Mass Spectrometry

Mass

Inertial Mass

$F = m \cdot a$

force, mass, acceleration

e.g. particles accelerated in a force field

⇓

mass spektrometry

microscopic technique

(down to femtomoles)

Gravitational Mass

•⟶ ⟵•

$F_W = g \cdot m$

Weight (force), gravitational acceleration

⇓

"weight measurement"

gravimetry

macroscopic technique

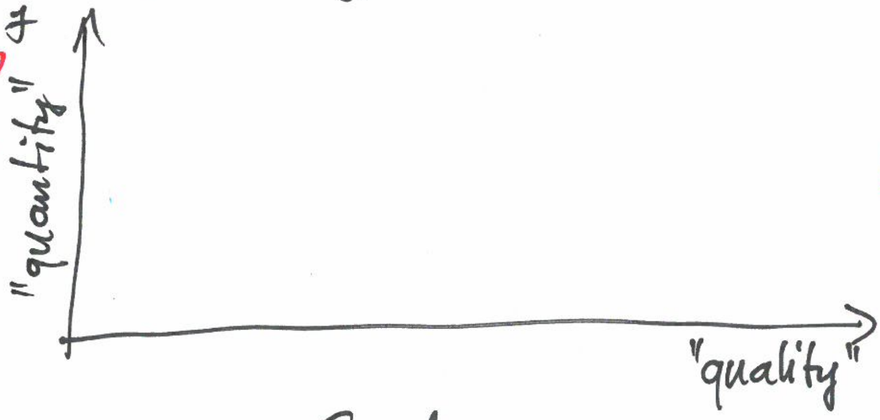
(down to mg)

Spectrum

A distinct type of distribution function

N, E, P, J

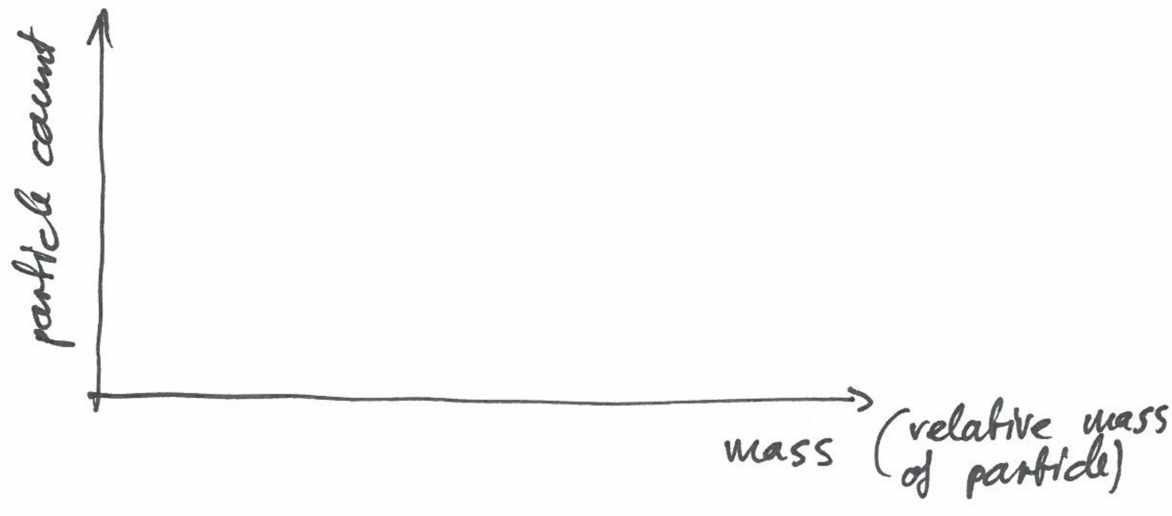
total energy → E; power → P; count → N; intensity → J



ε_{ph} ; λ ; f

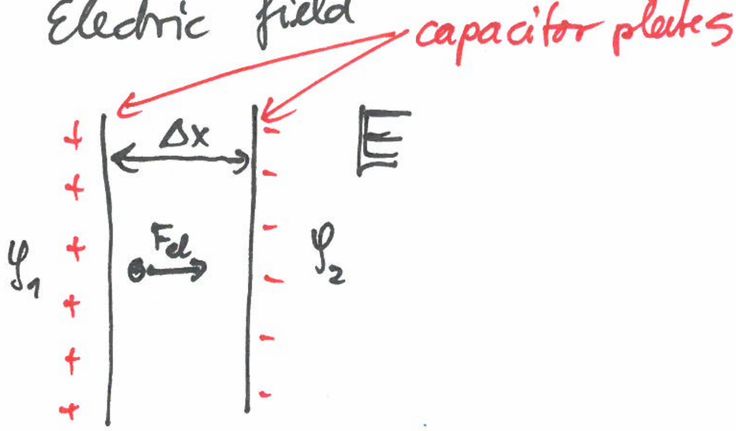
photon energy → ε_{ph}; wave length → λ; frequency → f

Mass Spectrum



How can a charged particle be accelerated

Electric field



$$F_{el} = E \cdot q$$

- F_{el} — electric force
- E — electric field strength
- q — charge of particle

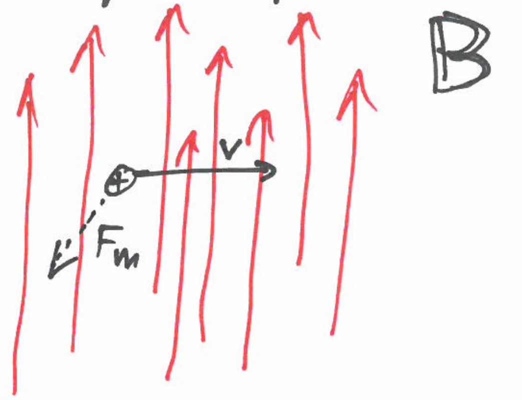
$$E = \frac{\Delta \varphi}{\Delta x}$$

- $\Delta \varphi$ — electric potential difference = voltage
- Δx — distance between plates

As a result of electric field, the magnitude of velocity will increase

$|v|$ increases

Magnetic field



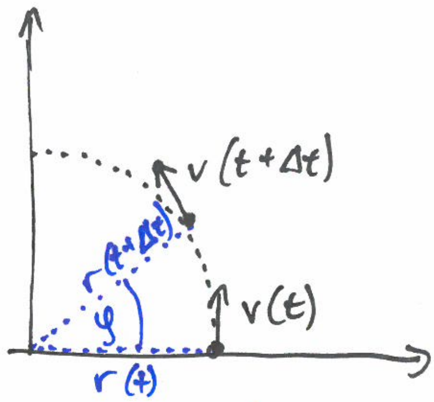
$$F_m = q \cdot v \times B$$

- F_m — magnetic force
- q — charge
- v — speed
- $\times$ — vectorial product
- B — magnetic field strength

KEEP IN MIND: RIGHT HAND RULE

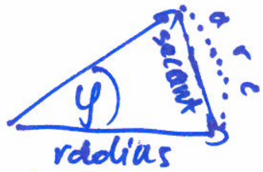
As a result of the magnetic field, the moving charged particle will be forced onto a curvilinear path

Circular motion & centripetal acceleration

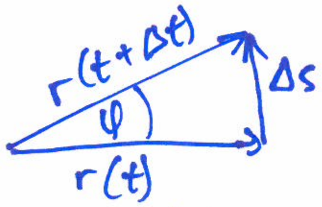


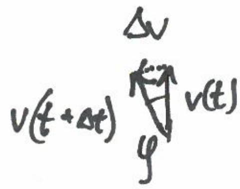
definition of angle:

$$\varphi = \frac{\text{arc}}{\text{radius}} \approx \frac{\text{secant}}{\text{radius}}$$



for small angles, the difference between arc and secant is negligible





$$\Delta v = v(t+\Delta t) - v(t)$$

$$\varphi \approx \frac{\Delta s}{r}$$

$$\varphi \approx \frac{\Delta v}{v}$$

$$\frac{\Delta s}{r} = \frac{\Delta v}{v}$$

Definition of speed:

$$v = \frac{\Delta s}{\Delta t}$$

$$v \cdot \Delta t = \Delta s$$

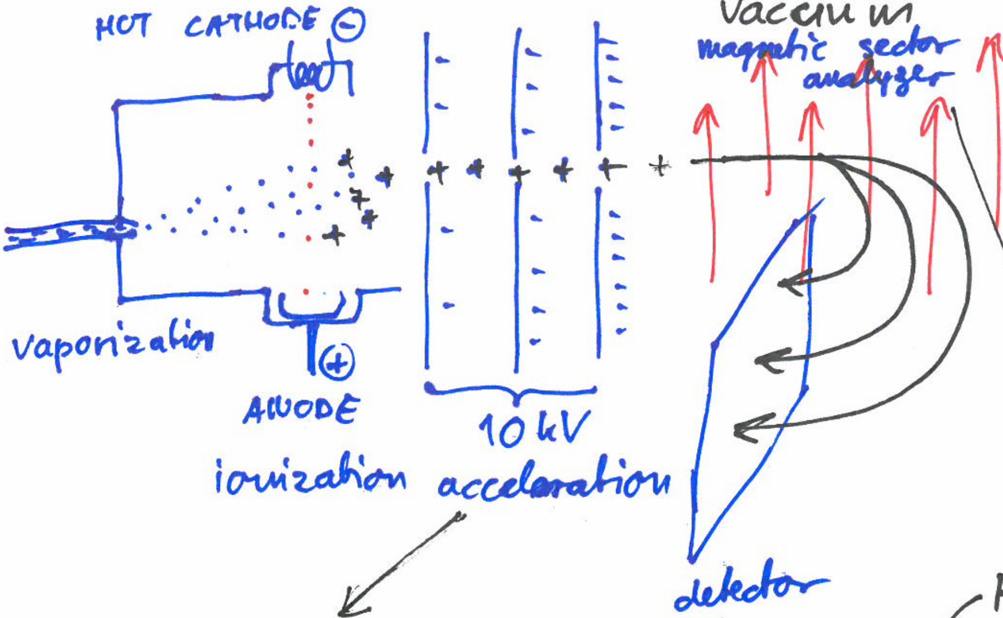
$$\frac{v \cdot \Delta t}{r} = \frac{\Delta v}{v}$$

centripetal acceleration $a_{cp} = \frac{\Delta v}{\Delta t} = \frac{v^2}{r}$

centripetal force $F_{cp} = a_{cp} \cdot m$

Basic Mass Spectrometer

Sample Inlet ⇒ [vaporization, atomization, ionization, fragmentation ⇒ mass analyzer ⇒ detector]



$B = 5000\ G = 0.5\ T$

the SI unit of B is tesla (T) the former cgs unit is gauss (G)
$1\ T = 10^4\ G$

detector ↓ charge multiplier tube

$E_{kin} = \frac{1}{2} m v^2 \qquad E_{el} = q \cdot U$

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

$$v = \sqrt{\frac{2qU}{m}}$$

$F_{cp} = a_{cp} \cdot m = \frac{v^2}{r} \cdot m$

$F_m = q \cdot v \cdot B$

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

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

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

e.g.

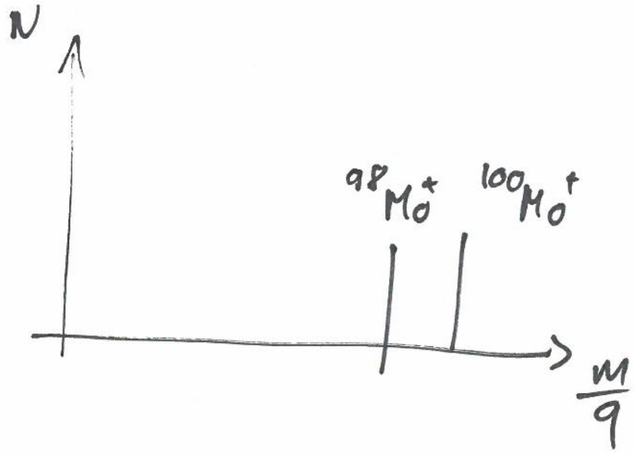
	m
$^{98}Mo^+$	1.6333×10^{-25} kg
$^{100}Mo^+$	1.6667×10^{-25} kg

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

$r(^{98}Mo^+) = 0.28577$ m

$r(^{100}Mo^+) = 0.2868$ m

$\Delta r = 2.9 \times 10^{-3}$ m $= 2.9$ mm



Types of Mass Spectrometers

1.) Ion sources (different ways of ionization)

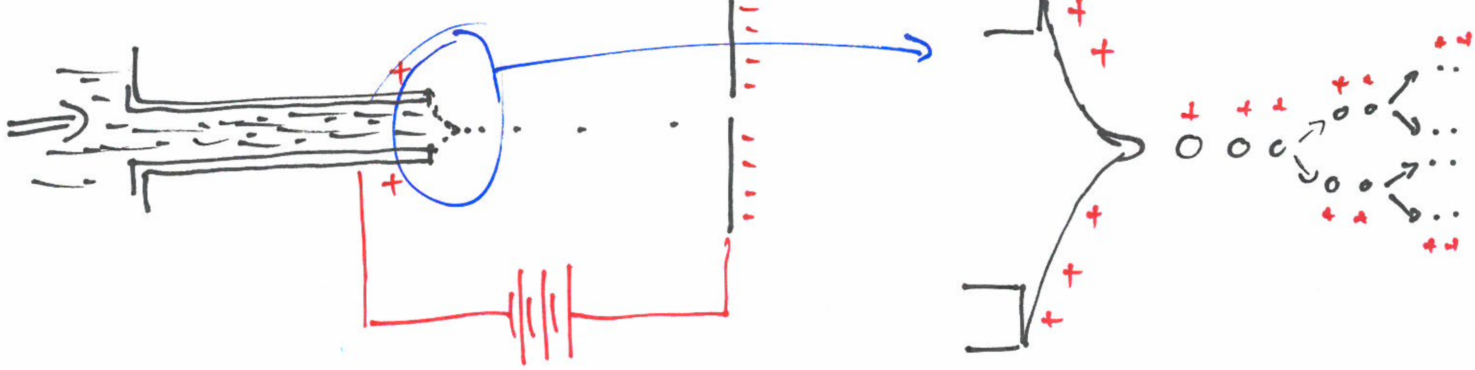
(A) Electron Ionization (EI) "hard" ionization (high degree of fragmentation) SEE ABOVE

(B) Chemical Ionization (CI)
- an inert substance (e.g. NH_3, CH_4) is brought into the ionization space (A)
- this gets ionized $A + e^- \longrightarrow A^+ + 2e^-$
- the sample (analyte) is introduced into the sample space (M)
- the A^+ transfers charge to the analyte

e.g.: $M + A^+ \longrightarrow M^+ + A$

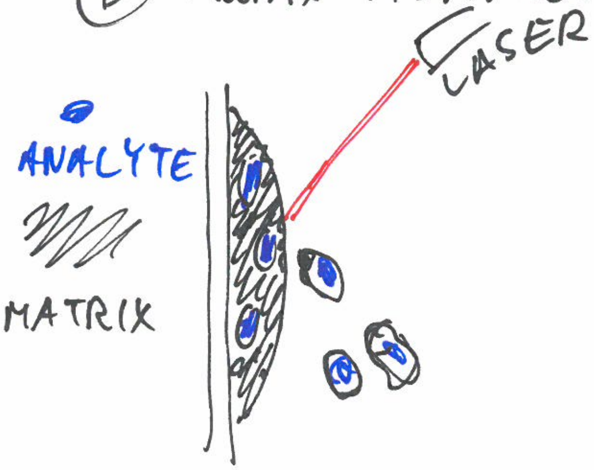
$M + A^+ \longrightarrow MA^+$

(C) Electrospray Ionization (ESI)



- the droplet becomes smaller due to evaporation
- the surface charge density will increase
- the droplet becomes unstable → explodes

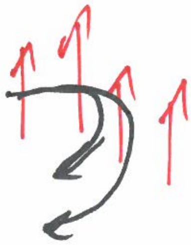
(D) Matrix Assisted Laser Desorption Ionization (MALDI)



Very mild ionization technique

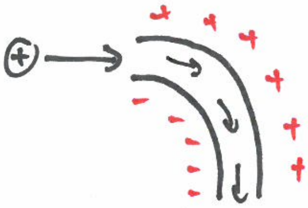
2) Mass analyzers

(A) Magnetic sector



$F_{cp} = F_m$

(B) Electric sector : bent capacitor



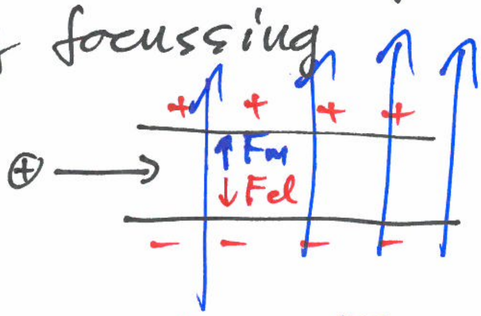
$F_{cp} = F_{el}$

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

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

- however, speed is a variable here
- we need to select a single speed

velocity focussing



it will go through:

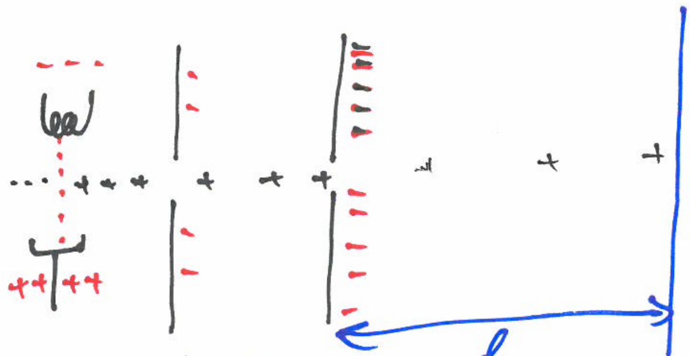
$$F_{el} = F_m$$

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

$$U = v \cdot B$$

$$v = \frac{U}{B}$$

(C) Time of flight (TOF)



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