Szervetlen komponensek analízise

A, Atomspektroszkópia

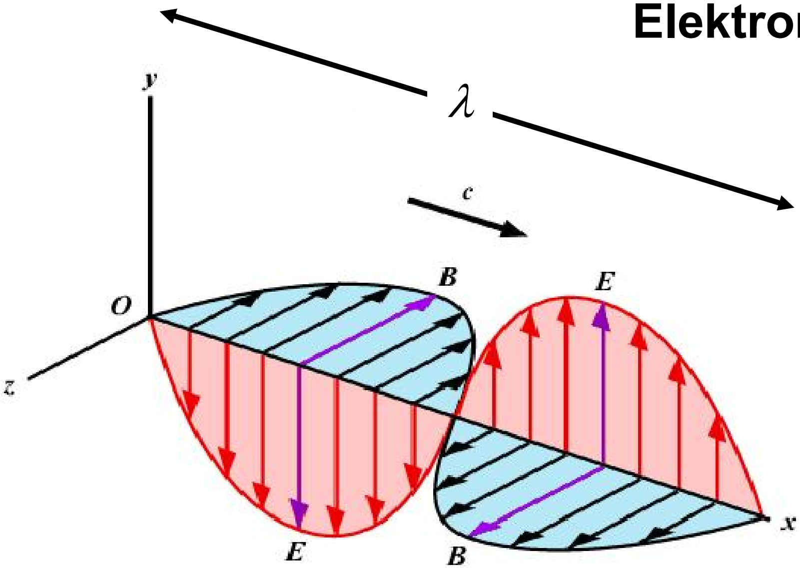
B, Molekulaspektroszkópia

C, Elektrokémia

D, Egyéb (radiokémia, termikus analízis, stb.)

A fény

Elektromágneses sugárzás



James Clerk Maxwell
(1831 – 1879)

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi_0)}$$

$$\text{tér}: \mathbf{E} = \mathbf{E}_0 \cos(kx) = \mathbf{E}_0 \cos\frac{2\pi x}{\lambda}$$

$$\text{idő}: \mathbf{E} = \mathbf{E}_0 \cos(\omega t) = \mathbf{E}_0 \cos(2\pi\nu t)$$

$$\lambda\nu = c$$

$\mathbf{k}$: hullámvektor, $\mathbf{E}$: elektromos tér

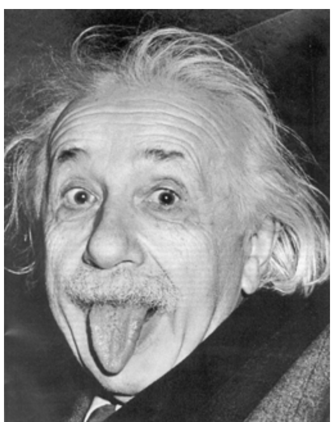
ω : körfrekvencia, λ : hullámhossz,

ν : frekvencia, c : fénysebesség

vákuumban :

$$c_0 = 2{,}99792458 \cdot 10^8 \text{ m/s}$$

$c = c_0 / n$ $\quad$ n : törésmutató



Albert Einstein
(1879 – 1975)

Részecsketermészet

1905: fotoelektromos jelenség

↓

fényenergia-kvantum: *foton*

$$E = h\nu\left(= \hbar\omega = \frac{hc}{\lambda} = hc\tilde{\nu}\right)$$

h : Planck – állandó, $\tilde{\nu}$: hullámszám

$$h = 6{,}62606876(52)\cdot 10^{-34}\ \text{Js}$$

Louis-Victor de Broglie
(1892 – 1987)

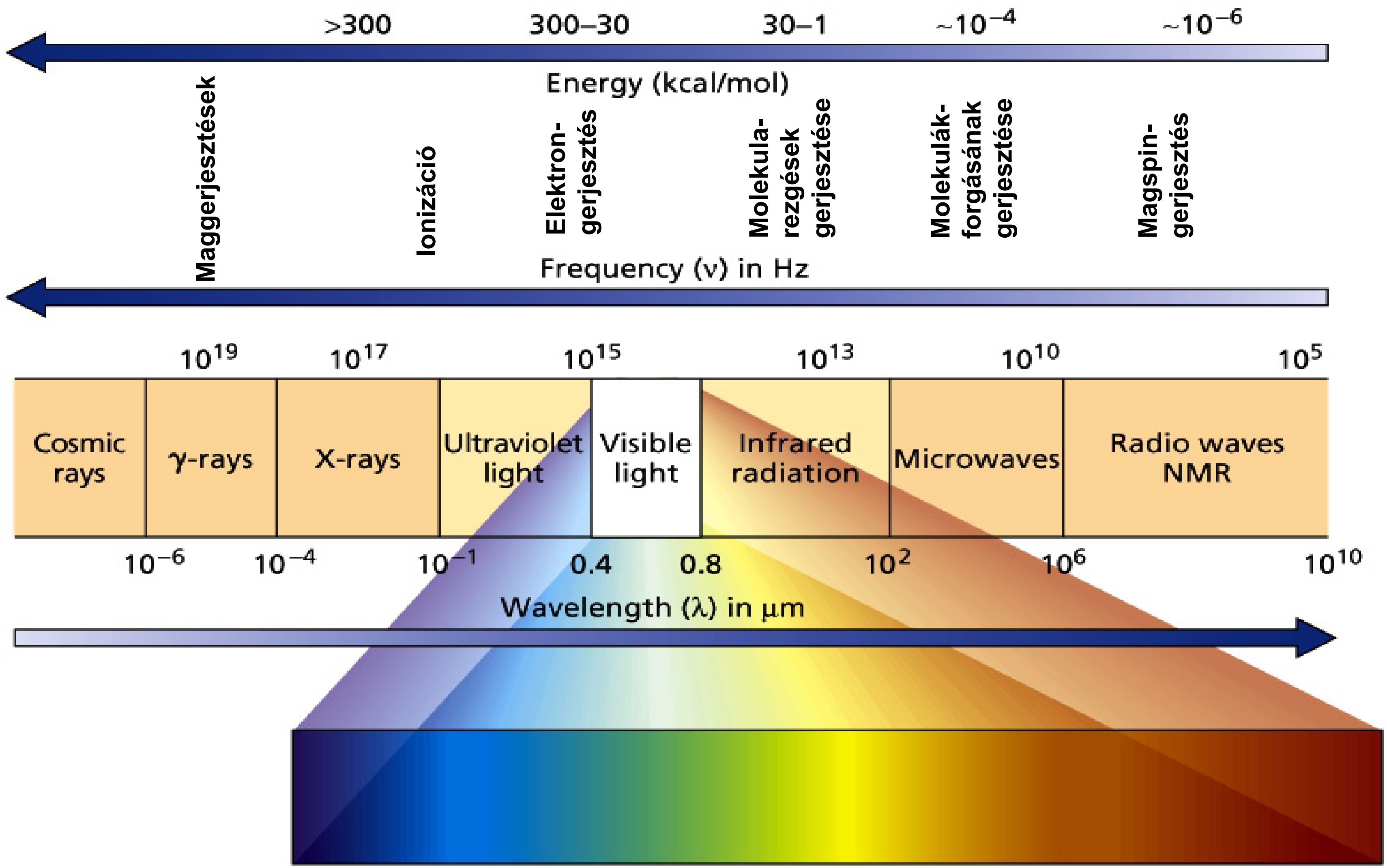
Kettőstermészet

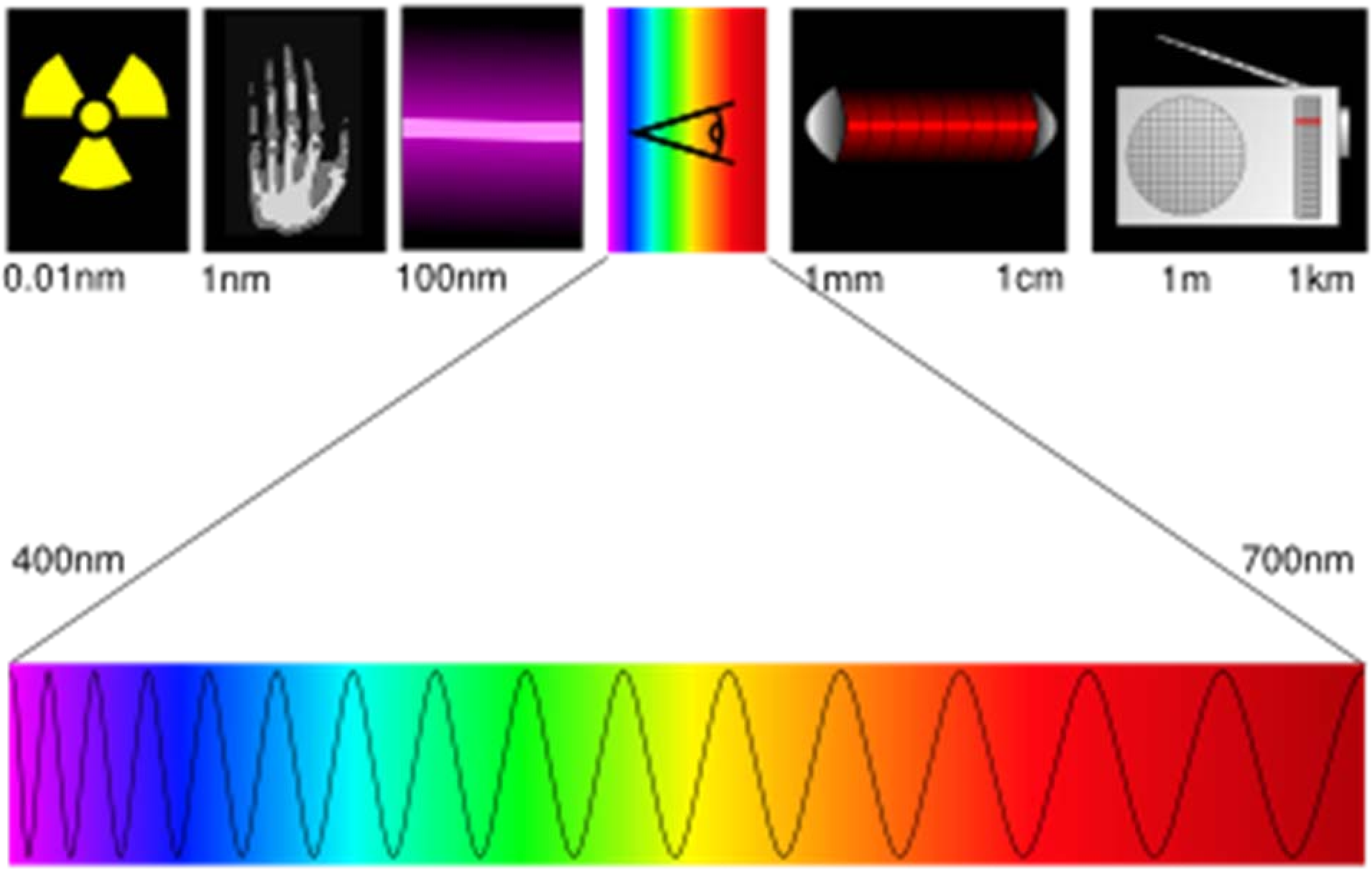
1924:
minden anyagra:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

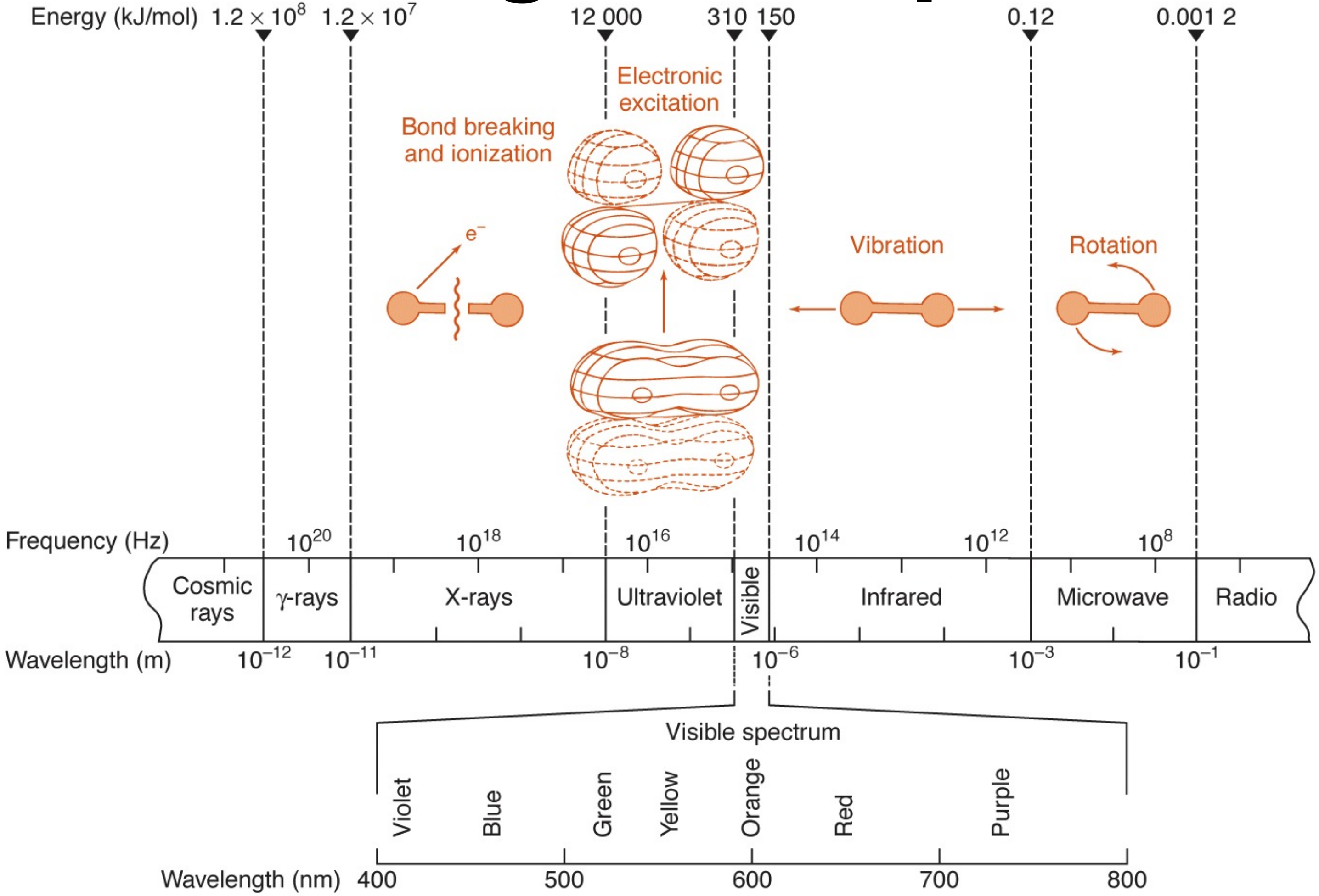
p : impulzus

A fény és az anyag kölcsönhatása

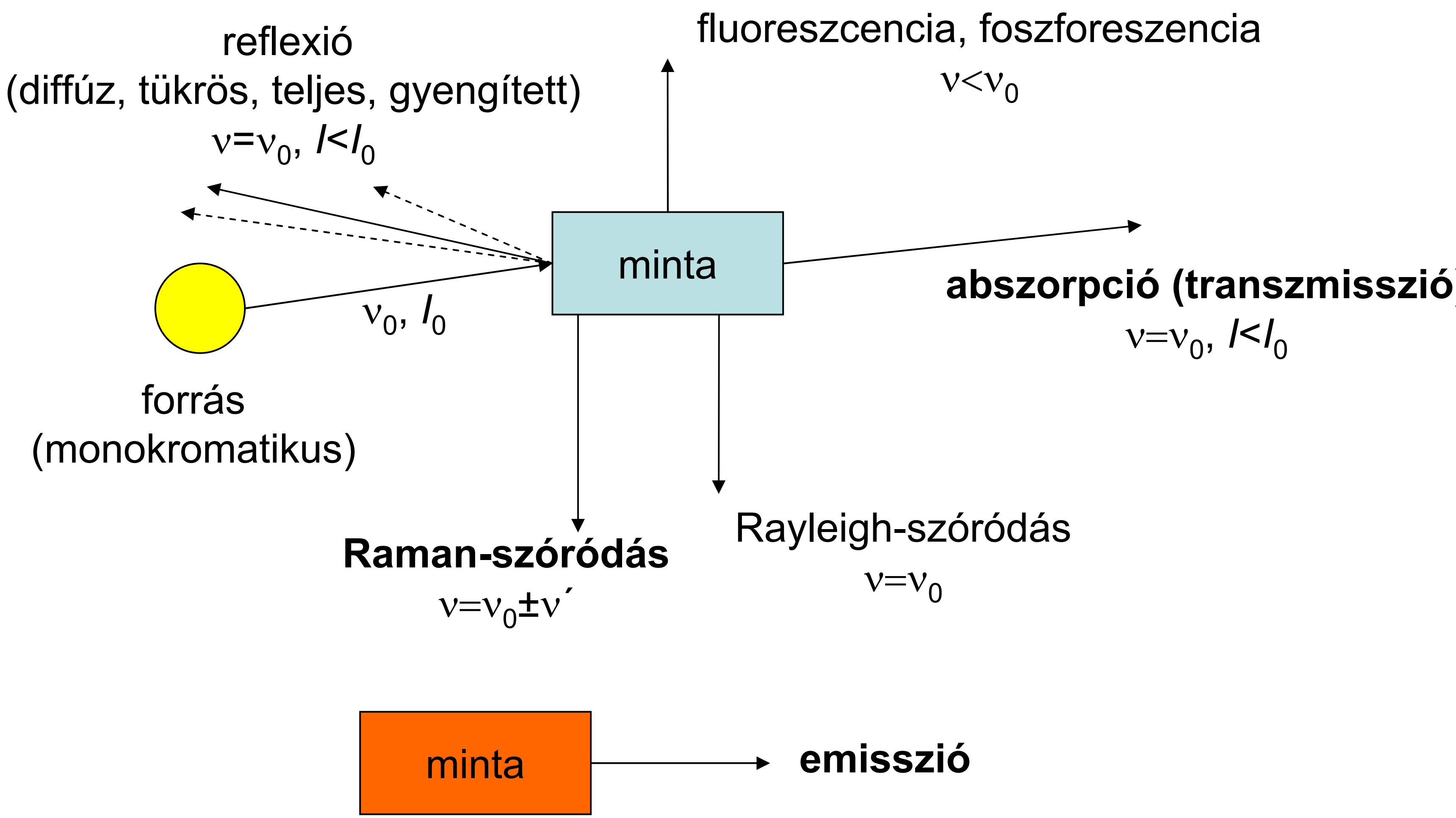



0.01nm
1nm
100nm
1mm
1cm
1m
1km
400nm
700nm

Regions of Electromagnetic Spectrum

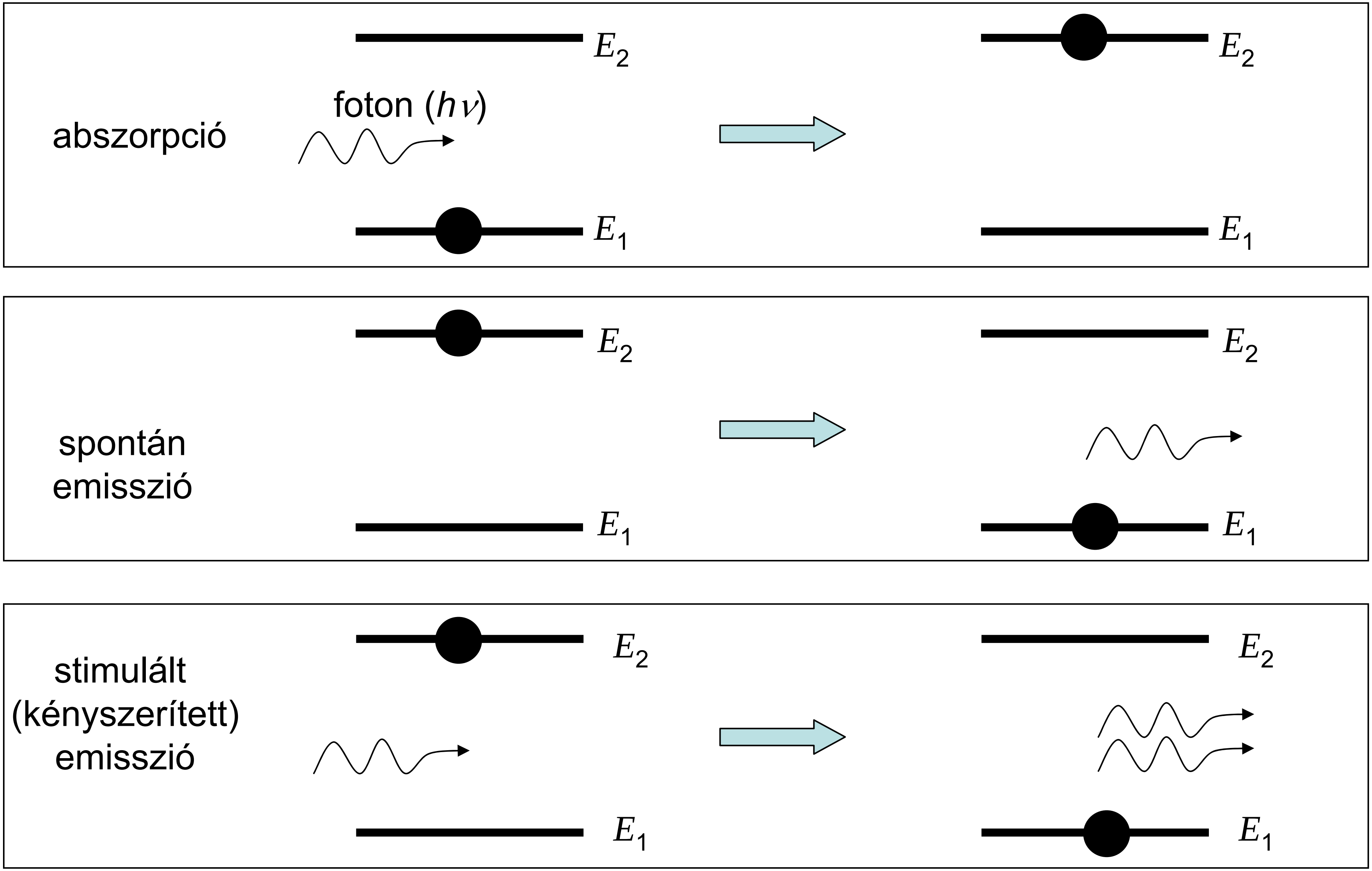


A fény és az anyag kölcsönhatása

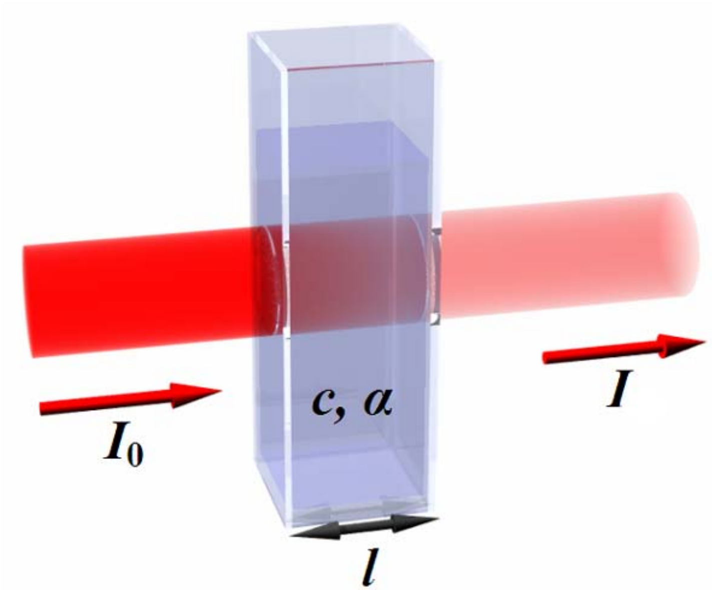


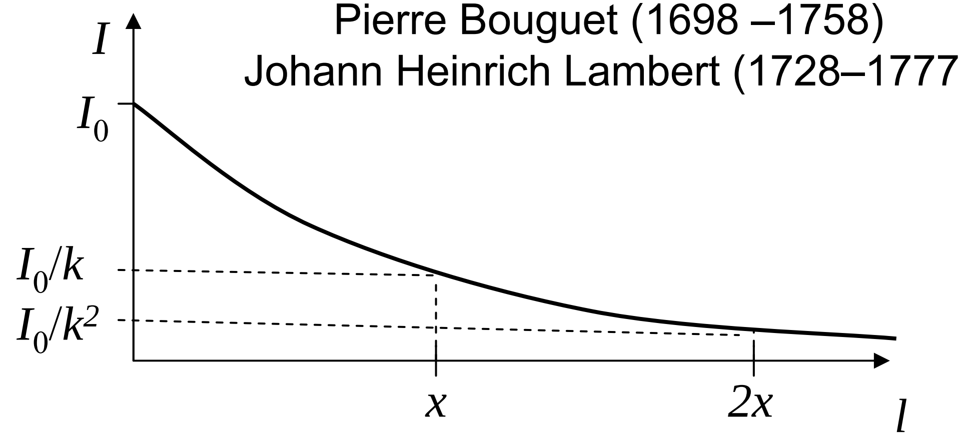
A fény és az anyag kölcsönhatása

„Bohr-feltétel”: $\Delta E = E_2 - E_1 = h\nu$



A fény és az anyag kölcsönhatása





August Beer (1825–1863)
Lambert–Beer-törvény:

$$I = I_0 10^{-\varepsilon c l}$$

$$-\log\frac{I}{I_0} = \varepsilon c l = A \quad \left(\ln\frac{I}{I_0} = -\mu l\right)$$

$$A = \log\left(\frac{1}{T}\right) \quad T(\%) = \frac{I}{I_0}\cdot 100$$

c : koncentráció

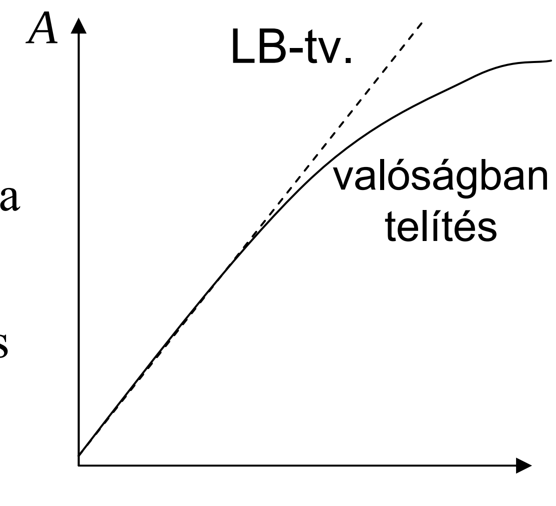
l : rétegvastagság

A : dekadikus abszorbancia

ε : dekadikus moláris abszorpciós koefficiens

μ : természetes absz. k.

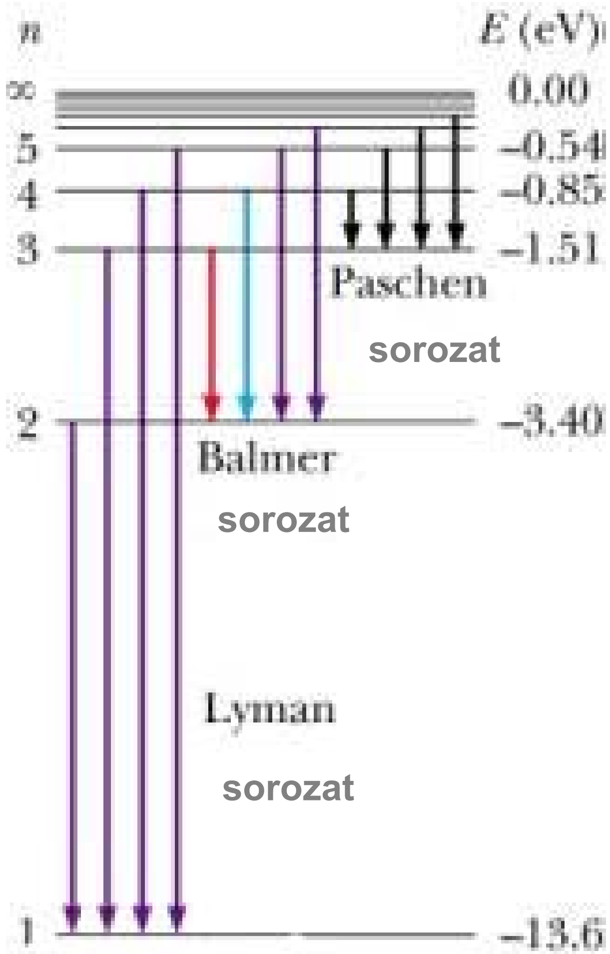
T : transzmittancia



→*kalibrációs görbe*

Atomspektroszkópia: H-atom

A hidrogénatom energiaszintjei

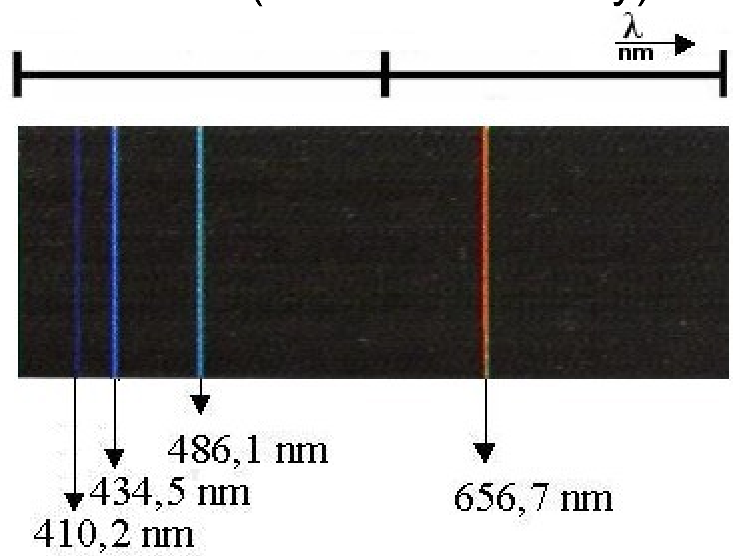


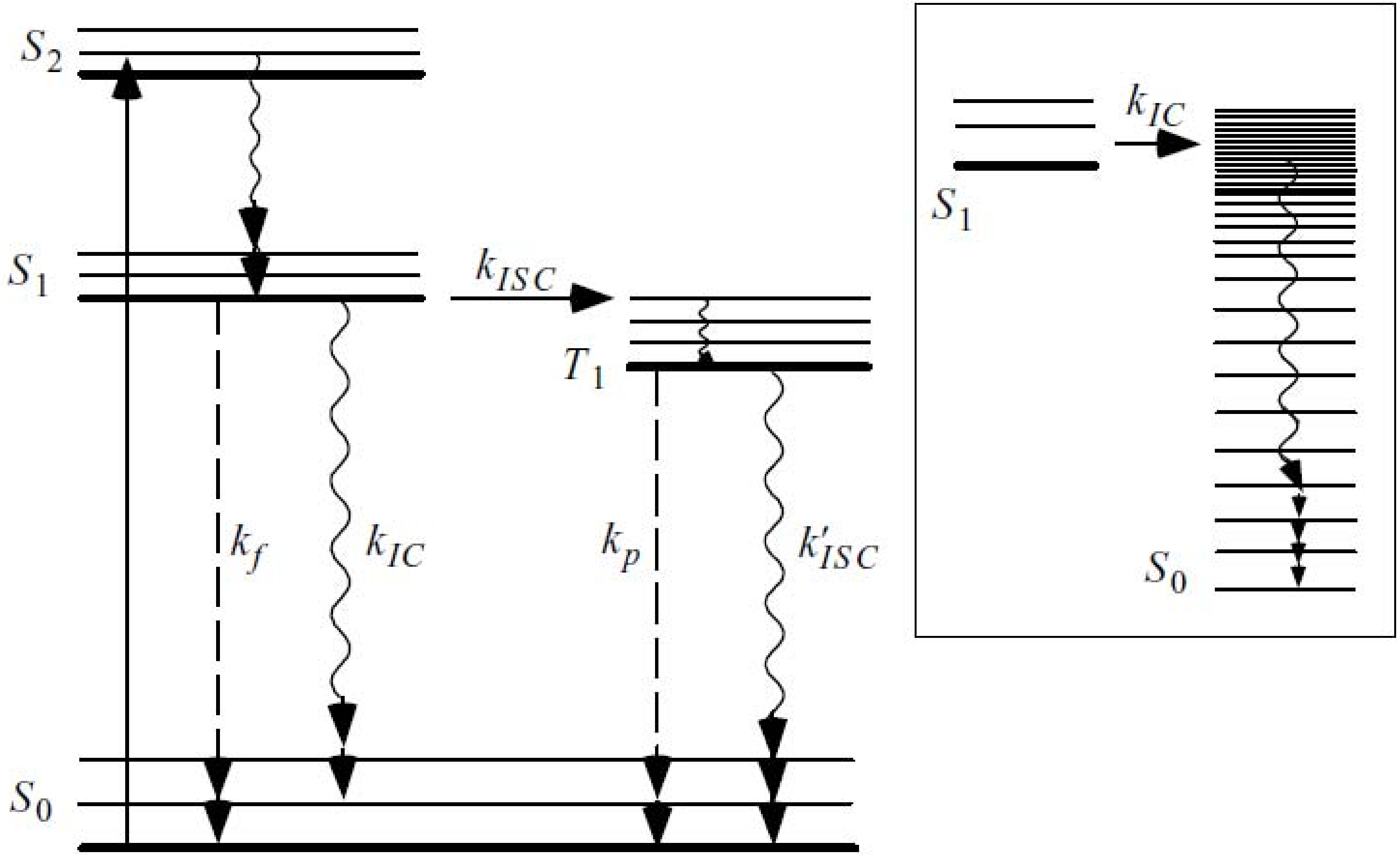
kiválasztási szabályok: $\Delta l = \pm 1$

$\Delta s = 0$

Hidrogénlámpa

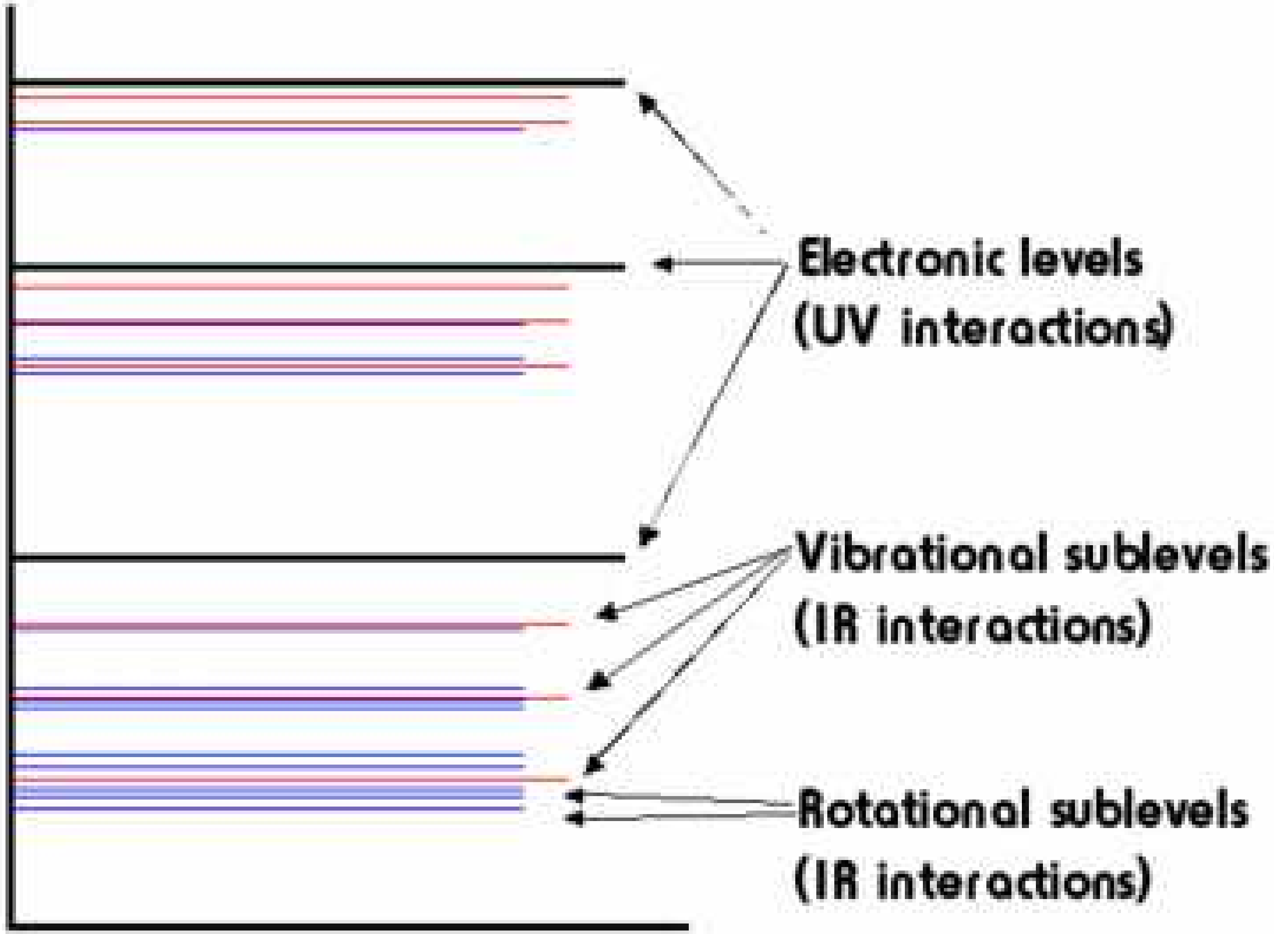
A hidrogénatom spektrumának részlete (látható tartomány)

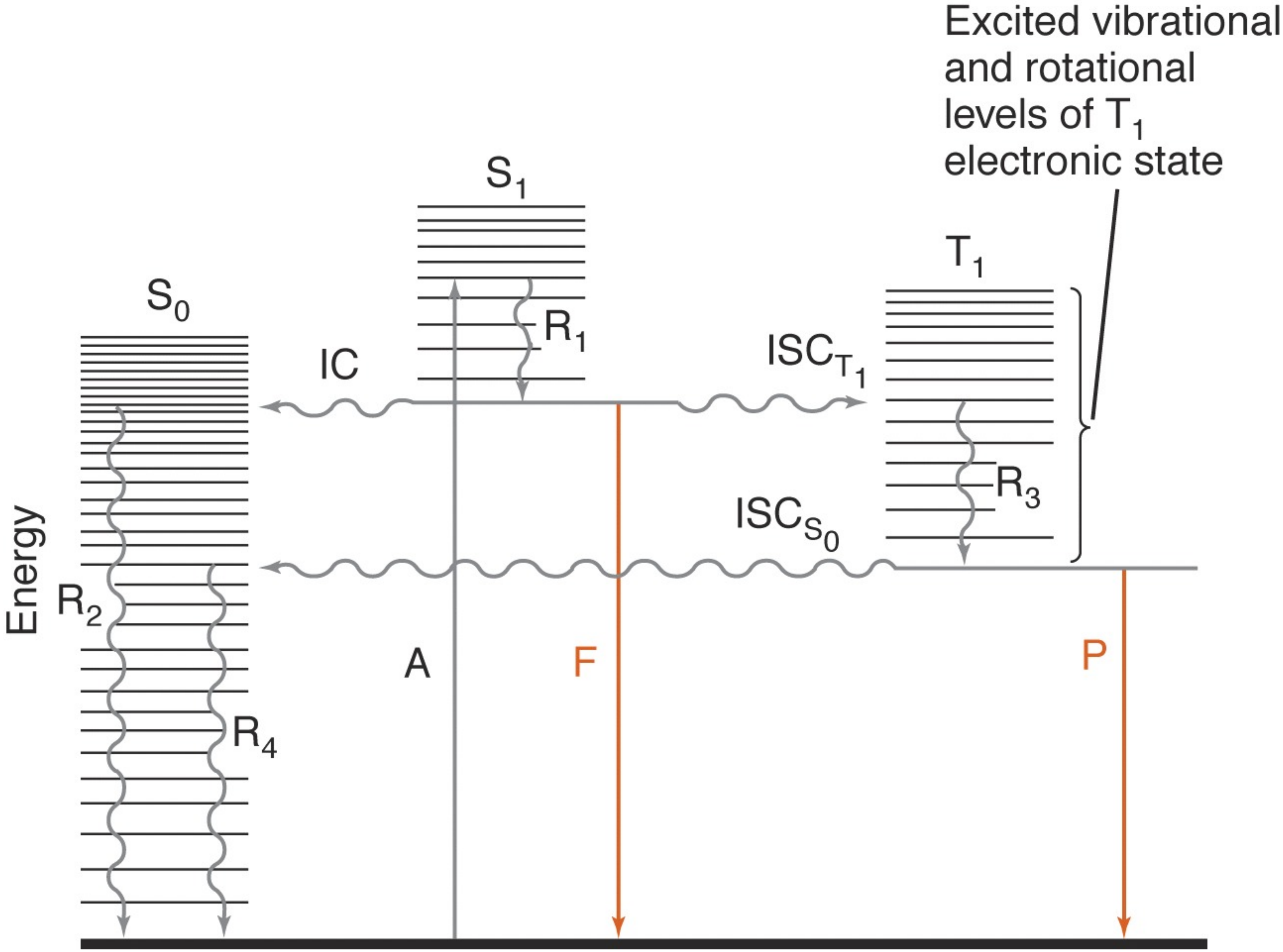




S_2
S_1
k_{ISC}
T_1
k_f
k_{IC}
k_p
k'_{ISC}
S_0
k_{IC}
S_1
S_0

The absorption process




Excited vibrational and rotational levels of T1 electronic state
S0
S1
T1
R1
R2
R3
R4
IC
ISCT1
ISCS0
Energy
A
F
P

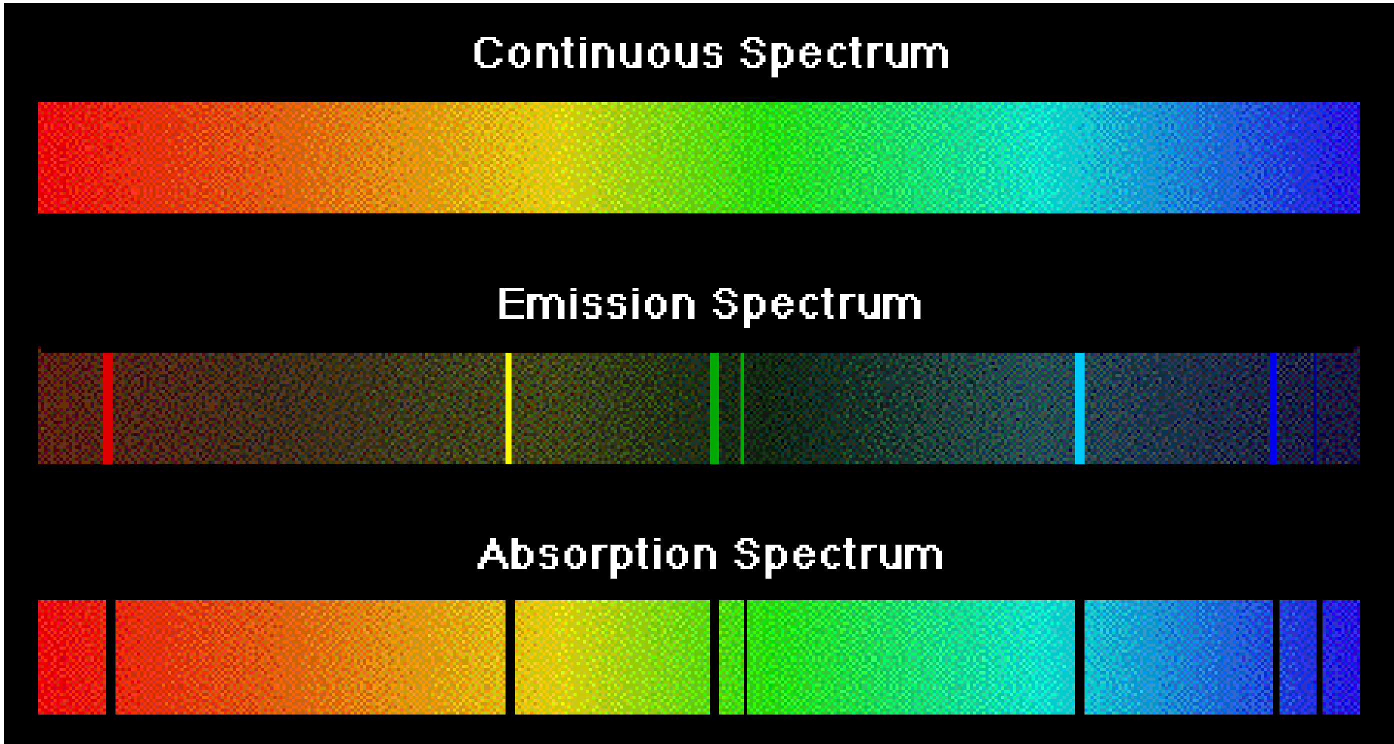
Atomspektroszkópia elmélete (abszorpció)

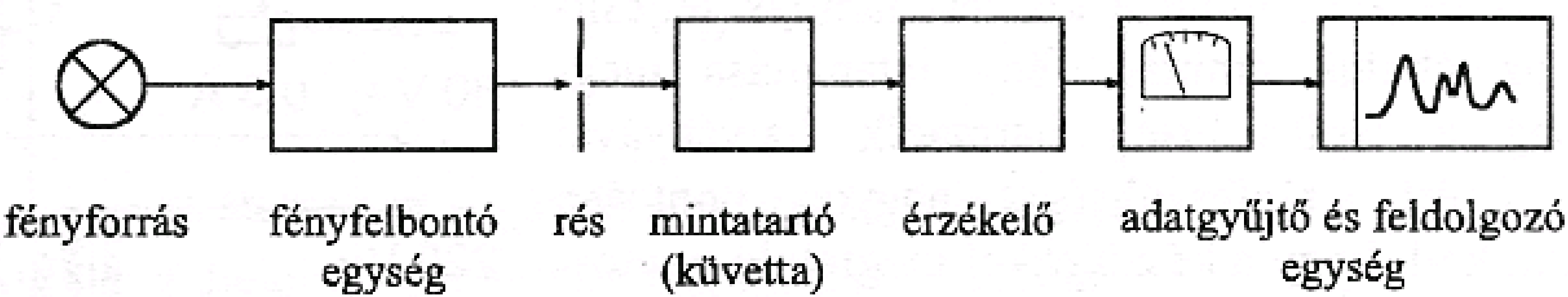
A vizsgálatokhoz gázfázisú és szabad (nem molekulárisan kötött) atomokra van szükség.

A szabad atomokat elektromágneses sugárzással besugározzuk (megvilágítjuk)

A megvilágító „fényből” elnyelik azokat a hullámhosszakat, amelyek az adott atom egy-egy elektronátmenetének megfelelő energiájú.

$$E = h \cdot \nu = h \cdot \frac{c}{\lambda}$$




fényforrás
fényfelbontó egység
rés
mintatartó (küvetta)
érzékelő
adatgyűjtő és feldolgozó egység

Excitation sources

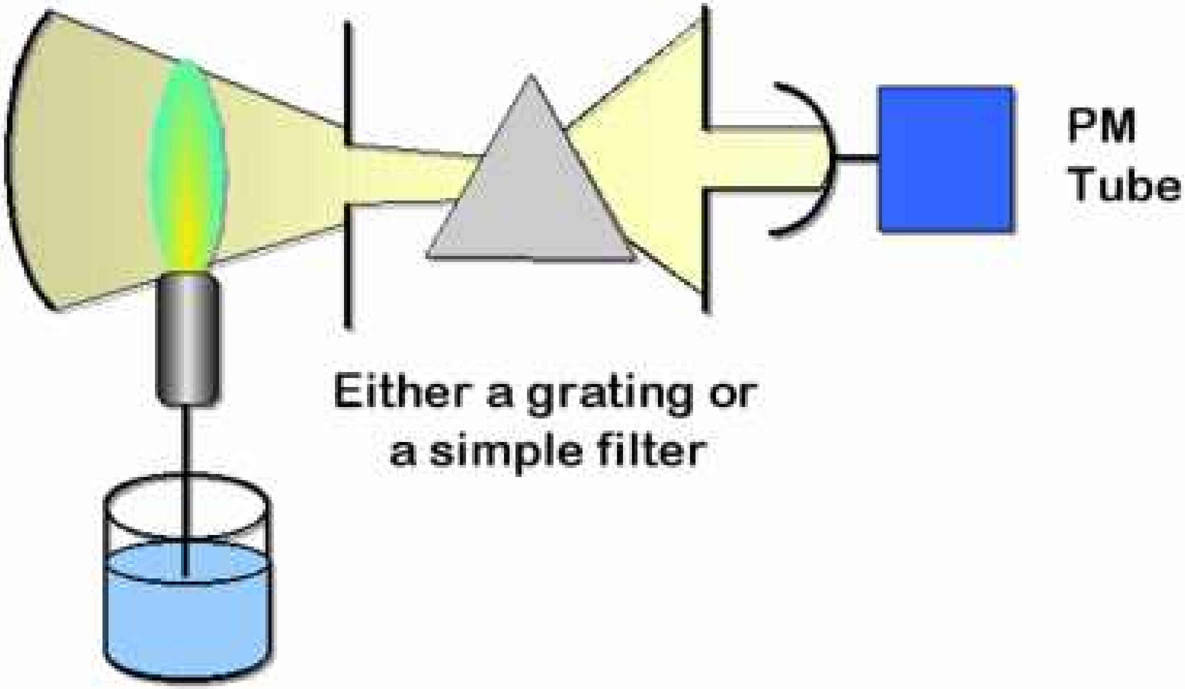
Flame excitation

This method of excitation is of relative low temperature:

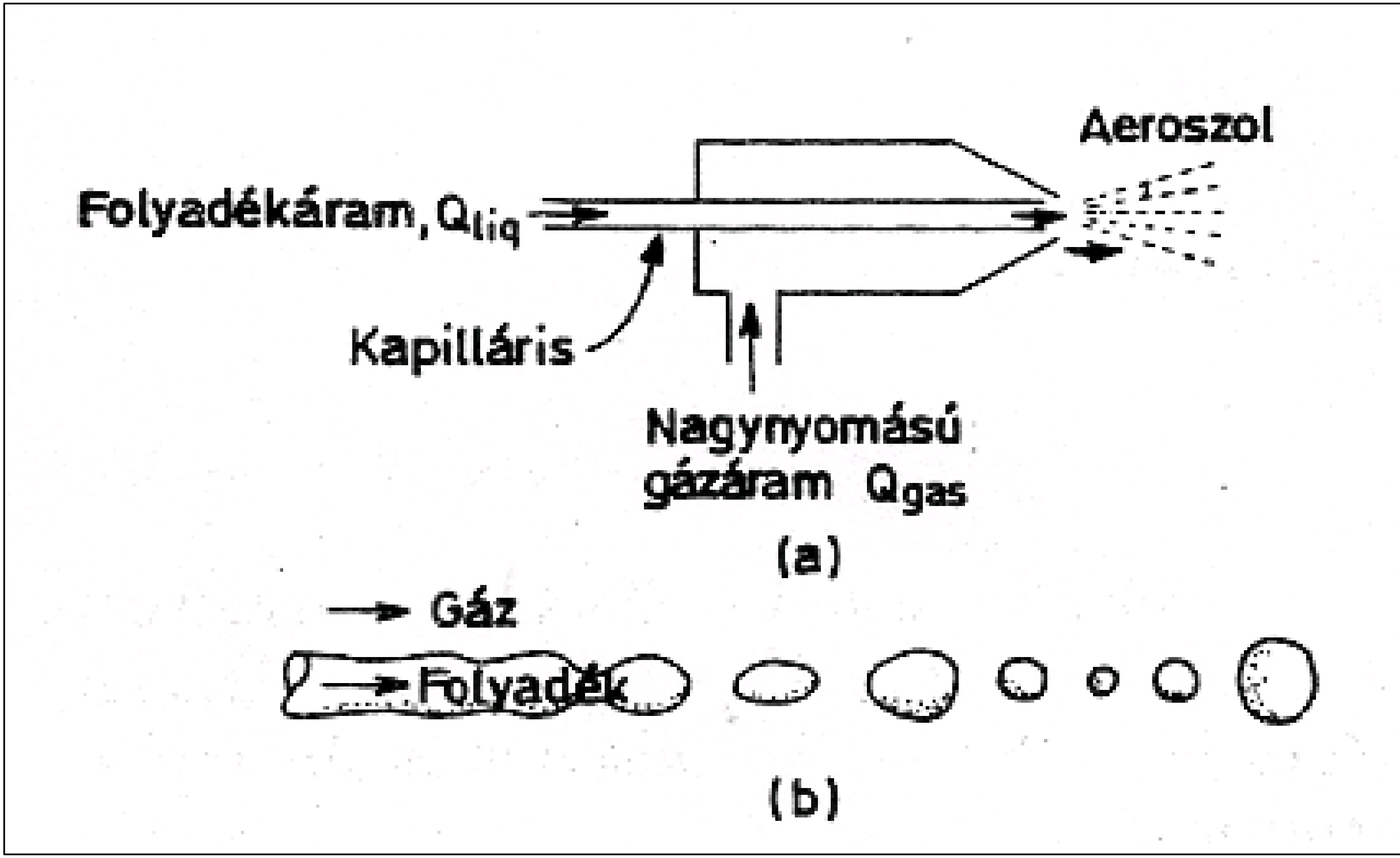
Air/H_2	2100°C
O_2/H_2	2700°C
N_2O/C_2H_2	3050°C

This results in only a very small percentage of the atoms being ionized (<1%). One option is to go to higher T - Plasma emission.

Flame photometer



II. porlasztás

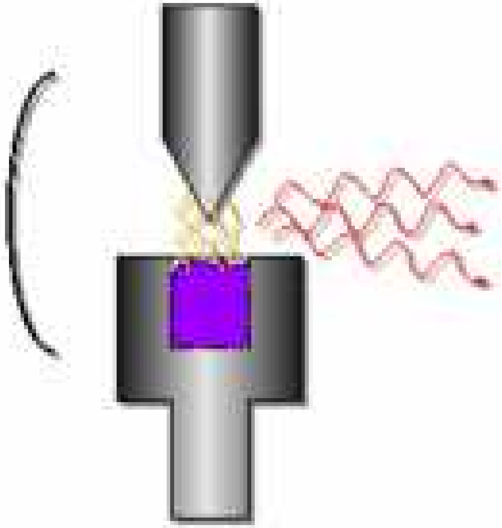


Hatásfoka általában 1-5%

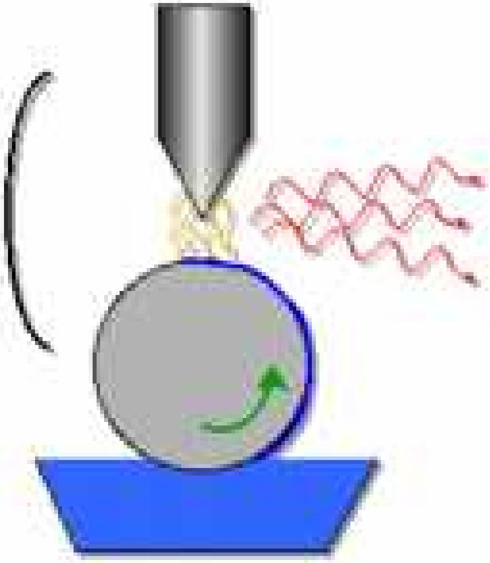
Excitation Sources

Electrical

The arrangement of the electrodes is based on the state of the sample.



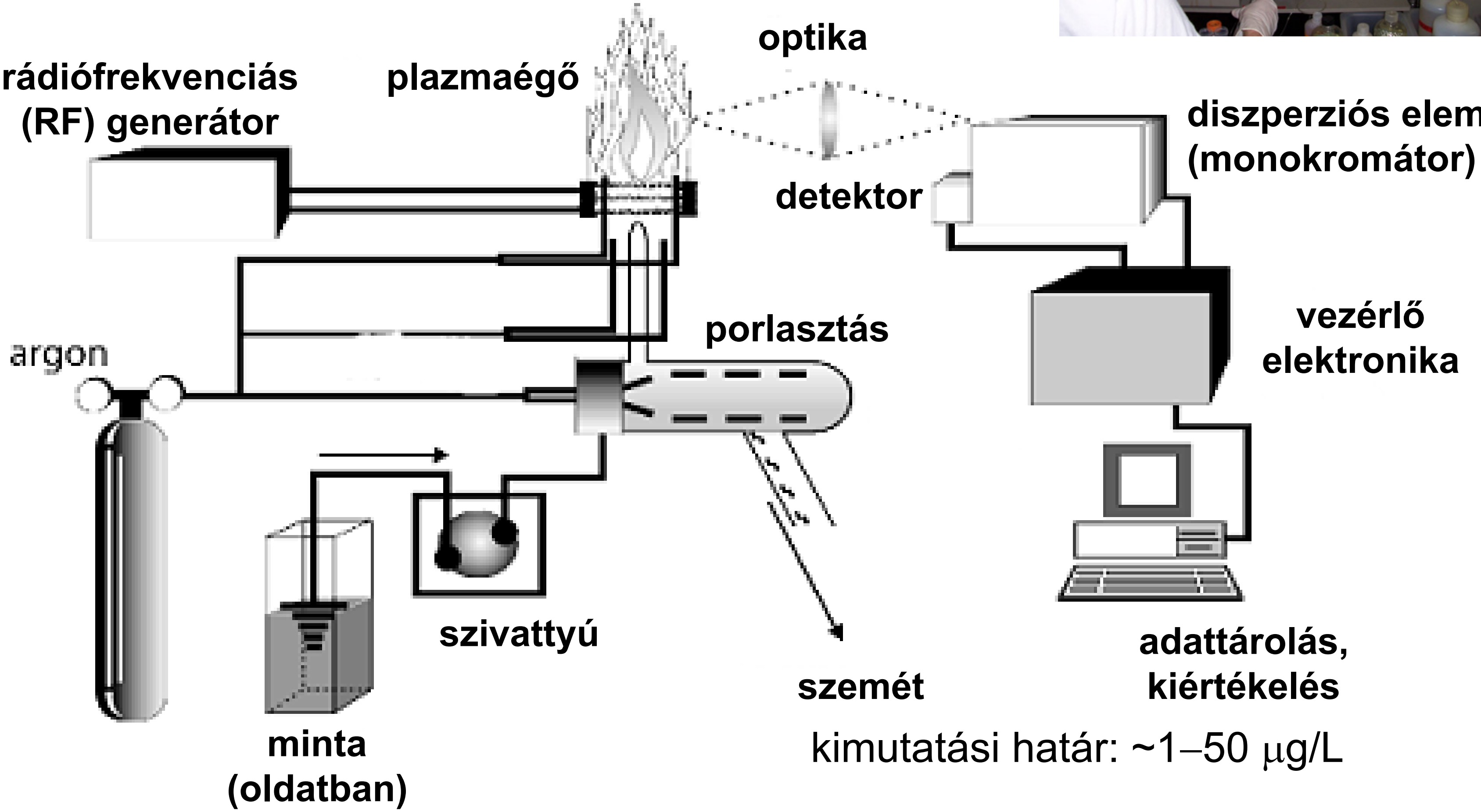
solids



liquids

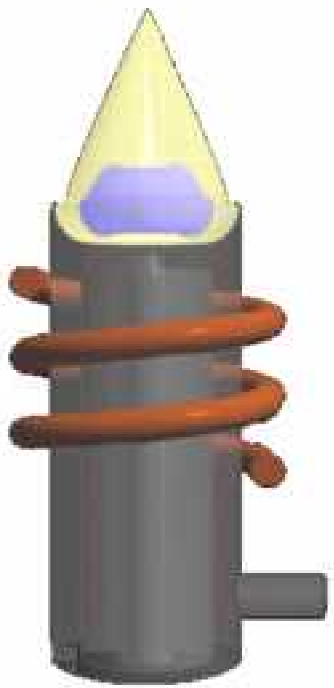
Atomi emissziós spektroszkópia (AES)

Egyik leggyakrabban alkalmazott technika:
Induktívan csatolt plazma (ICP) spektroszkópia



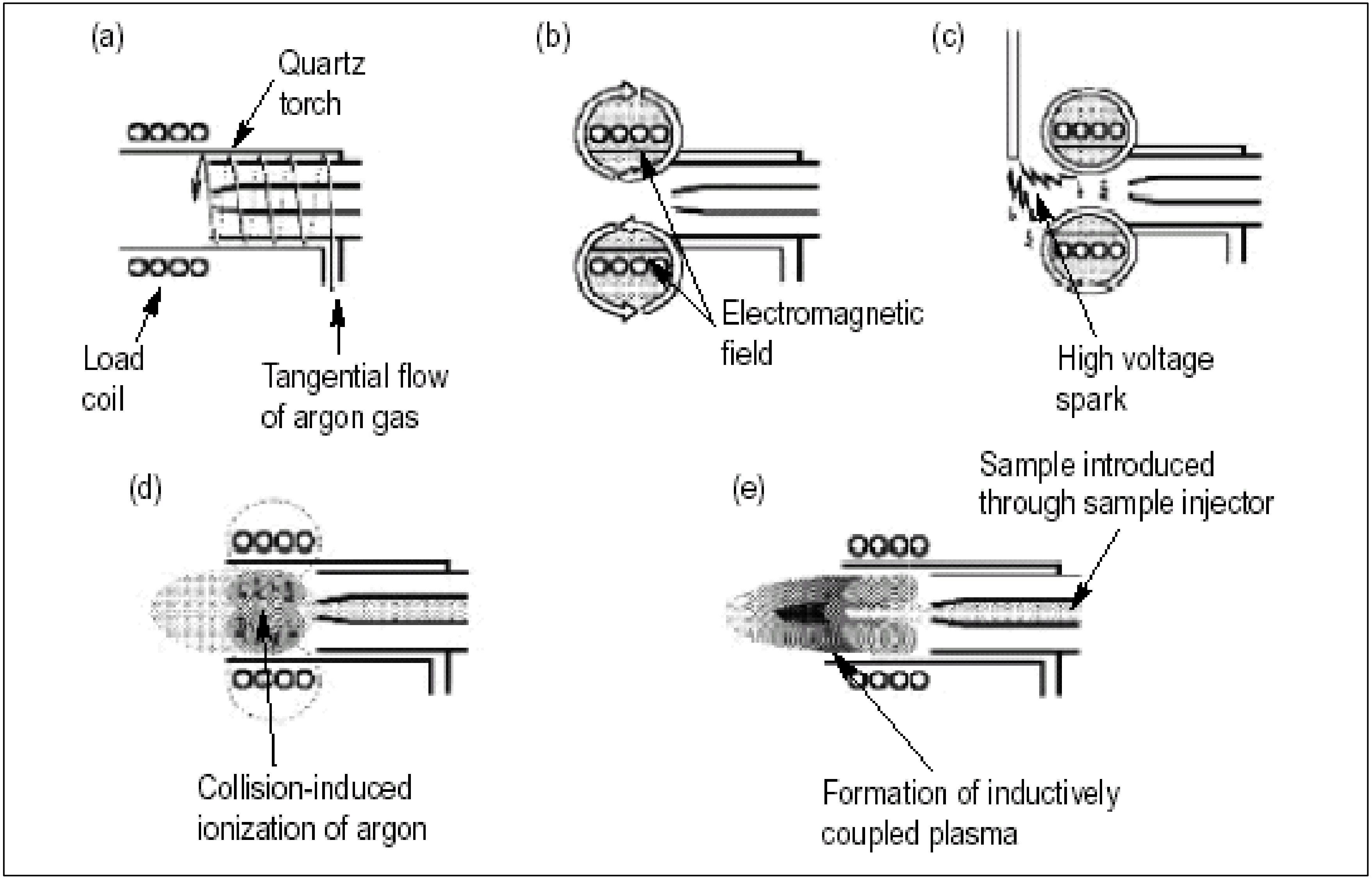
kimutatási határ: ~1–50 μg/L

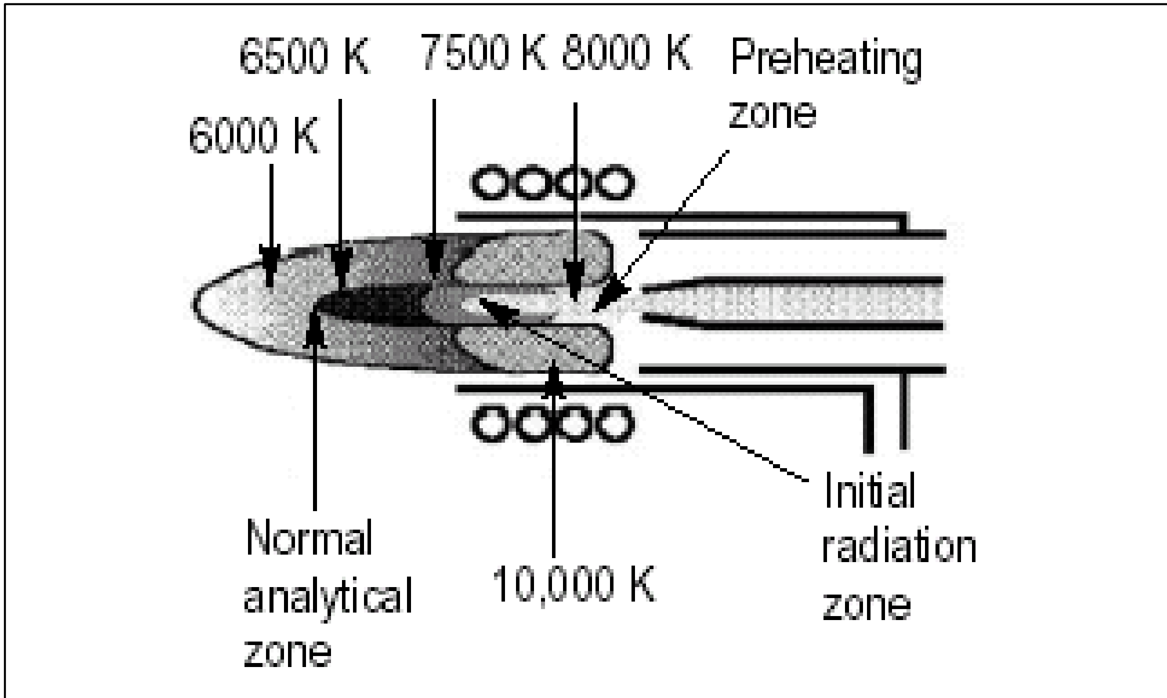
Excitation Sources

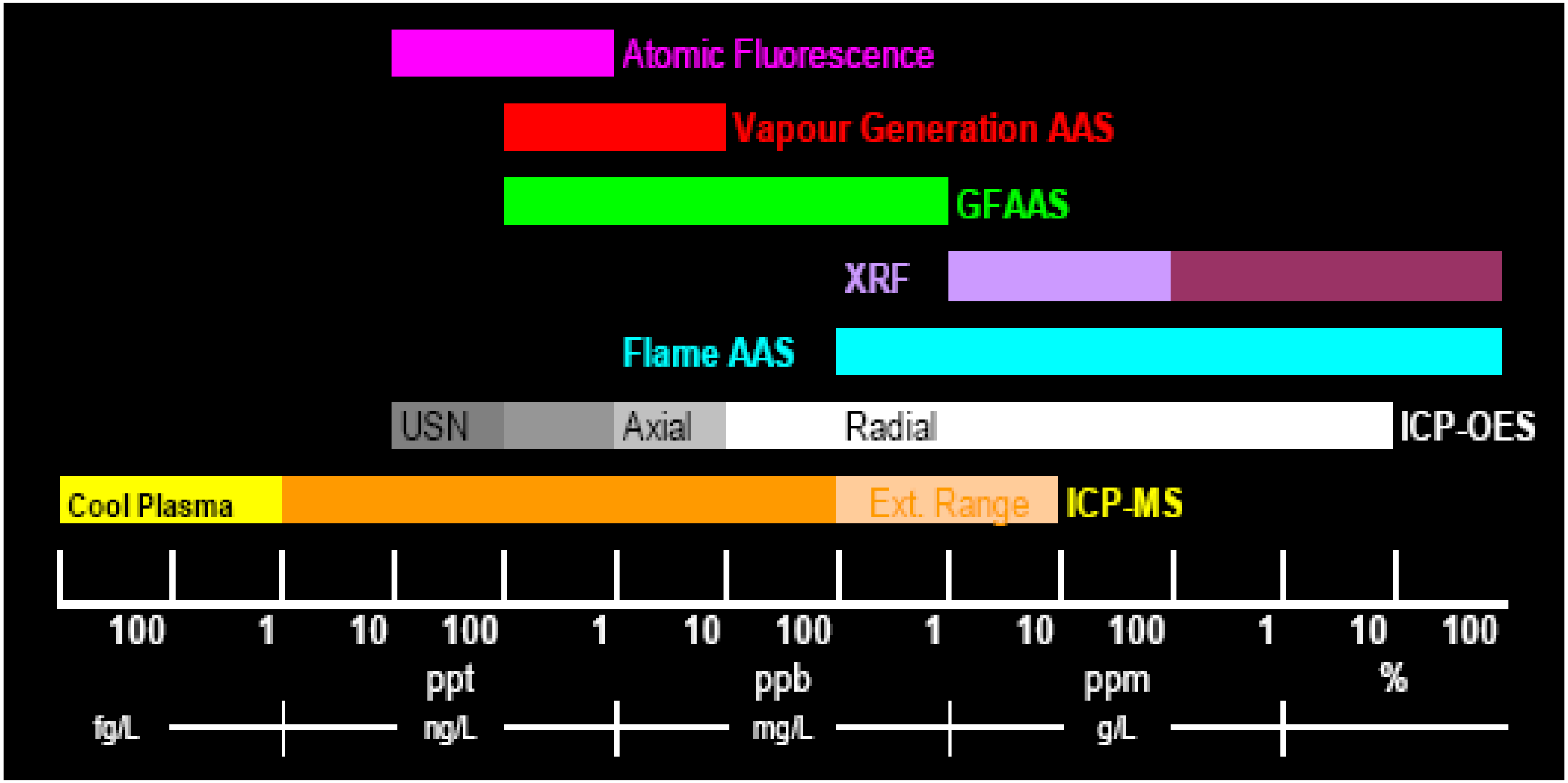


Inductively coupled
plasma source
(ICP)

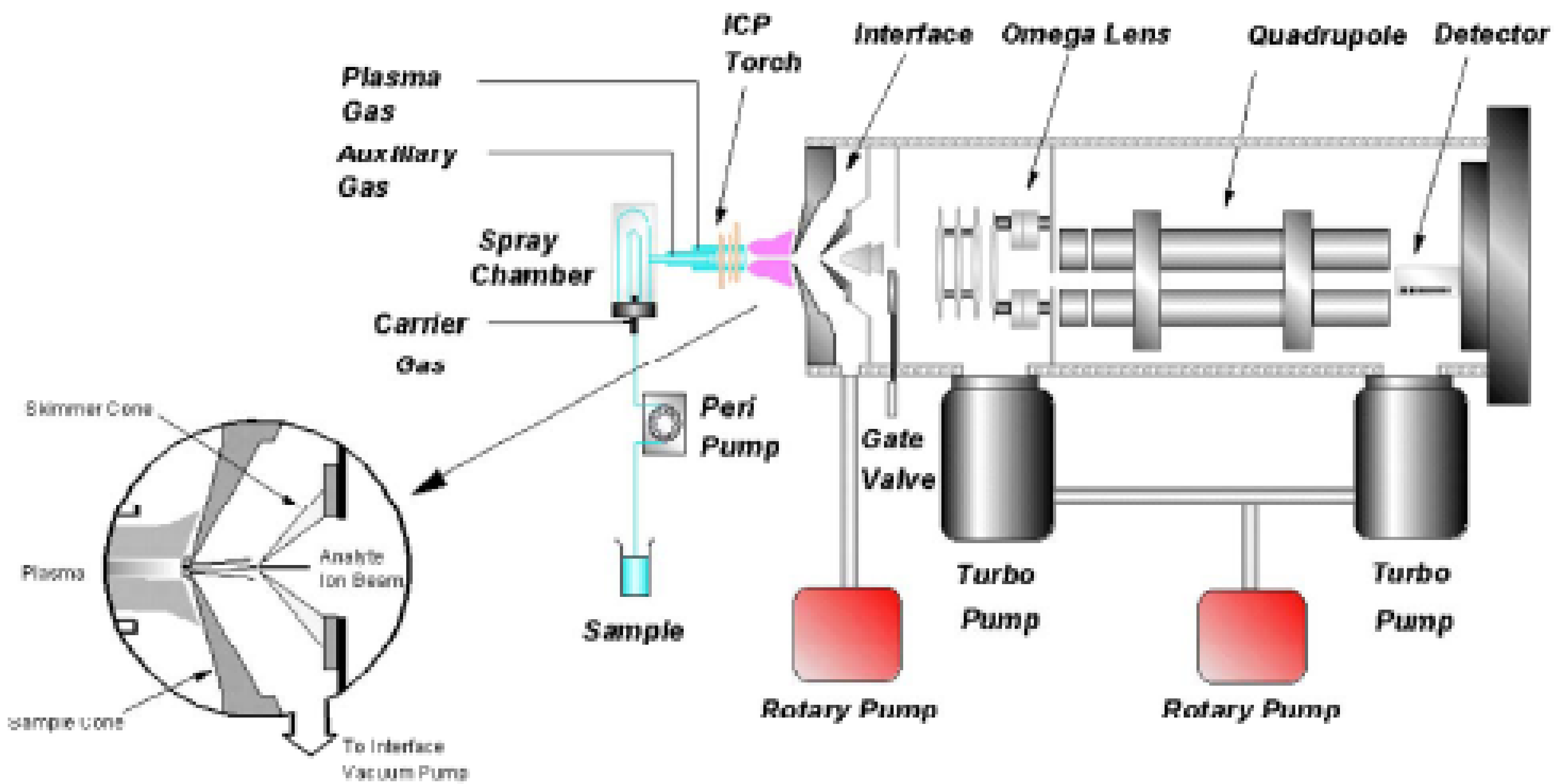
A plazma kialakulása




6500 K
7500 K
8000 K
Preheating zone
6000 K
Normal analytical zone
10,000 K
Initial radiation zone

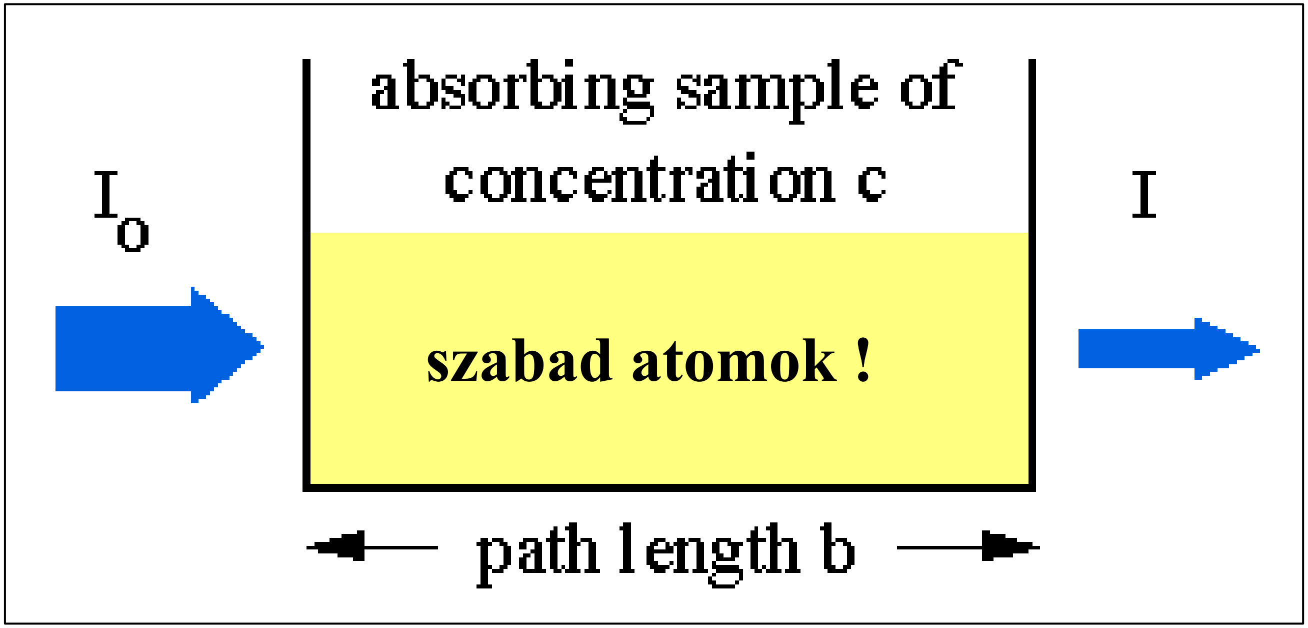


Atomic Fluorescence
Vapour Generation AAS
GFAAS
XRF
Flame AAS
USN
Axial
Radial
ICP-OES
Cool Plasma
Ext. Range
ICP-MS
100 1 10 100 1 10 100 1 10 100 1 10 100
ppt
ppb
ppm
%
fg/L
ng/L
mg/L
g/L



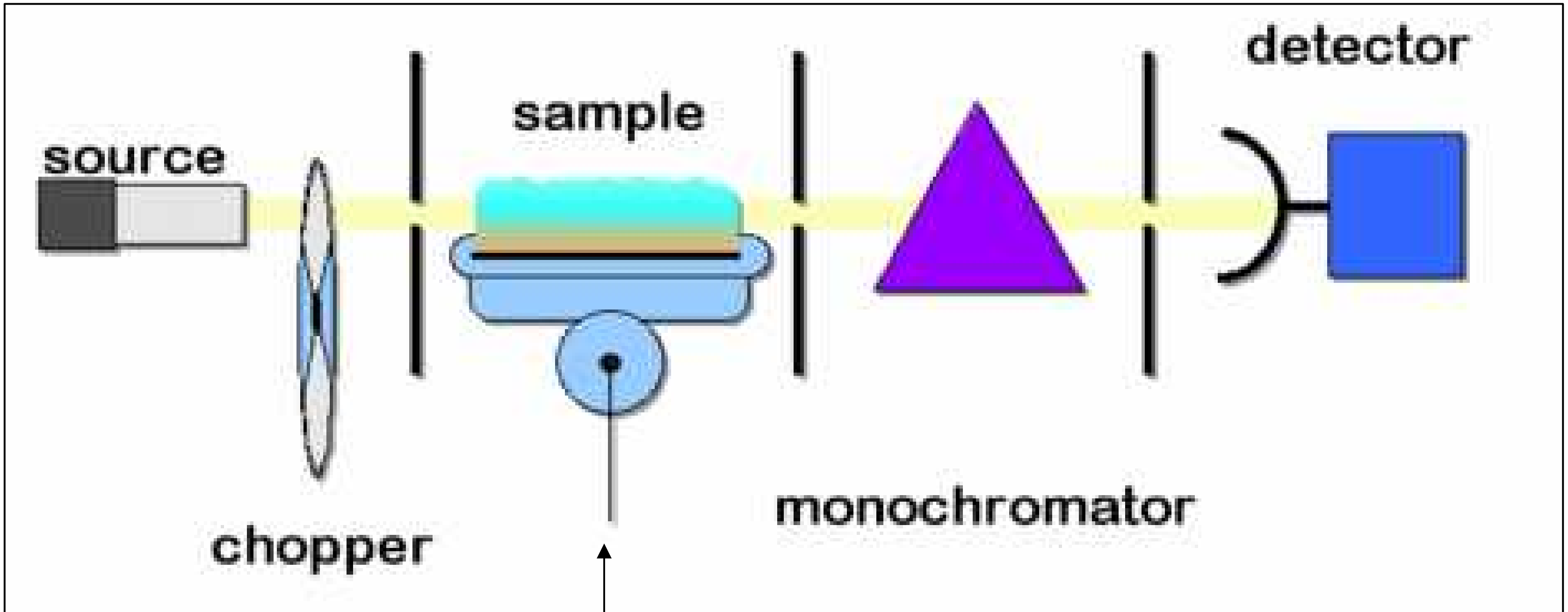
ICP Torch
Interface
Omega Lens
Quadrupole
Detector
Plasma Gas
Auxiliary Gas
Spray Chamber
Carrier Gas
Peri Pump
Gate Valve
Sample
Turbo Pump
Turbo Pump
Rotary Pump
Rotary Pump
Skimmer Cone
Plasma
Analyte Ion Beam
Sample Cone
To Interface Vacuum Pump

Abszorpciós módszerek



$$A = \lg\frac{I_0}{I} = \varepsilon \cdot l \cdot c$$

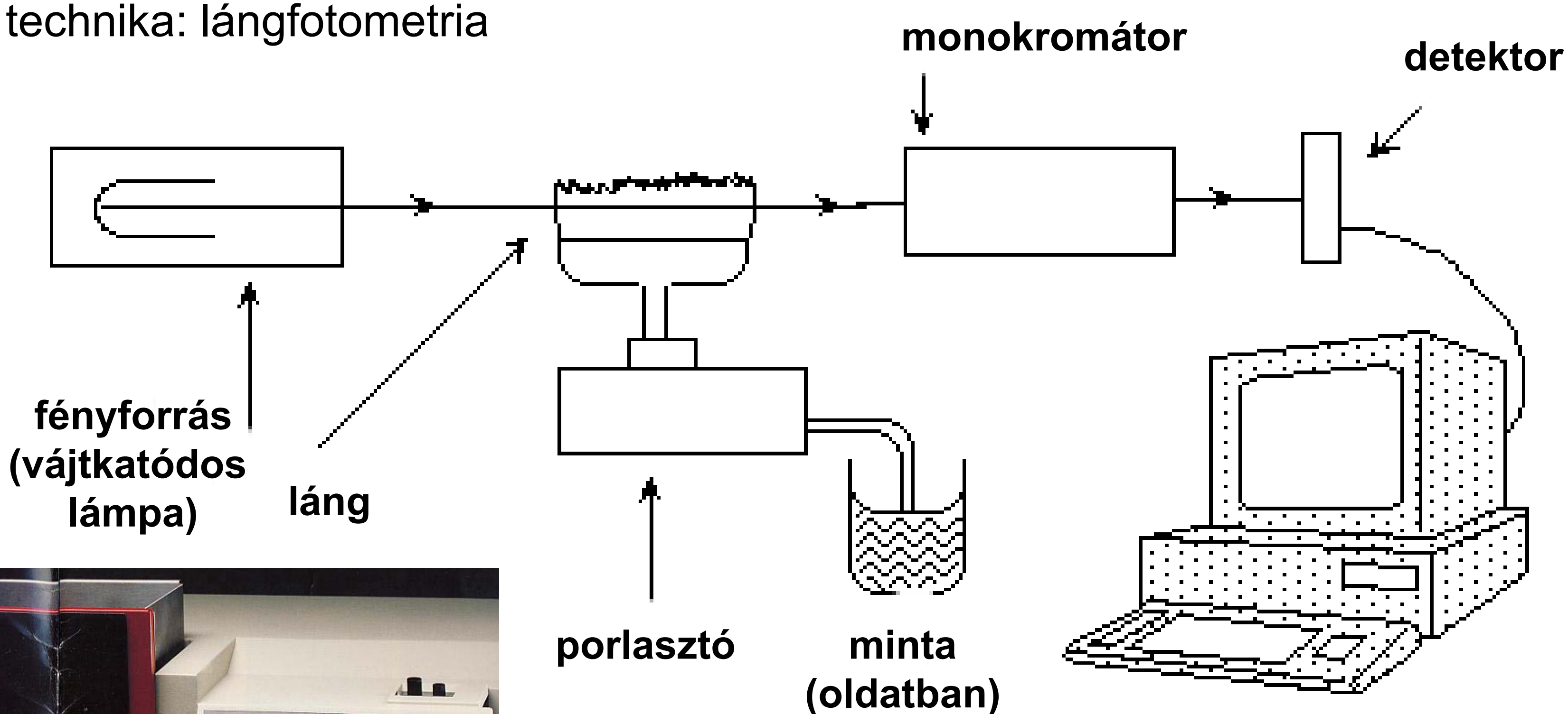
Láng-atomabszorpciós készülék

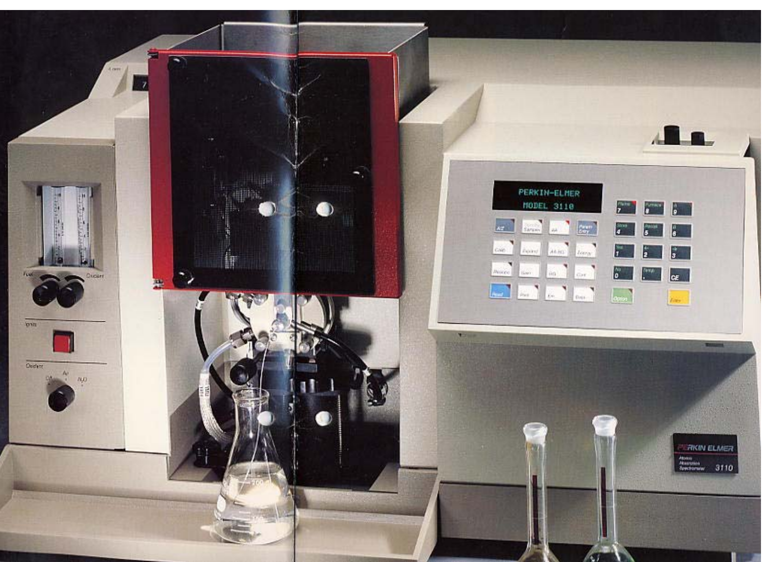


Minta (oldat)

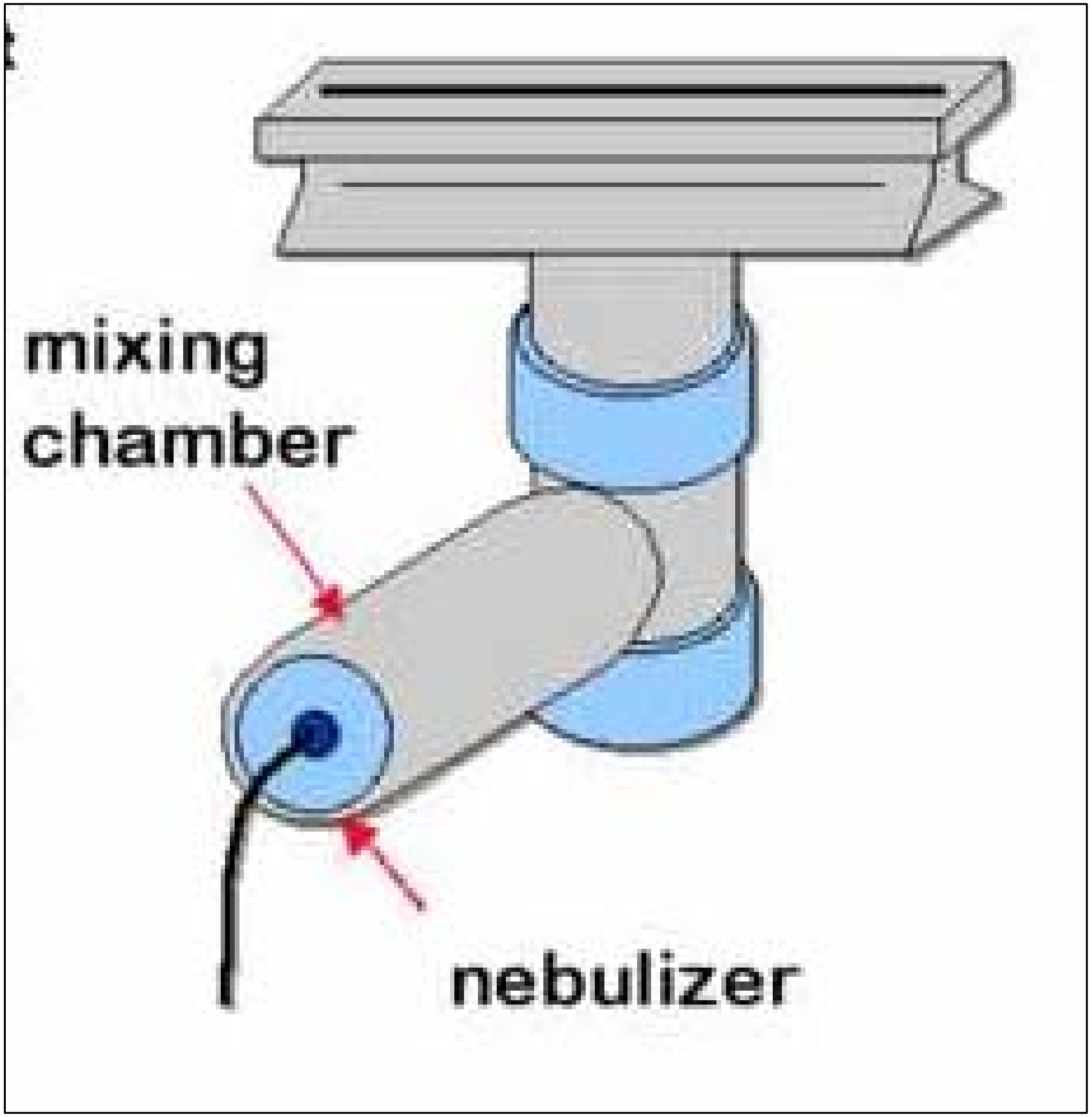
Atomi abszorpciós spektroszkópia (AAS)

Egyik technika: lángfotometria

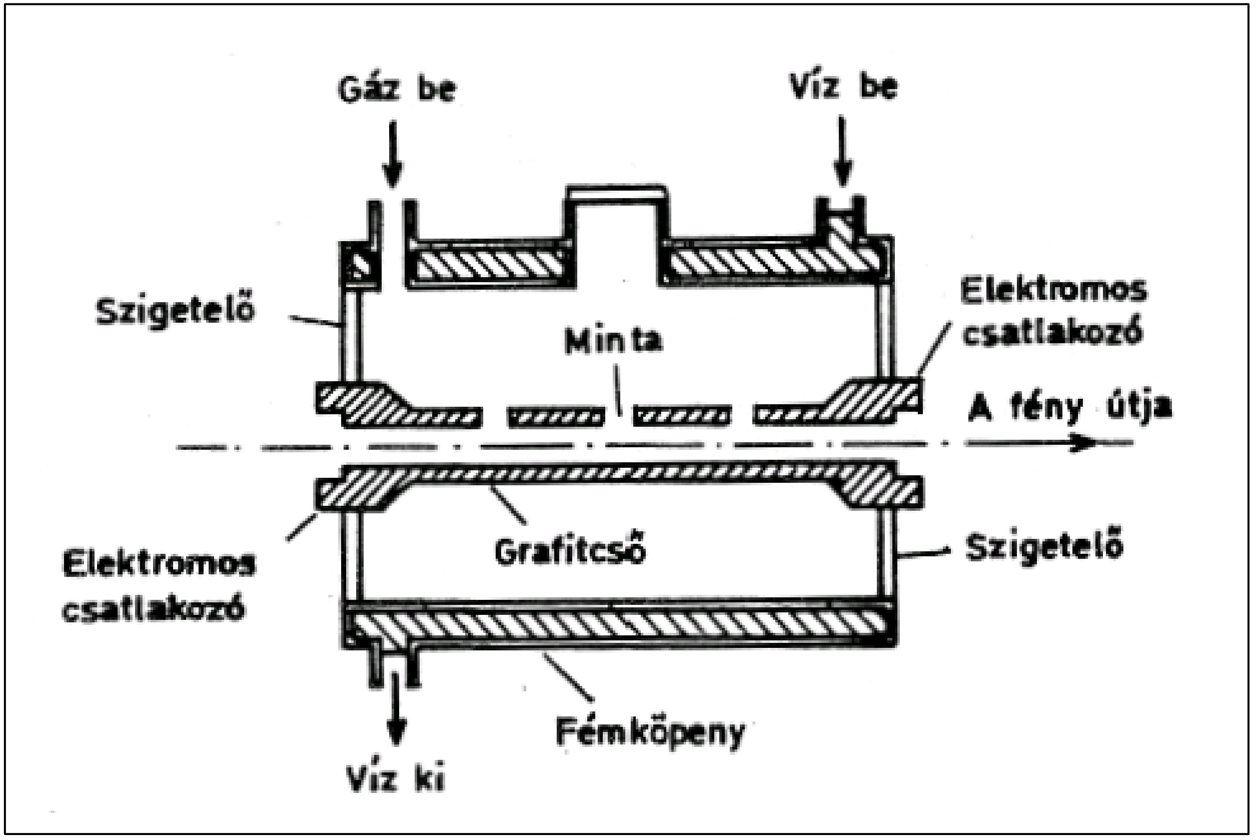


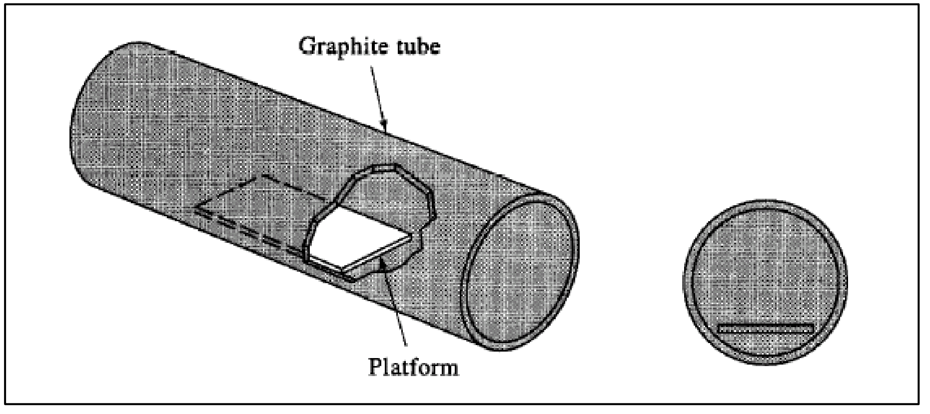


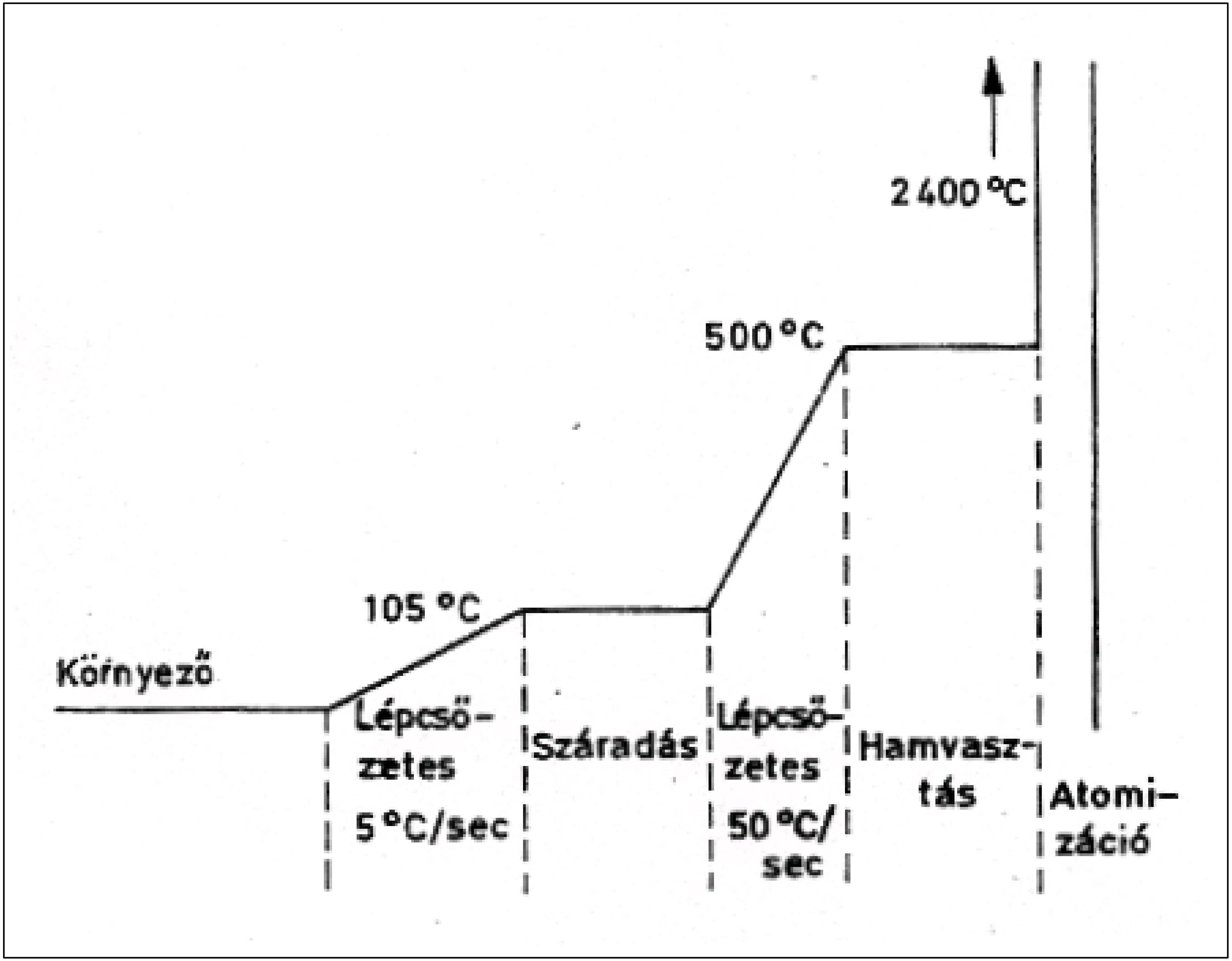
Láng-atomabszorpciós égő



Grafitkemencés atomizálás

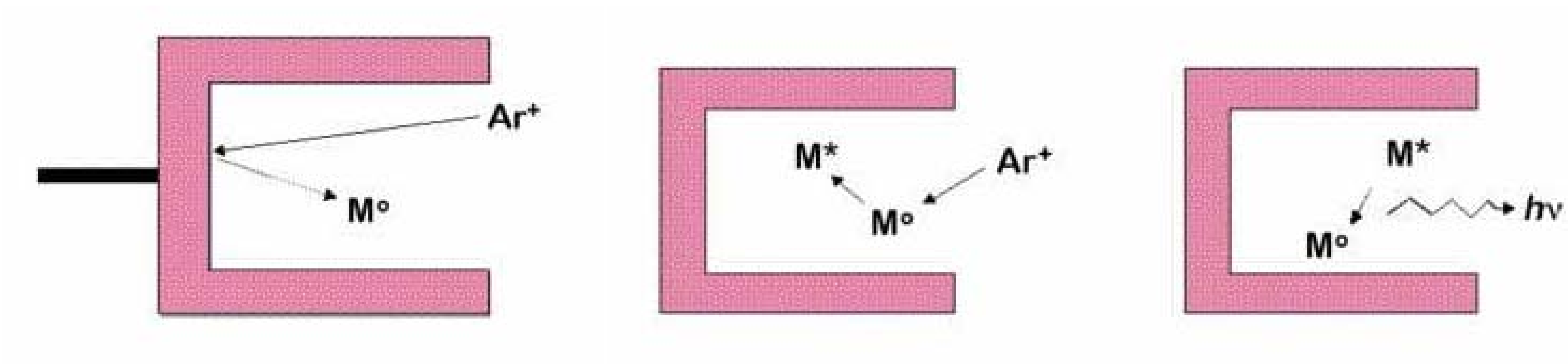


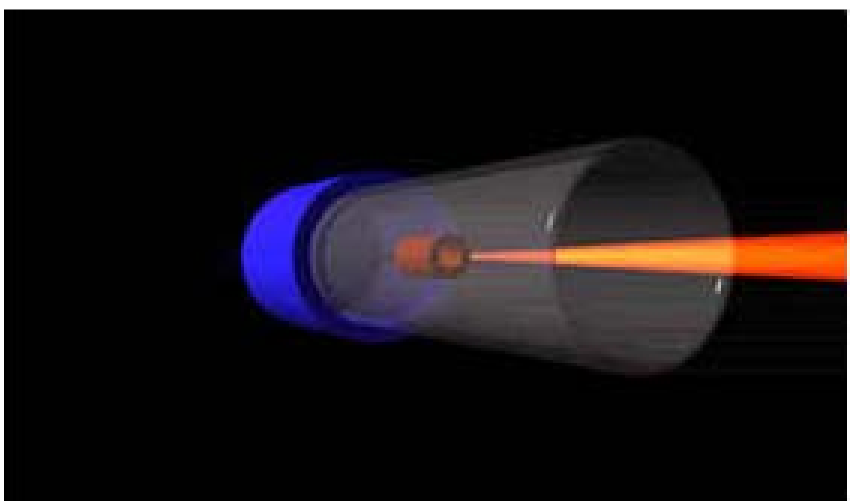


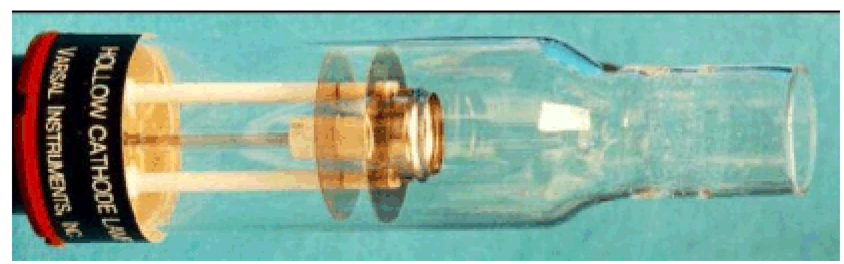

2400 °C
500 °C
105 °C
Környező
Lépcsö-
zetes
5 °C/sec
Száradás
Lépcsö-
zetes
50 °C/
sec
Hamvasz-
tás
Atomi-
záció

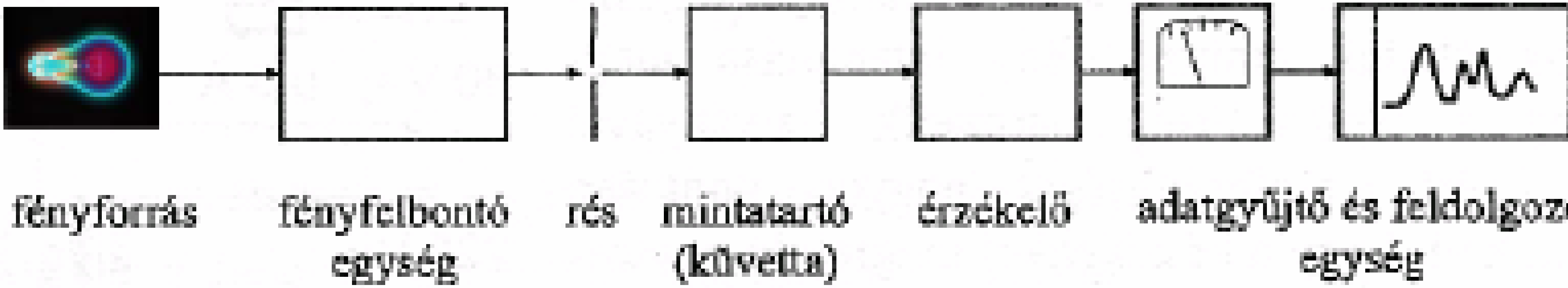
vájt katód llámpa (hollow cathode lamp)

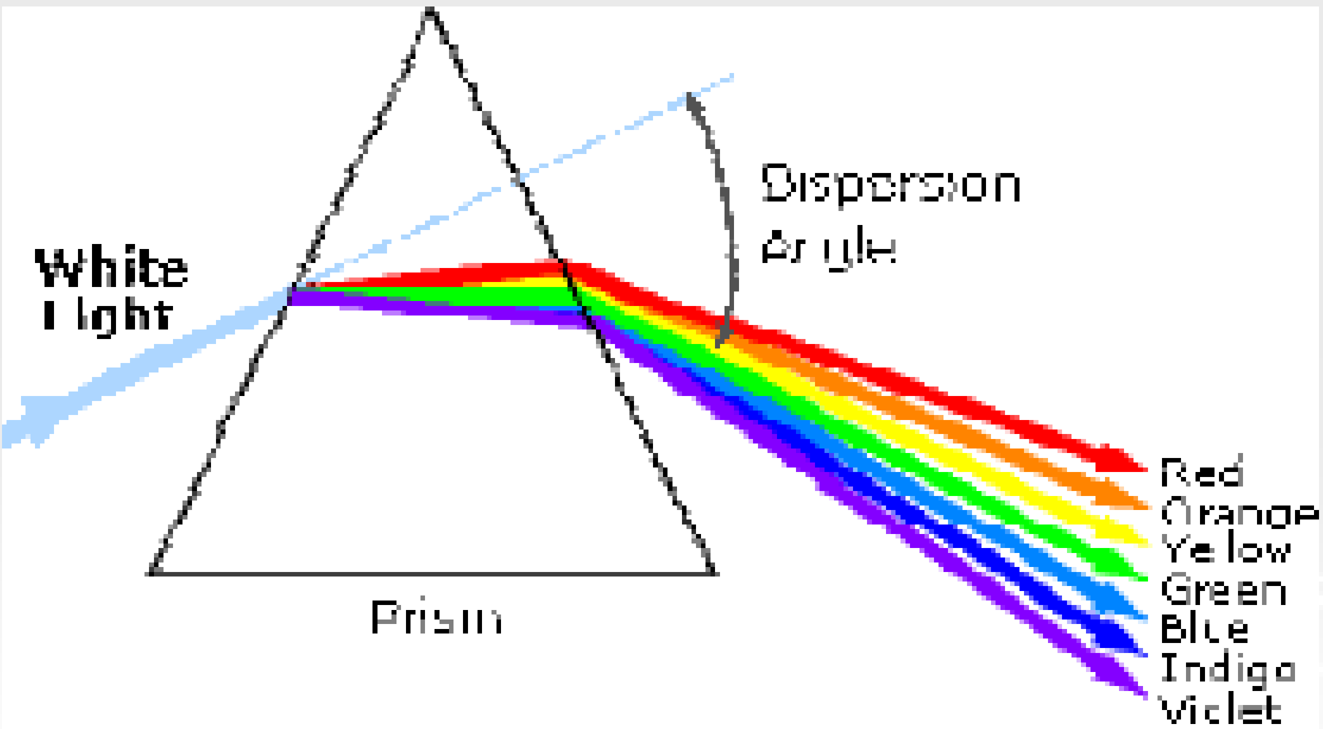
I. **II.** **III.**





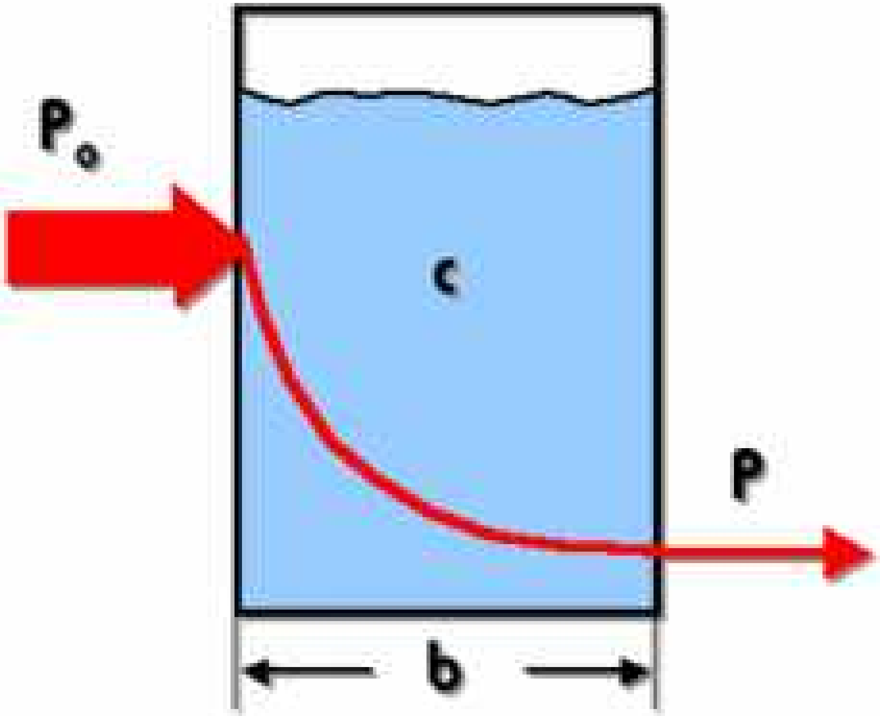



fényforrás
fényfelbontó egység
rés
mintatartó (küvetta)
érzékelő
adatgyűjtő és feldolgozó egység


White Light
Dispersion Angle
Prism
Red
Orange
Yellow
Green
Blue
Indigo
Violet

Quantitative Analysis

$\frac{P}{P_o}$ is a measure of the light that passes through the solution - transmitted



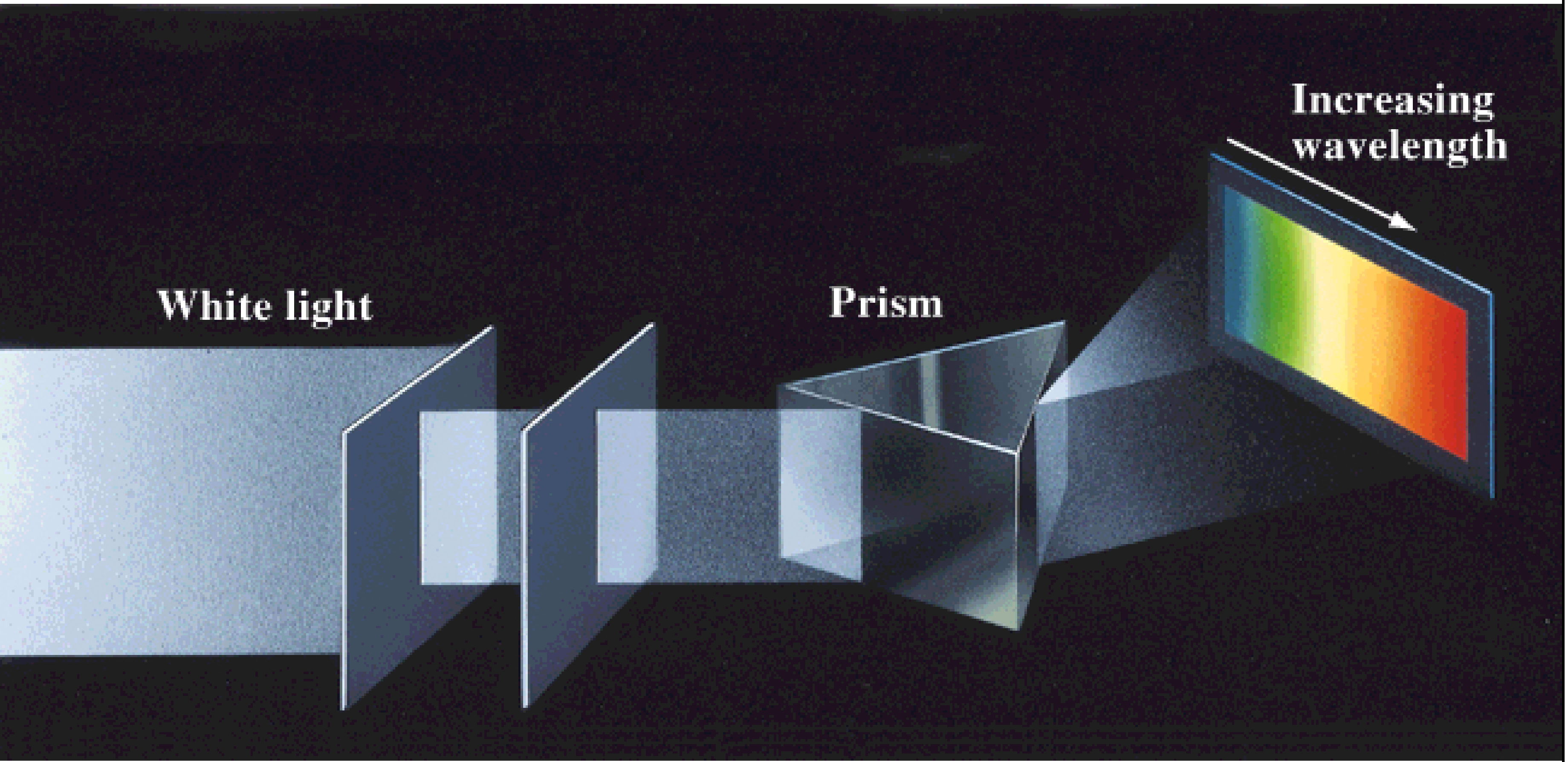
$\frac{P}{P_o}$ is also called the transmittance (T)

$-\log(T) = A$

A - absorbance

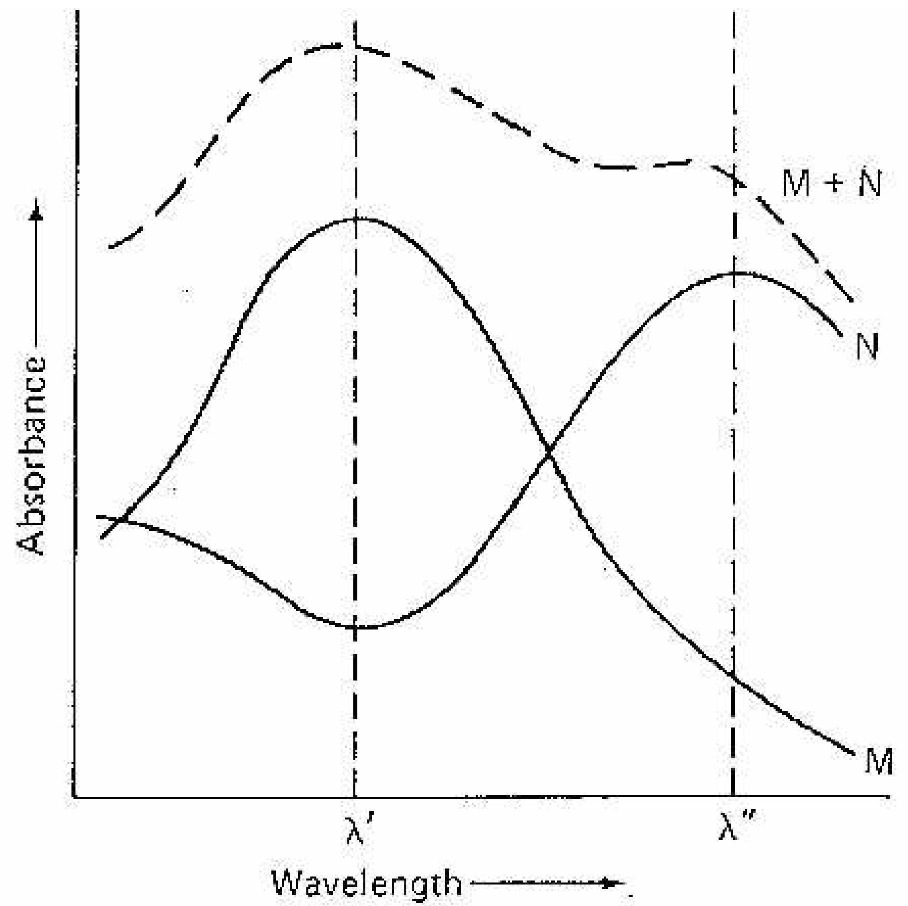
$A = abc$

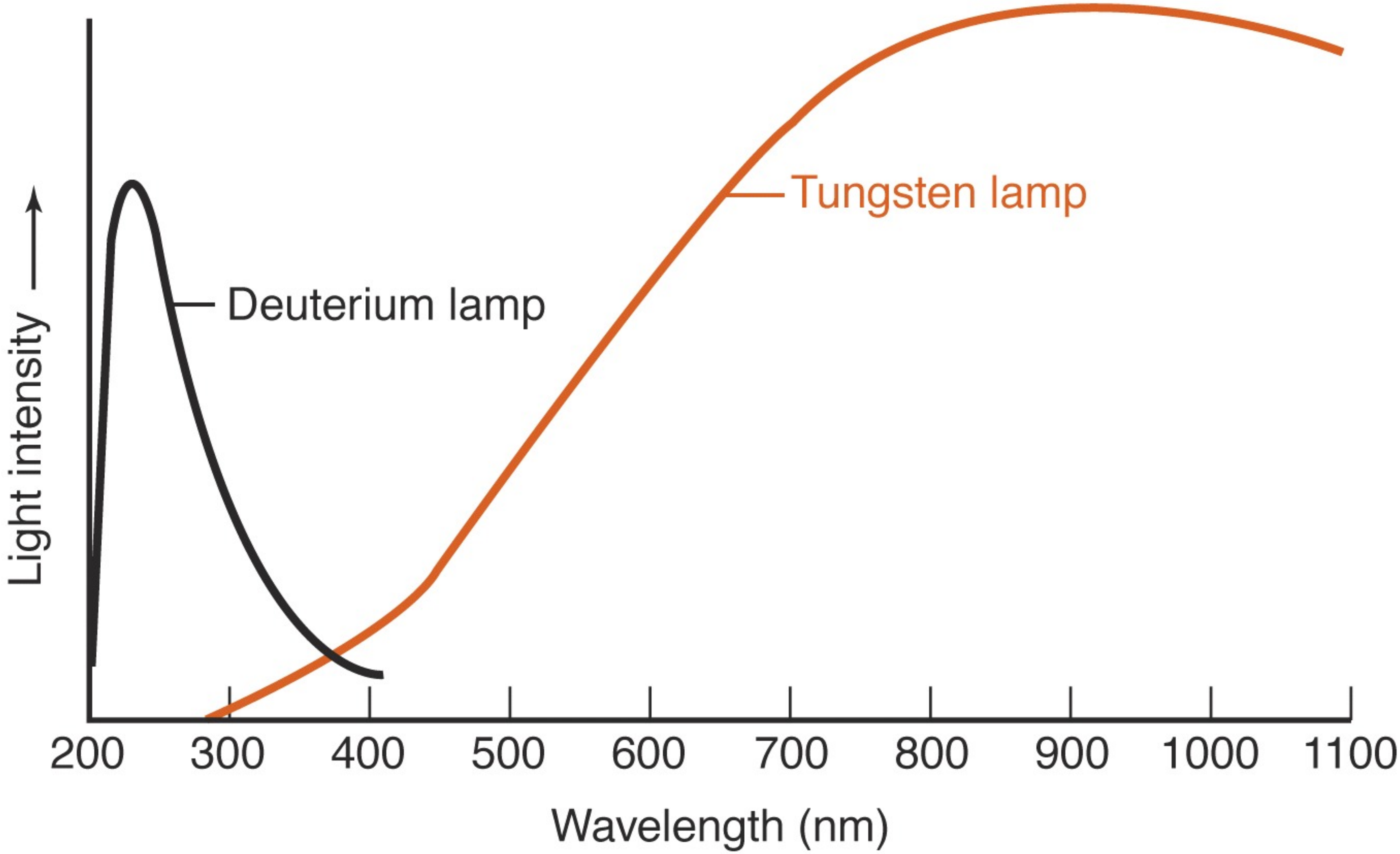
A spectrum of white light



Analysis of Mixtures of Absorbing Substances

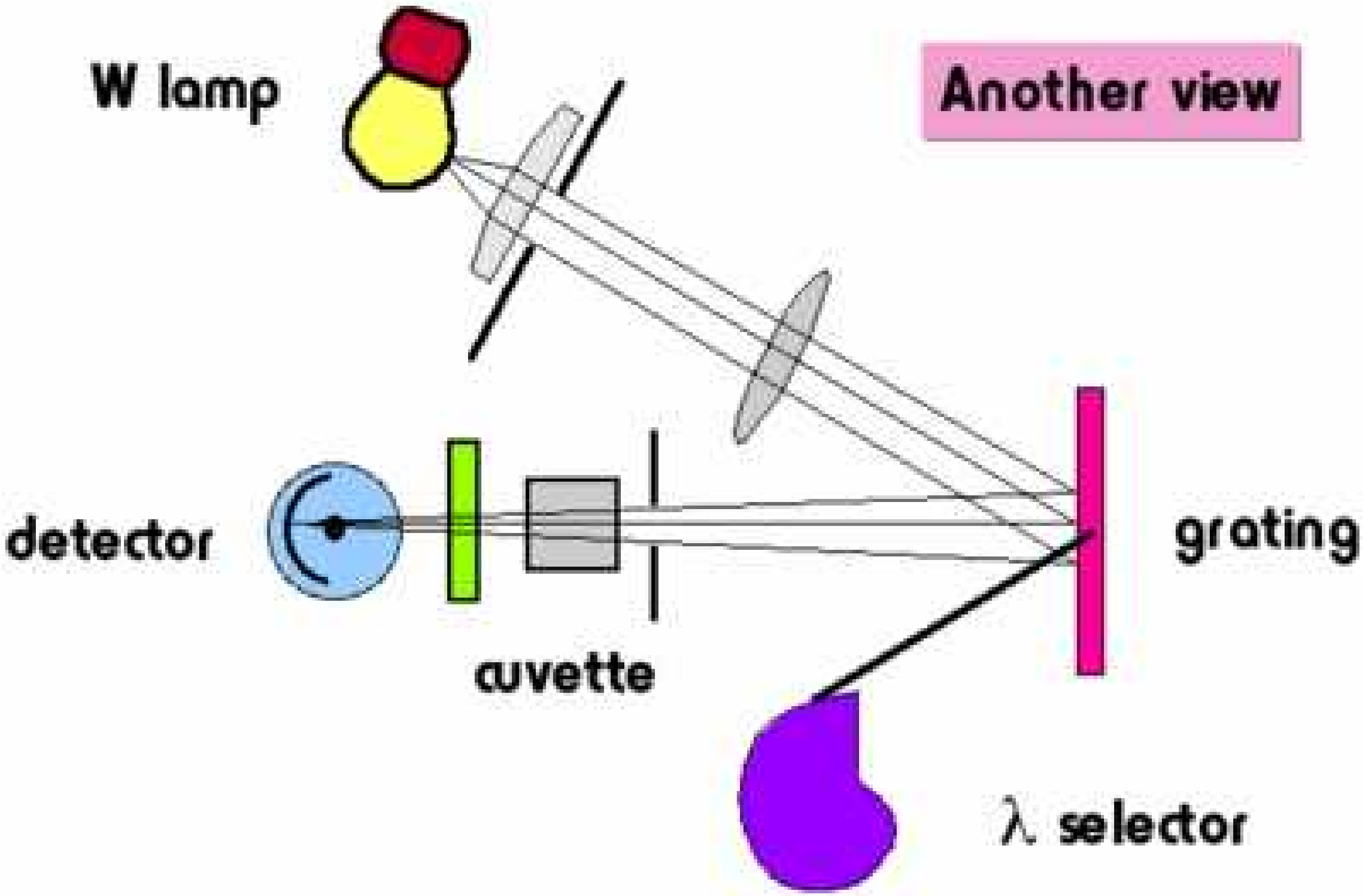
- Selection of Wavelength
- Fig. 14-14, pg. 345 "Absorption spectrum of a two-component mixture."





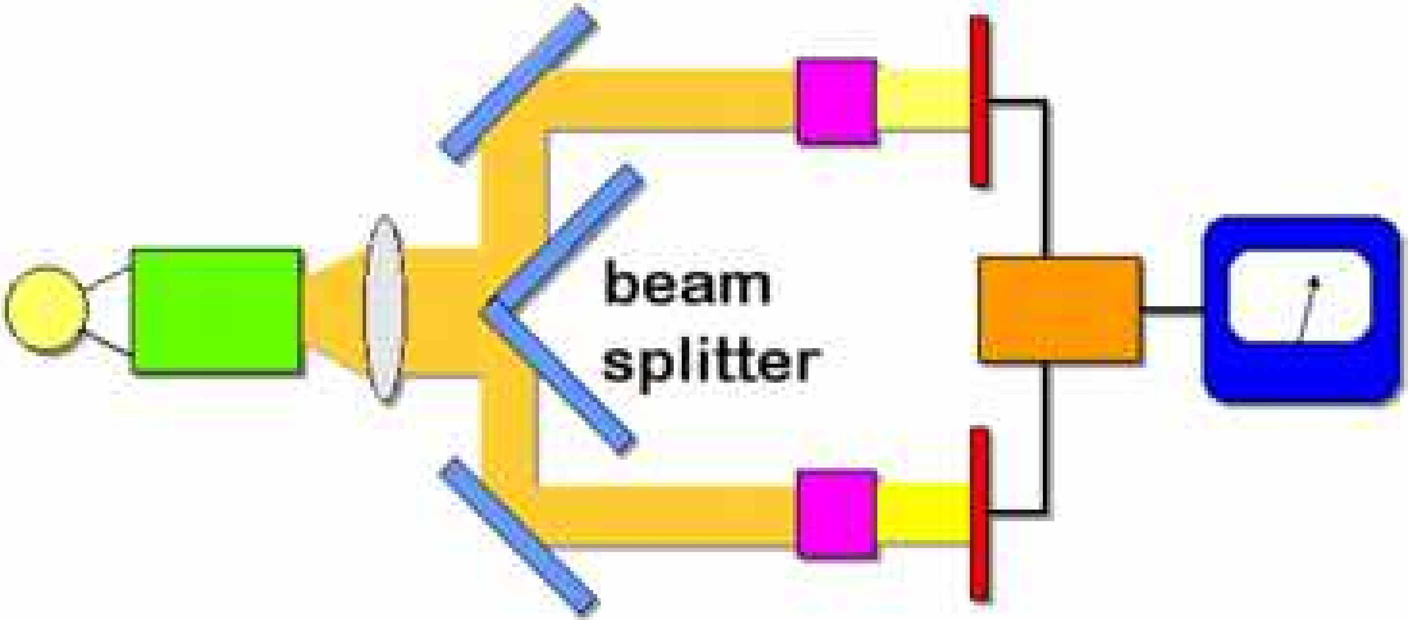
Light intensity
Deuterium lamp
Tungsten lamp
200
300
400
500
600
700
800
900
1000
1100
Wavelength (nm)

Single beam spectrophotometer

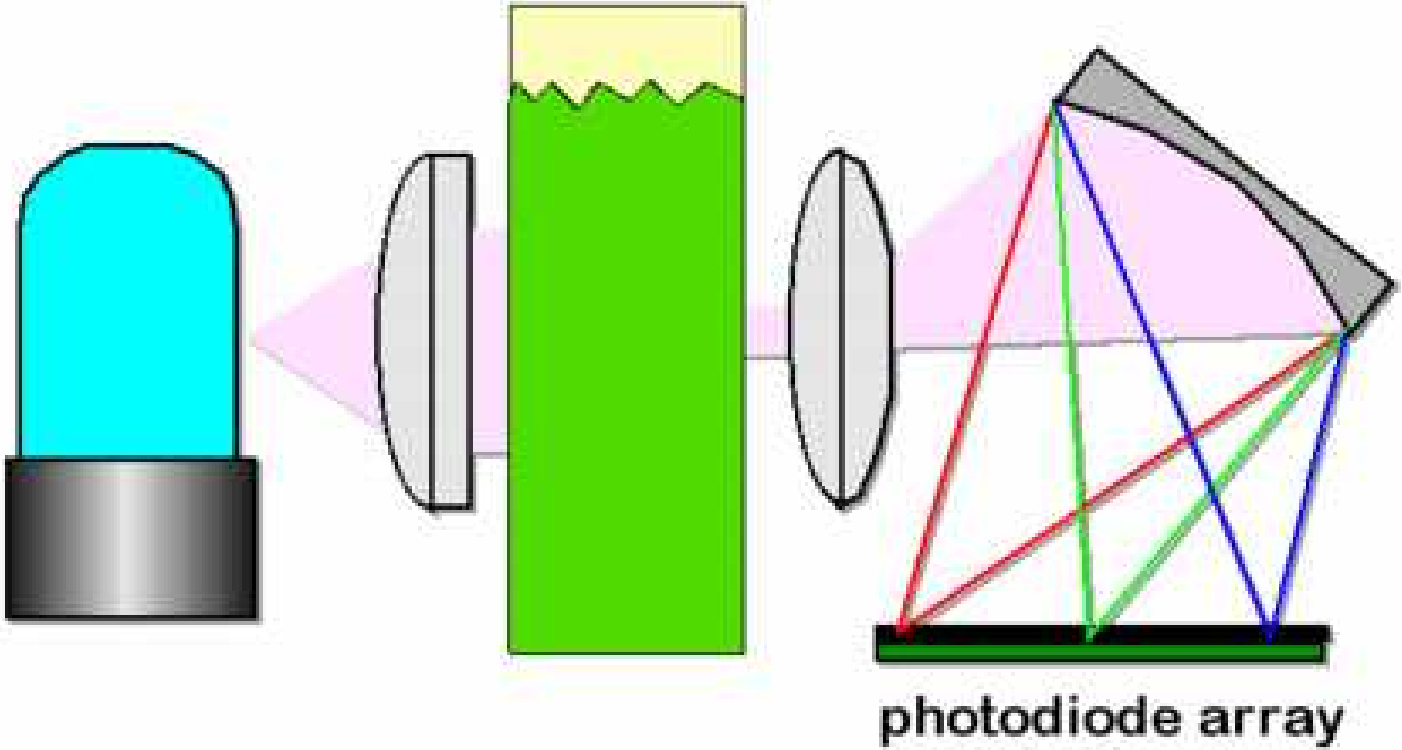


Double beam spectrophotometer

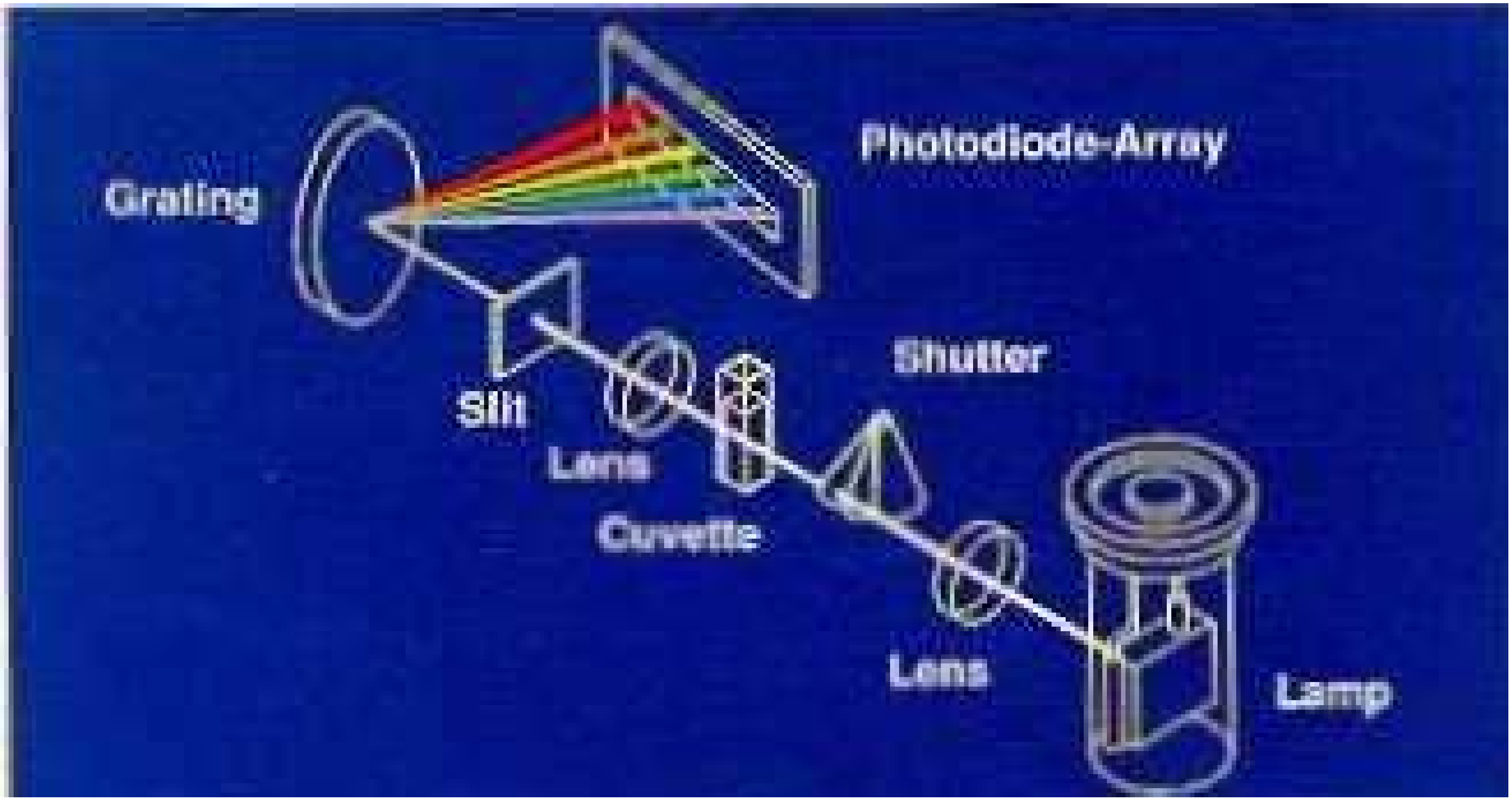
Double beam in space.

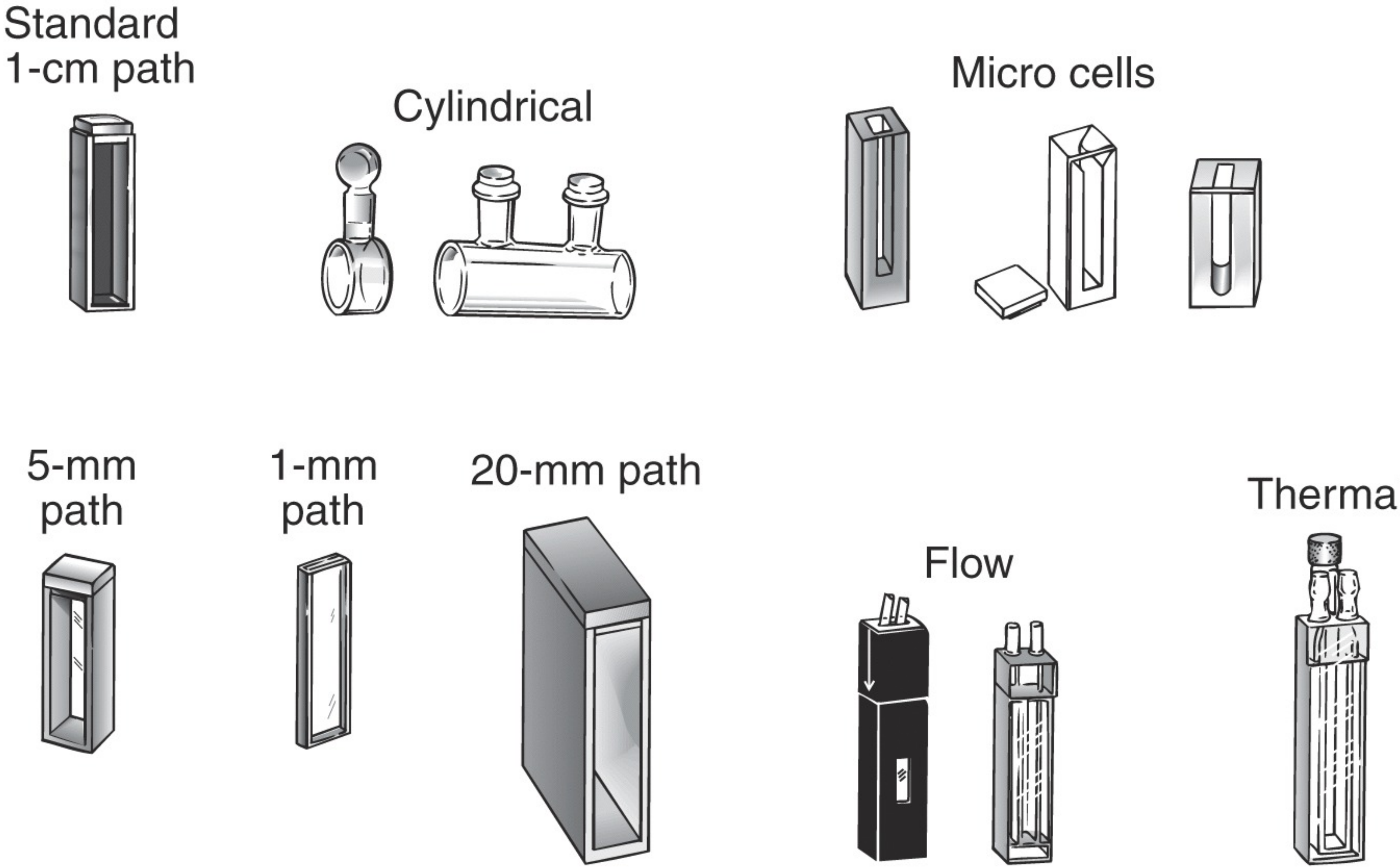


Multichannel spectrophotometers



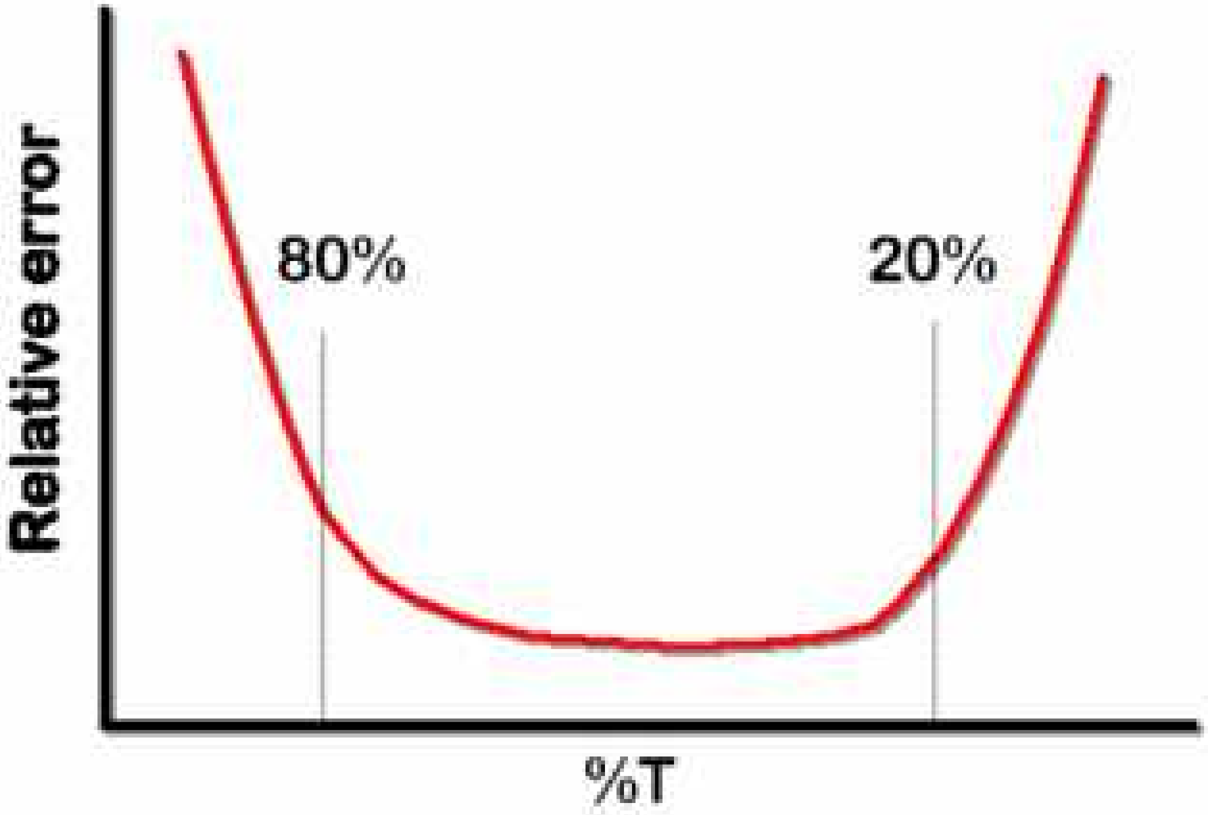
HP 8452a


Photodiode-Array
Grating
Shutter
Slit
Lens
Cuvette
Lens
Lamp


Standard
1-cm path
Cylindrical
Micro cells
5-mm
path
1-mm
path
20-mm path
Flow
Thermal

Measuring absorbance.

Relative error vs. %T



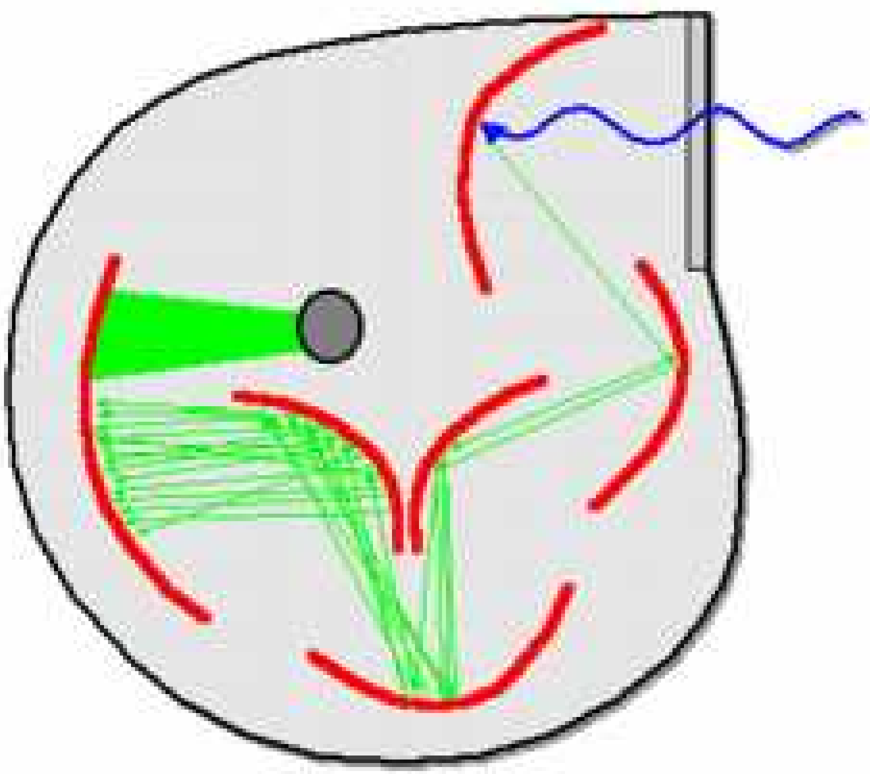
Detectors

PM Tube

A single electron is ejected at the conversion dynode.

Subsequent dynodes are ~90V more positive which results in the e⁻ being accelerated and ejecting additional electrons.

Amplifications of 10^6-10^7 are obtained.



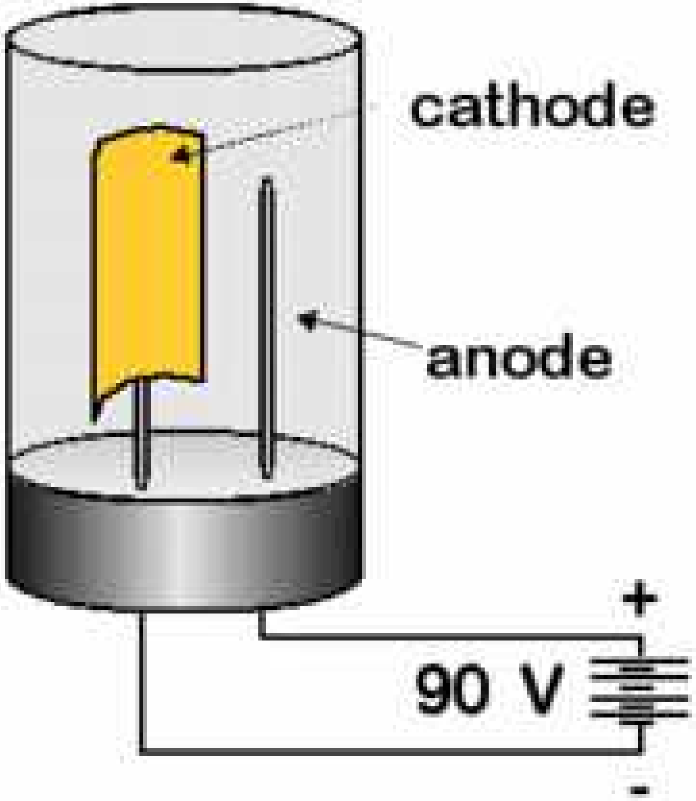
Detectors

Phototube Works via the photoelectric effect.

A photon hits the cathode which is covered with a photoemissive surface.

You get a current that is proportional to the intensity of the photons.

Tubes are subject to a small 'dark current' due to thermal effects.



ELEKTROKÉMIA

A határfelületen az egyensúlyi potenciál

$$\mu^0_{M^{2+}} + RT * \ln c_i - \mu^0_M = zF\varepsilon$$

Ahol: standard potenciál

R: egyetemes gázállandó (8,314 J/mol*K)

T: hőmérséklet (K)

z: töltés

F: Faraday állandó (96500 C/mol)

ε: elektród potenciál

Az oldat és a fém között létre jövő potenciál esés a konstansok összevonása és átrendezés után (és a fémion adatainak jelölésére mindenütt az i indexet használva):

ε = $\varepsilon^0 + \frac{RT}{z_i F} \ln c_i$ **Nernst egyenlet**

Walter Nernst

1864-1941

1920 Nobel-díj

$E=Eo+RT/nF \ln [ox]/[red]$

20°C-on

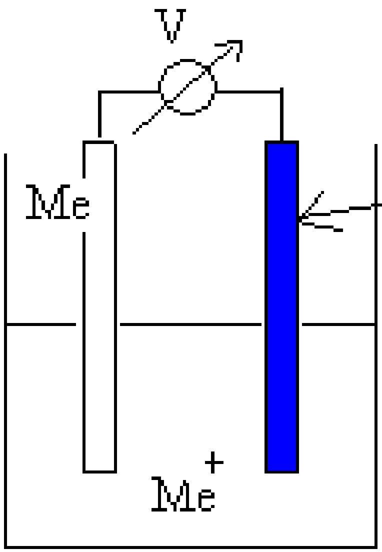
$E=Eo+0.058/n \lg [ox]/[red]$

$2H^+ + 2e^- = H_2$ $\qquad$ $Eo=0$

vagyis

$$E=RT/F \ln c_{H^+} = 0.058 \lg c_{H^+} = -0.058 \text{ pH}$$

Potenciálmérés



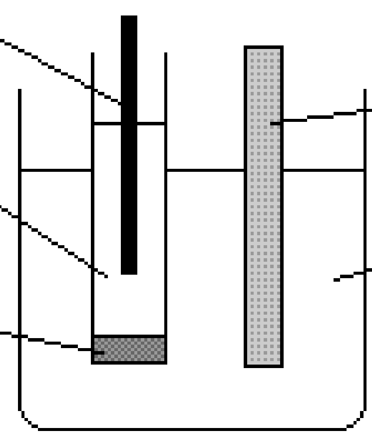
vonatkozási (vagy referencia) elektród potenciálja a mintától függetlenül állandó

Membránelektród

belső vonatkozási elektród

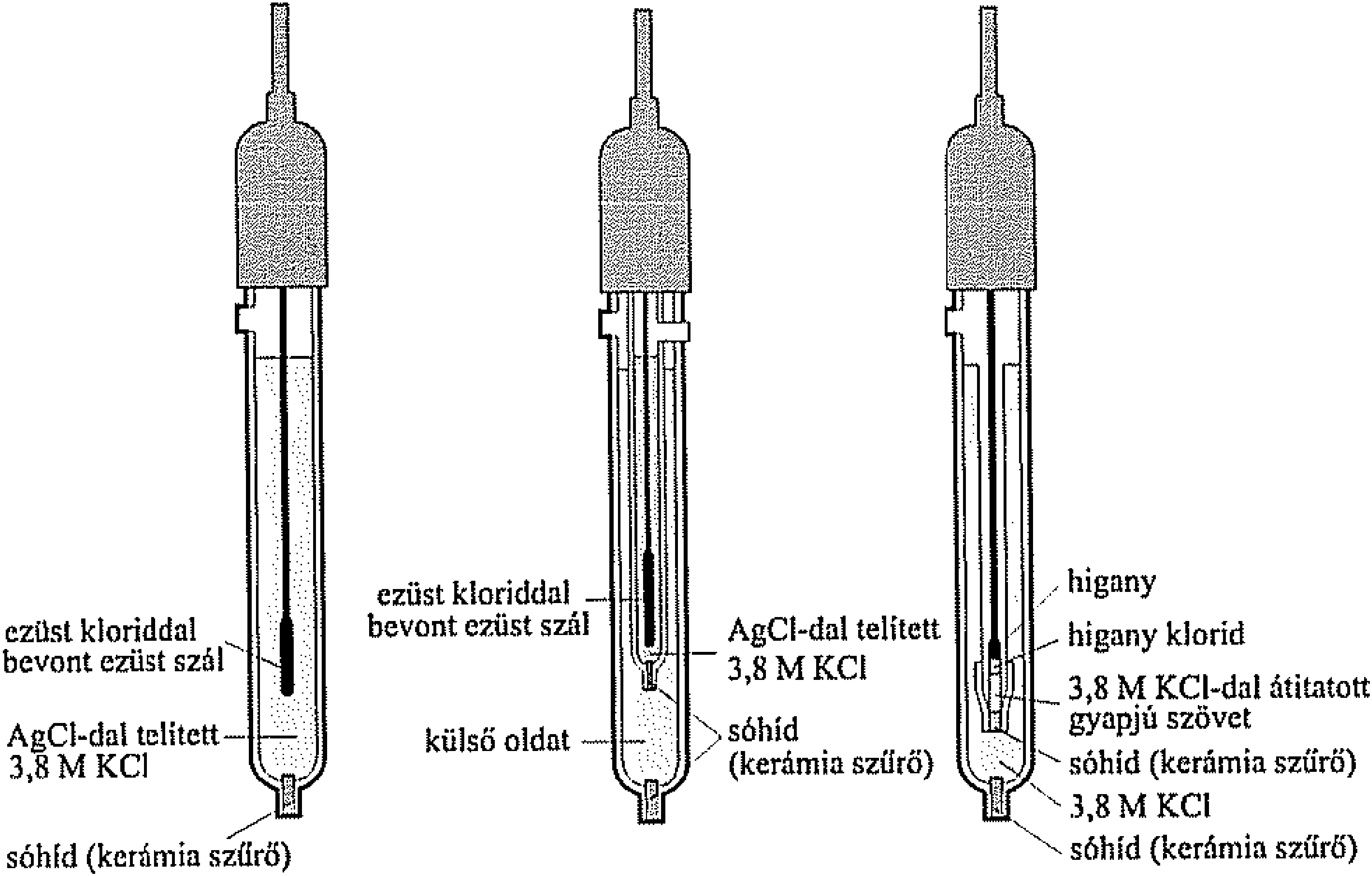
belső töltőoldat (internal electrolite)

mérőmembrán (nem porózus)



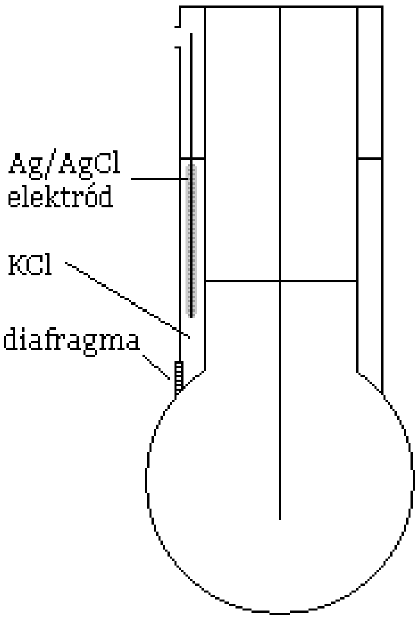
vonatkozási elektród

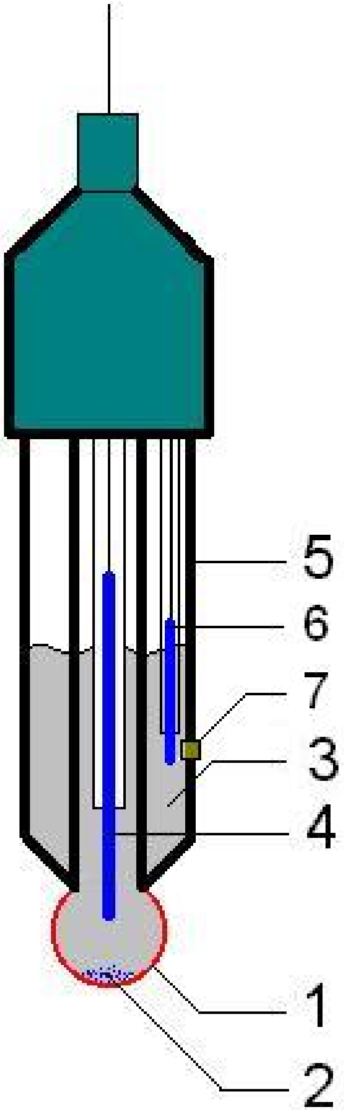
minta

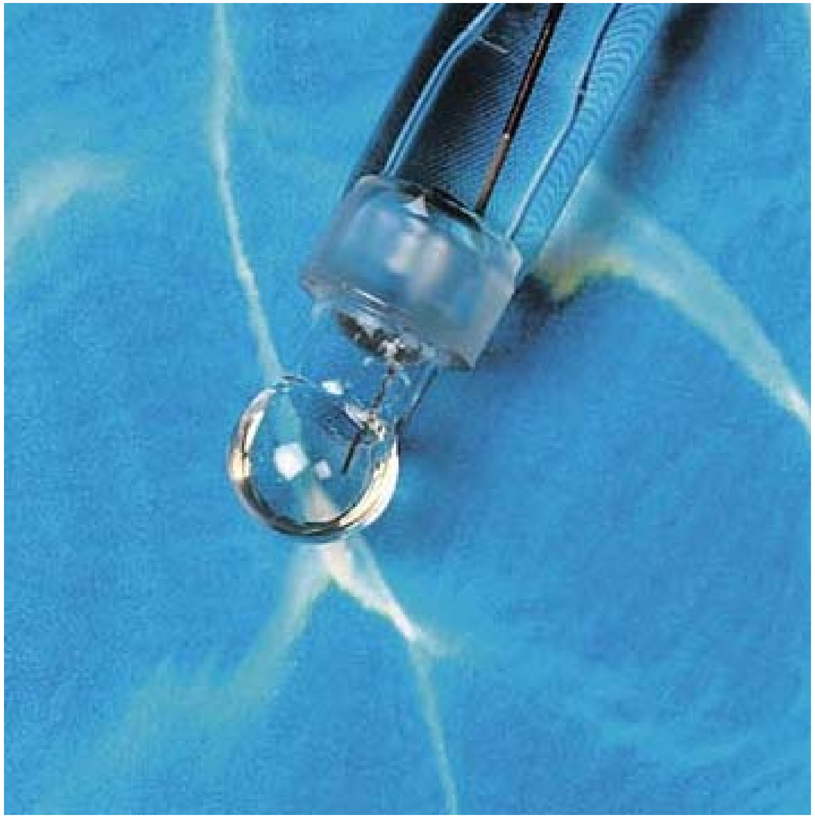


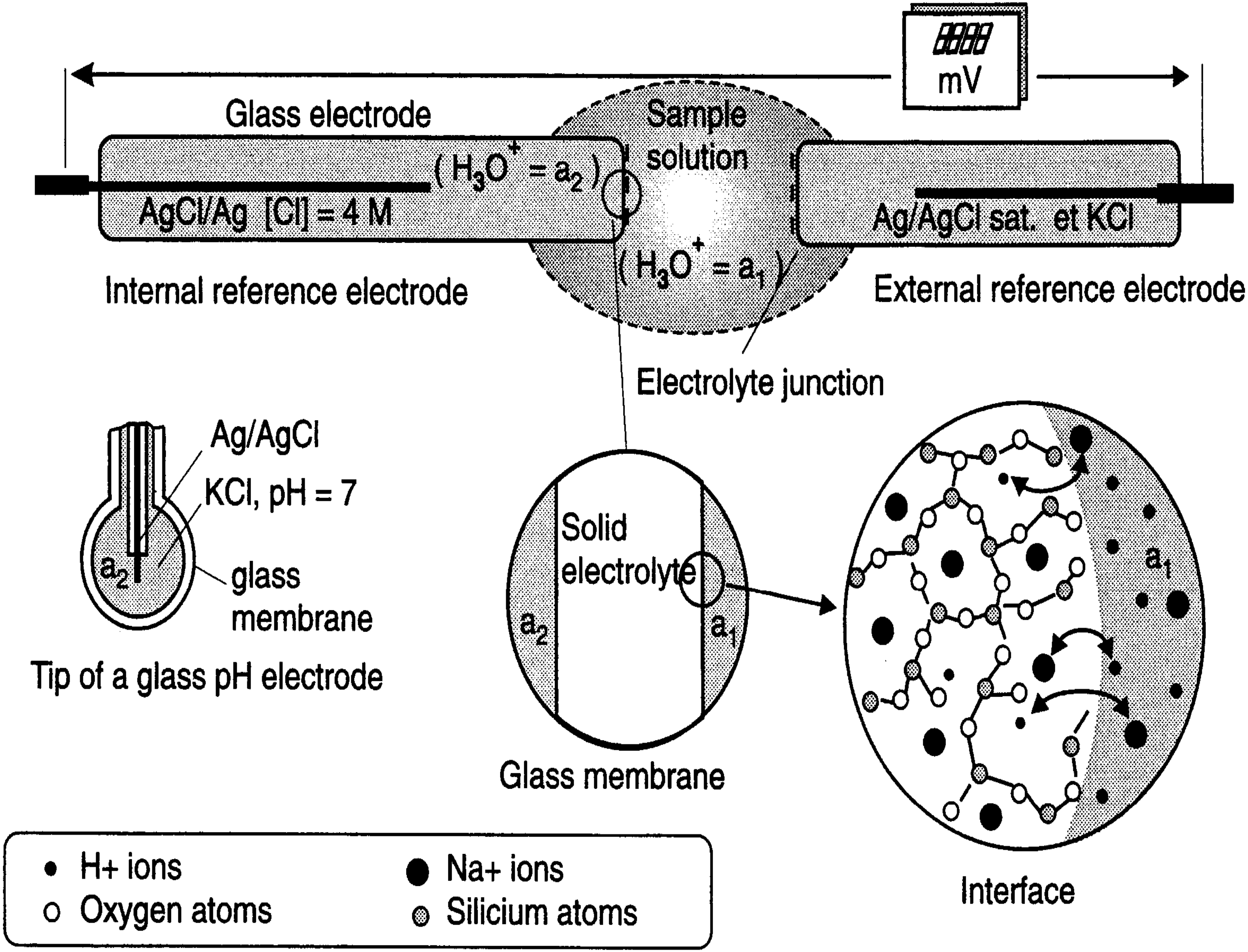
8.3. ábra Különböző vonatkozási elektródok

Üvegelektród (pH mérése)

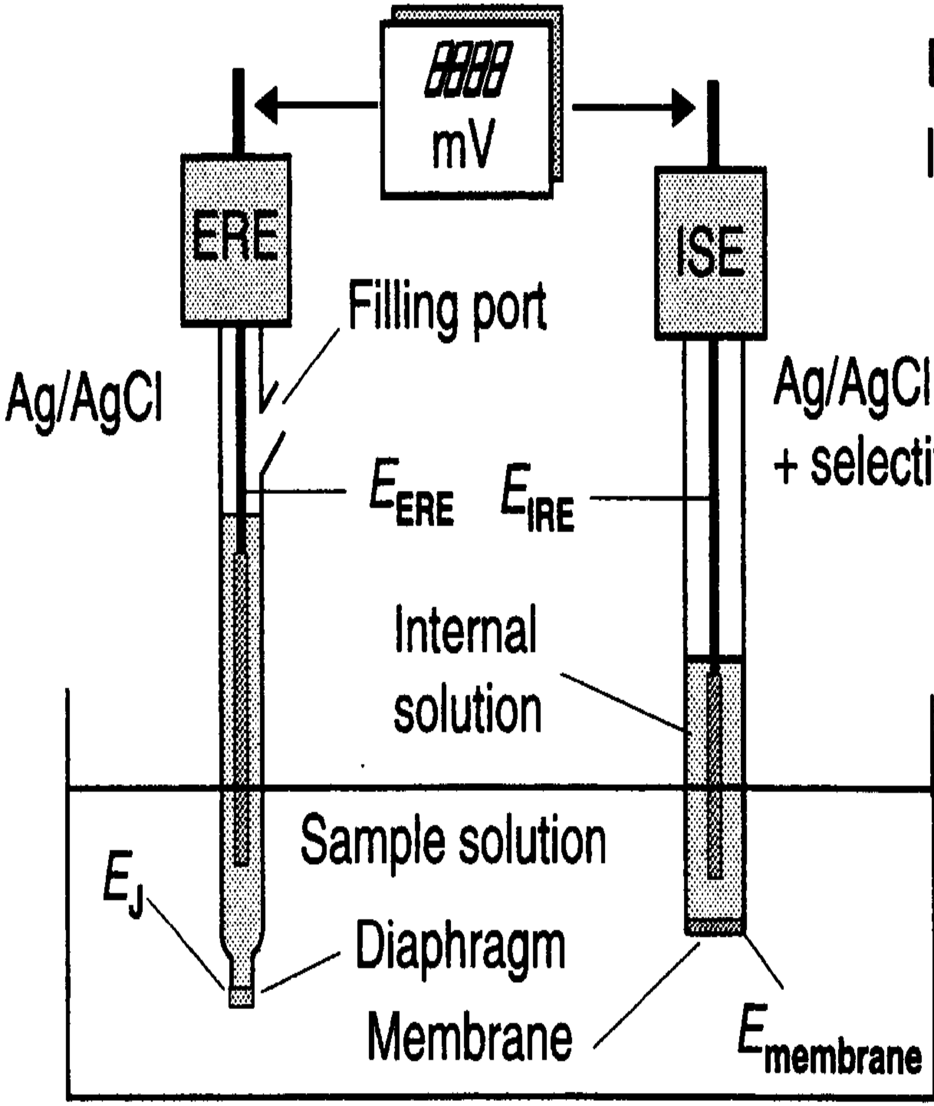








mV
Glass electrode
Sample solution
($H_3O^+ = a_2$)
AgCl/Ag [Cl] = 4 M
Ag/AgCl sat. et KCl
($H_3O^+ = a_1$)
Internal reference electrode
External reference electrode
Electrolyte junction
Ag/AgCl
KCl, pH = 7
a_2
glass membrane
Tip of a glass pH electrode
Solid electrolyte
a_2
a_1
Glass membrane
a_1
Interface
H+ ions
Na+ ions
Oxygen atoms
Silicium atoms

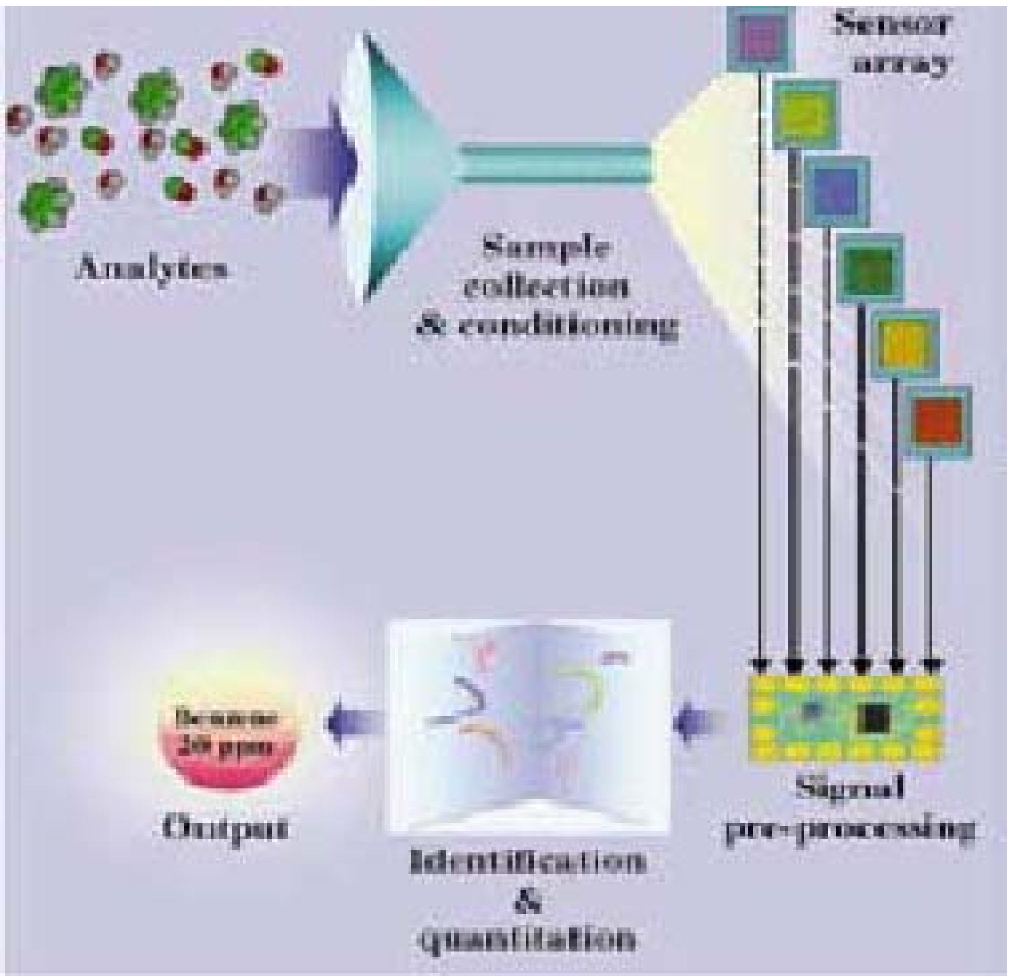


ERE External reference electrode

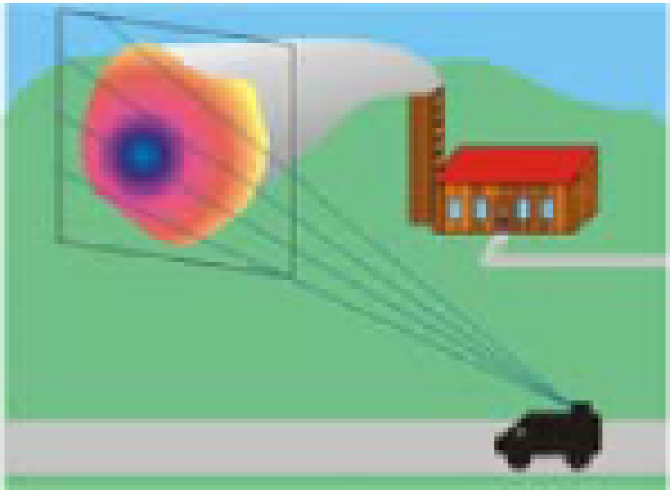
ISE Ion selective electrode

E_J	Junction potential
E_{ERE}	External reference electrode potential
E_{IRE}	Reference electrode potential for interior buffer
$E_{mem.}$	Global membrane potential

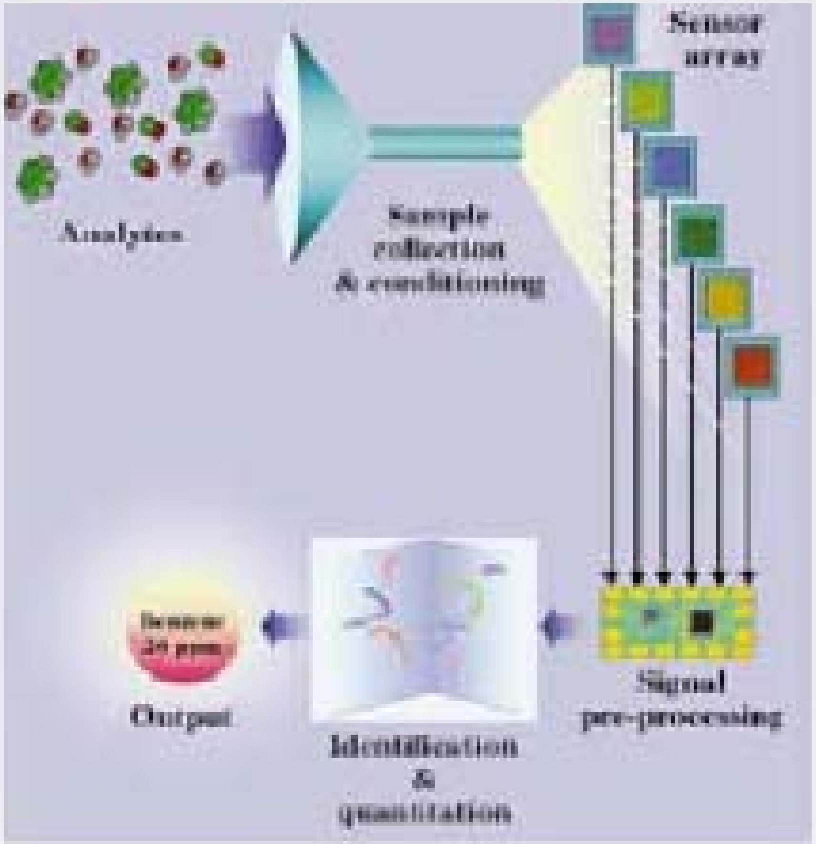
The membrane is permeable to the selective ion


Analytes
Sample collection & conditioning
Sensor array
Signal pre-processing
Identification & quantitation
Benzene 20 ppm
Output

Lidar (light detection and ranging)

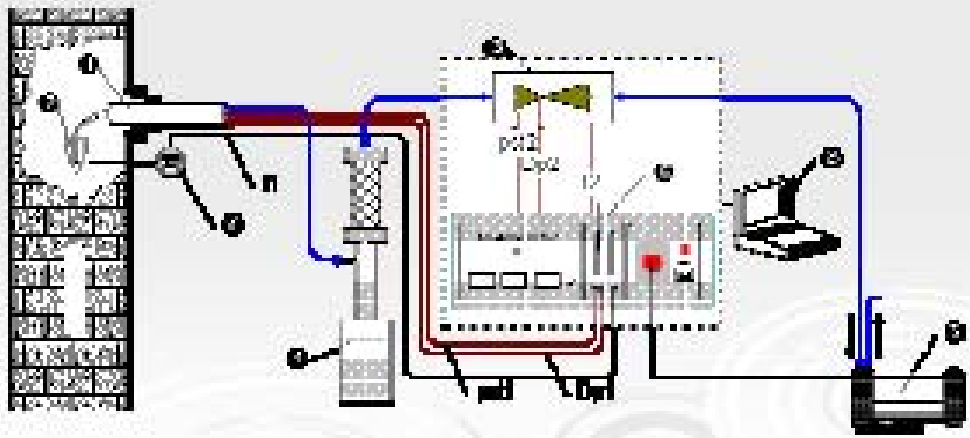


- lézer fény-impulzus
- anyagok elnyelése-kibocsátása jellegzetes
- távolságot a radar elven mérik – a megtett út alapján



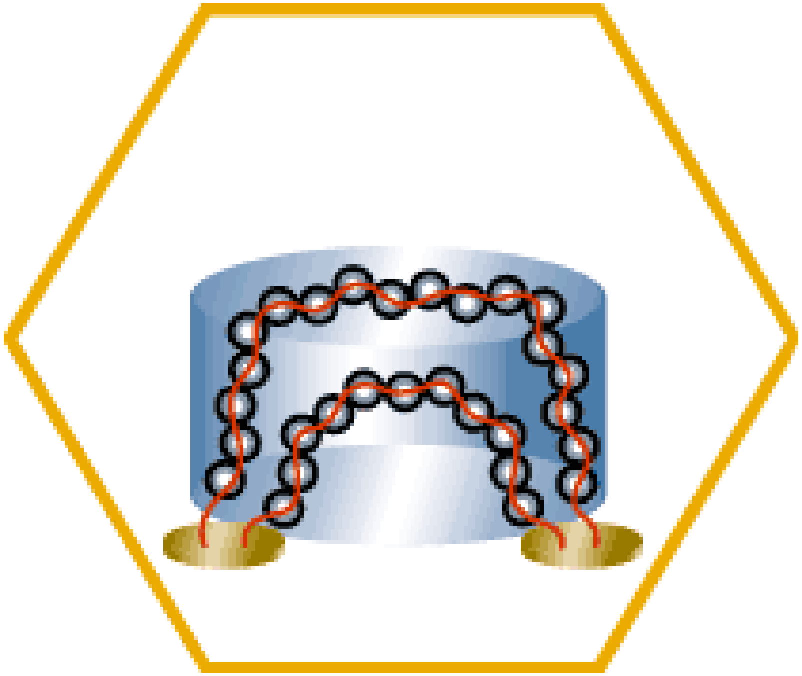
Kémiai szenzorok olyan eszközök amelyek a kémiai információt analitikai jellé alakítják. Adott vegyi anyag koncentrációjának megváltozására elektromos jel-változással reagálnak.

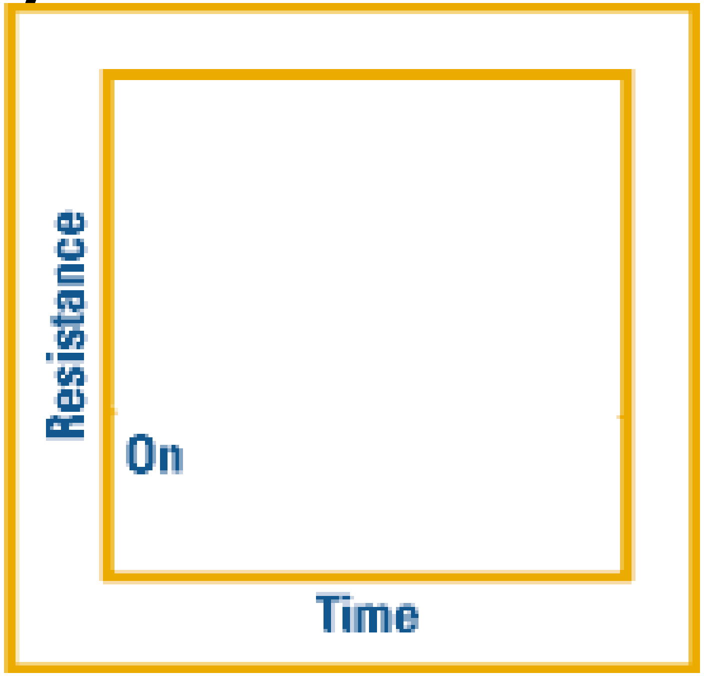
404 automatizált emissziós pormintavevő mérőkör



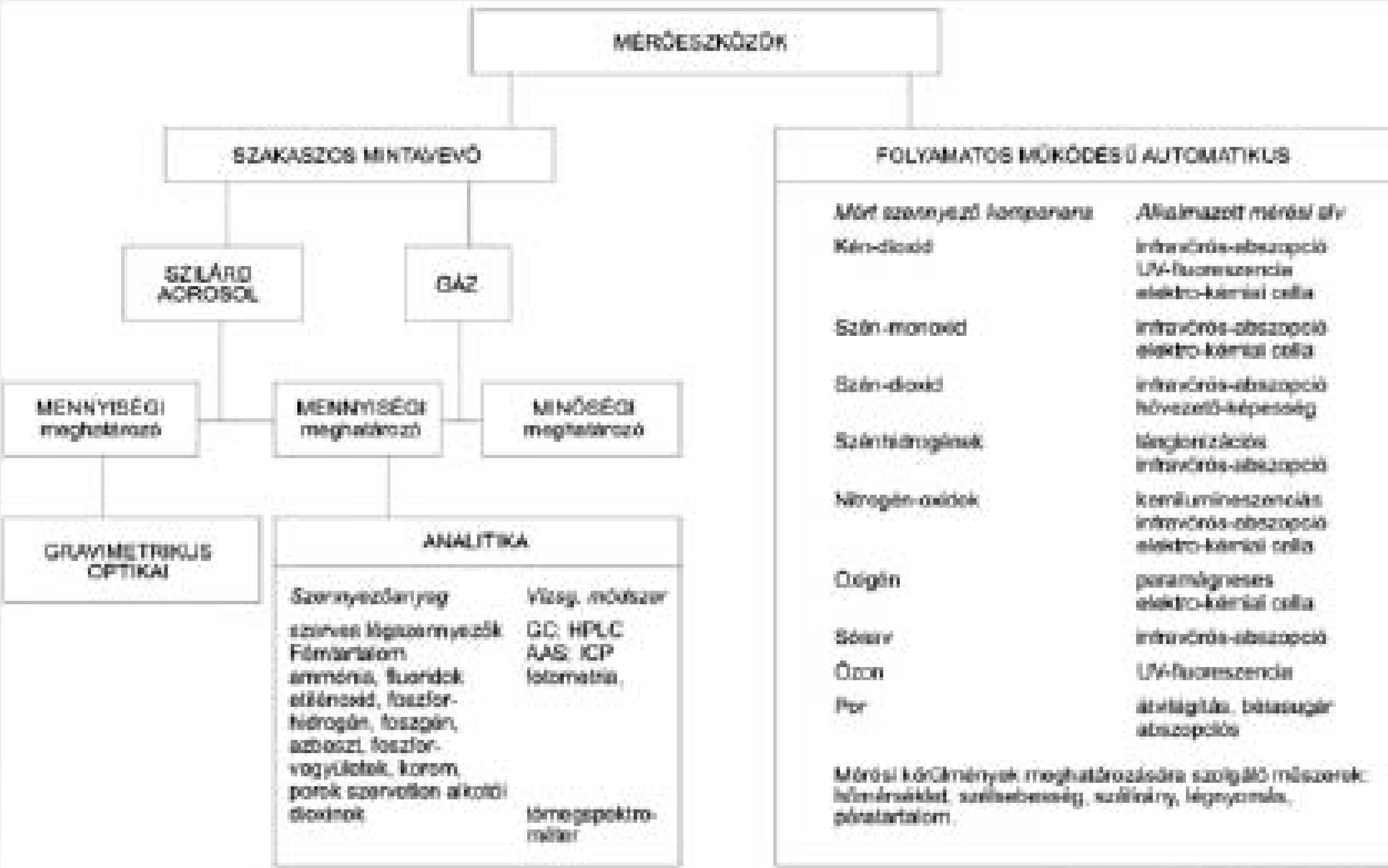
Az automatizált emissziós pormintavétel összeállítási rajza

Technology – Nanocomposite Arrays





- **Sensitive to chemical agents, toxic industrial chemicals, volatile organic compounds**
- **Stable to wide range of environmental conditions**



- Légszennyező anyagok mennyiségének mérésére szolgáló berendezések