Chapter 25

Instruments for Optical Spectrometry

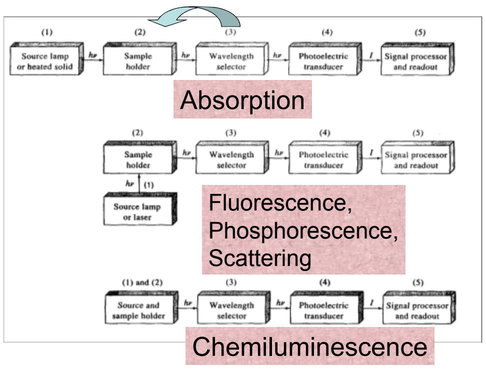
Optical Instruments

- Emission Flame Photometer (ICP—Inductively Coupled Plasma Emission Spectrometer)
- Flame Atomic Absorption Spectrometer (AA)
- Absorption Spectrometer (UV/Vis, FTIR)
- Fluorescence Spectrometer (Fluorimeter)
- Scattering Spectrometer (Raman Spectrometer)

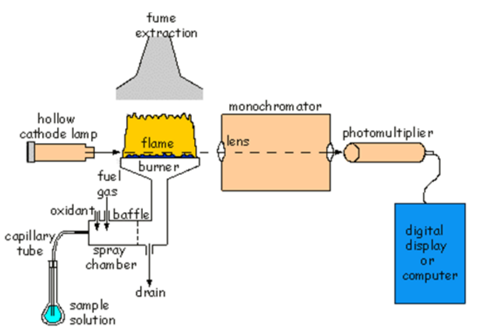
4 Basic Components of Instruments for Chemical Analysis

- signal generators
- detectors (input transducers)
- signal processors (circuits & electrical devices)
- readout devices

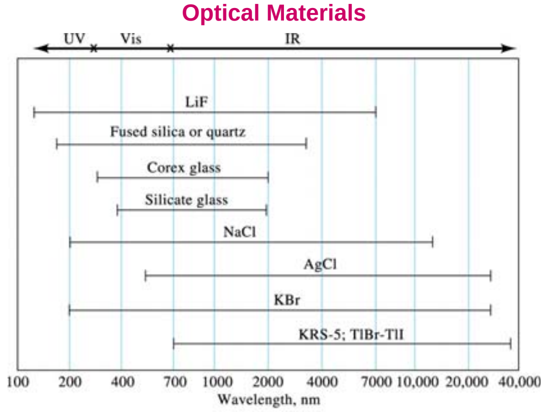
Optical Instrument Configurations



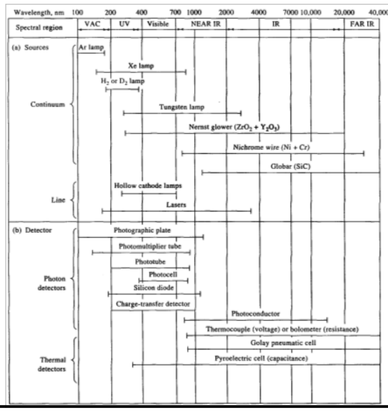
Atomic Absorption Spectrometer



Optical Materials



Optical Sources and Detectors



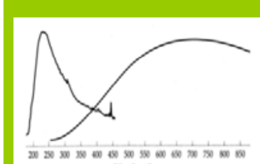
EMR Sources

- **Ideal Properties:**

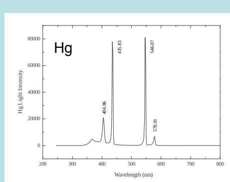
-High Intensity
easily measured
-Stable
low noise
-Tunable
provides desired λ's

Two Types of Sources

- Continuum -Band Spectrum (wide λ-range)

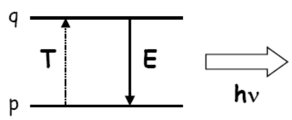


- Line Spectrum (discrete λ's)



Line Sources

- Most line sources rely on spontaneous emission from thermally-excited **gas-phase** atoms/ions:

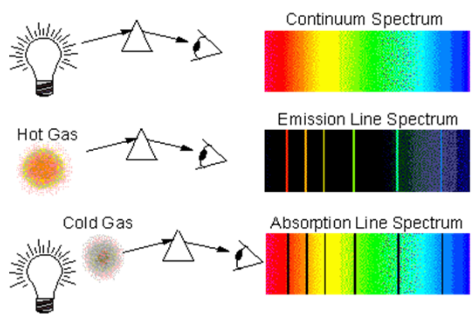


$$Emission \quad rate = -dN_q / dt = N_q A_{qp}$$

Excited state population

Einstein Spontaneous Emission Transition Probability

Continuum & Line Spectra



Most Commonly Used Sources

http://sales.hamamatsu.com/en/products/electron-tube-division/light-sources.php

- UV-Visible-Near IR Region

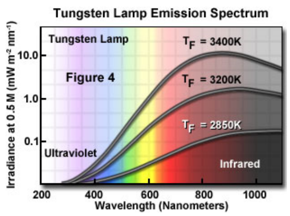
(a) H_2 or D_2 (deuterium) lamps (160-375 nm)

$D_2 + E_{electrical} \rightarrow D_2^* \rightarrow D_{(KE1)} + D_{(KE2)} + h\nu$

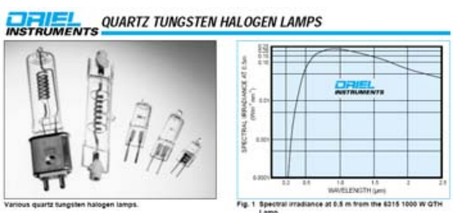
(b) Xenon Arc Lamps (250-600 nm)

λ_{max} ~ 500 nm

(c) Tungsten Lamps
(320-2500 nm)



(d) Quartz Tungsten Halogen Lamps (200-3000 nm)



high temperature (3500 K)

$$\text{Evaporation} \quad W(s) \rightarrow W(g)$$

$$W(g) + I_2(g) \rightarrow WI_2(g)$$

$$\text{Redeposition} \quad WI_2(g) + W(s) \rightarrow W(s) + I_2(g)$$

- IR Region
  - Nernst glower - rare earth oxides
  - globar - silicon carbide rod
  - incandescent wire - nichrome wire

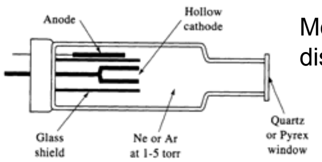
- Line Sources

(a) Hg Lamps
(b) Hollow Cathode Lamps
(Atomic Absorption Analysis)

Hollow Cathode Lamps

Hamamatsu Produces ~186 HCL Lamps

Can be used to detect ~70 metals

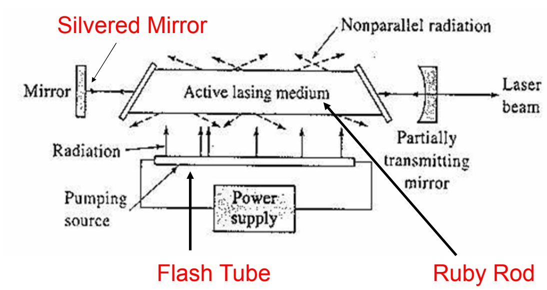


More Details will be discussed in Chapter 9

Sources

Lasers

Light Amplification by Stimulated Emission of Radiation



Sample Cells

- Must be transparent over desired λ-range

-- Visible:Glass or Plastic

-- UV/Vis:Quartz (fused silica)

-- IR:KBr/NaCl

- Needs to have a stable, fixed pathlength

--can be 1 mm to ~ few cm (varies)

- Should have minimal physical defects

--to keep losses due to scattering/reflection at a minimum

Wavelength Selectors

- Optical Filters
  - Interference
  - Absorbance
- Prism Monochromators
- Grating Monochromators
- Interferometers

Radiation Transducers:
(Detectors)

Ideally:

- high sensitivity
- low noise
- wide wavelength response
- linear output ($S=k \cdot I$)
- low dark current (small current when $I=0$) ($S=k \cdot I+k_d$)

Detectors

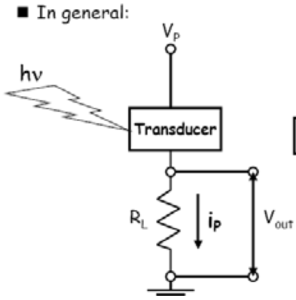
- *Earliest:* ***The Human Eye***
- can detect single photons
- limited to visible spectral region
- quantitation is problematic

- Two classes to consider:

1. **Single-Channel**
   - monitor intensity of a single resolution element at a time
2. **Multi-Channel**
   - monitor intensities of many resolution elements at a time

Single-Channel Detectors

- In general:

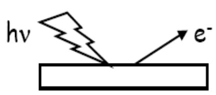


$$V_{out} = i_P R_L$$

Two common types:

1. **Photoemissive**

   Based on photoelectric effect:



•e^- released only if $h\nu > E_{min}$

•$\#e^- \propto \#photons$

2. **Photoconductive**

   -photons striking device cause an *increase* in electrical conductivity

   -e.g., photodiodes, semiconductors

Multi-Channel Detectors

- Monitors intensities of *many resolution elements* **simultaneously**

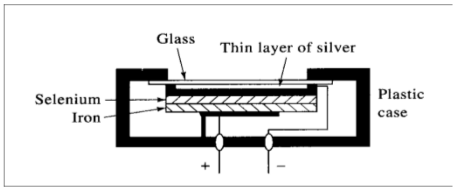
  -similar to FT-interferometry (multiplexed measurement), but in the *frequency domain*

  -**Examples:**

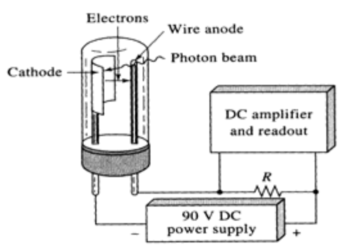
  -photographic plates
  -photodiode arrays (PDA)
  -CID and CCD detectors

  -Most commonly limited to UV/Vis

Detectors/Transducers Examples

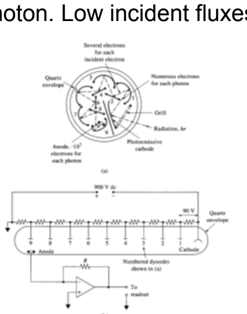


(A) Photovoltaic cells - metal-semiconductor-metal sandwiches that produce voltage when irradiated (350-750 nm)



(B) Phototube - electrons produced by irradiation of cathode travel to anode. I response depends on cathode material (200-1000 nm) (Photoelectric Effect)

(C) Photomultiplier tube (PMT) - irradiation of cathode produces electrons, series of anodes (dynodes) increases gain to 10^5-10^7 electrons per photon. Low incident fluxes only !



HAMAMATSU

PHOTOMULTIPLIER TUBES

R928, R955

Extended Red, High Sensitivity, Multialkali Photocathode
28mm (1-1/8 Inch) Diameter, 9-Stage, Side-On

FEATURES

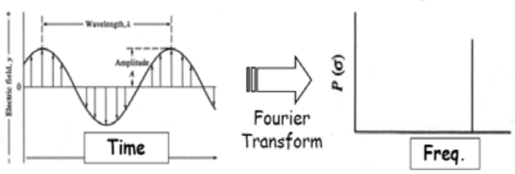
- **Wide Spectral Response**
  - R928 .... 185 to 900 nm
  - R955 .... 160 to 900 nm
- **High Cathode Sensitivity**
  - Luminous .... 250 μ A/lm
  - Radiant at 400nm 74mA/W
- **High Anode Sensitivity (at 1000V)**
  - Luminous 2500A/lm
  - Radiant at 400nm .... 7.4×10^5 A/W
- **Low Drift and Hysteresis**

The R928 and R955 feature extremely high quantum efficiency, high current amplification, good S/N ratio and wide spectral response from UV to near infrared. The R928 employs a UV glass envelope and the R955 has a fused silica envelope for UV sensitivity extension.
The R928 and R955 are well suited for use in broad-band spectrophotometers, atomic absorption spectrophotometers, emission spectrophotometers and other precision photometric instruments.

Non-Dispersive Methods

- **Fourier-Transform Interferometry**

What if we could measure the *oscillating wavefunction* of EMR *directly?*

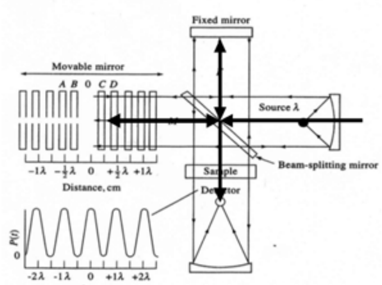


Time Domain

Frequency Domain

Michelson Interferometer

- EMR enters and hits *beamsplitter*
- Part goes to *fixed mirror*
- Part goes to *moveable mirror*
- Reflected beams recombine at *beamsplitter*



Advantages of Fourier Transform Spectroscopy

- Signal to noise enhancement—Multiplex Advantage;
- High throughtput advantage—few optical elements and no slits to attenuate radiation;
- High resolution.