Optical spectroscopy in materials science 10.
Ellipsometry
Emission spectroscopy

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Emission part by Hajnalka Tóháti, Wigner RCP

Ellipsometry

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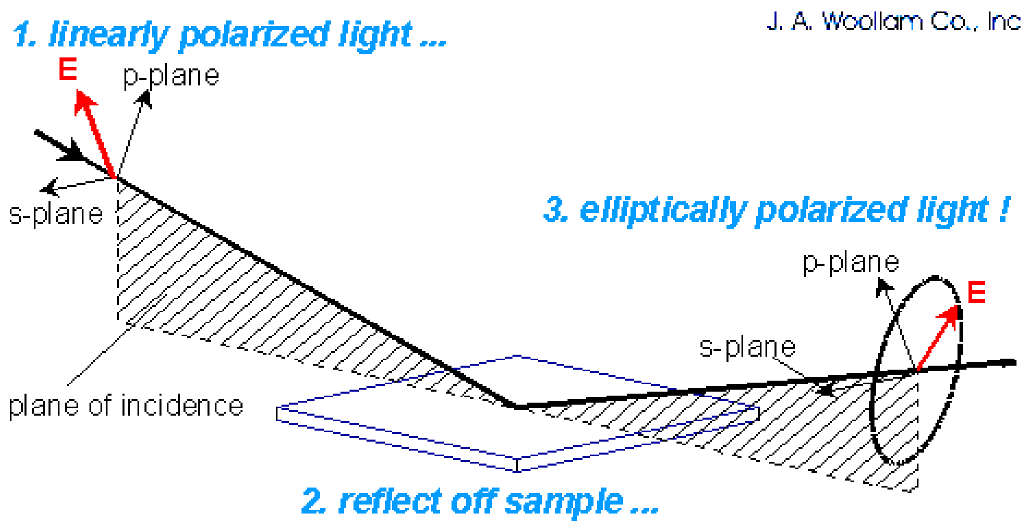
Petrik Péter
SOPRA →Semilab

Snell's law:
(Snellius – Descartes-törvény:
Snellius - Gesetz:)

$$n_a \sin\varphi_a = n_b \sin\varphi_b$$



From the boundary conditions of Maxwell's equations:
the tangential components of E and H are continous at the interface

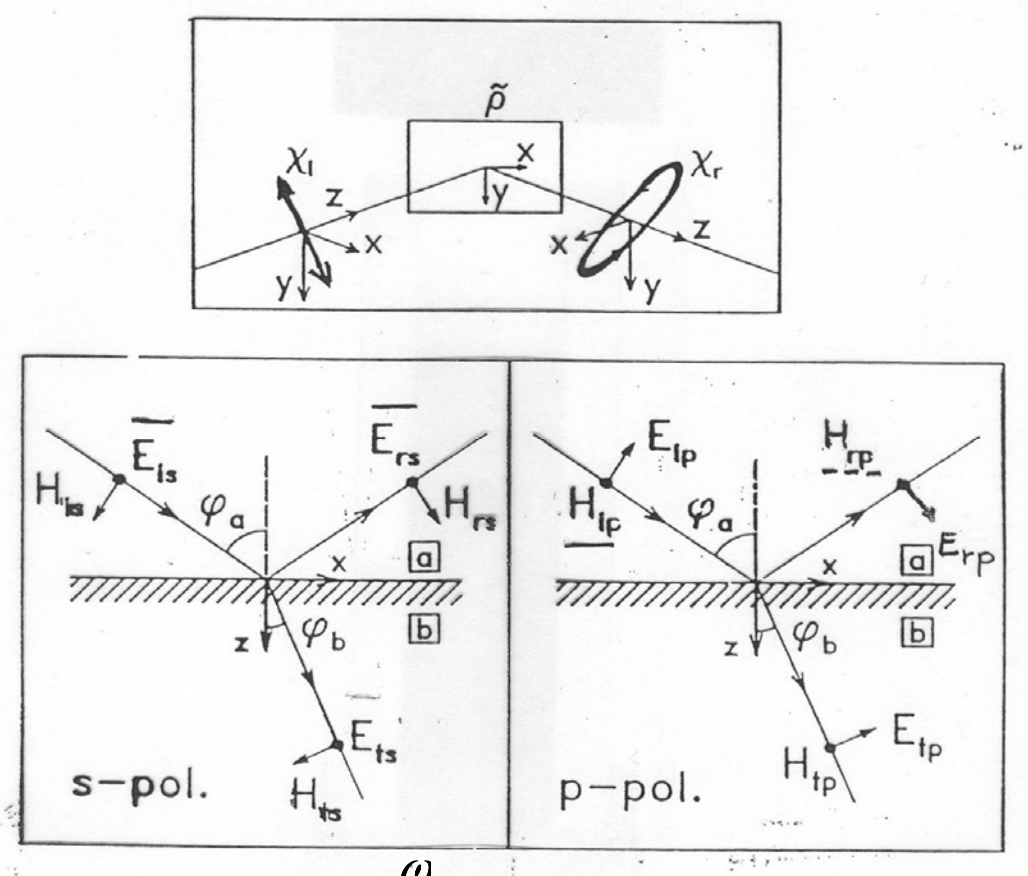
making use of

$$\mathbf{k}\times\mathbf{E} = \frac{\omega}{c}\mathbf{H}$$

$$|\mathbf{k}||\mathbf{E}| = \frac{\omega}{c}|\mathbf{H}|$$

$$H = \frac{kc}{\omega}E = nE$$

Fresnel's equations



$$\mathbf{k}\times\mathbf{E}=\frac{\omega}{c}\mathbf{H}$$

$$|\mathbf{k}||\mathbf{E}|=\frac{\omega}{c}|\mathbf{H}|$$

$$H=\frac{kc}{\omega}E=nE$$

$$E_{rs}+E_{is}=E_{ts}$$

$$n_a\cos\varphi_a(E_{rs}-E_{is})=-n_b\cos\varphi_b E_{ts}$$

$$n_a(E_{ip}-E_{rp})=n_b E_{tp}$$

$$\cos\varphi_a(E_{rp}+E_{ip})=\cos\varphi_b E_{tp}$$

Fresnel coefficients:

$$r_p=\frac{E_{rp}}{E_{ip}}\quad r_s=\frac{E_{rs}}{E_{is}}\quad t_p=\frac{E_{tp}}{E_{ip}}\quad t_s=\frac{E_{ts}}{E_{is}}$$

$$r_p=|r_p|e^{i\theta_{rp}}\qquad r_s=|r_s|e^{i\theta_{rs}}$$

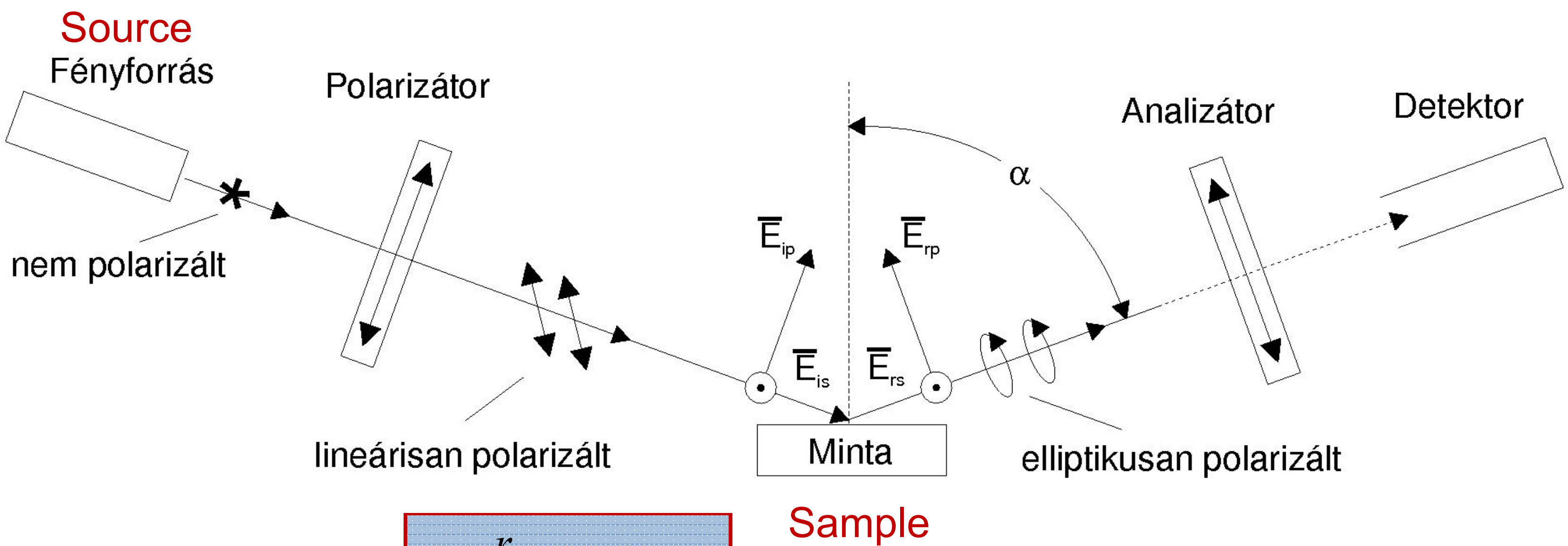
$$R=r^*r=|r|^2$$

$$r_p,r_s,t_p,t_s=f(n_a,n_b,\varphi_a,\varphi_b)$$

Measured quantities

Incident light: linear polarization

Reflected light: elliptical polarization



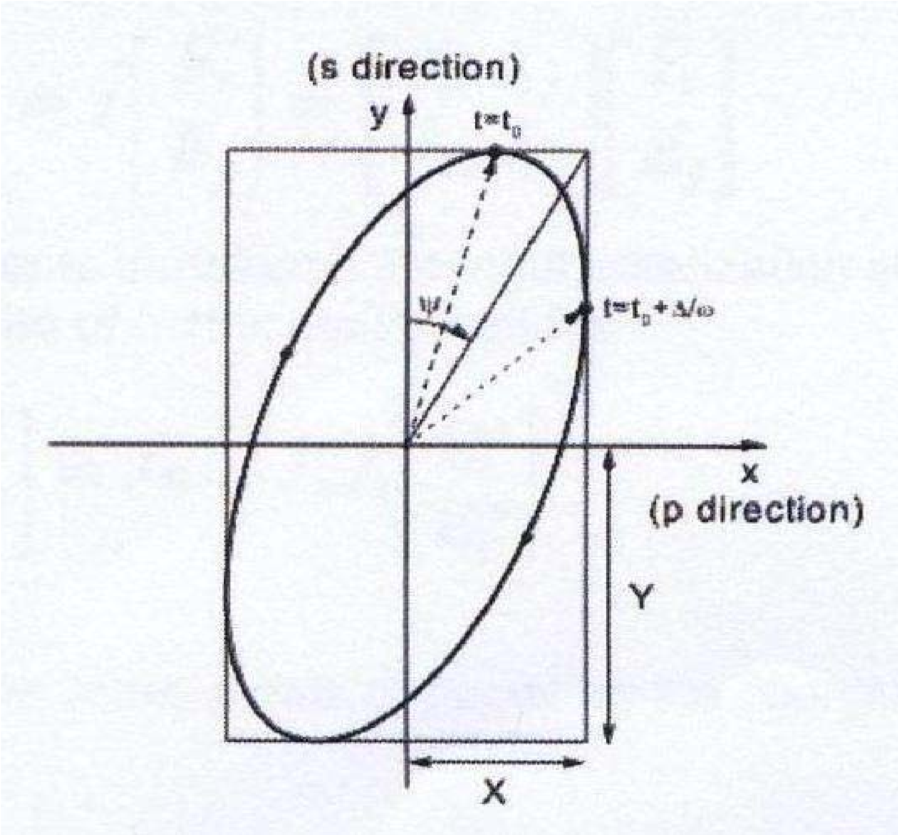
$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}$$

Ellipsometric angles: $\tan \Psi = \left| \frac{r_p}{r_s} \right|$ $\Delta = \theta_{rp} - \theta_{rs}$

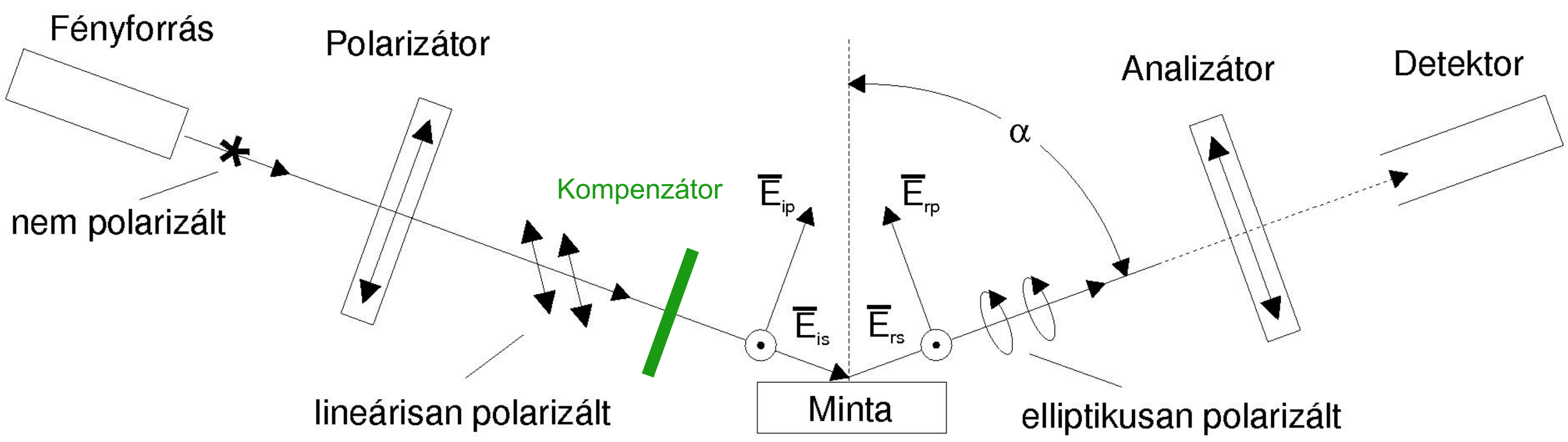
Spectroscopic ellipsometry: $\Psi(\omega), \Delta(\omega)$

Ellipsometric angles

Forrás: Tamáska István, 2009



Measurement: rotating analyzer setup



Polarizer: fixed angle (P)
Analyzer rotating: A(t)

$$I_{det}(A) = 1 + \frac{|\rho|^2 \cos^2 P - \sin^2 P}{|\rho|^2 \cos^2 P + \sin^2 P} \cos 2A + \frac{\mathrm{Re}(\rho) \sin 2P}{|\rho|^2 \cos^2 P + \sin^2 P} \sin 2A$$

$$I_{det}(A_i) \sim 1 + \alpha(\rho, P) \cos 2A_i + \beta(\rho, P) \sin 2A_i$$

$$\tan \Psi = \sqrt{\frac{1+\alpha}{1-\alpha}} \tan P \qquad \cos \Delta = \frac{\beta}{\sqrt{1-\alpha^2}}$$

Evaluation: Isotropic, infinite two-phase model

$$n_b^2 = \varepsilon_r(sample) = n_a^2\left(\sin^2\varphi_a + \frac{(1-\rho)^2}{(1+\rho)^2}\sin^2\varphi_a \tan^2\varphi_a\right)$$

$$\rho = \rho' + i\rho''$$

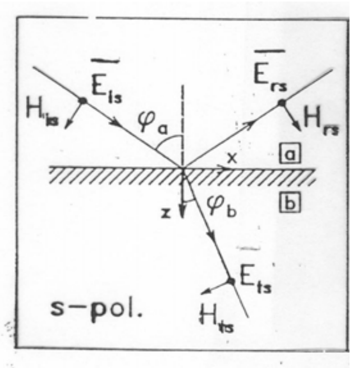
$$\boxed{\rho = \frac{r_p}{r_s} = \tan\Psi e^{i\Delta}}$$

If $n_a = 1$:

$$\varepsilon_r' = \sin^2\varphi_a + \frac{(1-\rho^2)^2 - 4(\rho'')^2}{1+\rho^2+2(\rho')^2}\sin^2\varphi_a \tan^2\varphi_a$$

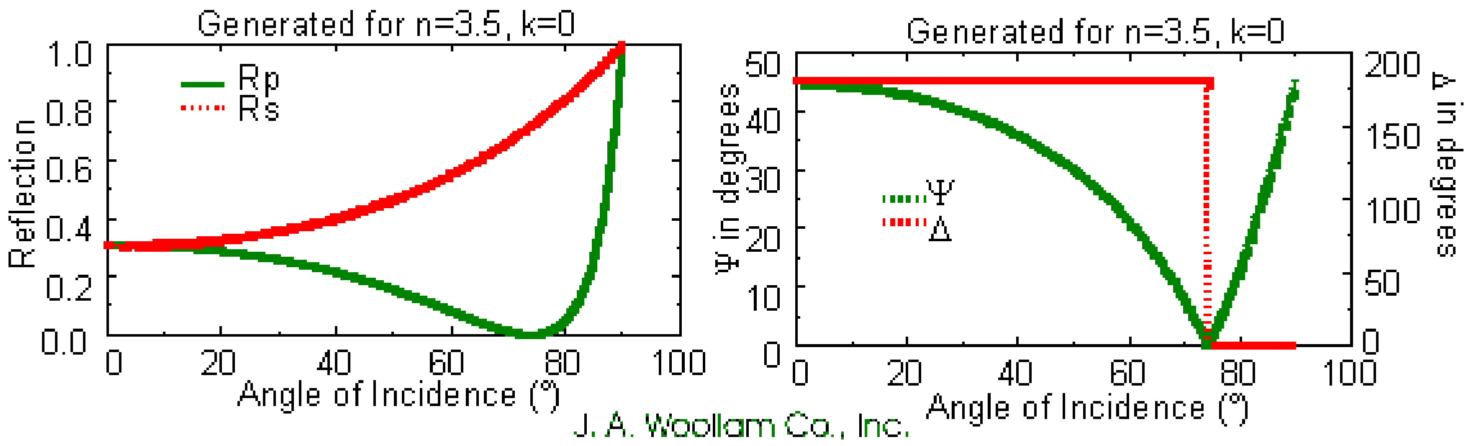
$$\varepsilon_r'' = -\frac{4\rho''(1-\rho^2)}{1+\rho^2+2(\rho')^2}\sin^2\varphi_a \tan^2\varphi_a$$

$$\varepsilon_r'' > 0 \Rightarrow \rho'' = \tan\Psi \sin\Delta < 0 \Rightarrow -\pi < \Delta < 0$$



convention! (measured quantity: cos Δ)

Accuracy of measurement

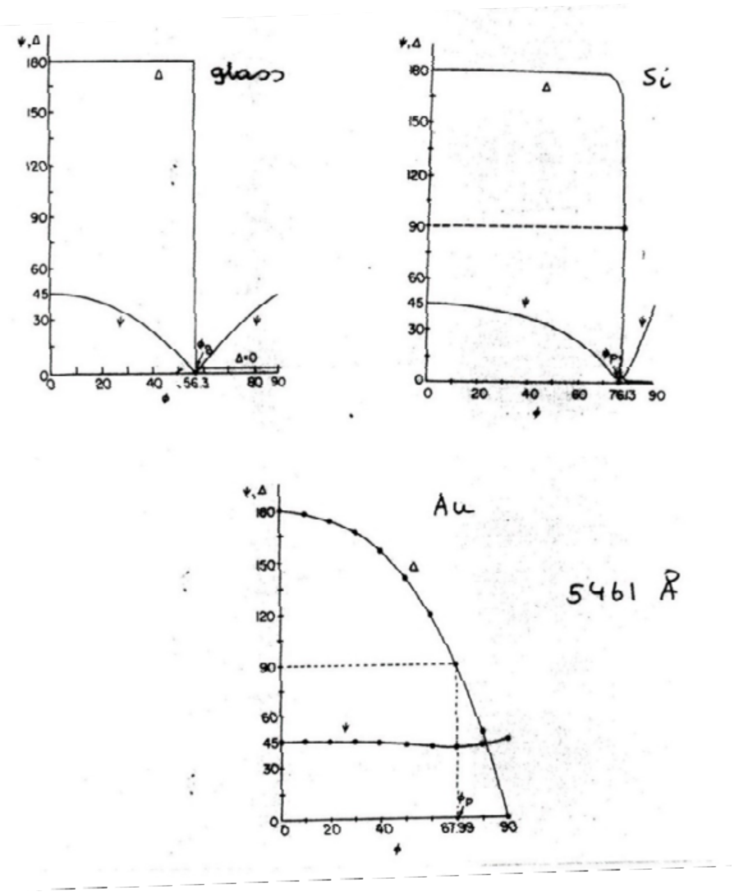


Brewster angle: $r_p=0$ $\Psi = 0, \Delta = \frac{\pi}{2}$

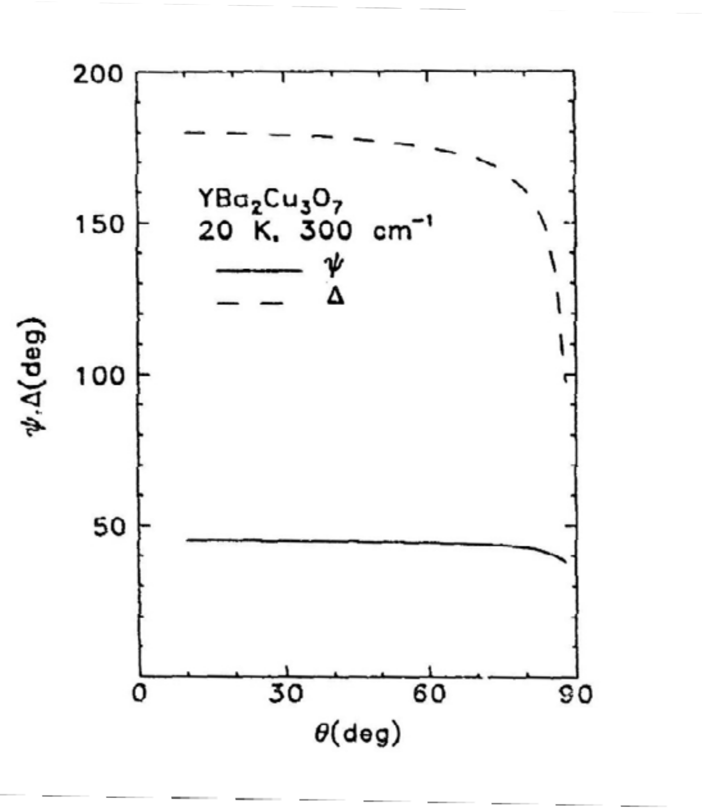
$\tan \varphi_a(B) = n_b/n_a$

cos Δ is the measured quantity – optimal range is where it is the most sensitive to Δ
however, sensitivity to angle of incidence is also large there
sensitivity of Ψ to angle is small around minimum

Dependence on angle of incidence



R.M.A. Azzam, N.M. Bashara: Ellipsometry and Polarized Light.
North-Holland, Amsterdam, 1977



$YBa_2Cu_3O_7$ 20 K

K.Kamarás, D.van der Marel, C.C.Homes, T.Timusk:
Physica C **235**, 1085 (1994)

Advantages - disadvantages

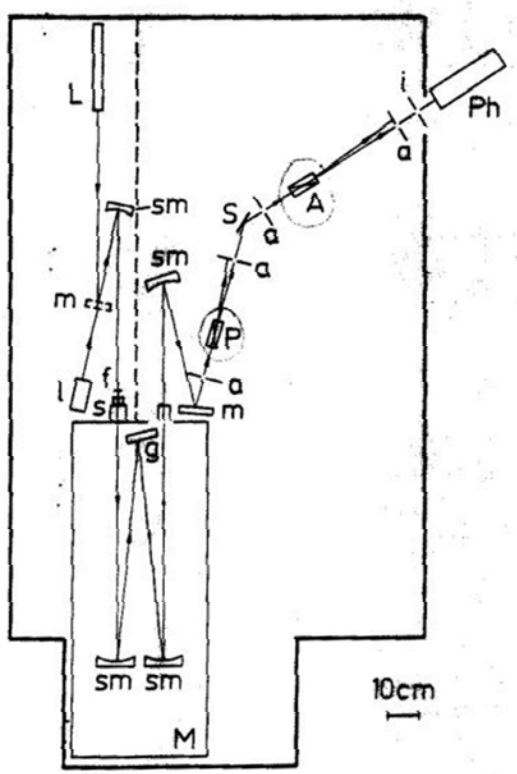
Advantages:

- direct determination of complex dielectric function (with appropriate model)
- no reference needed
- scattered light, small surface discontinuities cause small errors
- non-destructive
- remote sensing possible (visible range)

Disadvantages:

- large angle of incidence – large light spot, large sample area required
- evaluation complicated
- many parameters of the sample have to be known beforehand.

Experimental setup

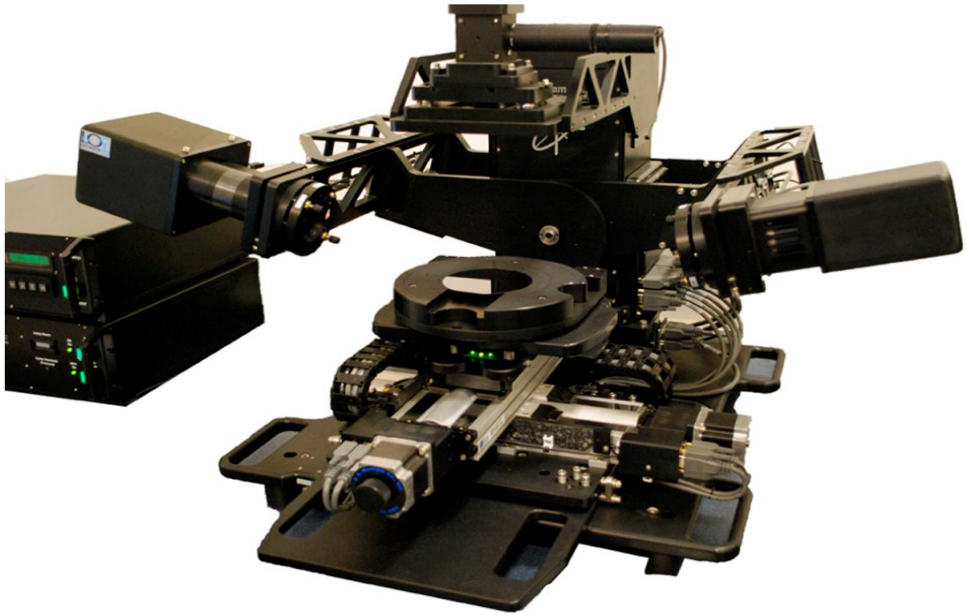


UV-VIS ellipsometer
(MPI Stuttgart)

$$I(A,\omega) \Rightarrow \Psi, \Delta(\omega) \Rightarrow <\varepsilon>(\omega)$$

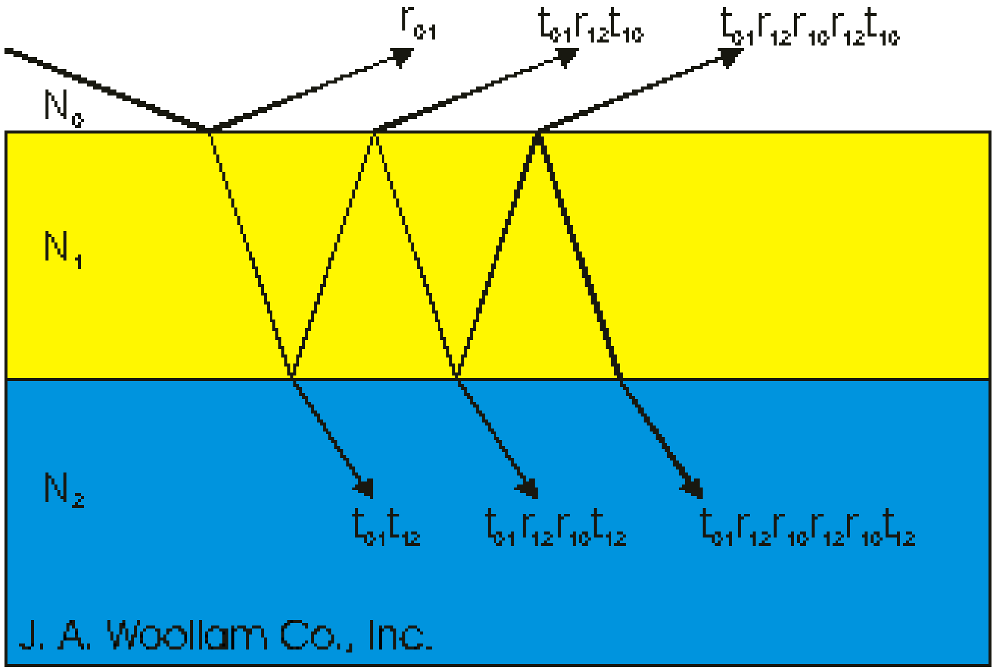
Pseudodielectric function <ε>:
approximation calculated with isotropic two-phase model
independent of angle of incidence!!!!
can be used for routine tasks with appropriate calibration

Modern ellipsometer



Woollam M2000DI – (MFA)
Rotating compensator
spectroscopic ellipsometer
range: **190-1700 nm**
minimum focus spot **0.15 mm**

Evaluation: multilayer systems



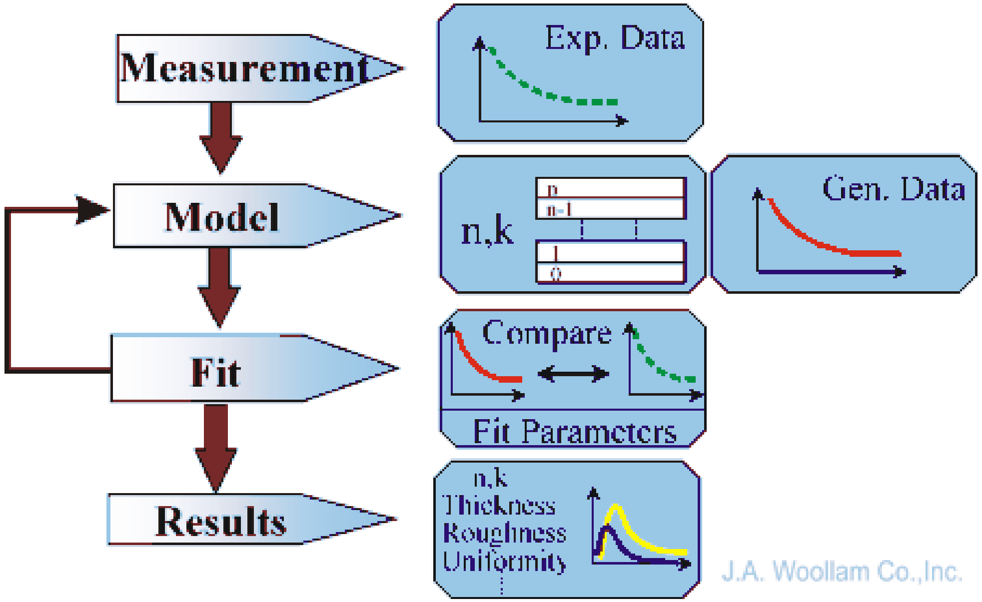
www.jawoollam.com

$$\rho(\varphi_a, \varepsilon_b, d_b, \varepsilon_c, d_c ...)$$

knowing (n-2) parameters,
any two unknown quantities
can be determined
(e.g. thickness)

Fitting procedures

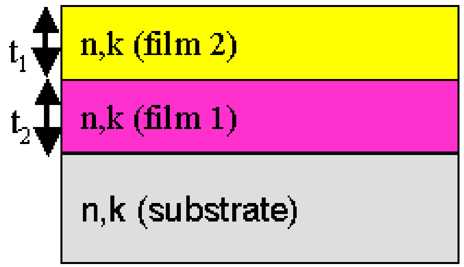
www.jawoollam.com



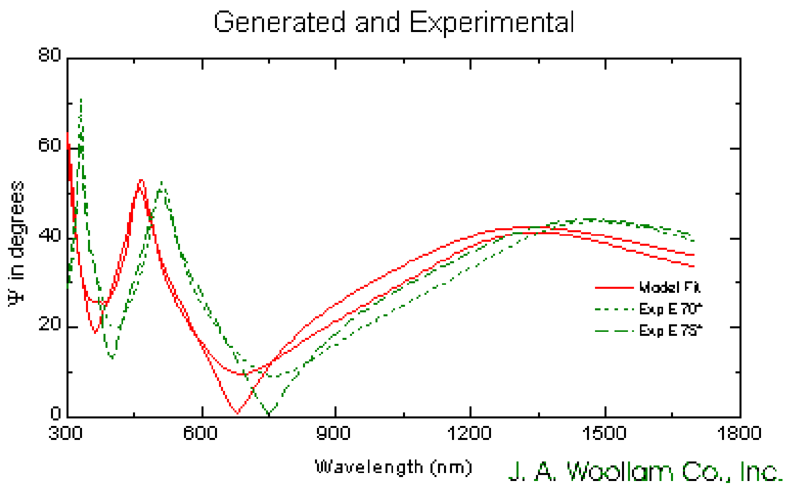
If n(ω) is known, more than two parameters can be fitted

more angles of incidence – more information

model



2	amorphous si	500 Å
1	sio2	1000 Å
0	si	1 mm



Sensitivity of ellipsometry

$\Psi, \Delta = 0.01 - 0.02°$ -> 0.01nm sensitivity on layer thickness

d (nm)	Δ	Ψ
0	179.257	10.448
0.1	178.957	10.448
0.2	178.657	10.449
0.3	178.356	10.450
0.4	178.056	10.451
0.5	177.756	10.453
1	176.257	10.462

Precise calibration (e.g. angle of incidence) is crucial!

Technology: process monitoring
process control

Source: Tamáska István, 2009

Application

- quick determination of dielectric function
- thickness measurement, technology control
- investigation of distribution in layered systems
  (comparison with model calculations)
- ideal for semiconductors, multilayers
- small sensitivity in case of transparent and strongly absorbing samples

"Kramers-Kronig transformation is arbitrary –
ellipsometry gives directly the dielectric function"

What's wrong with this sentence?

Combination of ellipsometry and Kramers-Kronig analysis

K. Kamarás, K.-L.Barth, F.Keilmann, R.Henn, M.Reedyk, C.Thomsen, M.Cardona, J.Kircher, P.L.Richards, J.-L.Stehlé:
J. Appl. Phys. **78**, 1235 (1995)

$SrTiO_3$

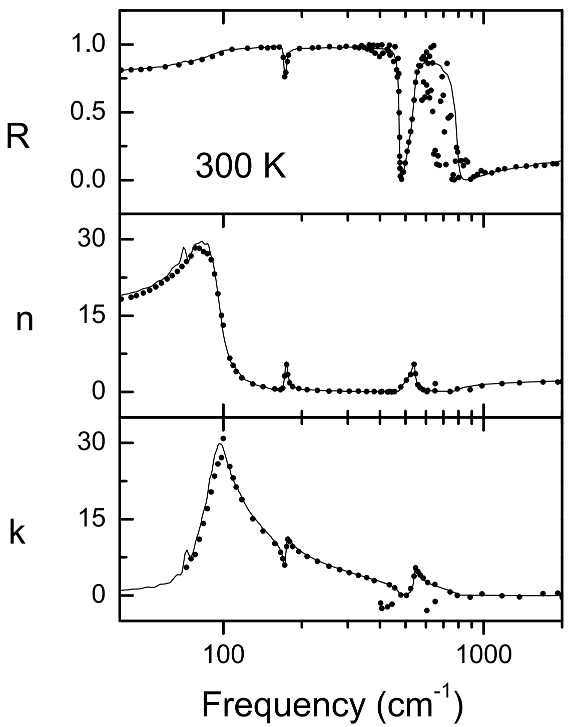


Fig. 1. Kamaras et al.

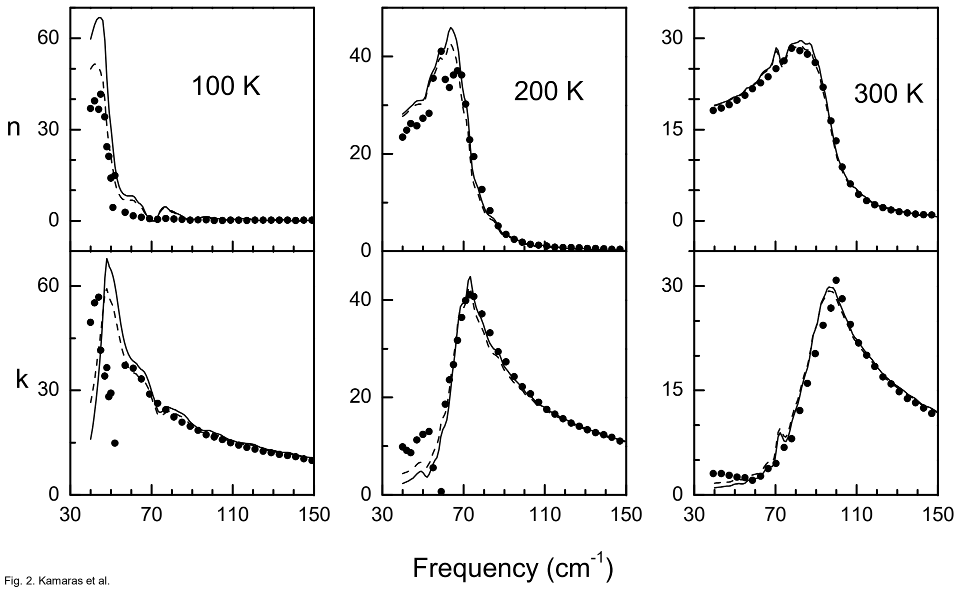


Fig. 2. Kamaras et al.

scaling of normal-incidence reflectance to ellipsometry
low-frequency extrapolations depend on slope of curve

Take-home message

- Basics of ellipsometry: illumination of sample with linearly polarized light under finite angle; analyzing polarization state of reflected (elliptically polarized) light
- Measured quantity: ratio of Fresnel coefficients $$\rho = \frac{r_p}{r_s} = \tan\Psi e^{i\Delta}$$
- Ellipsometric angles ψ, Δ depend on sample dielectric function and angle of incidence
- Pseudodielectric function (isotropic, infinite, two-phase model)
- Multilayer systems: any 2 parameters can be determined when the others are known (mostly thickness of known materials)
- Modeling, process control, remote sensing

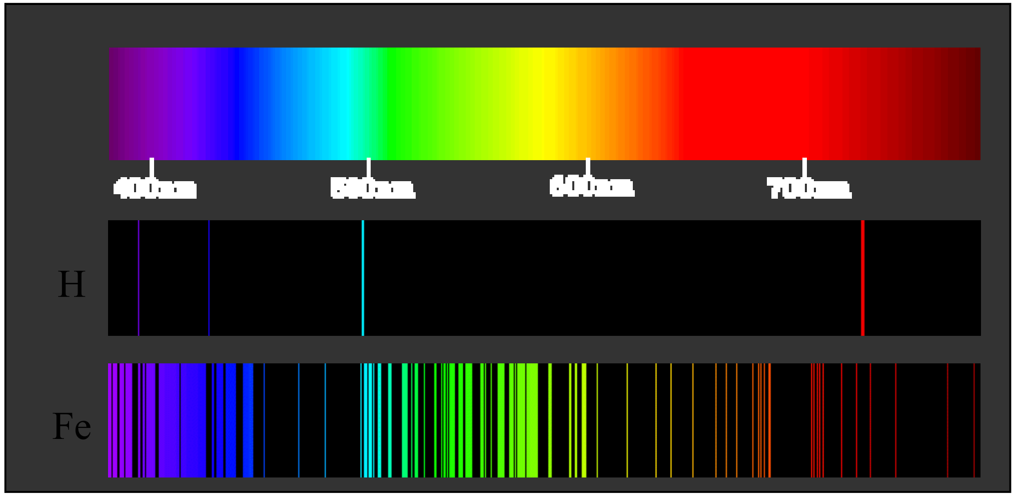
Összefoglalás

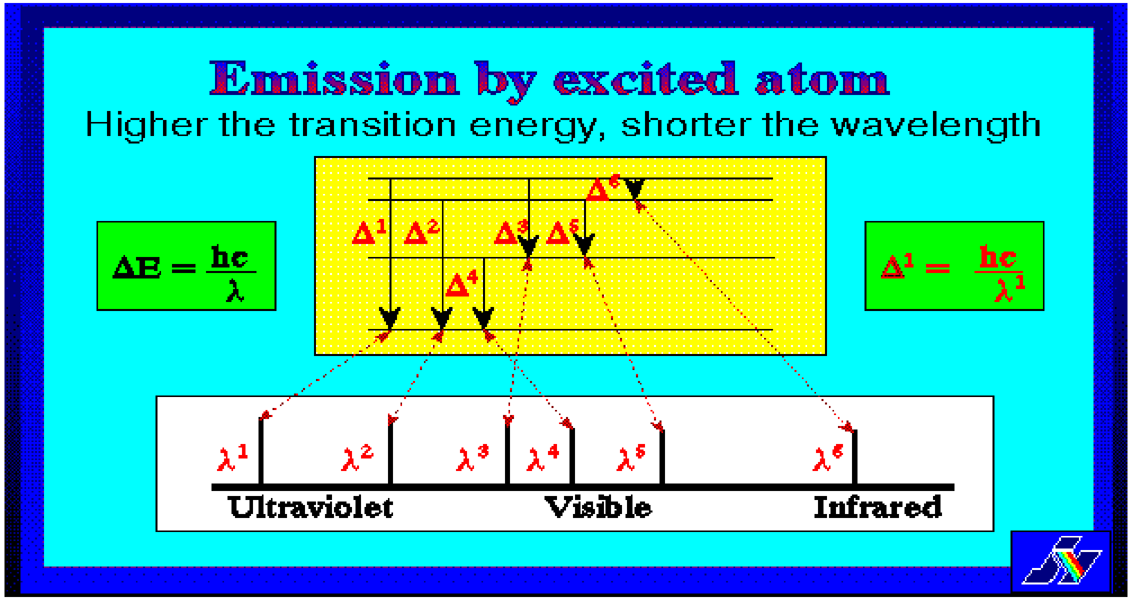
- Ellipszometria alapjai: minta megvilágítása lineárisan polarizált fénnyel véges beesési szöggel ; a visszavert (elliptikusan polarizált) fény analizálása
- Mért mennyiség: Fresnel-együtthatók aránya $\rho = \frac{r_p}{r_s} = \tan\Psi e^{i\Delta}$
- A ψ, Δ ellipszometrikus szögek a minta dielektromos függvényétől és a beesési szögtől függenek
- Pszeudodielektromos függvény (izotrop, végtelen, kétfázisú modell)
- Többrétegű rendszerek: bármely 2 paraméter meghatározható, ha a többi ismert (legtöbbször ismert anyagokból álló rétegek vastagsága)
- Modellezés, folyamatirányítás, távoli érzékelés

Emission spectroscopy

- **Atomic emission spectroscopy (AES)**
  - Flame test
  - Flame emission photometry
  - Atomic absorption spectrophotometry
  - Inductively coupled plasma
- Molecular spectroscopy
  - IR emission spectroscopy
  - Luminescence

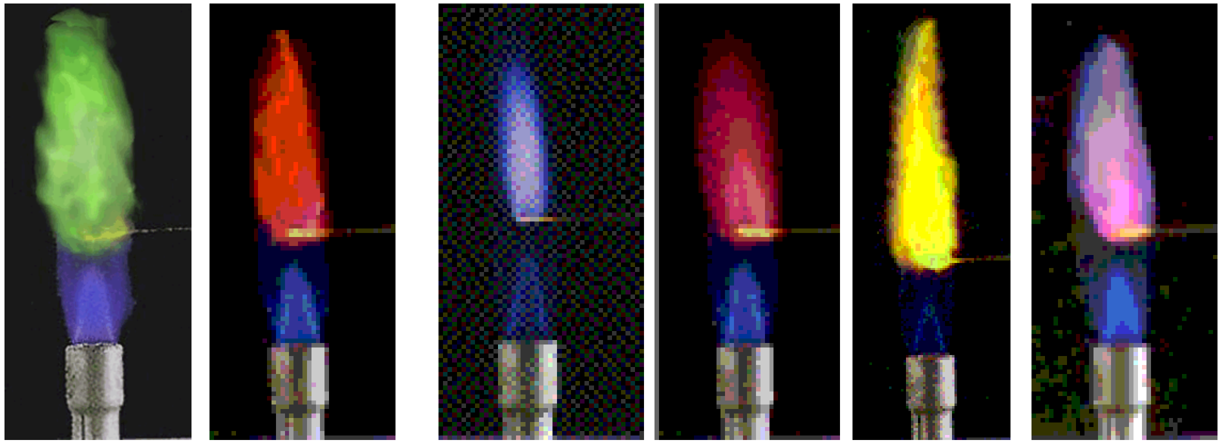
Emission spectroscopy





Atomic emission spectroscopy - Flame test

Walt Wolland, Bellevue Community College
http://www.800mainstreet.com/s/s.html

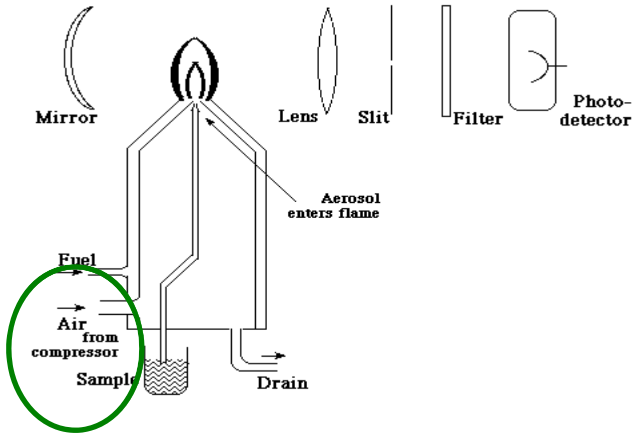


Ba **Ca** **K** **Li** **Na** **Rb**

Quantitative methods: flame photometry, atomic absorption spectroscopy (AAS)

Atomic emission spectroscopy

Flame Emission Photometry (FEP)

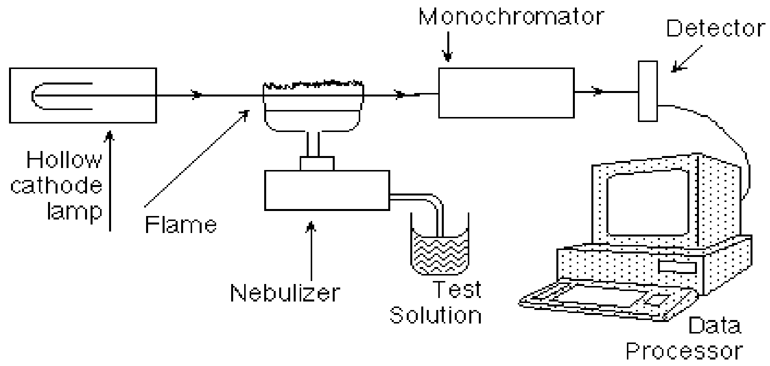


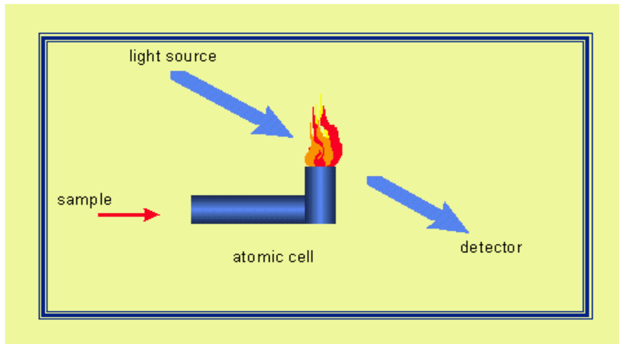
- **Excitation:** thermal energy of the flame
- **Flame:** - most frequent: acetylene and air

  - vaporization → homogeneous atomic cloud

  - excitation, but not ionization, of atoms
- **Vaporizer** → sample solution
- **Temperature:** 2000 – 3000 ˚C
- **Requirement**: constant composition, temperature and structure of the flame

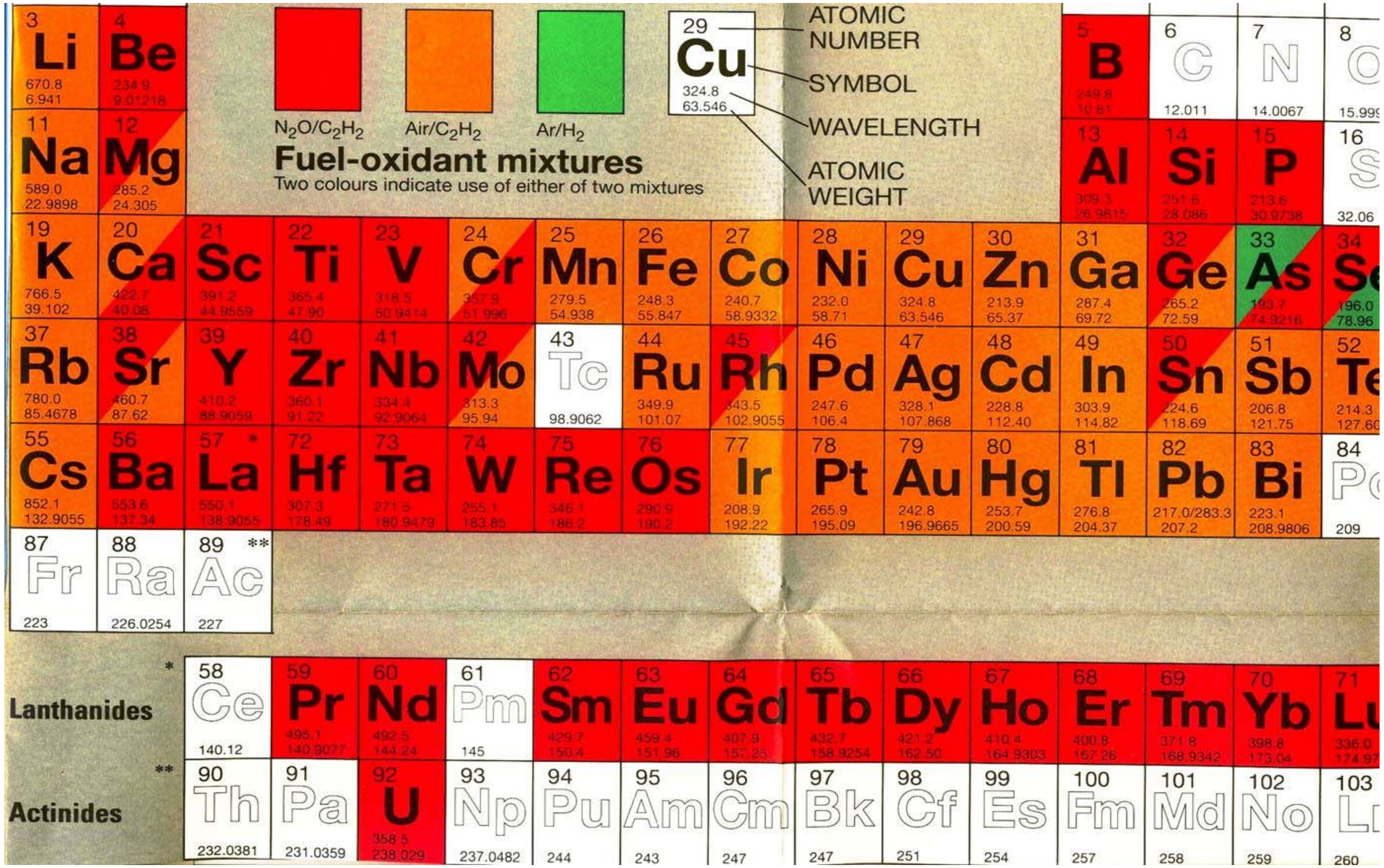
Atomic Absorption Spectroscopy (AAS)



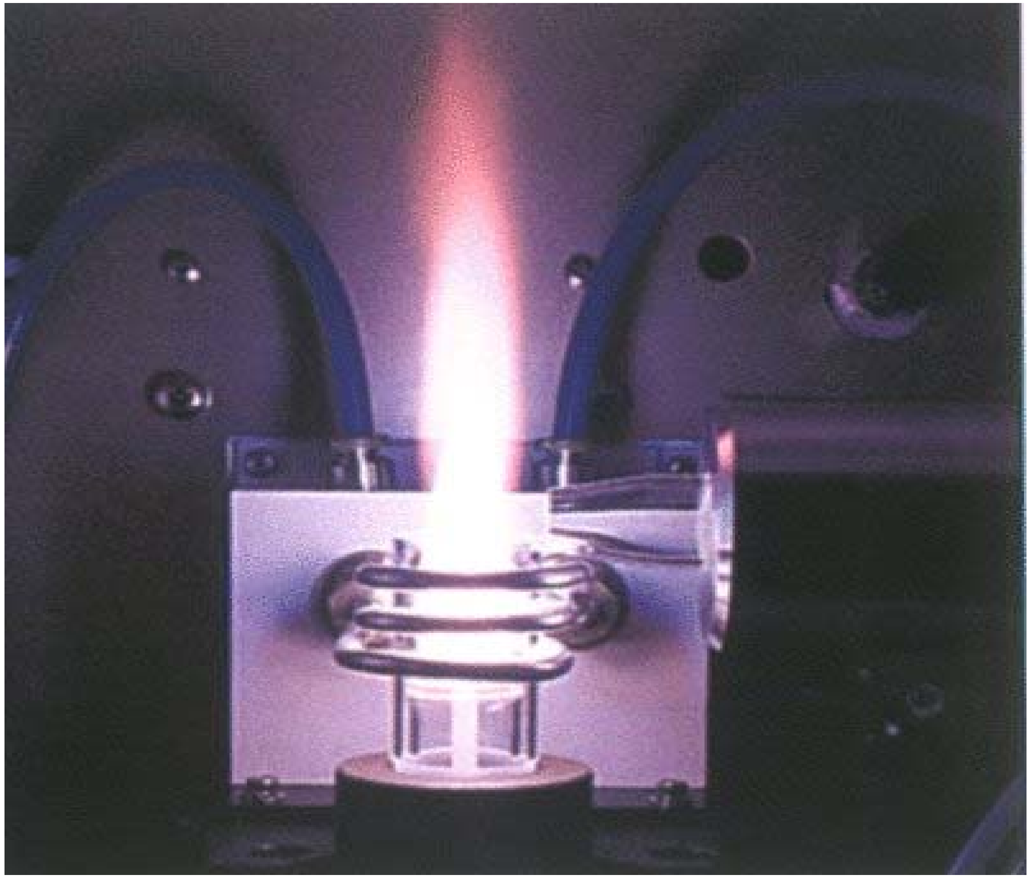


http://www.cee.vt.edu/ewr/environmental/teach/smprimer/aa/aa.html
http://www.resonancepub.com/atomicspec.htm

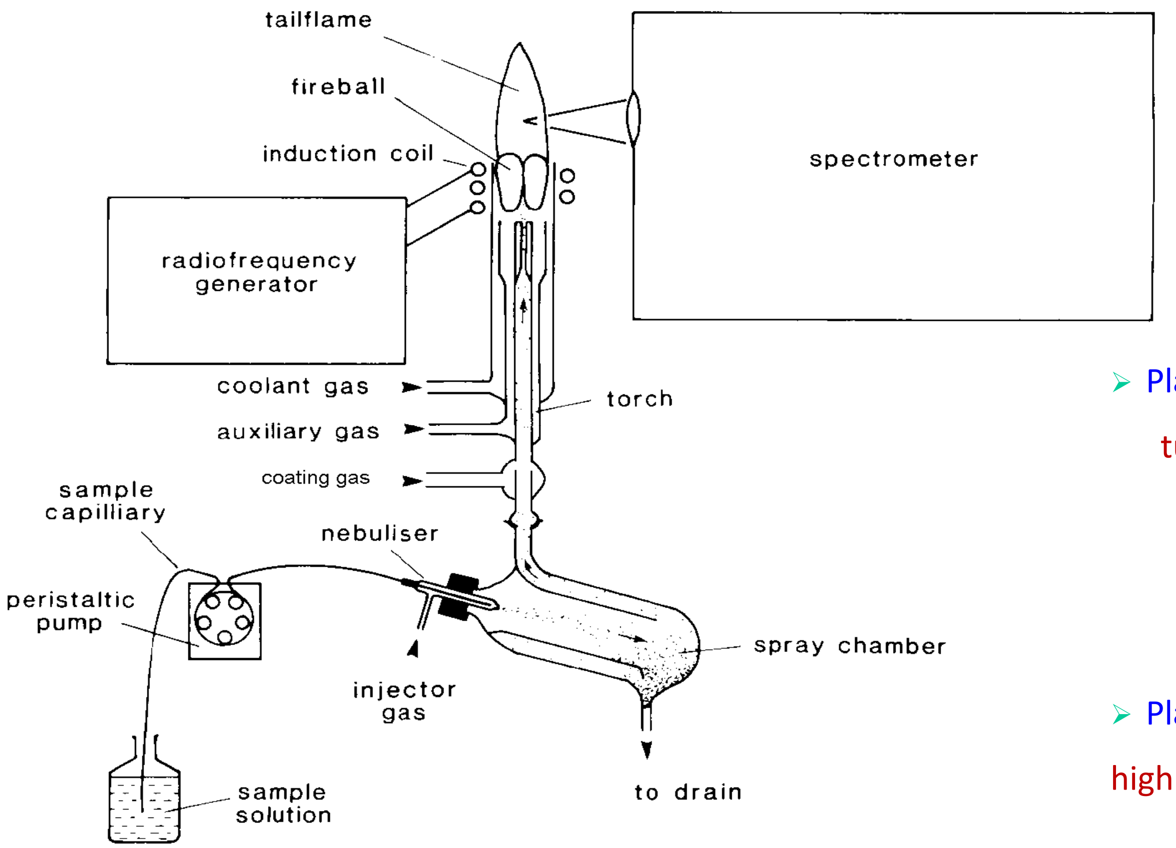
Detectable elements



Inductively coupled plasma (ICP)



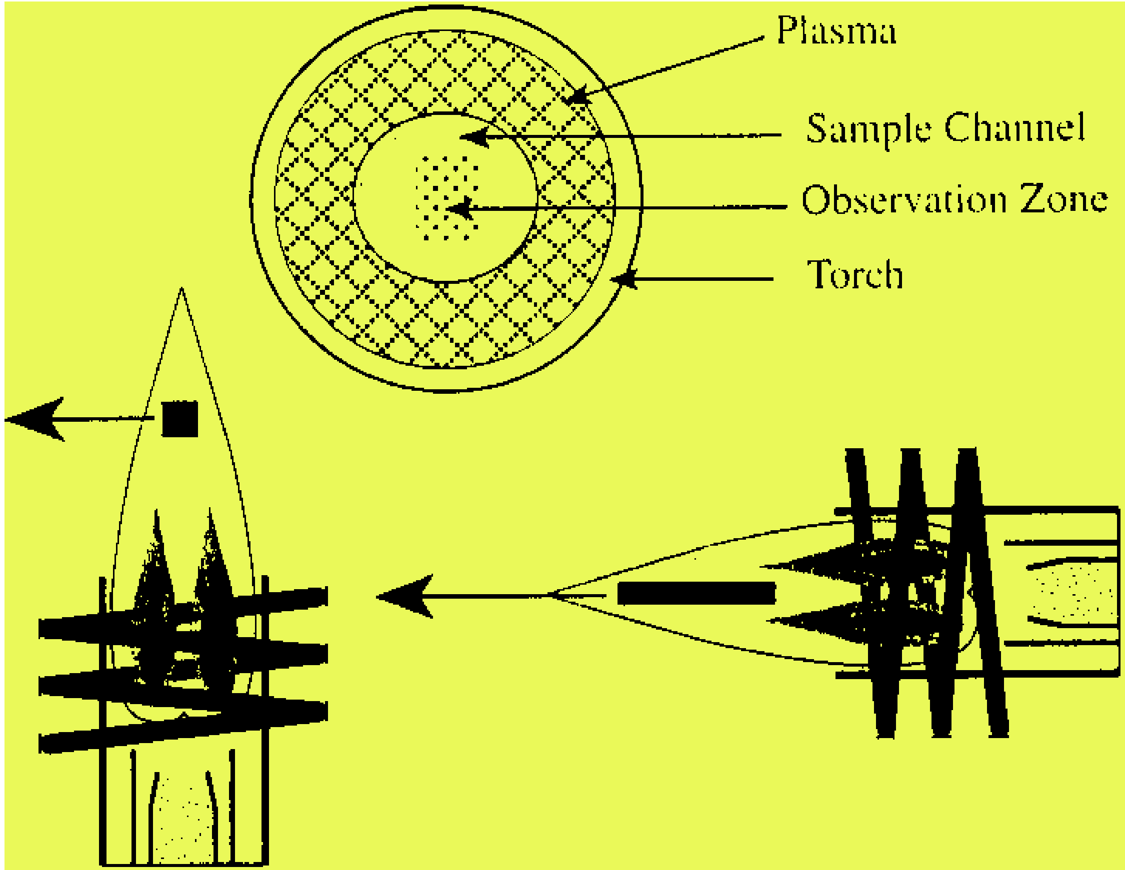
ICP Kitchen area



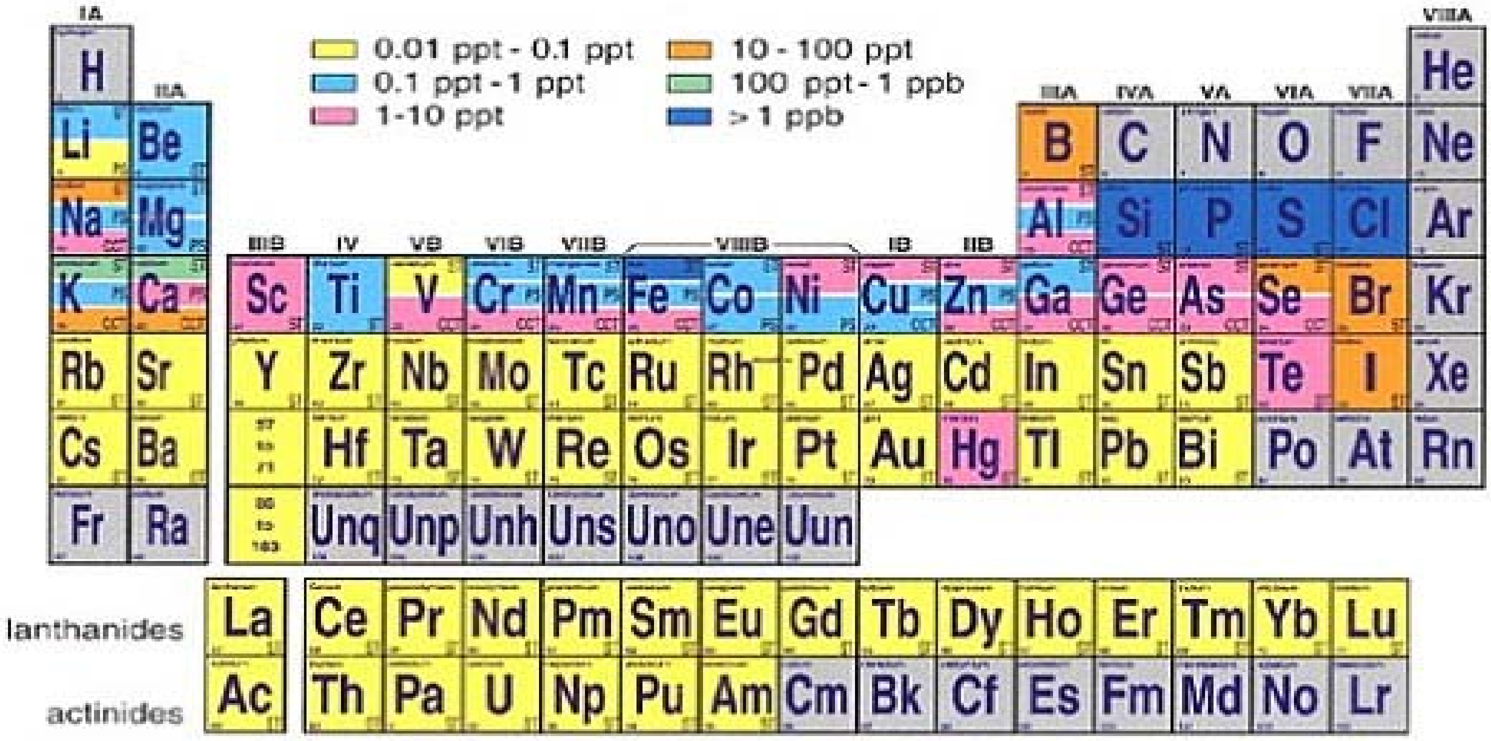
- Ar gas excited at radio frequency
- Temperature up to 8000° C
- Low concentration

- Plasma torch: 3 concentric quartz tubes, streaming Ar
  - Outside→ cooling
  - Central→ plasma
  - Inside→ carrier gas for sample
- Plasma state: electric excitation→ high temperature fireball

ICP plasma



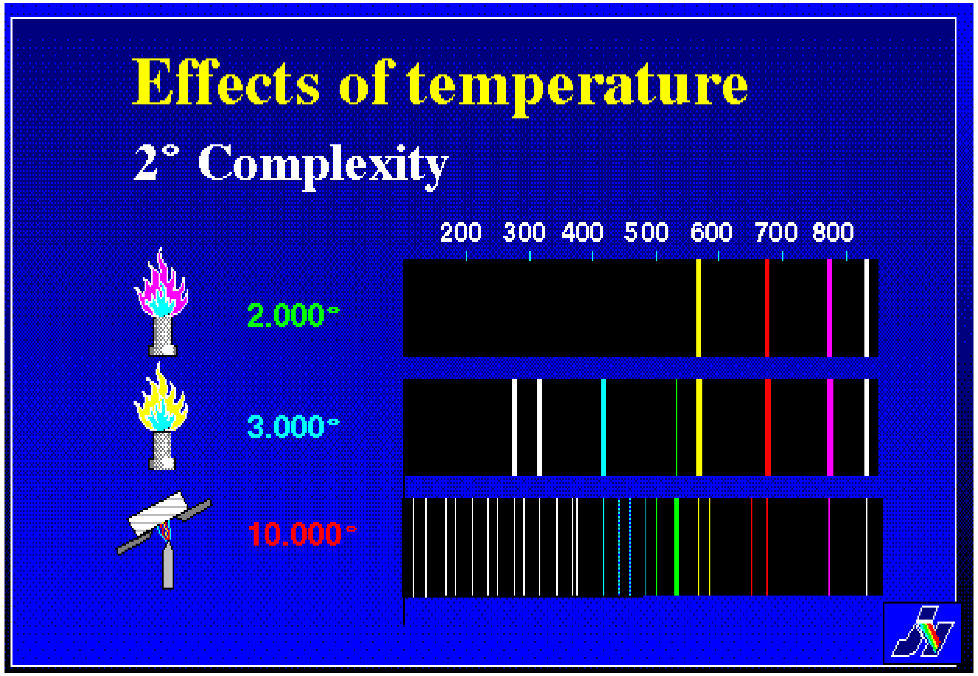
ICP-AES – Detection limits

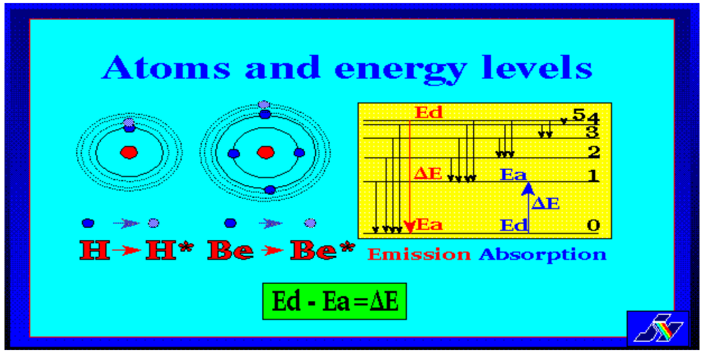


3 sigma detection limits in de-ionized water

ST = Standard PS = PlasmaScreen CCT = Collision Cell

Emission spectra: effect of temperature

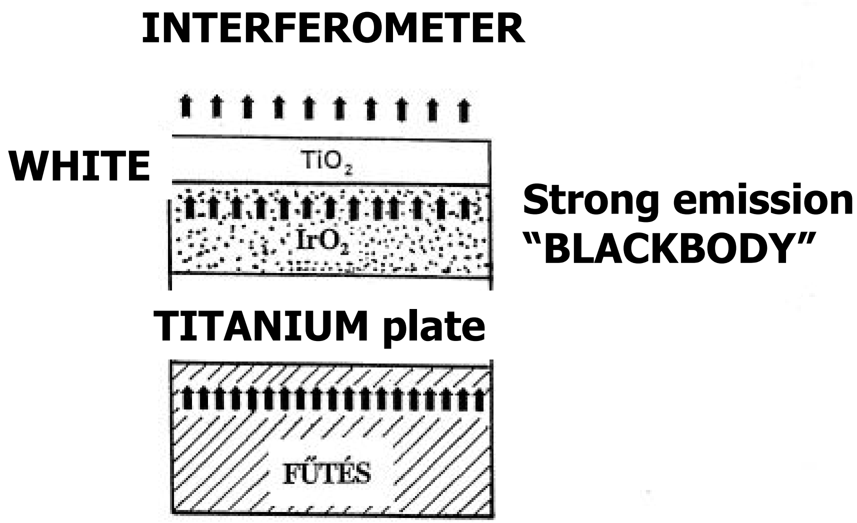




Infrared emission spectroscopy

Temperature: 100 – 200 ^{o}C

Keresztury Gábor, Mink János,
Kristóf János
MTA Kémiai Kutatóközpont,
Veszprémi Egyetem

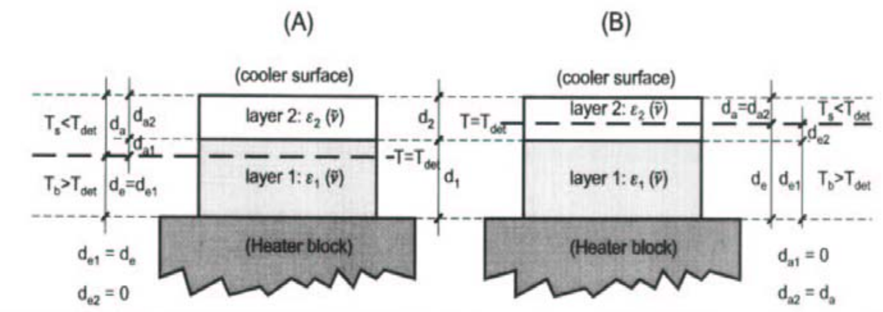


The model of layer structure

Self-absorption

The spectral shape depends on:

- effective thickness of the layers (d_1, d_2)
- thickness of emitting, absorbing layers (d_e, d_a)



G. Keresztury, J. Mink, J. Kristóf:
Anal. Chem. **67**, 3782 (1995)

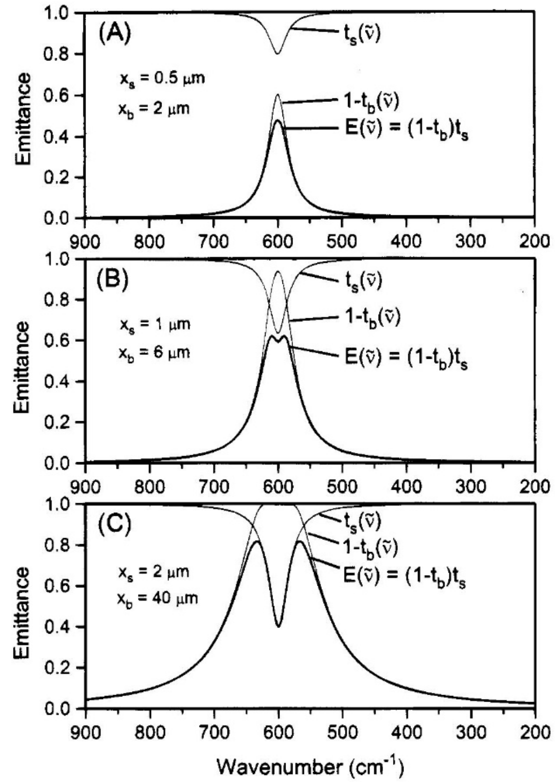


Figure 2. Simulation of the effect of self-absorption using eq 12 for different effective thicknesses of emitting bulk (x_b) and absorbing surface layer (x_s). (Lorentzian band shapes with $\tilde{\nu}_0 = 600$, $I_0 = 2000$, and $w = 30$ cm^{-1}.)

t_b – transmittance of the bulk

t_s – transmittance of the surface

E - emittance

Molecular spectroscopy – Luminescence

Light emission by excited molecules

Fluorescence of different sized CdSe quantum dots

Joseph R. Lakowicz – Principles of fluorescence spectroscopy, 3rd edition

Types of luminescence

(a) Excitation Mode	Luminescence Type
absorption of radiation (UV/VIS)	photoluminescence
chemical reaction	chemiluminescence, bioluminescence
thermally activated ion recombination	thermoluminescence
injection of charge	electroluminescence
high energy particles or radiation	radioluminescence
friction	triboluminescence
sound waves	sonoluminescence

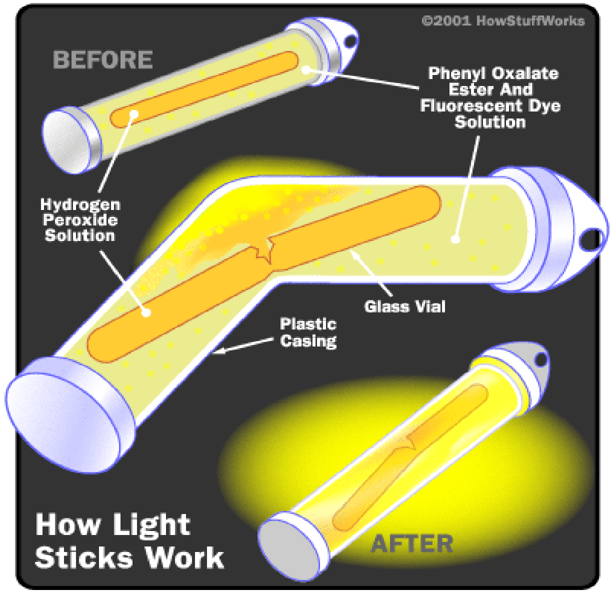
(b) Excited State (Assuming Singlet State)	Luminescence Type
first excited singlet state	fluorescence, delayed fluorescence
lowest triplet state	phosphorescence

Chemiluminescence/bioluminescence

Chemiluminescence – is the emission of light as the result of a chemical reaction

Bioluminescence – one type of chemiluminescence; the light is produced and emitted by a living organism

e.g. firefly, deep-sea fish, jellyfish, squids, bacteria, planktons, mushrooms

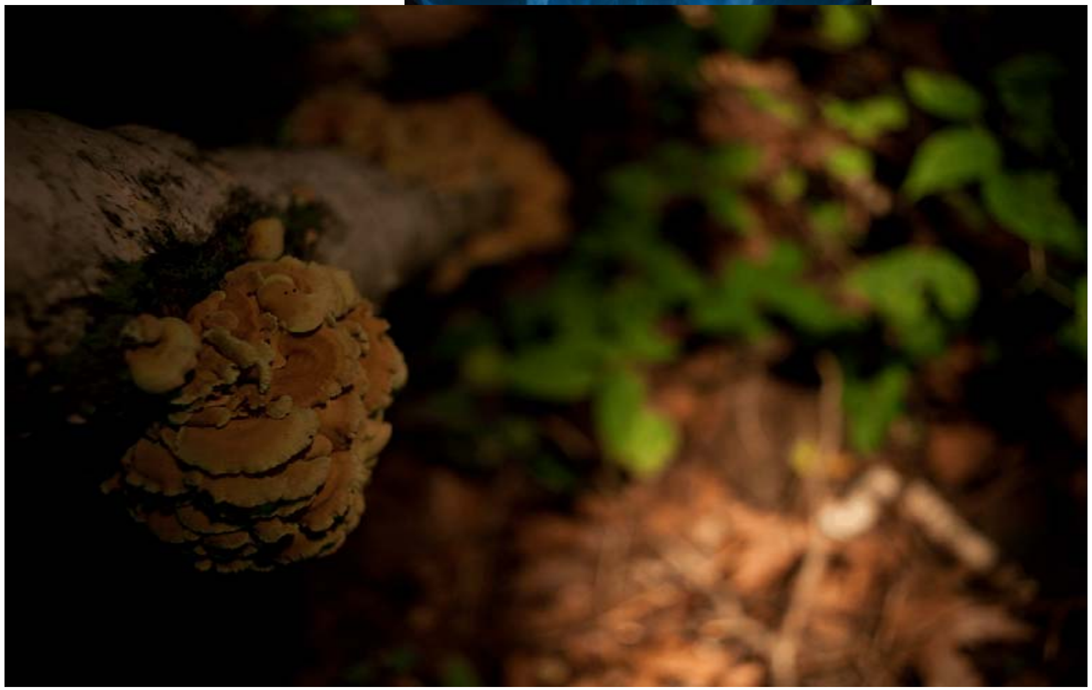


Female of *Lampyris noctiluca*, the Common Glowworm.

The ctenophore *Bathocyroë*

Praya dubia

Bioluminescent mushrooms



The fungus *Panellus Stipticus* displaying bioluminescence.

Luminescence

	Fluorescence	Phosphorescence
➢ Emission:	From excited singlet state	From excited triplet state
➢ Transition:	Allowed	„Forbidden"
➢ Emission rate:	Fast: 10^8 s^{-1}	Slow: $10^3 - 10^0$ s^{-1}
➢ Average lifetime:	1 – 10 ns	ms – s

➢ Example:

0 sec

1 sec

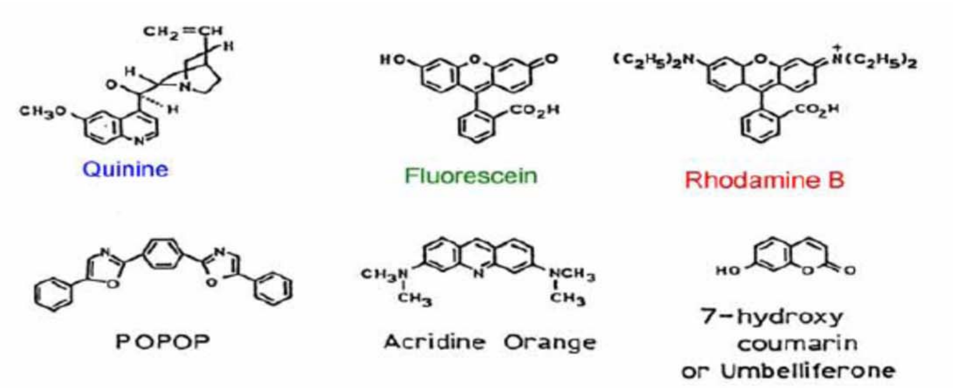
640 sec

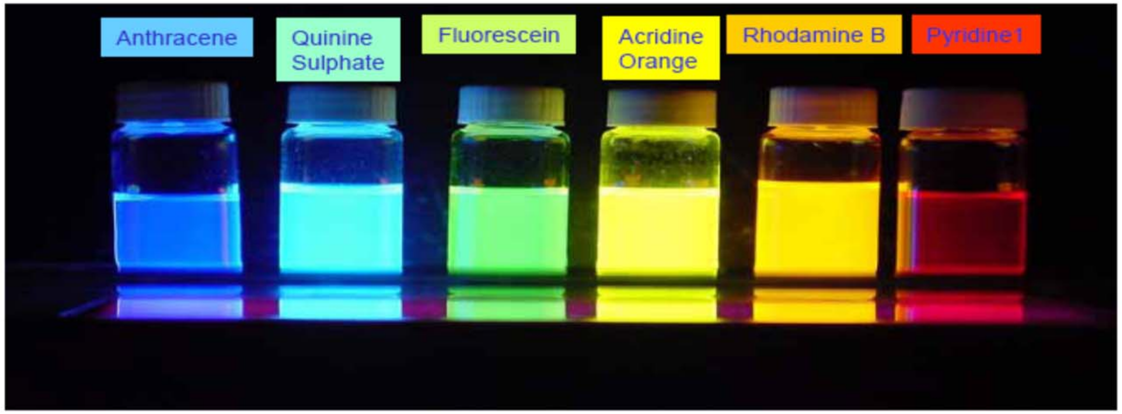
Molecular spectroscopy

Fluorescence – Typical fluorophores

- Typically aromatic molecules
- Usually no fluorescence

in condensed state





Molecular spectroscopy

Fluorescence – the beginning

Sir John Fredrich William Herschel

1792 – 1871

On a case of superficial colour presented by a homogeneous liquid internally colourless. By Sir John Frederick William Herschel, Philosophical Translation of the Royal Society of London (1845) 135:143–145. Received January 28, 1845 — Read February 13, 1845.

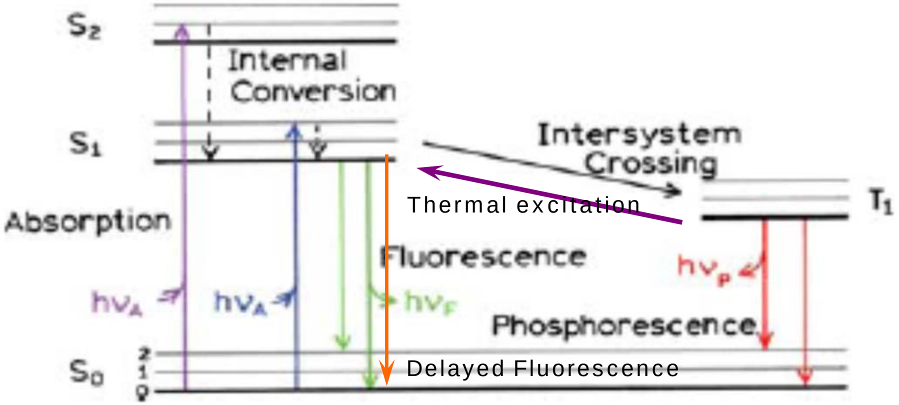
"The sulphate of quinine is well known to be of extremely sparing solubility in water. It is however easily and copiously soluble in tartaric acid. Equal weights of the sulphate and of crystallised tartaric acid, rubbed up together with addition of a very little water, dissolve entirely and immediately. It is this solution, largely diluted, which exhibits the optical phenomenon in question. Though perfectly transparent and colourless when held between the eye and the light, or a white object, it yet exhibits in certain aspects, and under certain incidences of the light, an extremely vivid and beautiful celestial blue colour, which, from the circumstances of its occurrence, would seem to originate in those strata which the light first penetrates in entering the liquid, and which, if not strictly superficial, at least exert their peculiar power of analysing the incident rays and dispersing those which compose the tint in question, only through a very small depth within the medium.

Fluorescence of quinine is the most widely used example up to now

Luminescence – Jablonski diagram

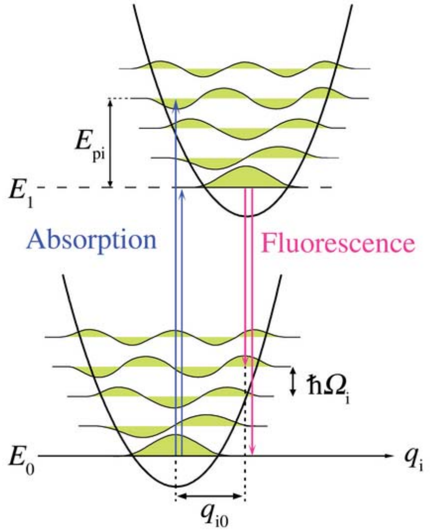
Professor Alexander Jablonski

1898 – 1980



One form of a Jablonski diagram.

Luminescence in molecules



Franck-Condon principle
R: configuration coordinate

absorption (vertical)

↓

relaxation

↓

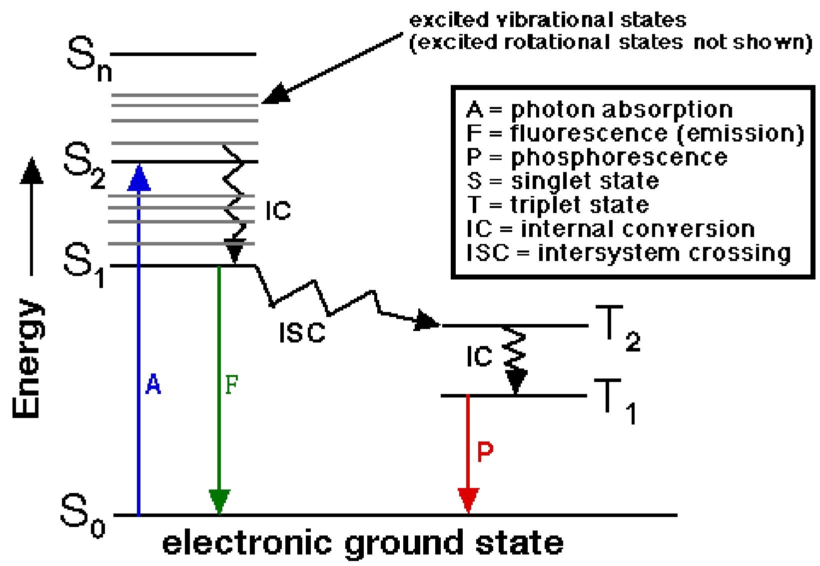
emission (vertical)

↓

relaxation

http://en.wikipedia.org/wiki/Franck-Condon_principle

http://www.shsu.edu/~chemistry/chemiluminescence/JABLONSKI.html

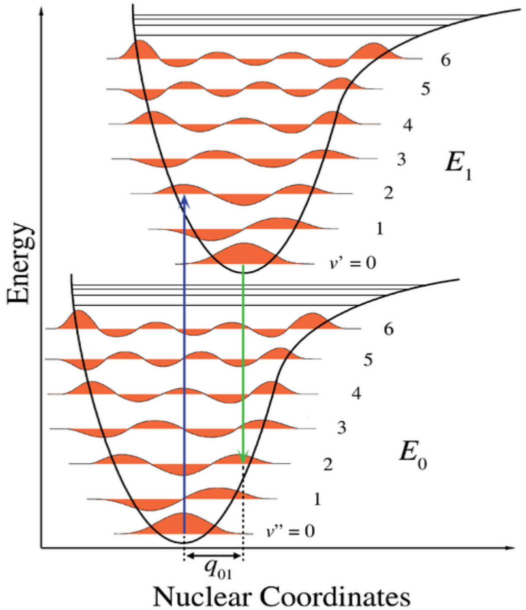


Jablonski diagram

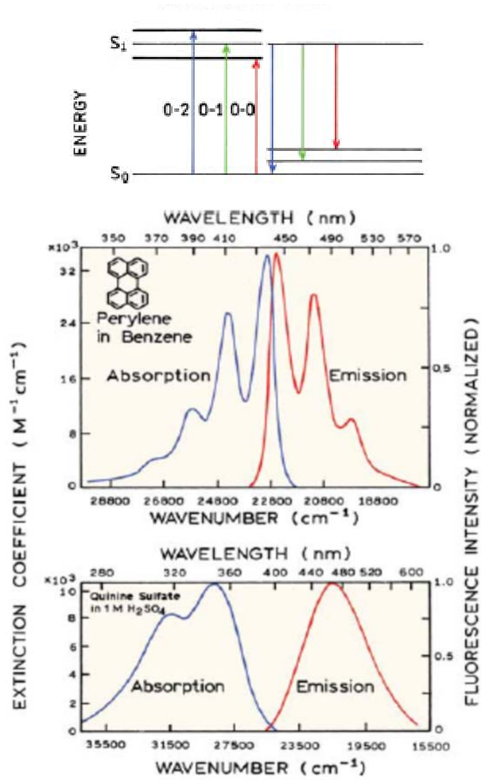
Intersystem crossing: singlet– triplet
Internal conversion: into vibrationally excited state of higher singlet
Fluorescence: singlet - singlet
Phosphorescence: singlet – triplet (delayed)

Fluorescence basics

Franck-Condon principle



Mirror image



During an electronic transition a change from one vibrational energy level to another will be more likely to happen if the two vibrational wavefunctions overlap more significantly

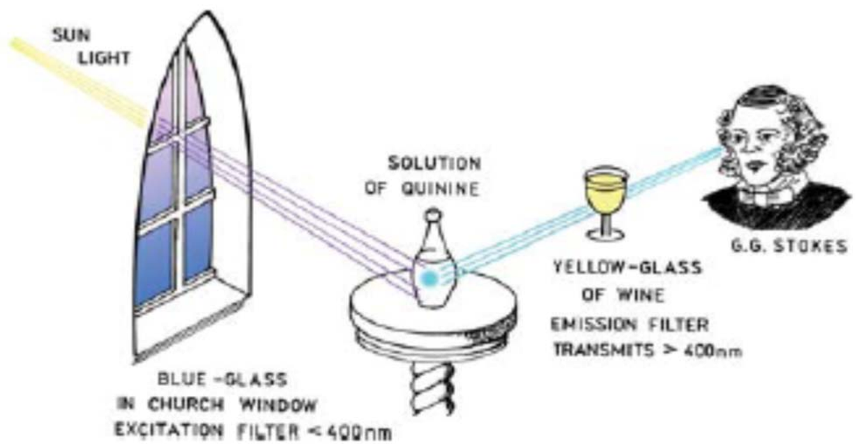
Electronic excitation does not greatly alter the nuclear geometry

Molecular spectroscopy

Fluorescence – Stokes shift

Sir George Gabriel Stokes

1819 – 1903



Experimental schematic for detection of the Stokes shift.

Visual observation of Stokes shift

Molecular spectroscopy

Fluorescence – Lifetime (τ) and quantum yield (Q)

- These are the two most important characteristics

$$\text{quantum yield} = Q = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} = \frac{\Gamma}{\Gamma + k_{nr}}$$

where Γ – emission rate of fluorophores

k_{nr} – number of non-radiative transitions to ground state S_0

if there is Stokes shift, $Q < 1$

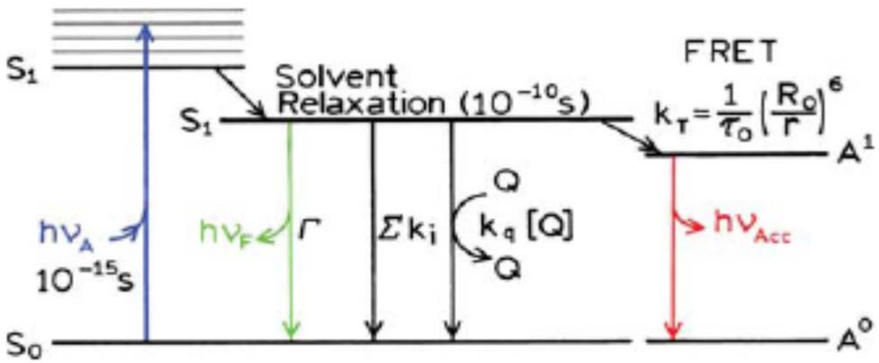
Lifetime: average time between excitation and emission

$$\tau = \frac{1}{\Gamma + k_{nr}}$$

if $k_{nr} = 0$, *intrinsic* lifetime

Fluorescence – Quenching

Quenching – intensity of fluorescence decreases



Jablonski diagram with collisional quenching and fluorescence resonance energy transfer (FRET). The term Σk_i is used to represent non-radiative paths to the ground state aside from quenching and FRET.

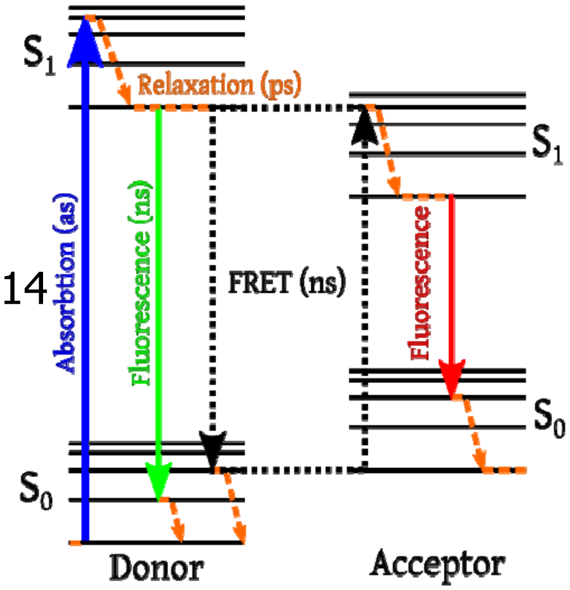
Reasons:

- collision with other molecules (quenchers)
- formation of non-fluorescent complexes
- resonance energy transfer (RET)

Molecular spectroscopy

Fluorescence – Resonance energy transfer

- emission spectrum of donor overlaps with absorption spectrum of acceptor
- no intermediate photon
- dipole-dipole interaction between donor and acceptor



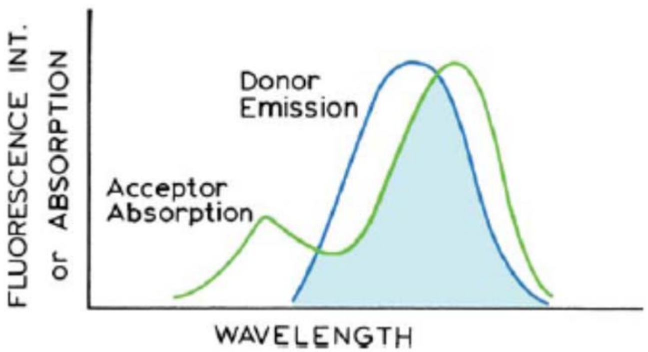


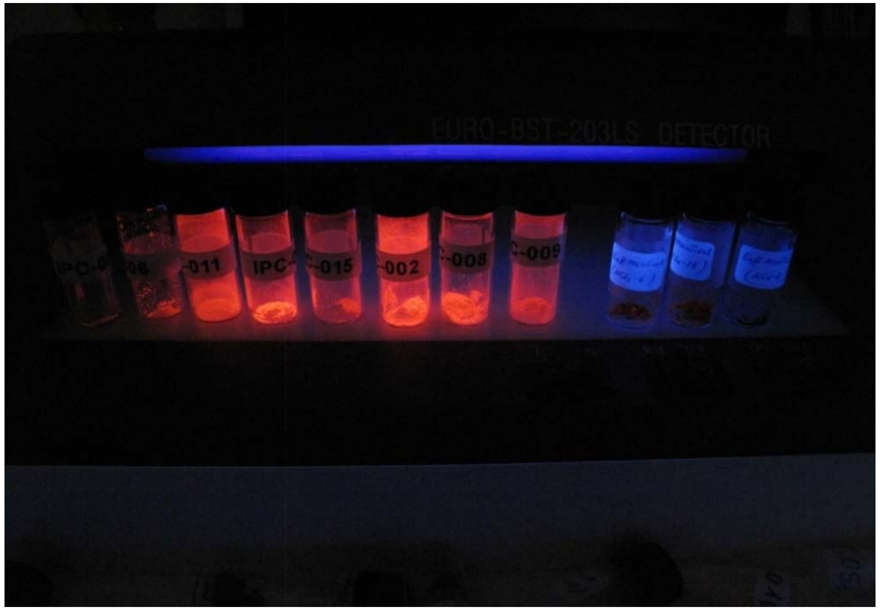
Figure 1.16. Spectral overlap for fluorescence resonance energy transfer (RET).

Molecular spectroscopy

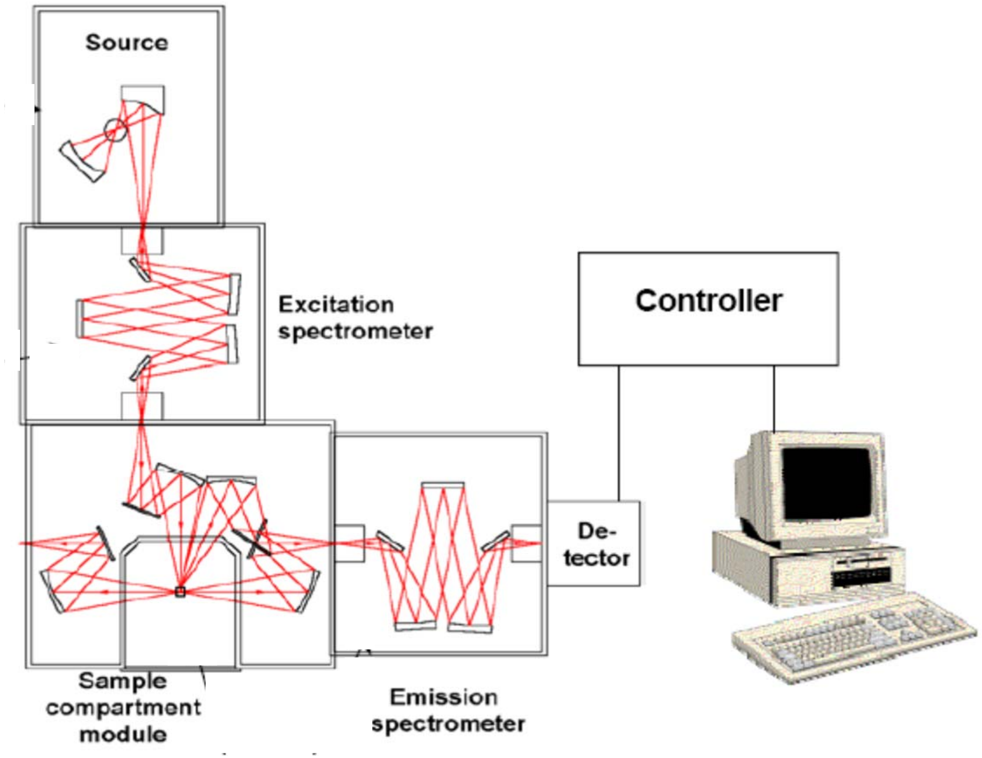
Fluorescence – Eu-based fluorophores

White llight illumination

UV light (365 nm)



Spectrofluorimeter – Fluorolog 3



Take-home message

- Atomic emission spectroscopy: flame test, flame emission photometry, atomic absorption spectroscopy, inductive coupled plasma
- Infrared emission spectroscopy: vibrational levels, self-absorption
- Molecular spectroscopy: types of luminescence
- Jablonski diagram: absorption, fluorescence, phosphorescence, internal conversion, intersystem crossing
- Quantum yield and lifetime
- Resonance energy transfer

Összefoglalás

- Atomi emissziós spektroszkópia: lángfestés, lángfotometria, atomabszorpciós spektroszkópia
- Infravörös emissziós spektroszkópia: rezgési szintek, önabszorpció
- Molekulaspektroszkópia: lumineszcencia típusok
- Jablonski-diagram: abszorpció, fluoreszcencia, foszforeszcencia, belső konverzió, intersystem crossing
- Kvantumhatásfok és élettartam
- Rezonáns energiatranszfer