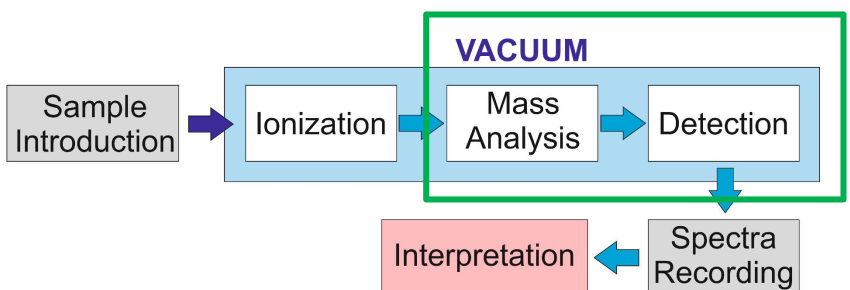
Mass analyzers

Literature: Jürgen H. Gross: Mass Spectrometry

Mass Analyzers

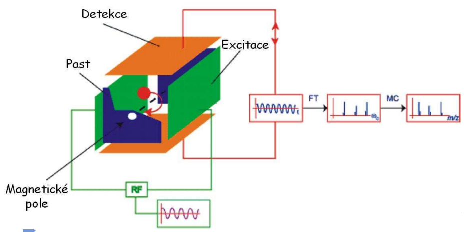


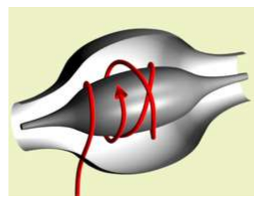
- Magnetic analyzer
- Electrostatic analyzer
- Time-of-flight analyzer
- Quadrupoles
- Quadrupolar traps
- High resolution analyzers – ICR, Orbitrap
- Detection

High resolution

FT ICR

Orbitrap





Ion cyclotron resonance (ICR)

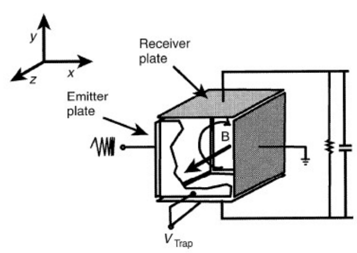
Penning trap

- electric trapping in a magnetic field

→ pulsed analysis

1. Ions are trapped
2. Ions are excited (emitter)
3. Ions circulate in the magnetic field at their cyclotron resonance (dependent on m/z)
4. Oscillating ions generate a current (receiver)

ICR can be also used for mass selection and CID experiments similarly to the quadrupole ion traps



From Hoffmann

Figure 2.50
Diagram of an ion cyclotron resonance instrument. The magnetic field is oriented along the *z*-axis. Ions are injected in the trap along the *z*-axis. They are trapped along this axis by a trapping voltage, typically 1 V, applied to the front and back plates. In the *x*,*y* plane, they rotate around the *z*-axis due to the cyclotronic motion and then go back along the *z*-axis between the electrostatic trapping plates. The sense of rotation indicated is for positive ions. Negative ions will orbit in the opposite direction

http://www.youtube.com/watch?v=a5aLlm9q-Xc&feature=related

FT-MS

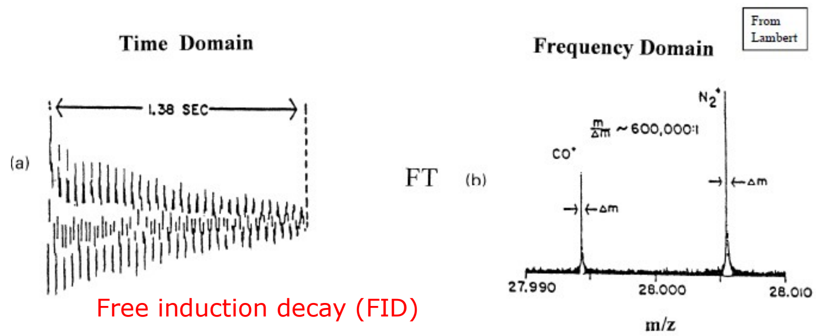


Figure 13-25 (a) Time domain signal (transient) recorded for a mixture of $CO^{+\cdot}$ and $N_2^{+\cdot}$ ions of nominal *m/z* 28 and (b) the corresponding frequency (mass) domain signal. (Courtesy of A.G. Marshall.)

Instruments with highest resolution

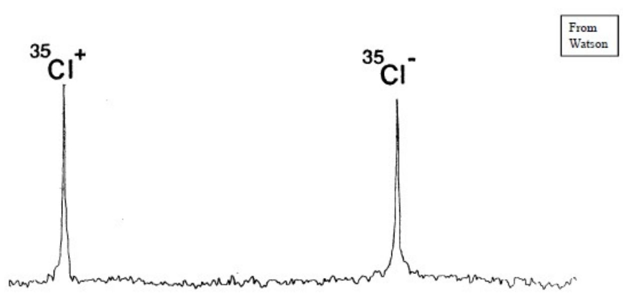
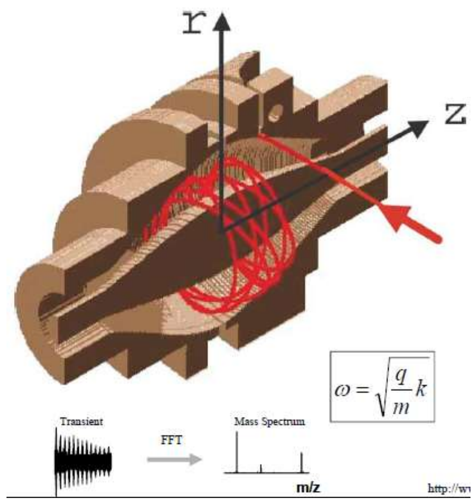


FIG. 4.22. Segment of mass spectrum in region of nominal mass 35 showing a resolution greater than 1,000,000 (FWHM definition) when using FT-MS. The peaks represent the positive and negative ions of ^{35}Cl that have a difference in mass equivalent to the mass of two electrons. The spectrum was obtained using a FT-ICR mass spectrometer with a superconducting magnet (4.7 tesla); the instrument was switched from the positive-ion-detection mode to the negative-ion-detection mode during the scan between the two peaks (Courtesy of Spectrospin AG.)

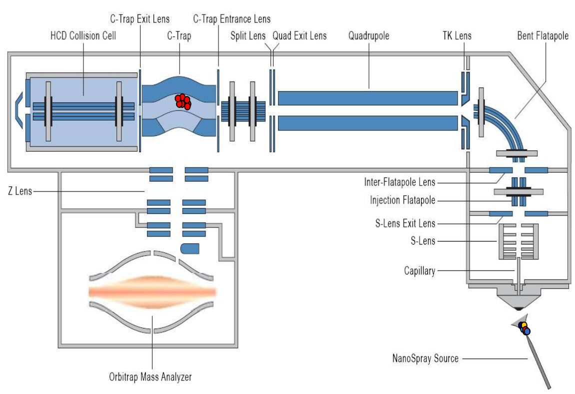
Orbitrap



- Ions introduced perpendicular to the z-axis (red arrow)
- Distance of the entrance point to z = 0 determines potential energy along z-axis

- Perspective: The Orbitrap: a new mass spectrometer. Q. Hu, R.J. Noll, H. Li, A. Makarov, M. Hardman, R. Graham Cooks. *J. Mass Spec.*, 40(4): 430 – 443, 2005.

Orbitrap



- High precision (1 – 2 ppm)
- High mass resolutions (up to 200 000)
- High dynamic range (~ 5000)
- Easy to operate
- Often used for determination of an exact mass

- https://www.youtube.com/watch?v=fqfyyravJkA

Comparison of mass analyzers

Mass analyzer	Mass range Resolution	Advantages	Disadvantages
Quadrupole	Range m/z ~ 3000 R ~ 2000	Well suited for ESI Small, cheap	Small mass range, poor adaptability to MALDI
Ion traps	Range m/z ~ 2000 R ~ 1500	Small, cheap CID: up to MS^{12}	Small mass range
Magnetic sector	Range m/z ~20 000 R ~ 10 000	High resolution High dynamic range Reliable	Not tolerant to high pressures Expensive Slow scanning
TOF	Range m/z ∞ R ~ 10^3 - 10^4	Good resolution Very fast scanning Cheap	Suboptimal adaptability to ESI
Orbitrap	Range m/z 6 000 R ~ 10^5	High resolution Easy to operate (compared to ICR)	Requires high vacuum Expensive
ICR	Range m/z 10 000 R ~ 10^6	High resolution CID: up to MS^4	Superconducting magnet → expensive, massive Requires high vacuum

Summary

- High resolution mass analyzers
  - Time of flight (reflectron)
  - Penning trap (ion cyclotron resonance)
    - high magnetic field, ions circulate in the magnetic field at their cyclotron frequency → AC current (frequency and amplitude → m/z and intensity)
    - proteomics
  - Orbitrap
    - ions oscilate in a harmonic electrostatic field → AC current (frequency and amplitude → m/z and intensity)
    - biochemical applications
    - chemistry – exact mass analysis