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MASS SPECTROMETRY

analytical methods
- qualitative : kind of components — SPECTROSCOPY
- ~~qualitative~~ quantitative : kind and amount of components — SPECTROMETRY

"kind" = chemical species :
- atoms
- molecules
- ions (monatomic or polyatomic)
- molecule fragments

What is MASS?

"gravitative mass"
- creates and interacts with gravity

$$F_{gravit.} = \gamma \cdot \frac{m_1 m_2}{r^2}$$

(γ: gravitational constant)

for everyday use on the Earth:

$$F_W = g \cdot m$$

(F_W: weight, g: grav. acceleration, m: mass)

- use: gravimetry (2nd year)
  - measure the weight to find out the amount
  - e.g. determination of Ba^{2+} concentration by weighing $BaSO_4$
- "oldschool" but precise method

macroscopic method (greater amounts)

"inertial mass"
- Newton's 2nd law: mass resists acceleration:

$$\sum F = a \cdot m$$

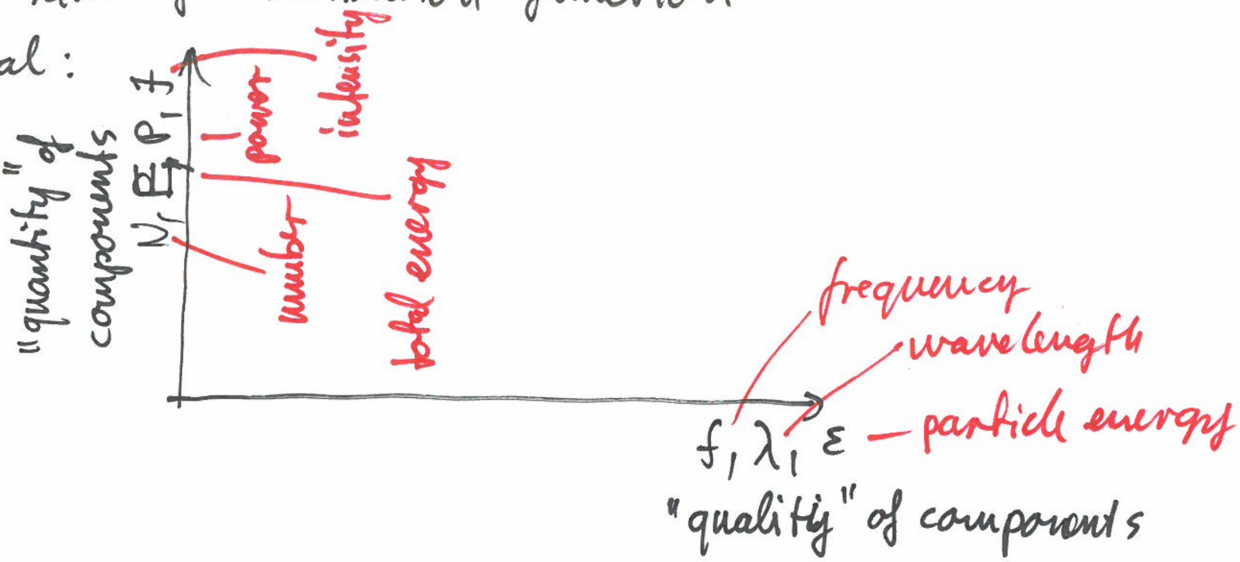
($\sum F$: total force, a: acceleration, m: mass)

use: mass spectrometry

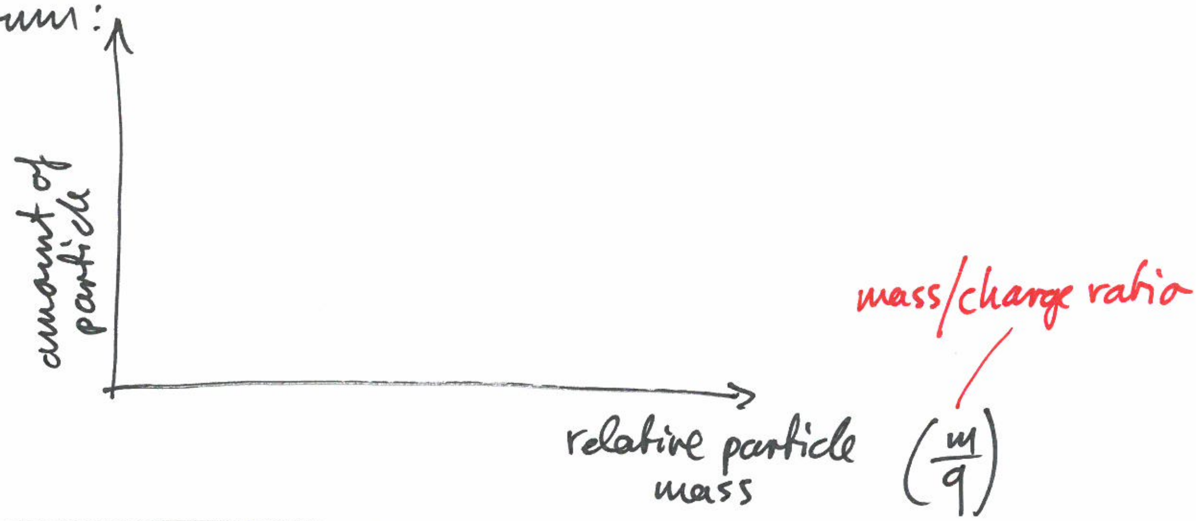
microscopic methods
sensitivity can be as low as a few 100 particles
"cutting edge" method

What is a SPECTRUM

- a special kind of distribution function
- in general:

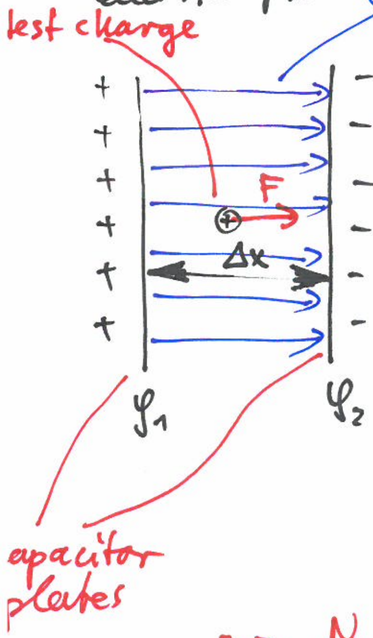


- mass spectrum:



Basic interactions involved in MS

electric field ($\vec{E}$)



$$E = \frac{F_{el}}{q} = \frac{\Delta\varphi}{\Delta x}$$

(F_{el}: electric force, N; q: charge, C; $\Delta\varphi$: potential difference between plates, V; Δx: distance between plates, m)

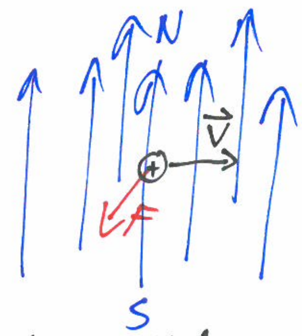
effect: linear acceleration

$$m \cdot \vec{a} = \vec{F_{el}} = \vec{E} \cdot q$$

$|\vec{v}|$ = increases

$$[E] = \frac{N}{C} = \frac{V}{m}$$

magnetic field ($\vec{B}$)



effect: radial acceleration

$$m \cdot \vec{a} = \vec{F_L} = q \cdot \vec{v} \times \vec{B}$$

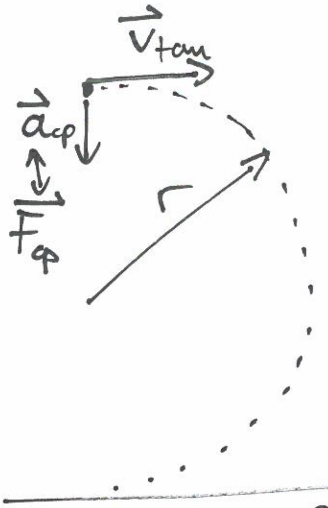
($\times$: vector product, right hand rule)

$|\vec{v}|$ = const.

$[B]$ = T (SI) or G (CGS)

$1\,T = 10^4\,G$

circular motion: caused by radial acceleration = acceleration normal to the actual speed $\vec{a} \perp \vec{v}$



$$\vec{F}_{cp} = \vec{a}_{cp} \cdot m$$

centripetal or radial acceleration

centripetal or radial force

$$a_{cp} = \frac{v_{tan}^2}{r}$$ — tangential speed

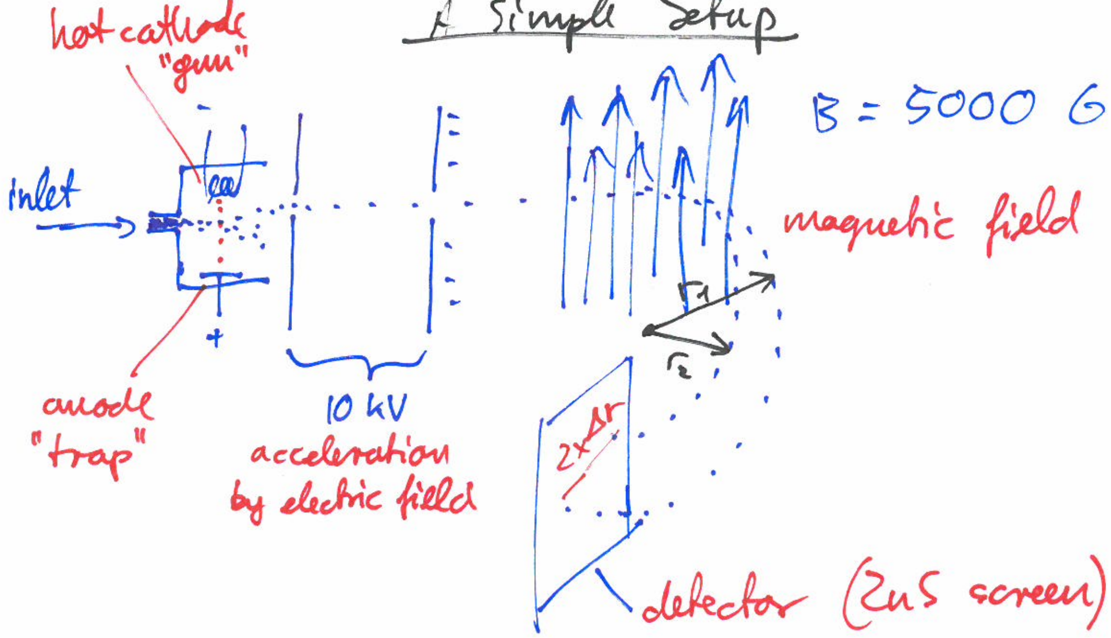
Schematic of a Mass Spectrometer

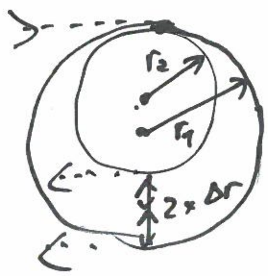
sample inlet → atomization, ionization, fragmentation → mass analyzer → detector

vacuum

atomization: physically disintegrate the sample volume
ionization: add charge to the particle (typically ⊕ charge)
fragmentation: chemical disintegration of bigger molecules

<u>A Simple Setup</u>





- acceleration by electric field:

electric energy $\varepsilon_{el} \longrightarrow \varepsilon_{kin}$ kinetic energy

$$q \cdot U = \frac{1}{2} m v^2 \qquad v = \sqrt{\frac{2 \cdot q \cdot U}{m}} \quad \#1$$

- acceleration by magnetic field:

$$|F_L| = q \cdot v \cdot B \;=\; F_{cp} = m \cdot \frac{v^2}{r}$$

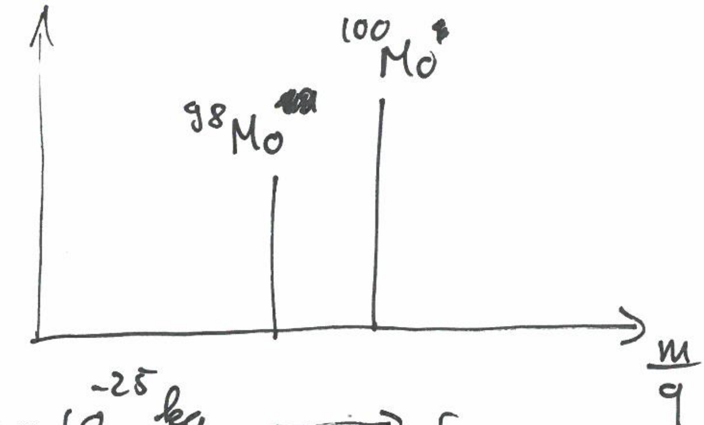
$$r = \frac{m \cdot v^{\cancel{2}}}{q \cdot \cancel{v} \cdot B} = \frac{m v}{q B} \quad \#2$$

- combine equations #1 & #2:

$$r = \frac{m \cdot \sqrt{\frac{2 q \cdot U}{m}}}{q \cdot B} = \frac{1}{B} \cdot \sqrt{\frac{m^{\cancel{2}} \cdot 2 \cdot \cancel{q} \cdot U}{\cancel{m} \cdot q^{\cancel{2}}}} = \frac{1}{B} \cdot \sqrt{\frac{m \cdot 2 \cdot U}{q}}$$

this is what we want to know! ($\frac{m}{q}$)

- e.g. Mo isotopes:



$m(^{98}Mo^+) = 1.633 \times 10^{-25}$ kg $\longrightarrow r_2$

$m(^{100}Mo^+) = 1.667 \times 10^{-25}$ kg $\longrightarrow r_1$

$q = e = 1.6 \times 10^{-19}$ C

settings: $U = 10$ kV $\quad B = 0.5$ T

$r_2(^{98}Mo^+) = 0.28574$ m

$r_1(^{100}Mo^+) = 0.28870$ m

$\Big\} \Delta r = 0.00296$ m $= 2.96$ mm

Ion Sources

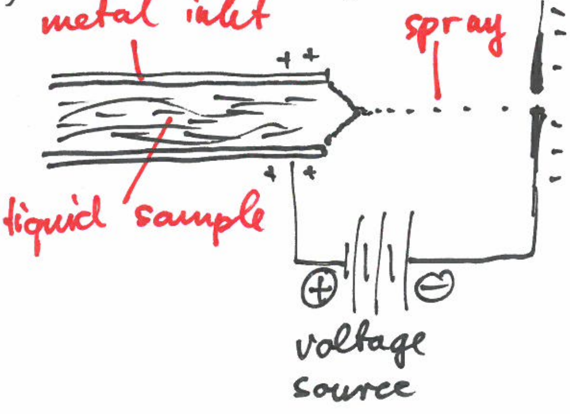
1) Electron Ionization (EI)

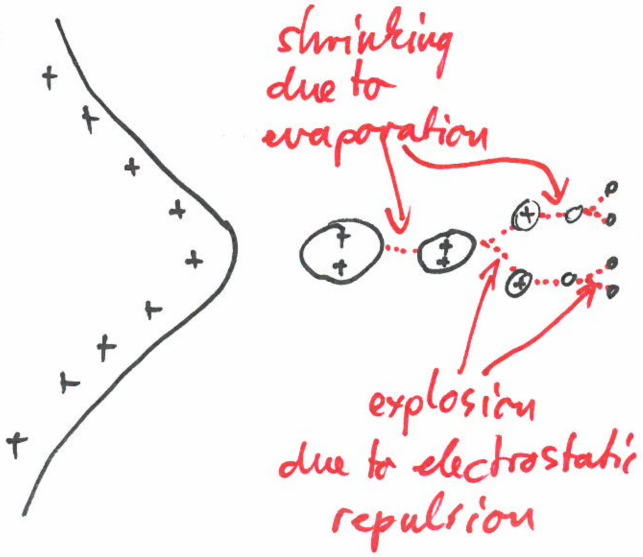
- a beam of electron ray is generated between ~~an~~ cathode and an anode
- the electrons will collide with sample particles removing electrons and eventually also causing ~~disin~~ fragmentation
- hard ionization: high degree of fragmentation

2) Chemical Ionization (CI)

- an inert chemical is introduced into the ionization space (A)
- then it gets ionized: $e^- + A \longrightarrow A^+ + 2e^-$
- then the sample (M) is introduced and charge will be transferred from the "A" to the "S" particles:
  - $M + A^+ \longrightarrow M^+ + A$
  - $M + A^+ \longrightarrow [M\,A]^+$
- ~~mild~~ soft ionization process

3.) Electro Spray Ionization (ESI)



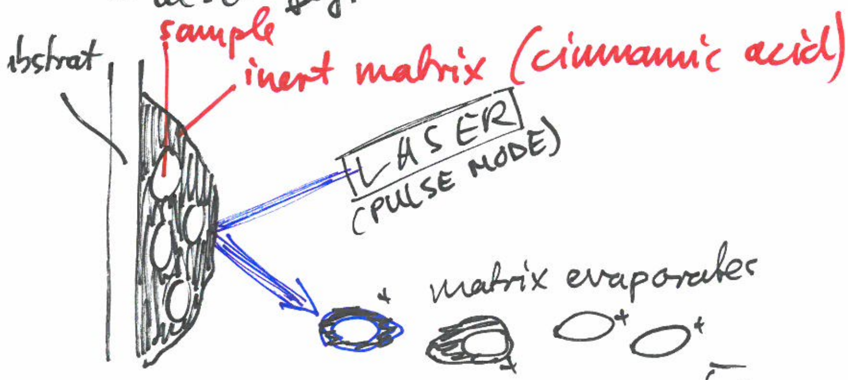


- also soft ionization

4.) Matrix Assisted Laser Desorption/Ionization (MALDI)

- also soft

Desorption ↑ removal from surface



Mass Analyzers

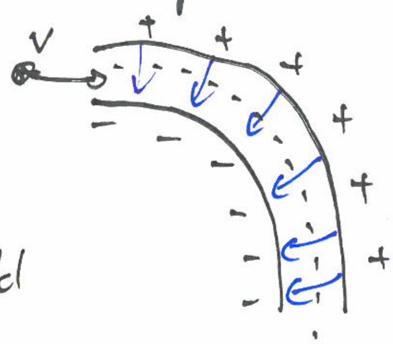
1.) Magnetic Sector
(see above)

$$F_{cp} = F_L$$

$$m \cdot \frac{v^2}{r} = q \cdot v \cdot B \}$$

2.) Electric Sector : curved capacitor

charges are forced to follow a circular path in the curved capacitor's electric field



$$\varepsilon_{el} = \varepsilon_{kin}$$

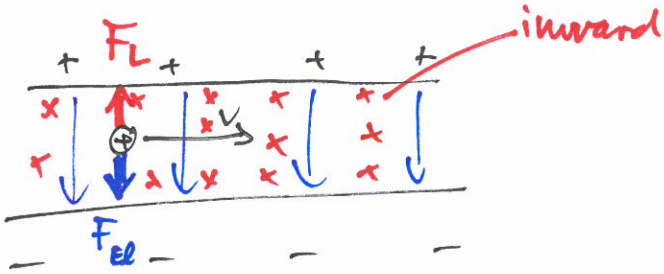
$$qU = \frac{1}{2} m v^2$$

$$F_{cp} = F_E$$

$$m \cdot \frac{v^2}{r} = E \cdot q$$

$$r = \frac{m \cdot v^2}{q \cdot E}$$

3.) Speed Focusing

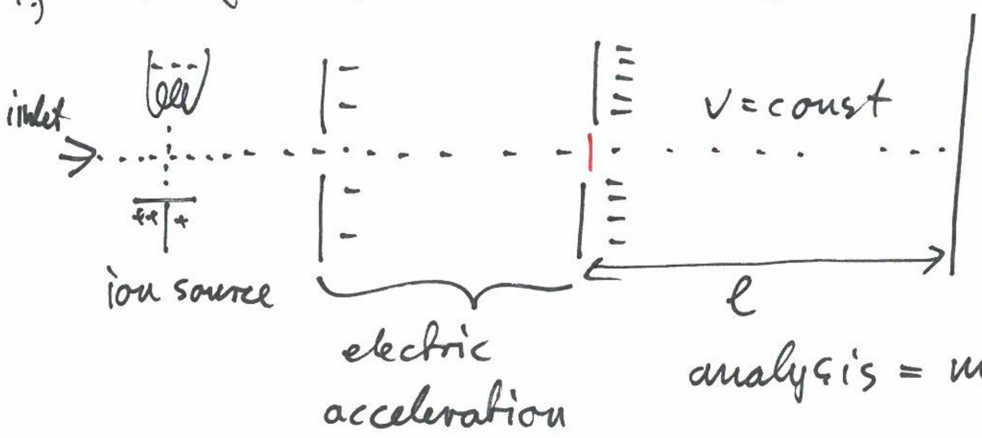


particle can pass through if $F_L = F_{El}$

$$q \cdot v \cdot B = q \cdot U$$

$$v = \frac{U}{B} \} \text{ speed selection}$$

4.) Time of Flight (TOF) analyzer



$$v = \frac{\Delta x}{\Delta t} = \frac{l}{\Delta t}$$

known (l), measured (Δt)

$$t = \frac{l}{v} = \frac{l}{\sqrt{\frac{q U \cdot 2}{m}}}$$

analysis = measuring flight time: Δt