

Principles of spectral analysis methods

Nanomaterials characterization I

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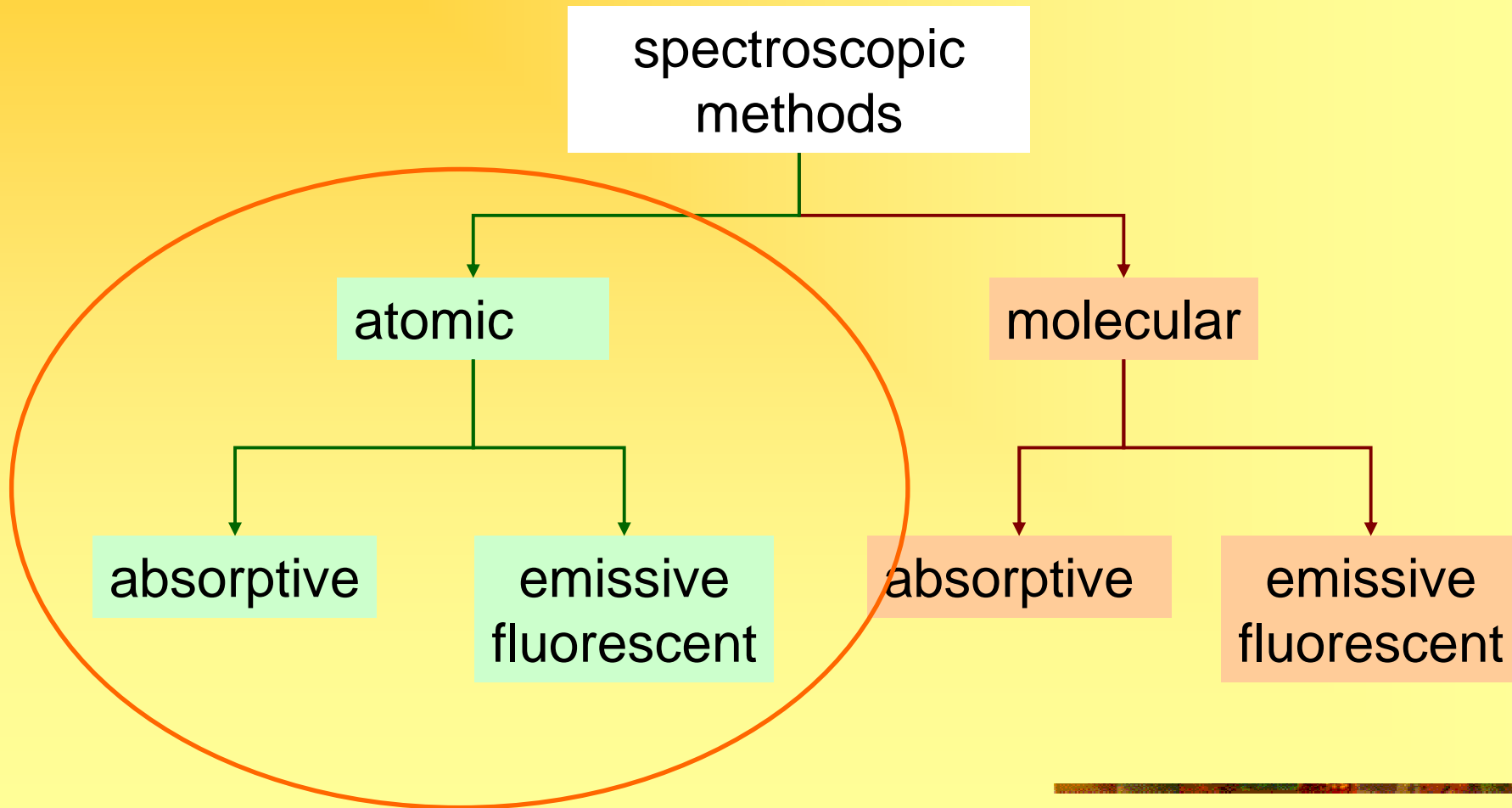
OP Vzdělávání
pro konkurenceschopnost

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Spectral analysis methods

- Optical methods for **determination of material chemical composition**
 - Methods are based upon interaction material – electromagnetic radiation
 - interaction material – radiation → **energy-changing** (non spectroscopic methods – polarimetry, refractometry → without energy – changing)
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Spectroscopic techniques



Spektroskopische methods: atomic x molecular

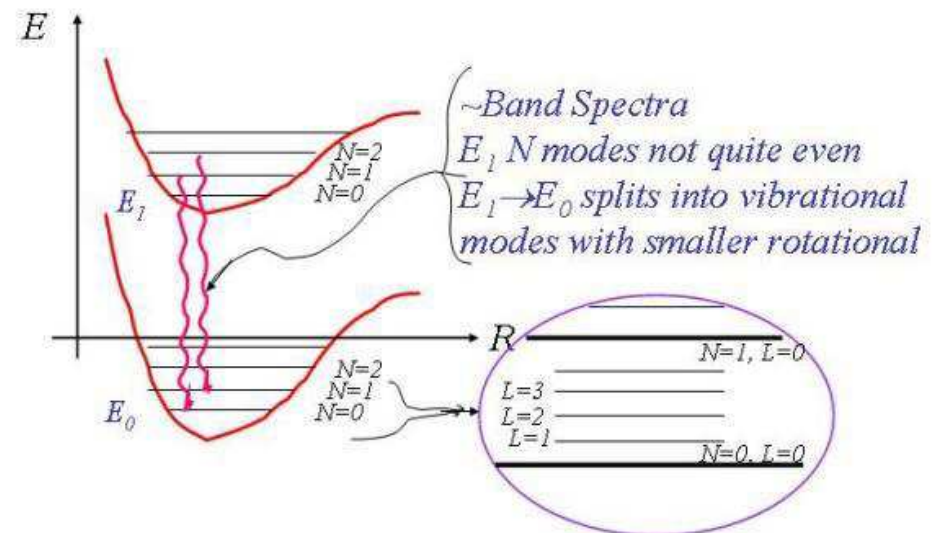
❖ atoms and molecules can change their energy stage due to absorption or emission of discrete energy values only

❖ in atoms interchange is mediated only due to electrons, in molecules energy levels are splited (vibrational and rotation sub-levels)

❖ For differences between energy levels:
 $\Delta E_{\text{rot}} \ll \Delta E_{\text{vibr}} \ll \Delta E_{\text{el}}$

Molecular spectra

Selection Rules: $\Delta N = \pm 1$ & $\Delta L = \pm 1$ at a fixed n electronic



9/13/2006

Physics 13 - Fall 2001 -
 Goldstein Physics 13 - Fall 04 - G.R.
 Goldstein

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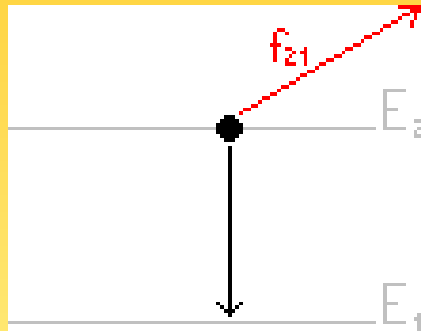
Optical atomic spectroscopy

- Method that makes use of processes connected with **valence electrons transitions**

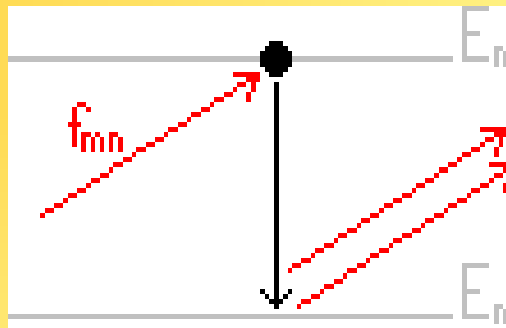
Processes leading to the change of quantized valence electron energy:

- spontaneous emission → *atomic emission spectral analysis*
- absorption of radiation → *atomic absorption spectrometry*
- secondary emission → *atomic fluorescent spectrometry*
- stimulated emission → *lasers*

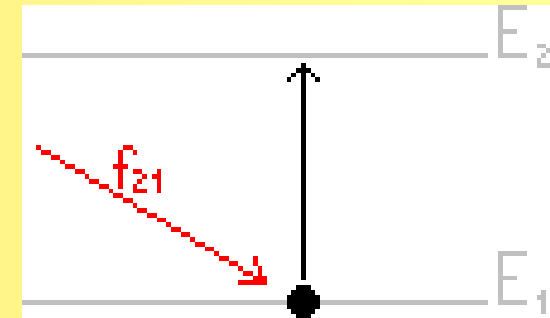
Electron transitions diagrams:



Spontaneous emission



Stimulated emission



Absorption

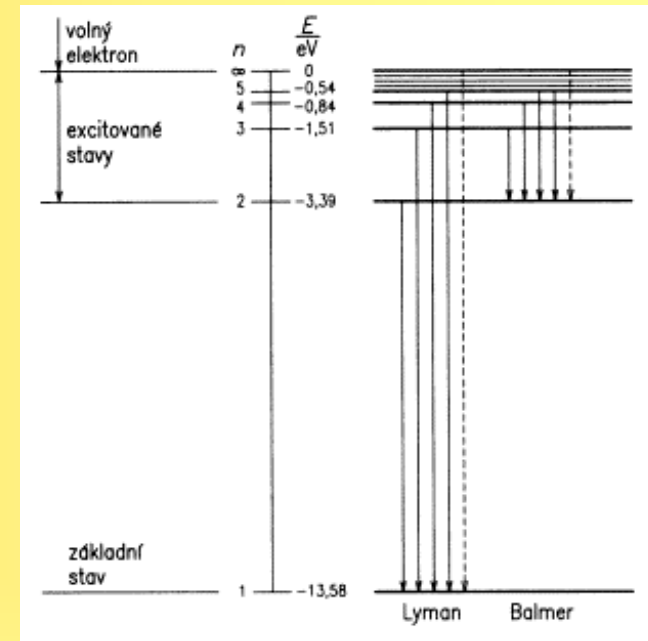
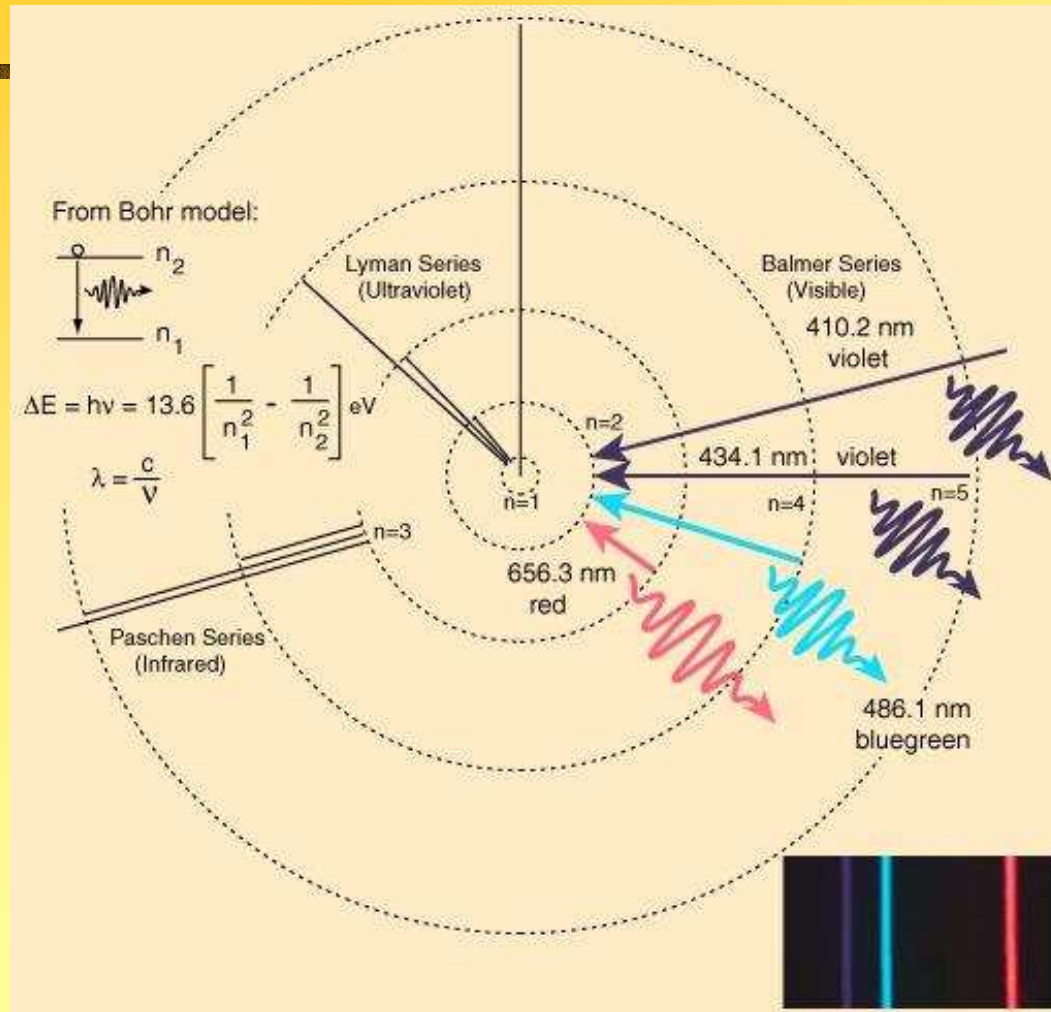
Photon absorption ($E = \Delta E_{mn}$) by electron on higher energy level $E_m \rightarrow$ **emission of other photon** with the same energy, direction and phase of oscillation like excitant photon.

Avalanche effect is used in lasers \rightarrow formation of an intensive beam of monochromatic, parallel and coherent radiation

Optical emission spectroscopy (OES)

- One of the most sensitive methods of qualitative and quantitative elemental analysis
- Method is based on the registration of photons that arise by **transitions of valence electrons from higher energy levels to lower energy levels**
- Registration of radiation emitted by atoms or ions → **emission spectrum**
- Line character of spectrum – spectral lines corresponding with separate transitions
- Area 110 – 900 nm is used for an analysis only

The simplest spectrum - atomic hydrogen



Bohr's model of hydrogen atom

Hydrogen



Helium



Lithium



Oxygen



Carbon



Nitrogen



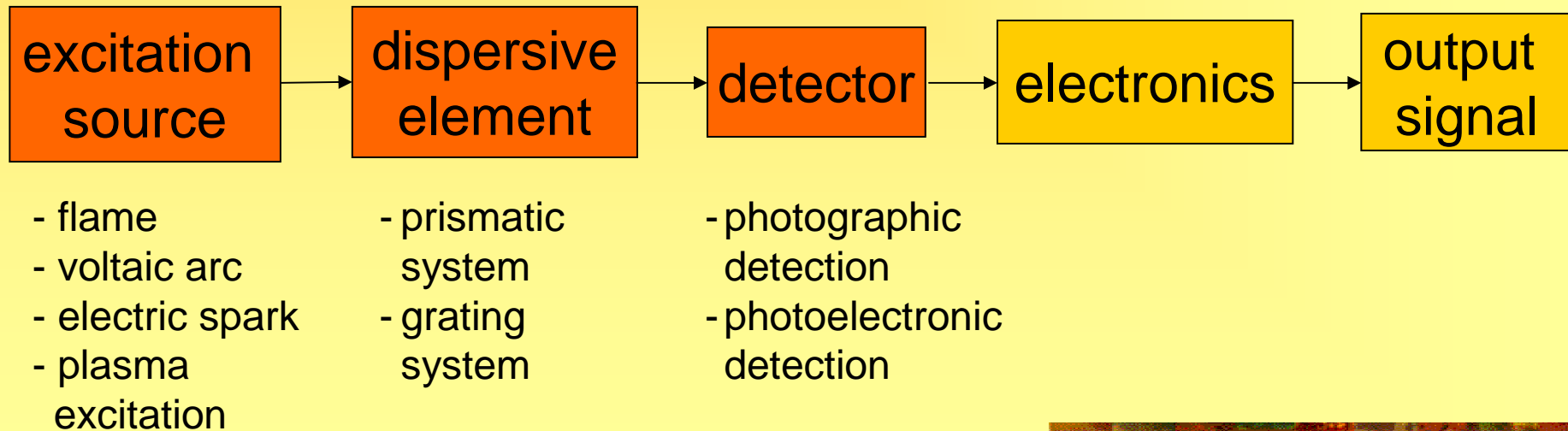
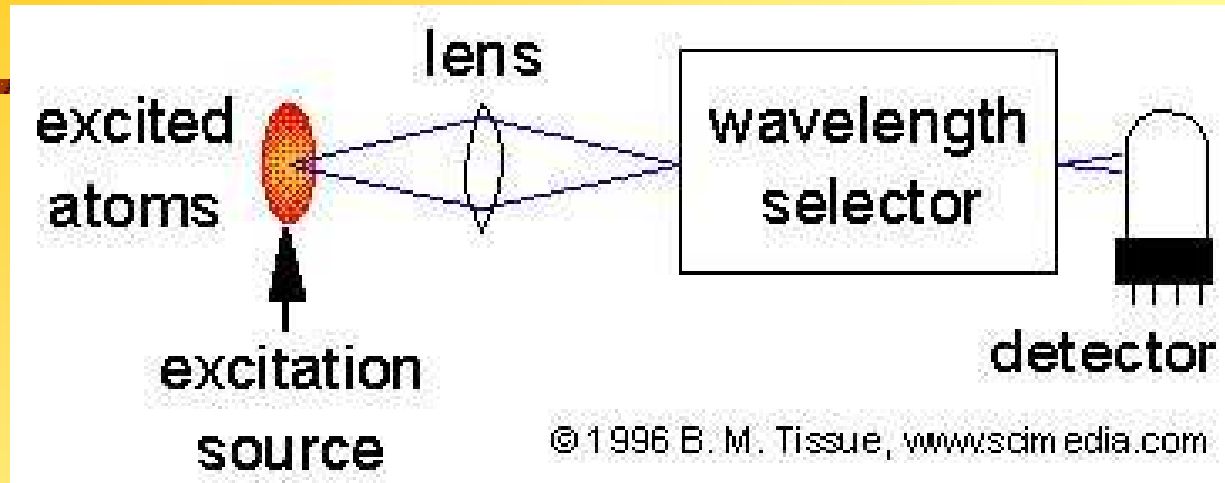
OES - atomic spectrum registration

- **Lines position** (wavelength) defines elements included in the specimen → ***qualitative composition***
 - **Lines intensity** defines elements concentration in the specimen → ***quantitative composition***
-
- **number of lines** in the spectrum is increasing with number of electrons on valence shell
 - similarity of atoms and ions spectras with the same number of electrons (Li⁺ a H for example) or spectras of elements with the same number of electrons on the top-shell
 - spectras of alcali metals – number of lines 1-n.10, spectras of Fe, W, V, Ta, Mo – a few thousands of lines

OES - atomic spectrum registration

- **Conditions:**
 - elements must be in atomic state
 - elements must be excited to higher energy state
 - Realization – by **thermic excitation**
 - The number of spectral lines is increasing with increasing temperature of excitation source (multiple ionization, realization of forbidden transitions)
 - The most intensive lines – so called **resonance spectral lines** (transitions from higher levels to ground state)
-

Basic scheme of optical emission spectroscopy



Spectroscopic instruments → distribution and registration of light

- **Spectrograph** → photographic registration of arc spectrum
- **Spectroscope** → visual observation
- **Spectrophotometer** → measuring of separate wavelength
- **Kvantometer** → modern spectrograph, detector ≡ photomultiplier

- **Dispersion** - angle $D_\varphi = \frac{d\varphi}{d\lambda}$
- linear $D_l = \frac{dl}{d\lambda}$
 - **Resolution** $R = \frac{\lambda}{d\lambda_{\min}}$
- Characteristics of spectral instruments**

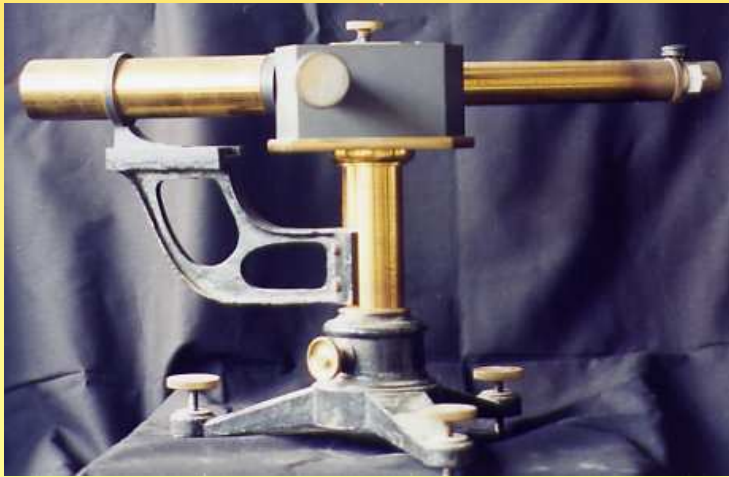
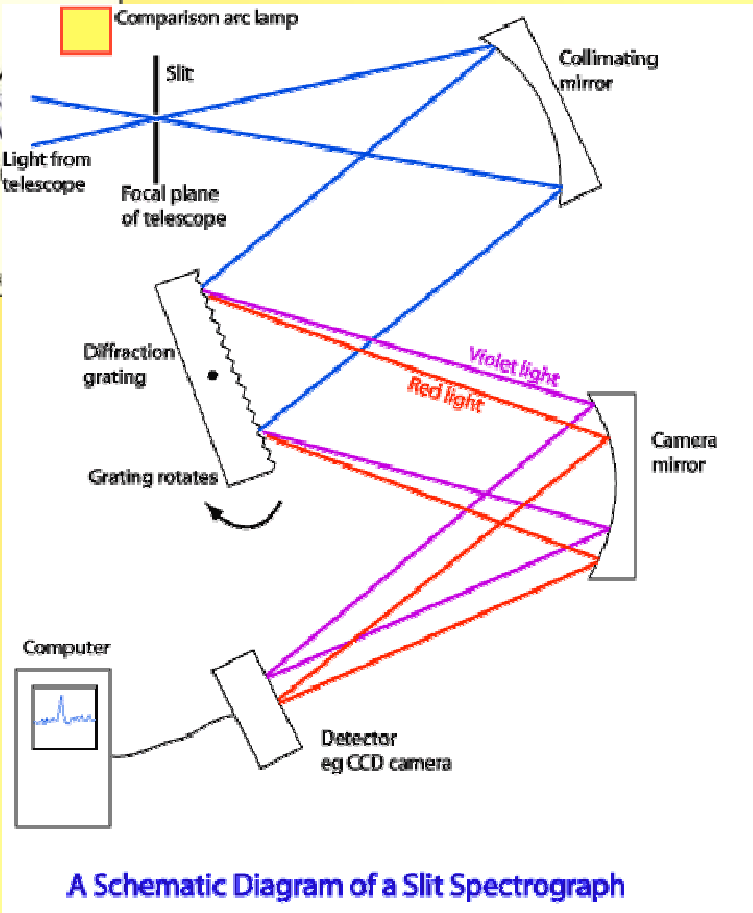
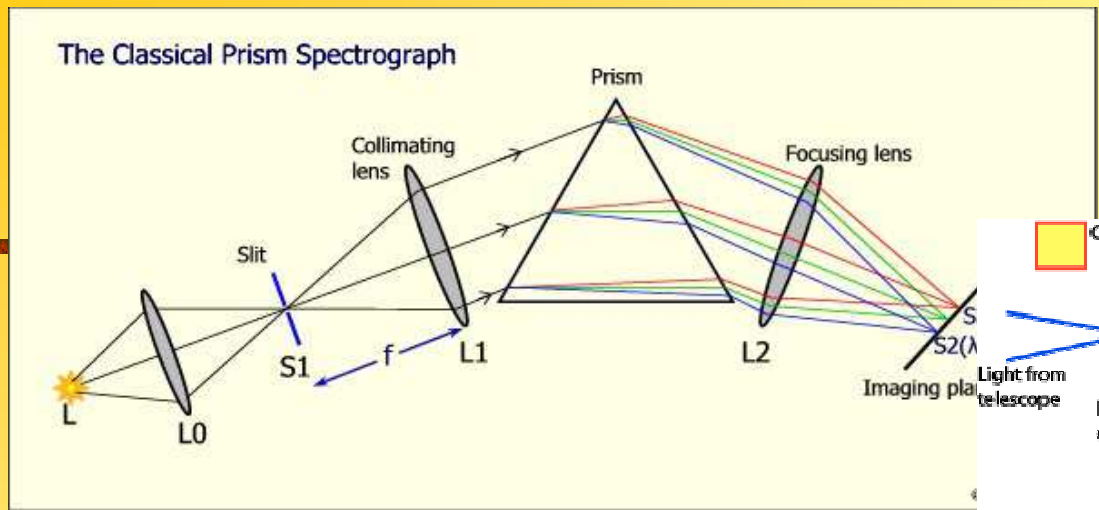
OES classic methods

- **Flame photometry**

- Flame excitation (low temperature \Rightarrow analysis of easy excited elements - Na, K, Li, Ca, Mg)

- **Spectrography**

- historical method, excitation – voltaic arc, electric spark
- dispersive element: prism, grid
- optics: lenses, concave mirror
- advantage: high sensitivity
- disadvantage: less reproducibility (less stability of discharge)
- Semi-quantitative analysis (method of homologous pairs, method of spectra comparison)
- Quantitative analysis – element concentration is defined from spectral line intensity (Lomakin relation)



Grating spectrograph Steinheil, 1910

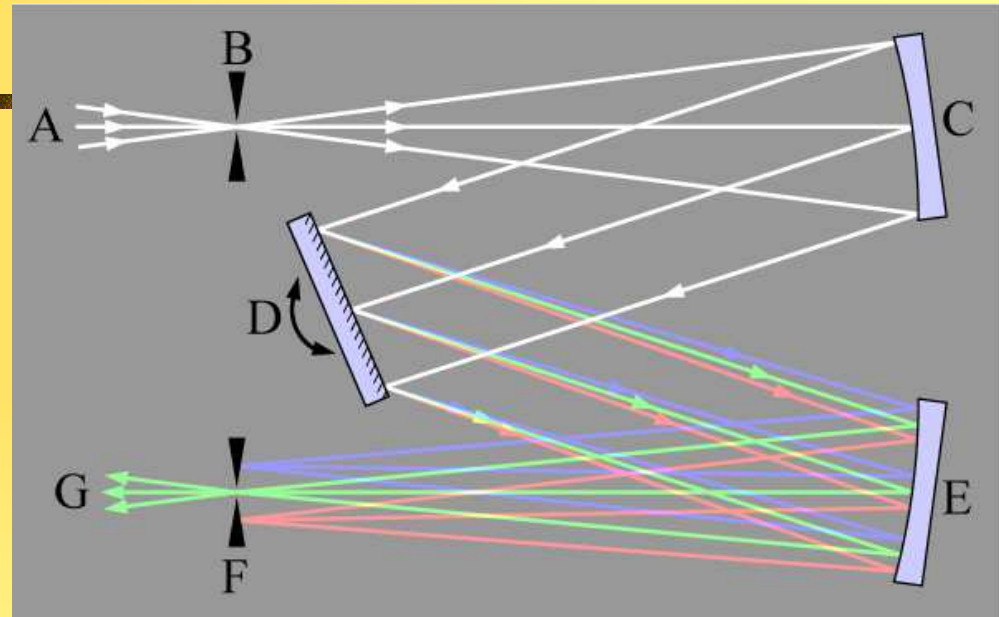
Modern methods of OES

- **Sequence** spectrometers
spectrum is taken **subsequently** (incident radiation intensity is measured, **subsequent** change of λ) \Rightarrow lower speed, higher flexibility of analysis)
- **Simultaneous** spectrometers
exit slits are set to the concrete λ , incident radiation intensity is measured simultaneous \Rightarrow high speed, but possibilities of analysis are limited (it is possible to scan only elements that are set to the „channels“ (slit + photomultiplier system)
- **Simultaneously - sequence** spectrometers
combination of both types and advantages, scanning of integral emission spectrum

Scheme of sequence spectrometer

(dispersion element = monochromator)

Czerny-Turner
monochromator



F...entrance slit

E, C...concave mirrors → focusing of radiation on grid, event. on output slit

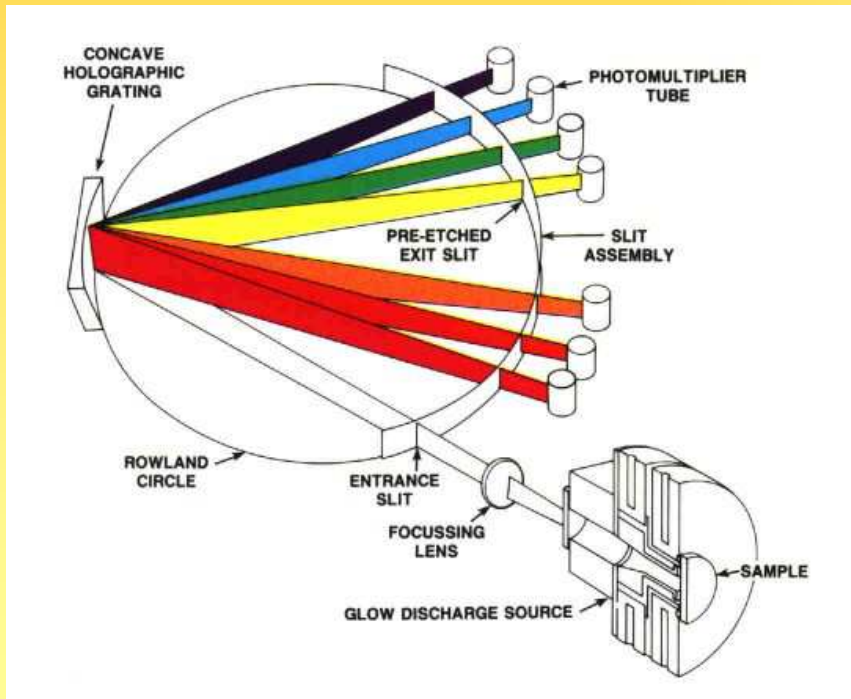
D...diffraction grating → dispersion of polychromatic radiation

(narrow interval $\Delta\lambda$ incidents to exit slit B, choice of interval - tilt of grating)

Scheme of simultaneous spectrometer

(dispersion element = polychromator)

Paschen-Runge polychromator



- separate channels (slit + photomultiplier + electronics) are installed on the Rowland's circle
- channels are optimized for accordant line
- plane-parallel plate is used for correct setting of λ

Specificity of metals emission analysis

- **Excitation**

- excitation sources
 - arc discharge – high sensitivity, low reproducibility;
 - spark discharge – lower sensitivity, high reproducibility
- excitation conditions (discharge in air, discharge in argon)
- excitation process:
 1. spark pre-ejection (remelting of surface → homogenization)
 2. analytic spark ejection

- **Quantitative analysis**

- Calibration (calibration standarts, analytic curves for main matrix elements)
- Spectral-line interference – elimination through mathematical correction

Specificity of metals emission analysis

- Spectrometers for special analytic programme
 - **Mobile spectrometers** – for analysis of only two material bases ⇒ material verification
 - **Laboratory spectrometers** – configured for a wider analytic programme ⇒ accurate analysis
 - **Automatic spectrometric centre** – full automatized system, special container ⇒ very fast and accurate analysis for smelting industry, high price
 - Sample preparation
 - according to the type of the spectrometer – smooth-surfaced usually (polishing)
 - main problem – contamination from abrading material!
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Glow Discharge Spectrometry (GDS)

- Glow (Grimm's) discharge
- Cathode: analysed specimen
- Excitation in argon atmosphere

- **Advantages:**
 - Reproducibility better than for spark excitation
 - Less effects of matrix
 - Less width of lines → better resolution of near lines

- **Disadvantages:**
 - Longer time of analysis
 - High-quality preparation of specimen surface is necessary

- **Possibilities:**
 - surface analysis
 - in-depth profiles

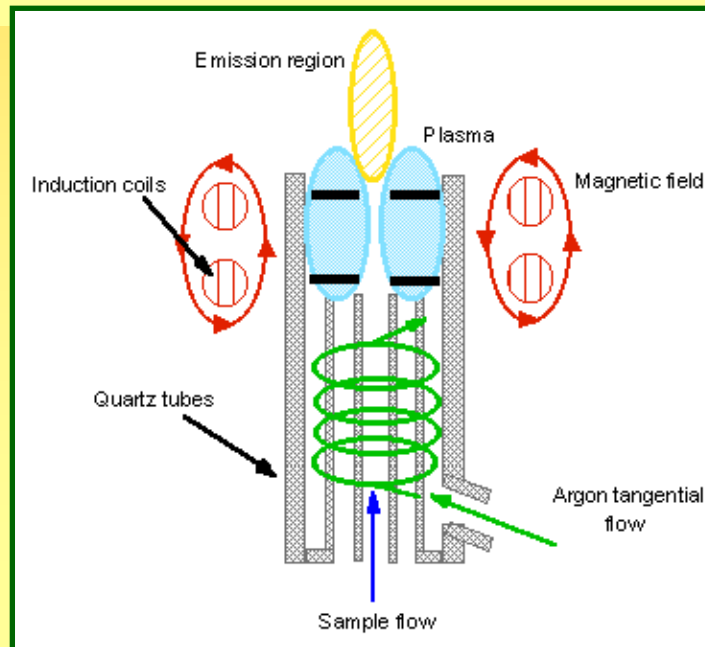
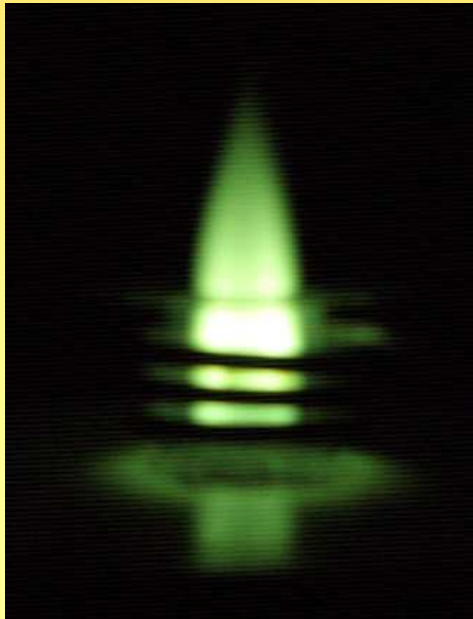


Plasma spectroscopy

- Classic sources of excitation → many negative properties → instability, effects of matrix, ... ⇒ searching of alternative excitation sources
- **Plasma jets** – different types (according to supply – direct current or high frequency energy supply)
- **Transition gas-plasma: by means of energy supply**
($>$ ionization energy of present atoms) by heating to high T usually
– cca n.1000K

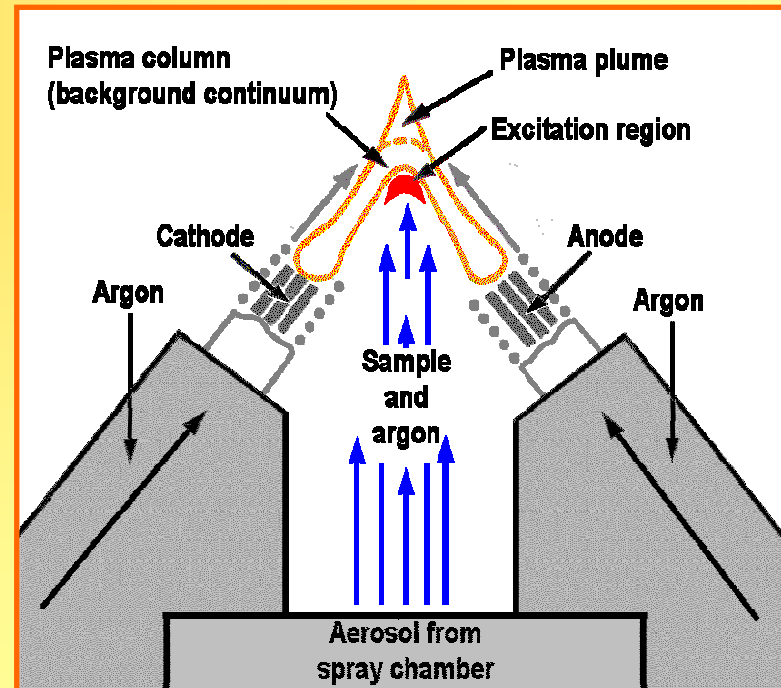
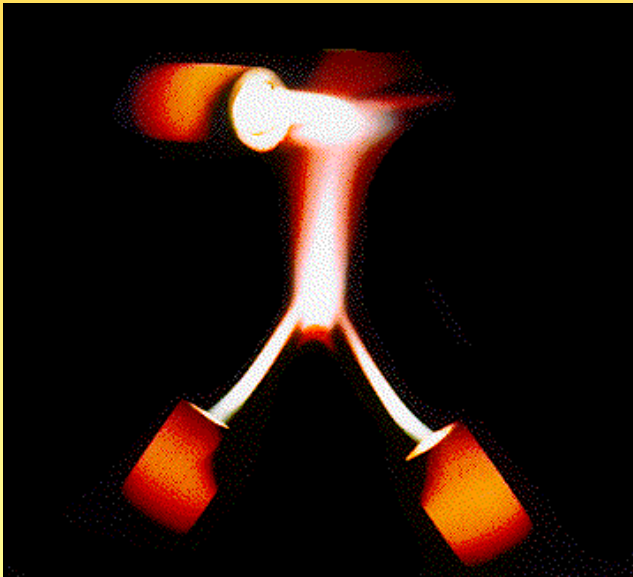
Plasma spectroscopy

- **ICP (Inductively Coupled Plasma)**
- (high-frequency inductively coupled plasma – microwave generators)
- analysis of all specimen states is possible, mainly for analysis of solutions
- Solid state phase analysis – special techniques (direct transfer of the specimen in the plasma, electrothermic evaporating, discharge abrasion, laser ablation)



Plasma spectroscopy

- **DCP (Direct Current Plasma)**
(direct supply of plasma jet) – three-electrode system usually, argon plasma, aerosol of specimen



ICP OES spectrometer

- generator of high-frequency current, ICP burner, gas unit
- specimen transfer system
- spectral instrument (optics + grating + detector)
- control unit and signal processing

