Updated: 11 September 2019

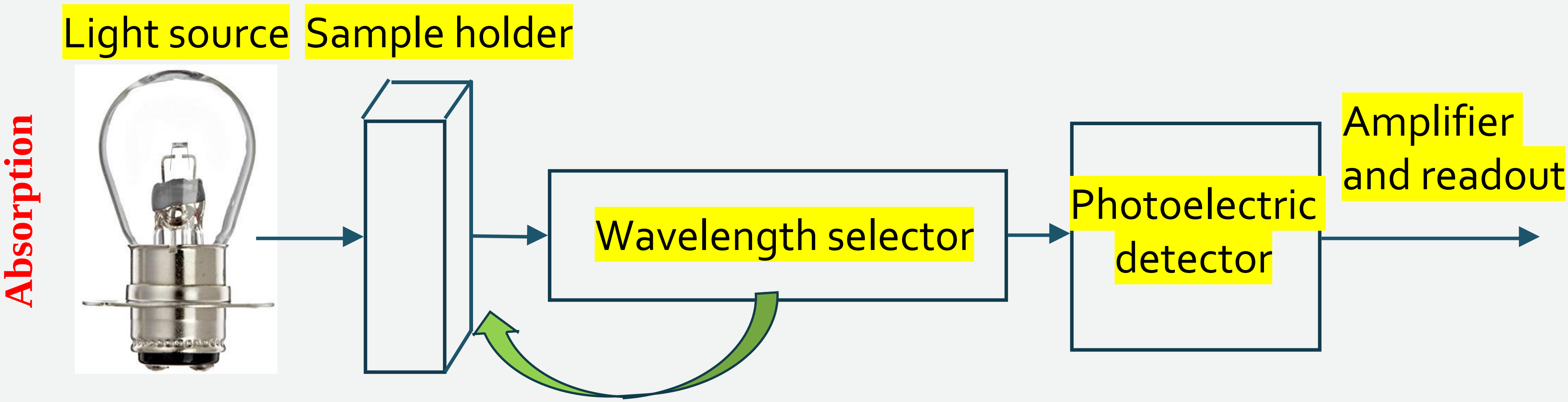
CEE 772: INSTRUMENTAL METHODS IN ENVIRONMENTAL ANALYSIS

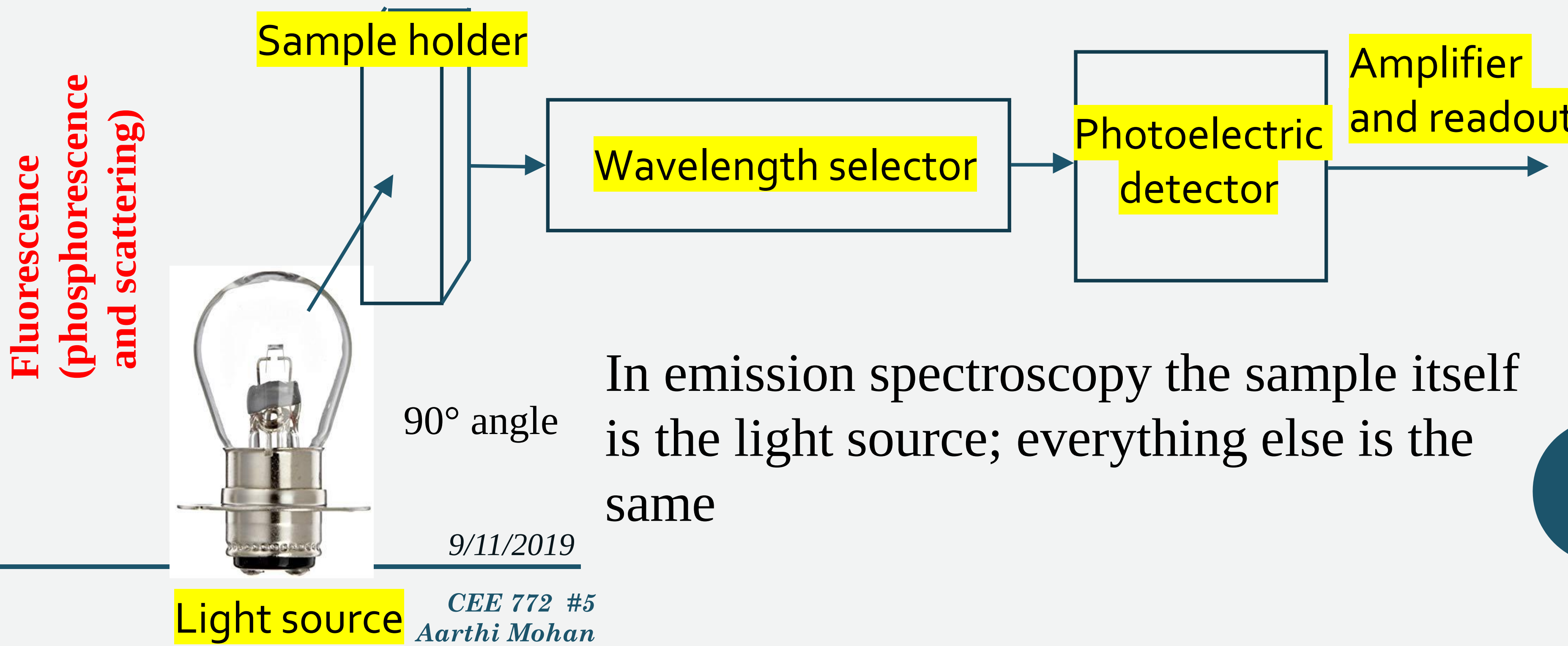
Lecture #5

Optical spectroscopy: (Skoog, 4th edition, Cha 6)

Types of optical spectrophotometers

- UV-Vis Spectrophotometer
- Atomic Spectrophotometer (AS)
  - Flame atomization
  - Atomic Absorption Spectroscopy (AAS)
  - Flame Emission Spectroscopy (FES)
  - Atomic Fluorescence Spectroscopy (AFS)
- Infra-red absorption Spectroscopy (IR)
- Raman Spectroscopy
- X-Ray spectroscopy
- Nuclear Magnetic Resonance (NMR) Spectroscopy





In emission spectroscopy the sample itself is the light source; everything else is the same

Light Sources

Line	For discrete wavelengths
Continuous	For all (or broader) wavelengths

Line

AAS, atomic and molecular fluorescence spectroscopy, Raman spectroscopy

Continuous

Absorption and fluorescence

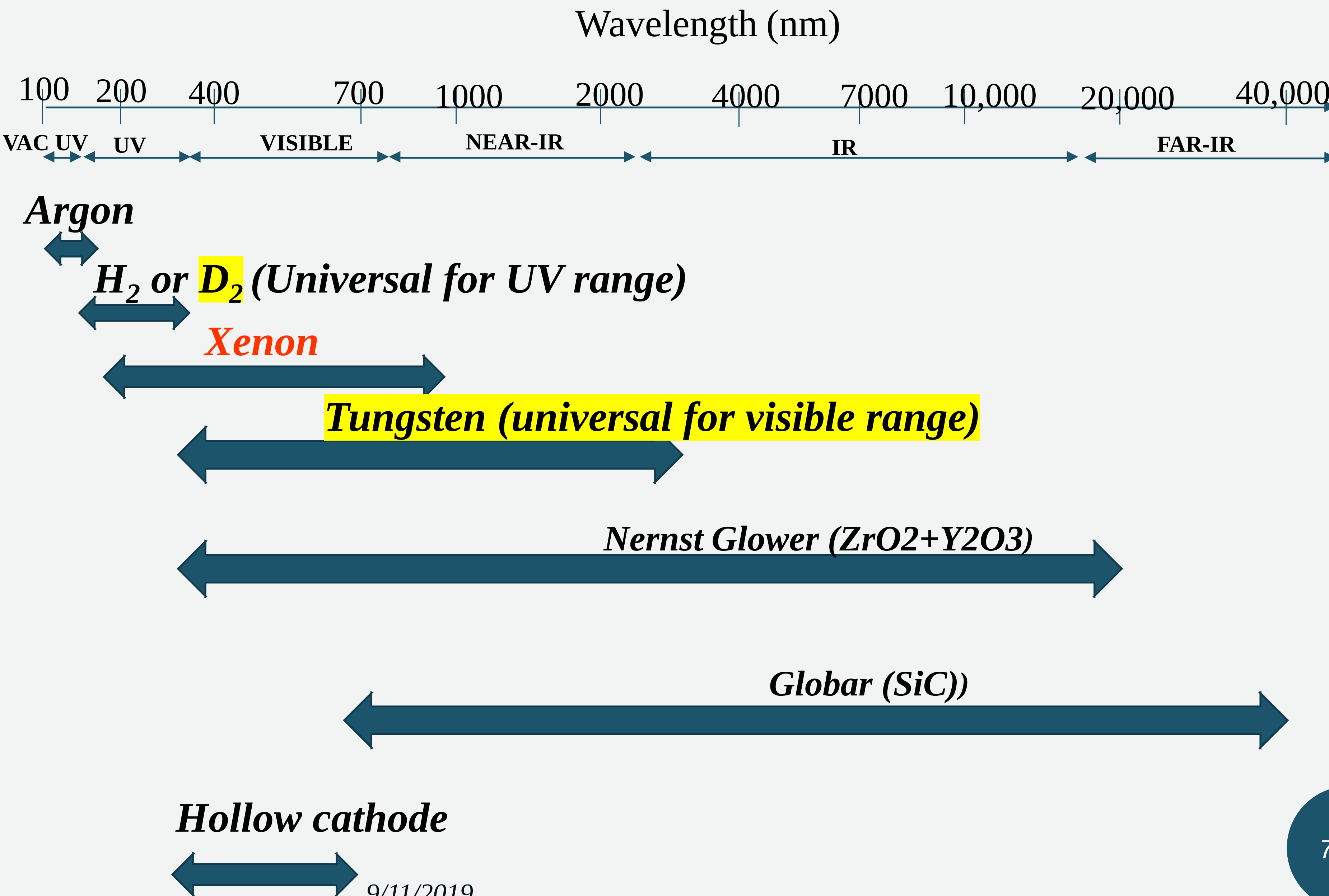
Considerations for source lamps

1) Spectral distribution i.e., intensity vs. λ (continuum vs. line sources)

2) Stability – short term fluctuations (noise), long term drift

3) Cost and life

4) Geometry – match to dispersion device



(Adapted and modified from Figure 6-2 on Skoog, 4th ed.)

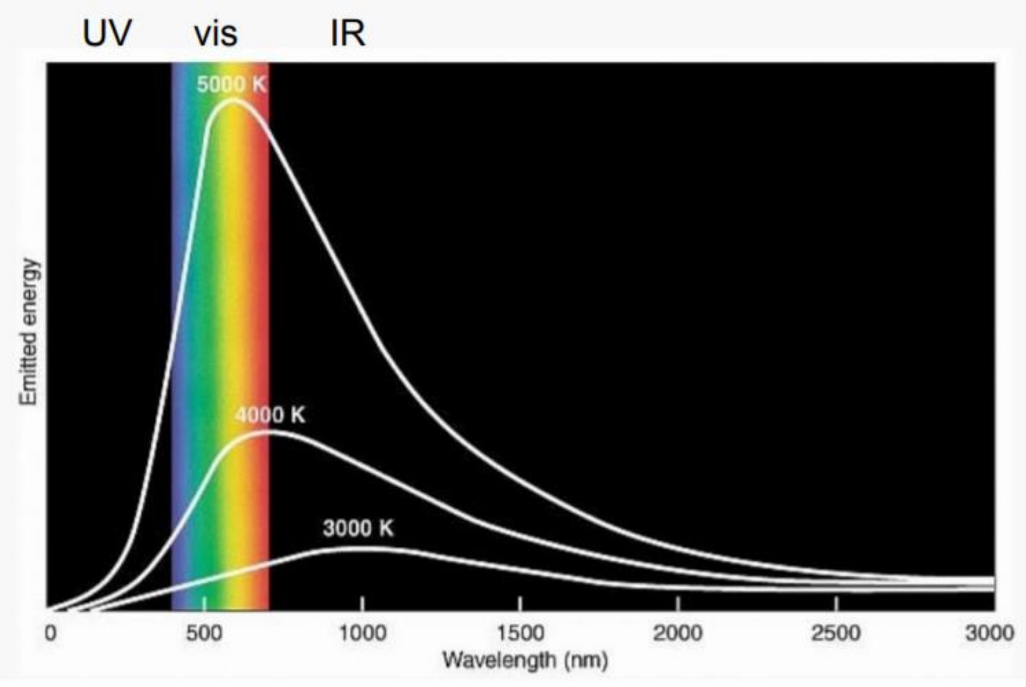
Tungsten Lamp

-Incandescent light

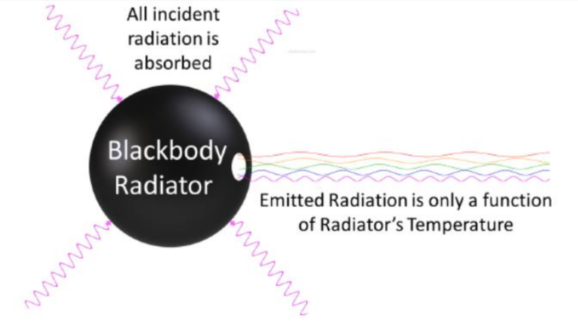
-Visible and near-IR region (350-2500nm)

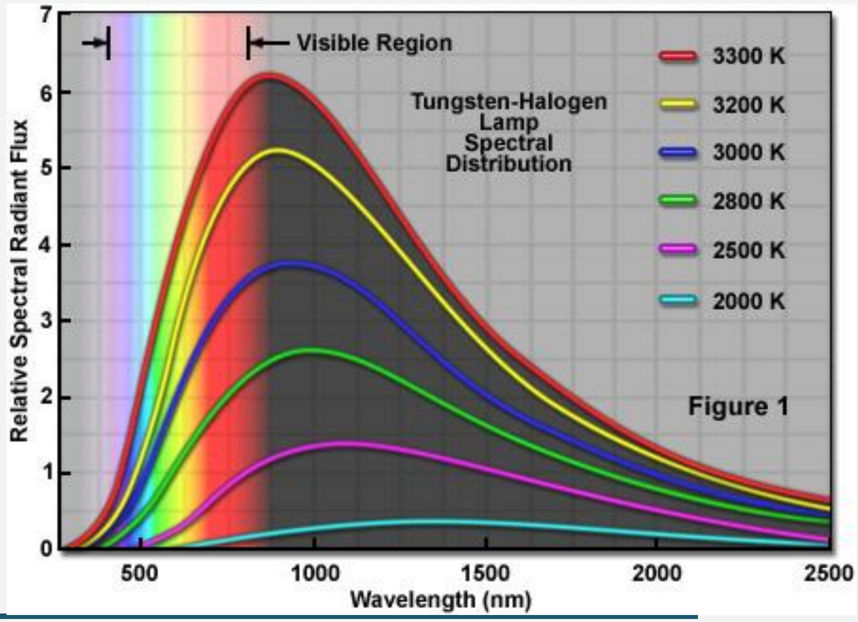
-generate light by heating a metal wire or filament with electricity until it glows.

- *Better than predecessors (carbon (2500 °C max) or osmium filaments)*
- *Tungsten M pt. = 3380 C; Best operating temperature : 2870 -3500K (2600-3230 °C).*
- $E \infty (Voltage)^4 \infty (Temp)^4$



http://faculty.uml.edu/david_ryan/84.314/Instrumental%20Lecture%204.pdf





http://zeiss-campus.magnet.fsu.edu/articles/lightsources/tungstenhalogen.html

Quartz enclosure because of high operating temperature; iodine filled (WI_2 formation)

Deuterium and hydrogen Lamp

- Deuterium provides more power than hydrogen (λ distribution same as H_2).
- 1000 h life-time
- Operates at very high temperature (can not use glass)
- Deuterium lamps are always used with a Tungsten (halogen) lamps to allow measurements to be performed in both the UV and visible regions.

Deuterium and hydrogen Lamp

- Electrical excitation of H2/D2 at low pressure

$$H_2 + E_e \rightarrow H_2^* \rightarrow H' + H'' + h\nu$$ (applies to H_2 and D_2)

$$E_e = E_{H_2\,*} = h\nu + E_{H'} + E_{H''}$$

- $h\nu$ ultraviolet photon
- E_e electrical energy absorbed
- E- kinetic energies of the two atoms H' and H

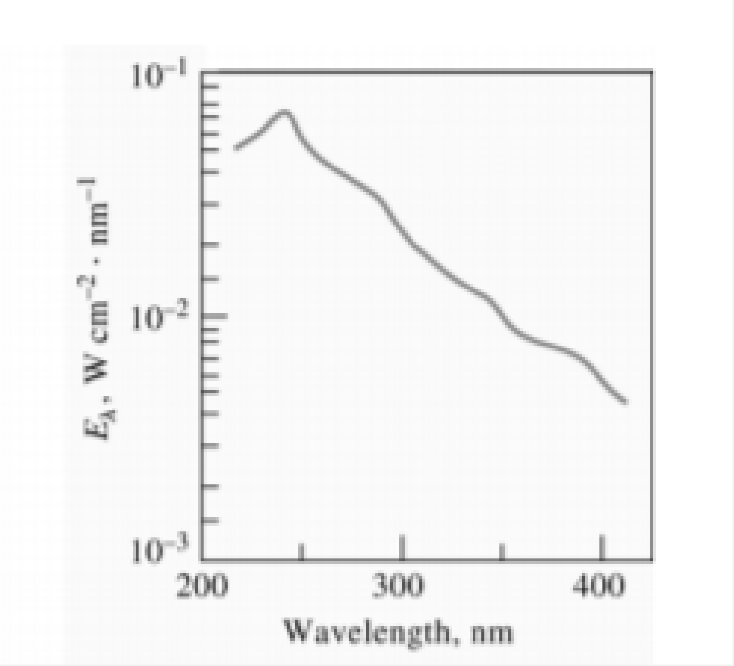
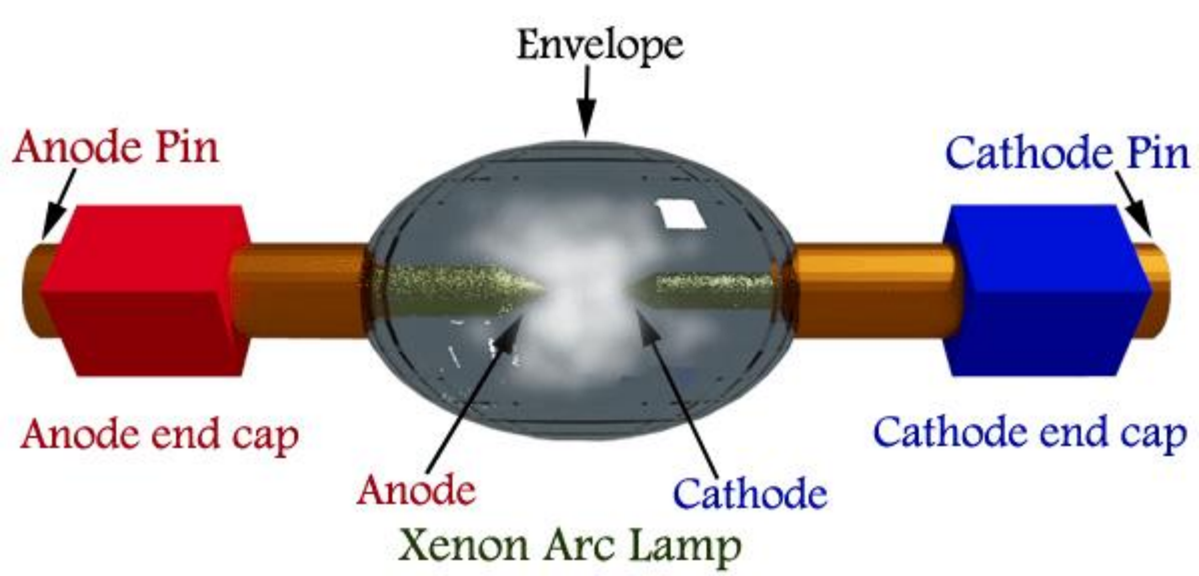
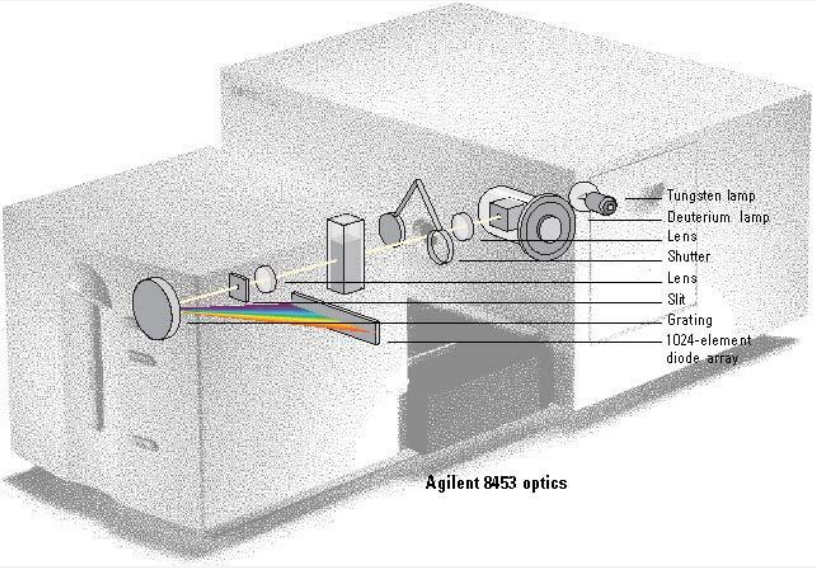


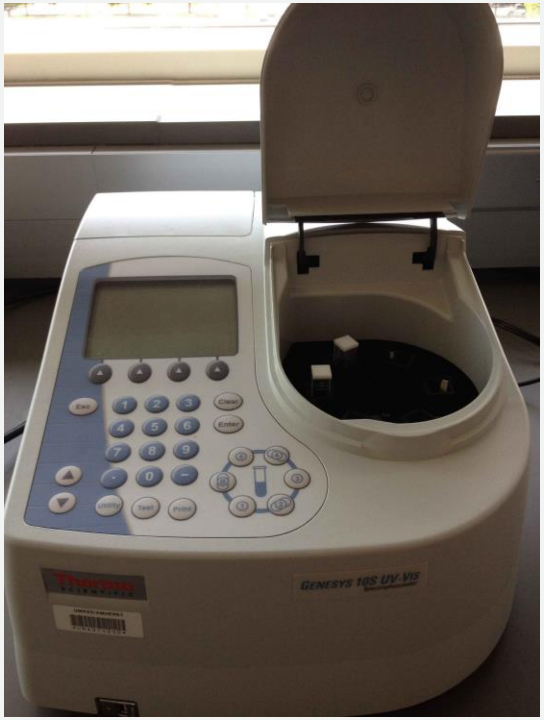
Fig 7-3 from Skoog, 4th ed.

Xenon (gas-discharge lamp)

- Intense radiation by passing current through atmospheric xenon
- high energy light source with a short warm up time and long lamp life.
- UV and Visible regions

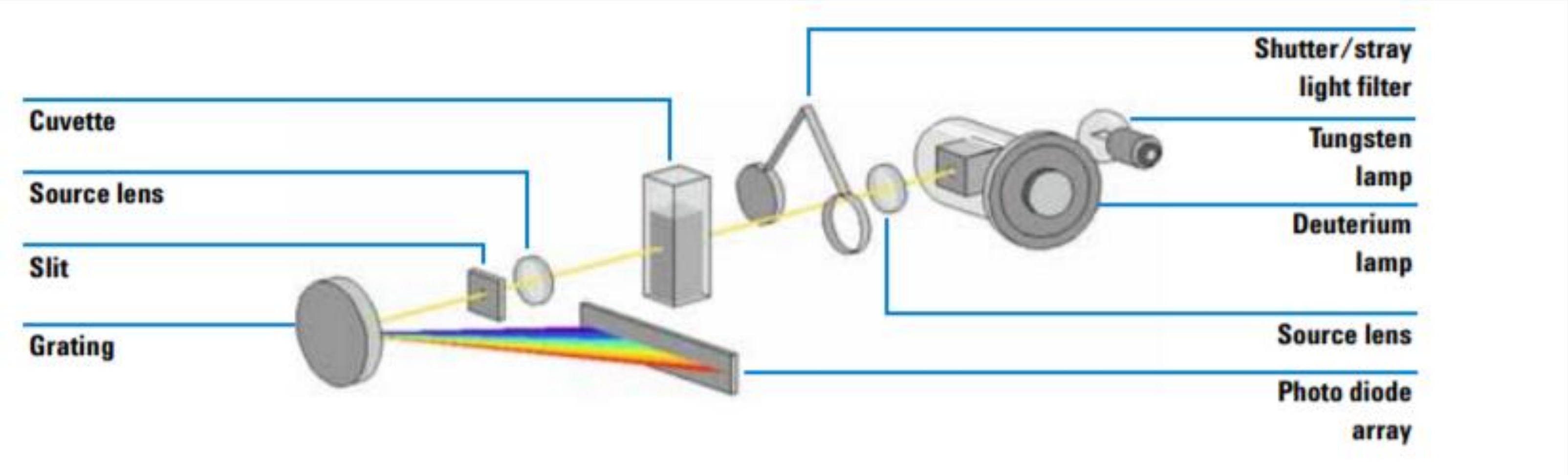




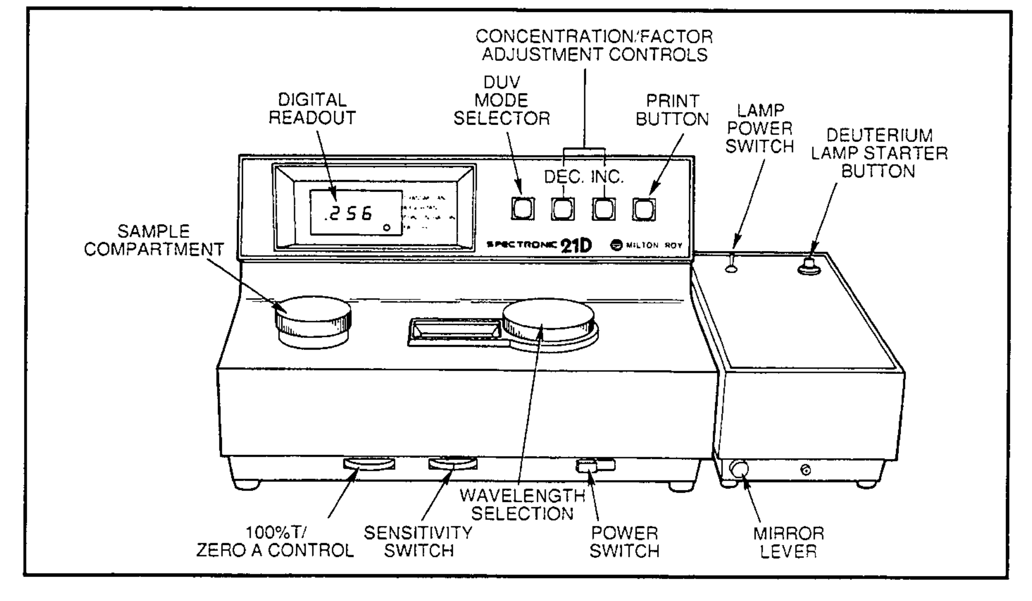


Internal xenon lamp- strong fundamental line at 529 nm

UV- deuterium
Vis- Tungstan filament lamp



Milton Roy Spectronic 21D UV-Visible Spectrophotometer (Hyland Scientific)



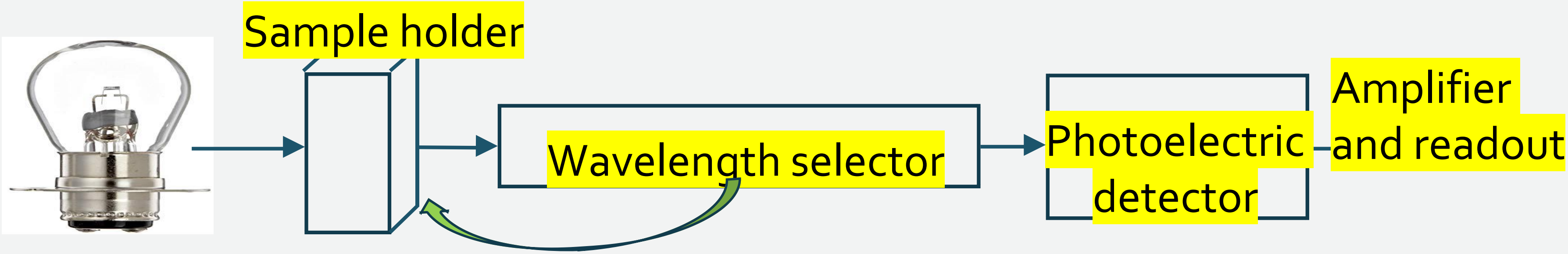
UV-Vis Spectrophotometer

- UV-Vis analysis is suitable:
  - UV and visible light absorbing compounds (pi bonds or atoms with non-bonding orbitals)
  - For analytes that can be dissolved in solvents like water, ethanol and hexane.
  - For single or multiple analytes as long as there is no overlapping of peaks
- Unsuitable for:

  -Analytes that have a photochemical reaction at (or above) the wavelength range of interest.

  -Unclear or colloidal samples.

Sample holder



Sample holder: (not for emission spectroscopy)

-Quartz or fused silica for UV region (below 350 nm), visible, IR (upto 3 µm)

-Silicate glasses (350-2000nm)

-Plastic- visible region

Typical 1 cm , 0.1 – 10 cm available

Spacers to transform path length available.

Cylindrical cells (prone to errors)

Fingerprints, grease and other deposits on the walls cause transmission

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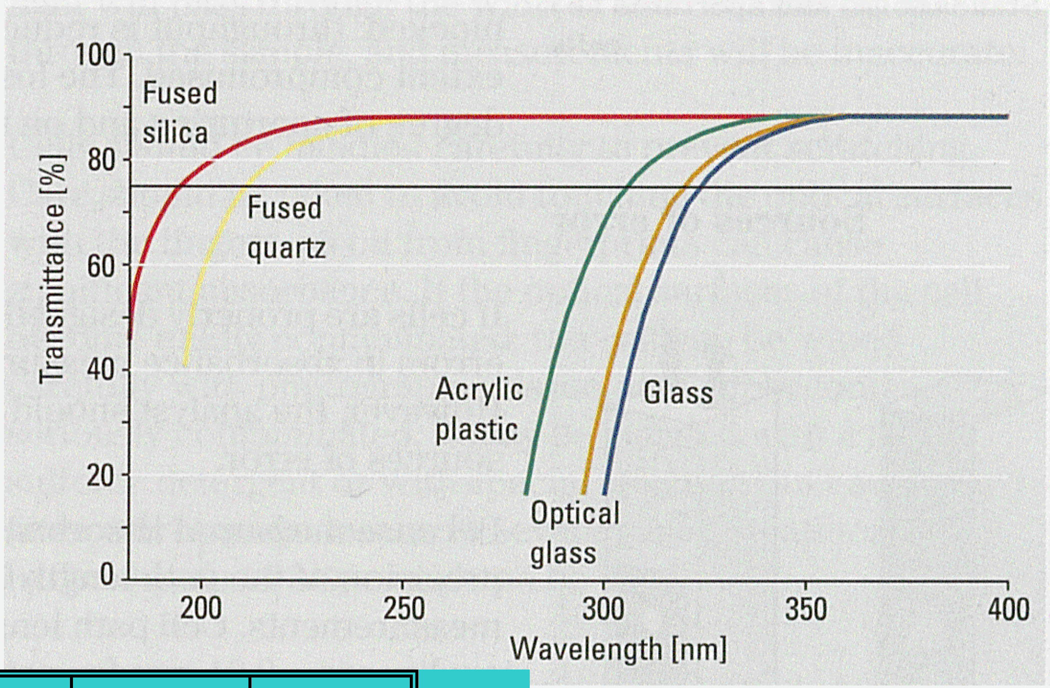
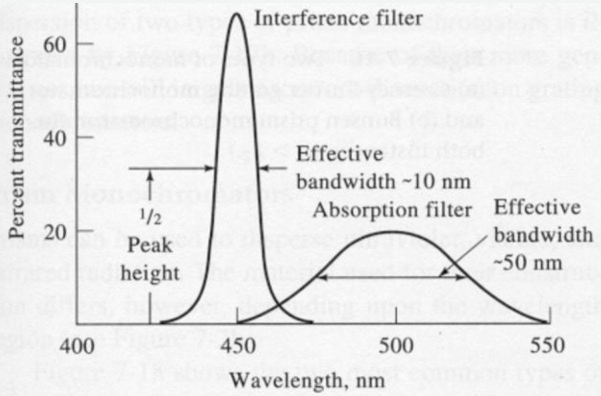
Sample Cells



Window	Wavelength Range (nm)	Letter Code	Lot #s	Color Code
Optical Glass	360 - 1000	OG		yellow
Near-UV Glass or Special Optical Glass	300 - 1000	OS or SG	180's	green
Standard Silica	220 - 2500			
Supracil Quartz or Quartz UV	165 - 2600, 2850 - 3600	QS or UV	280's	blue
Infracil Quartz or Quartz IR	220 - 3600	QI or IR	300's	red

Wavelength selectors: Filters



From Skoog, 4th edition, Cha 6

- -Narrow bandwidth
- -Filters and monochromators

Filters

- Adsorption (vis)
  - Less expensive (colored glass or dye)
- Interference (UV,Vis,IR)
  - Dielectric materials (filters or wedges)

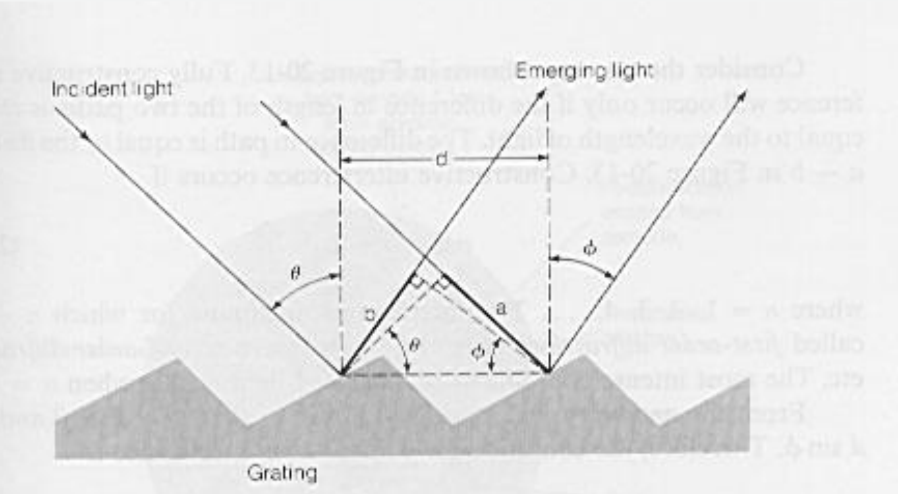
Wavelength selectors: Monochromators

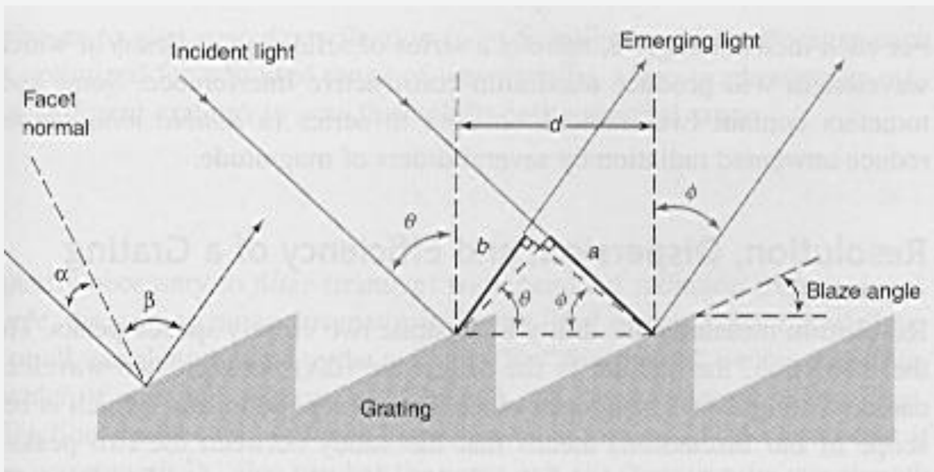
-Spectral scanning

-Combination of slits, lens, mirrors, windows, gratings or prisms

Reflection Gratings (3-10cm length)

- Most common
- Construction is expensive and tedious
- Replicate gratings from master grating using liquid resin casting process; gold/platinum/aluminium coating
- Geometry provides efficient diffraction of radiation

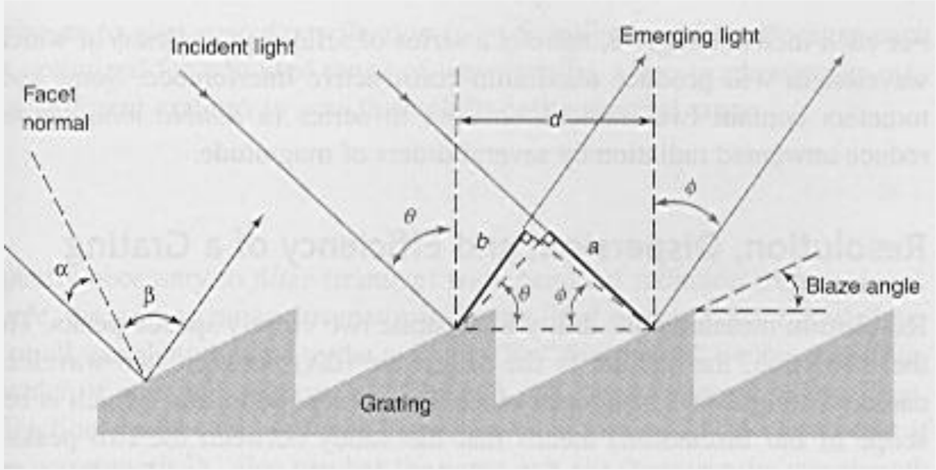




UV-Vis- 300-2000 grooves/mm (1200-1400 typical); IR-10-200 grooves/mm

- For constructive interference:
  - The difference in length of adjacent light paths is equal to an integral multiple of the wavelength.

$$n\lambda = a - b$$



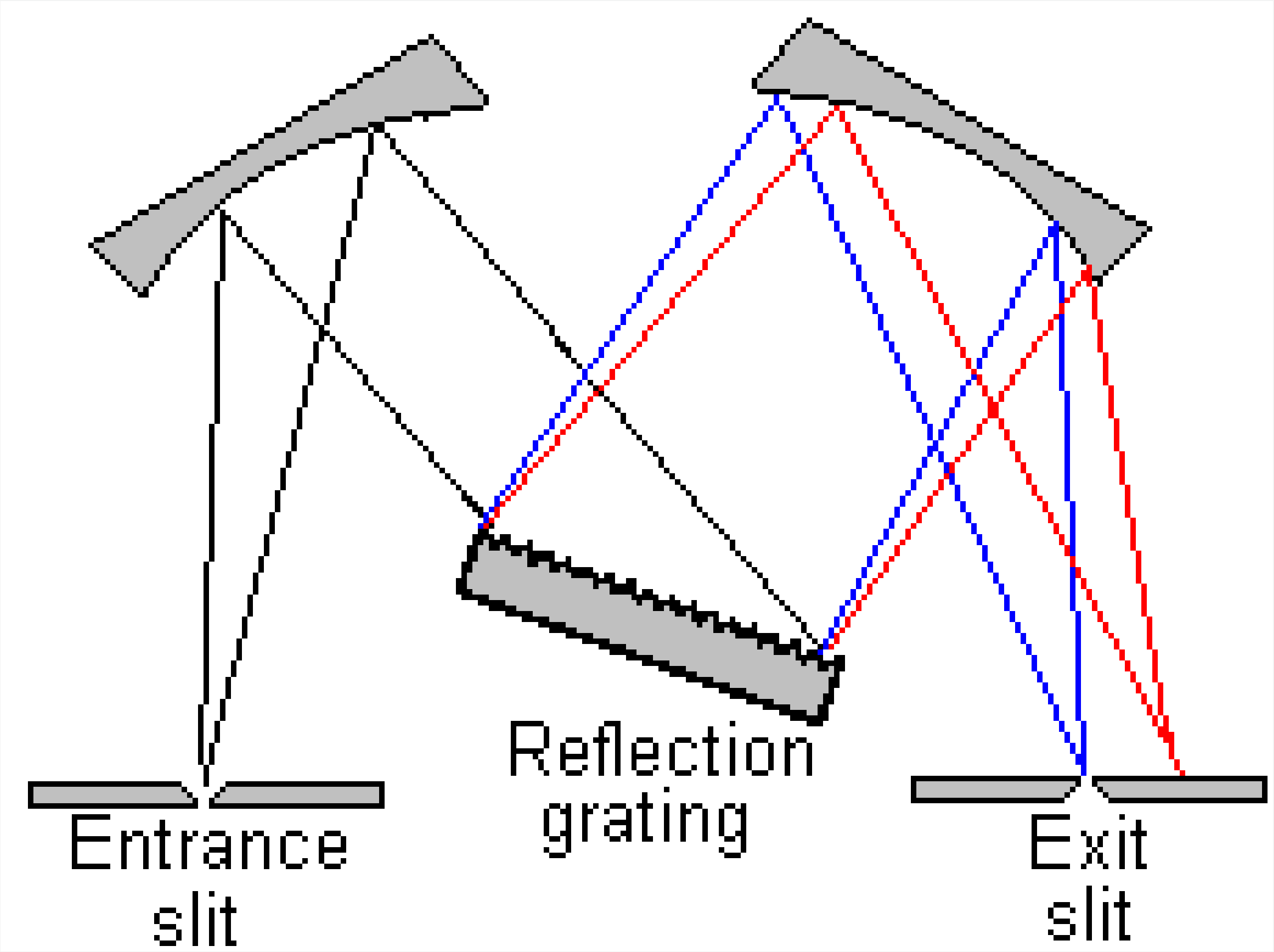
$$a = d\sin\theta$$

$$b = d\sin\phi$$

$$n\lambda = d\left(\sin\theta - \sin\phi\right)$$

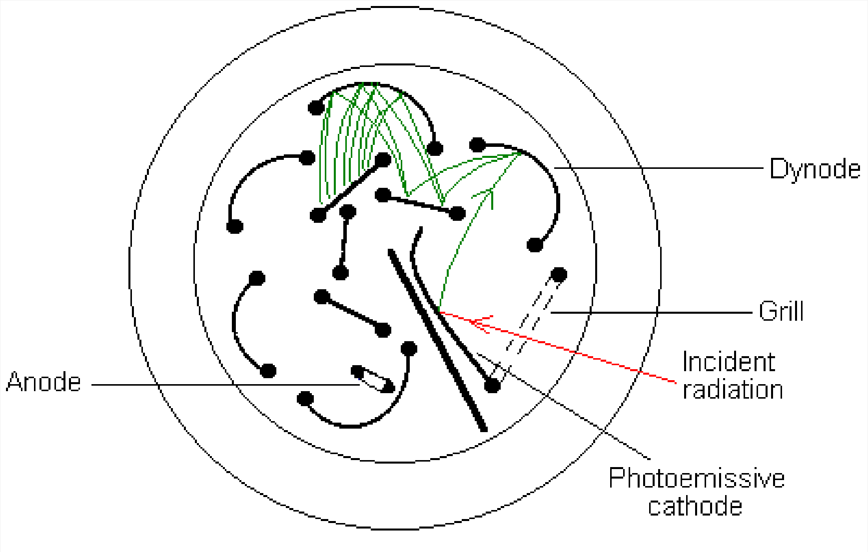
Condition for constructive interference to occur (higher amplitude)

Reflection gratings

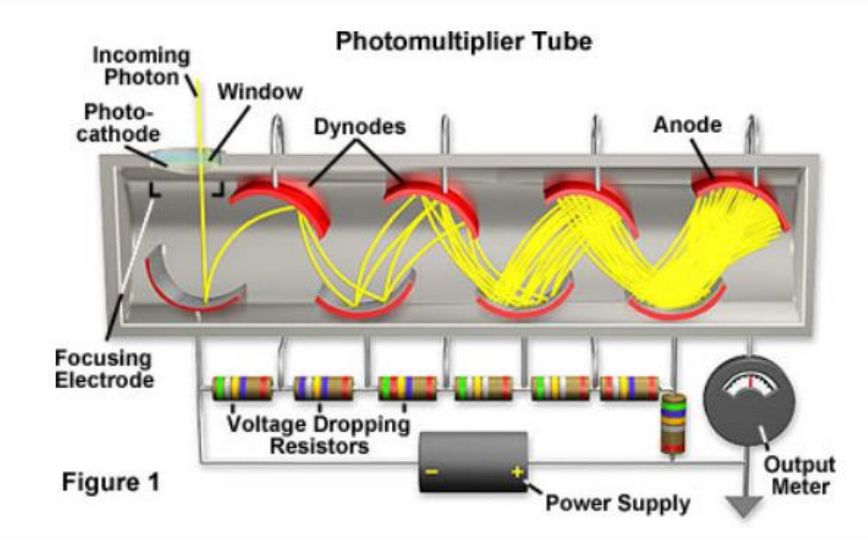


Detectors

- **Photomultipliers**



https://micro.magnet.fsu.edu/primer/digitalimaging/concepts/photomultipliers.html



Detectors

- **Photomultipliers**

-consists of a photocathode and a series of dynodes in an evacuated glass enclosure.

-When a photon of sufficient energy strikes the photocathode, it ejects a photoelectron due to the photoelectric effect.

-The photocathode material is usually a mixture of ***alkali metals***, sensitive to photons throughout the ***visible region*** of the electromagnetic spectrum.

-The ***photocathode is at a high negative voltage***, typically -500 to -1500 volts. The photoelectron is accelerated towards a series of additional electrodes called dynodes. These electrodes are each maintained at ***successively less negative potentials***. Additional electrons are generated at each dynode.

-This cascading effect creates ***10^5 to 10^7 electrons*** for each photoelectron that is ejected from the photocathode.

-The amplification depends on the ***number of dynodes and the accelerating voltage***. This amplified electrical signal is collected at an anode at ground potential, which can be measured.

Detectors

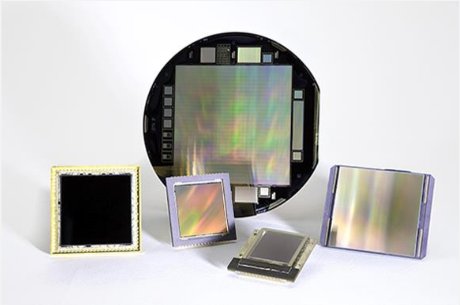
- Phototubes
  - similar to photomultipliers, but consist of only a photocathode and anode.
    - Since phototubes do not have a dynode chain to provide internal amplification, they are used in less sensitive applications such as absorption spectrometers

- **CCD – charge coupled device (integrated circuits etched on silicon surface)**

A charge coupled device (CCD) consists of row an area of photodiodes which releases an electron when a photon reaches the material (the photoelectric effect). This charge is converted to electrical signal.

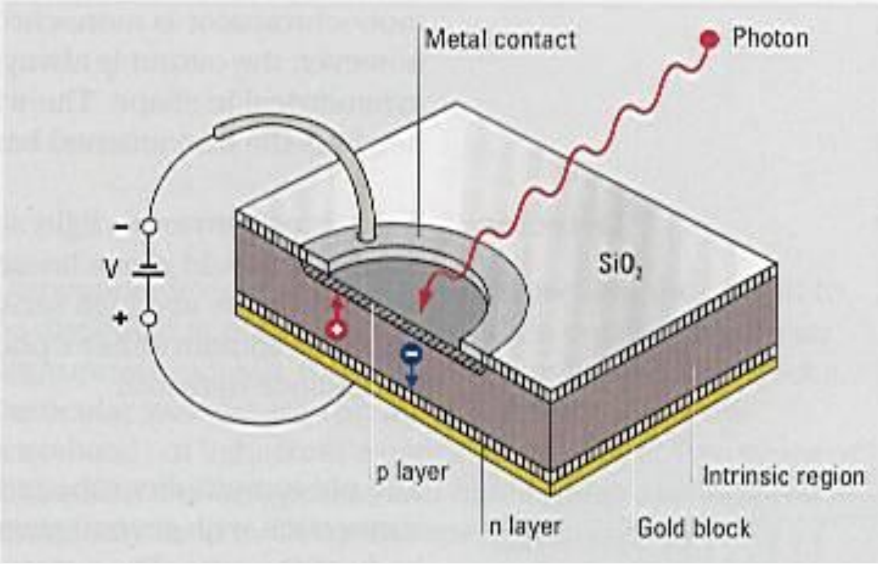
A CCD can record a full spectrum at once.

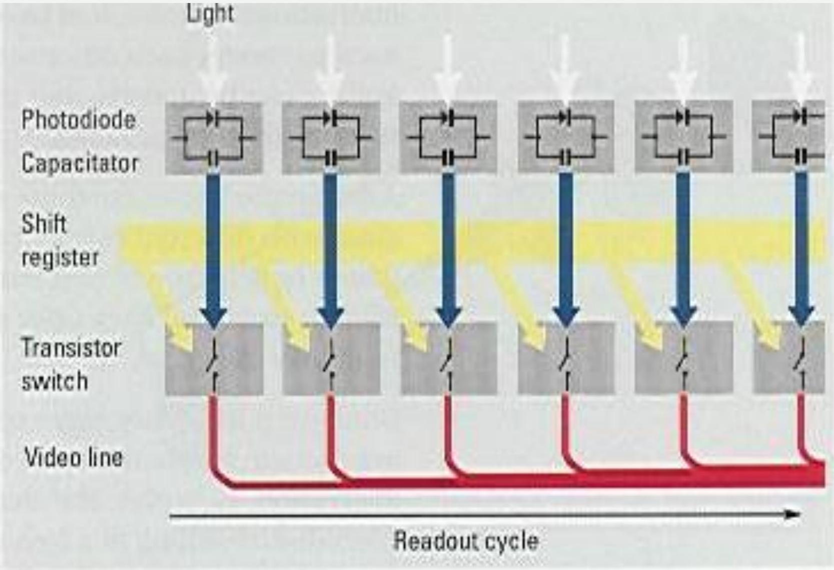
Eg) Digital camera



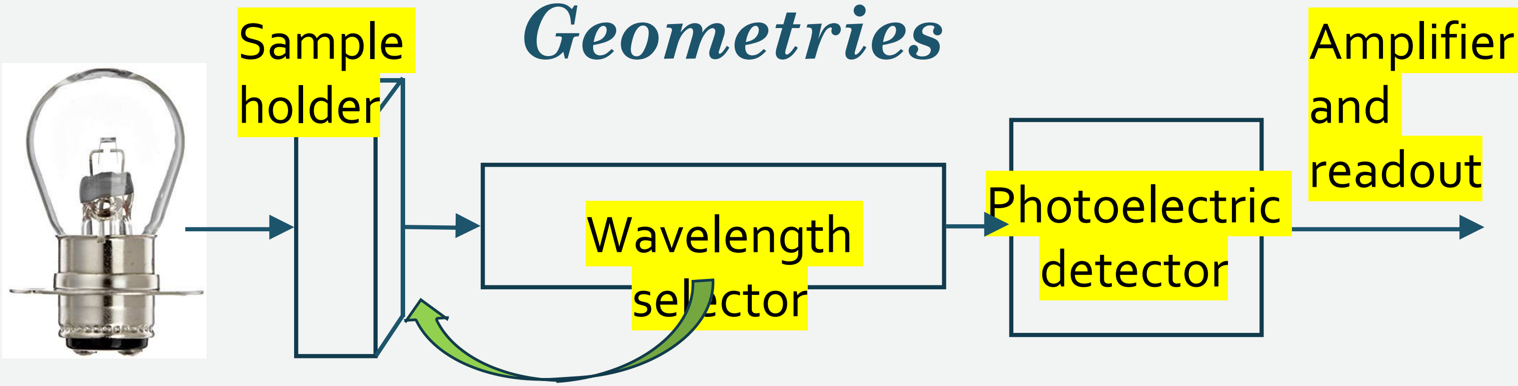
Photodiode detector

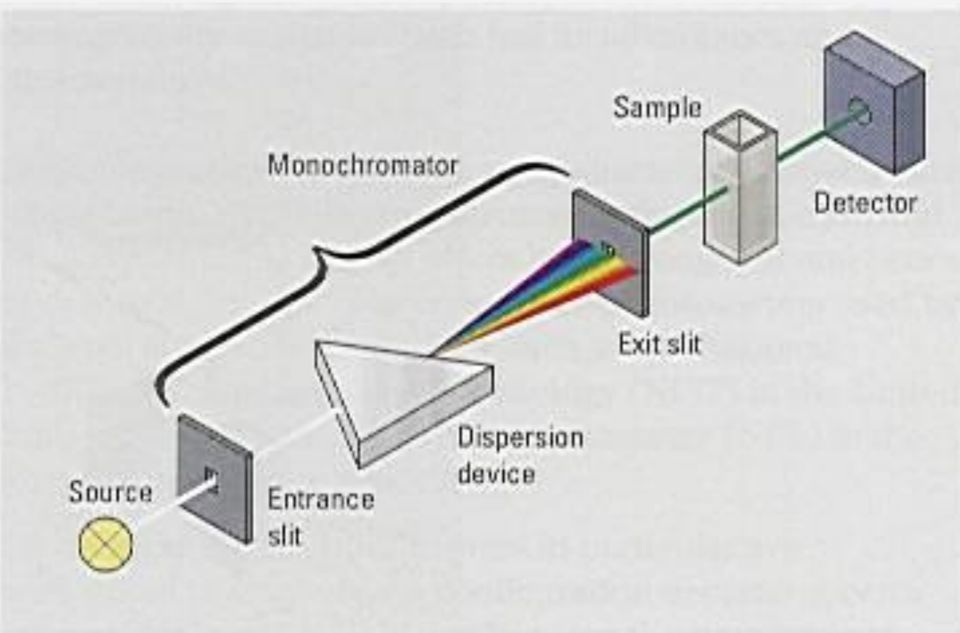
- Solid state- incident light to current (solar cell analogy)
  - More robust than photomultipliers
  - Range: 170-1100 nm
  - Arrays may contain 200-1000 elements
- Mechanism
  - Light hitting the semiconductor stimulates the flow of electrons *(inner photoelectric effect)*
  - This partly discharges the associated capacitor
  - Capacitors are recharged at regular intervals
    - The measurement period for each scanning cycle



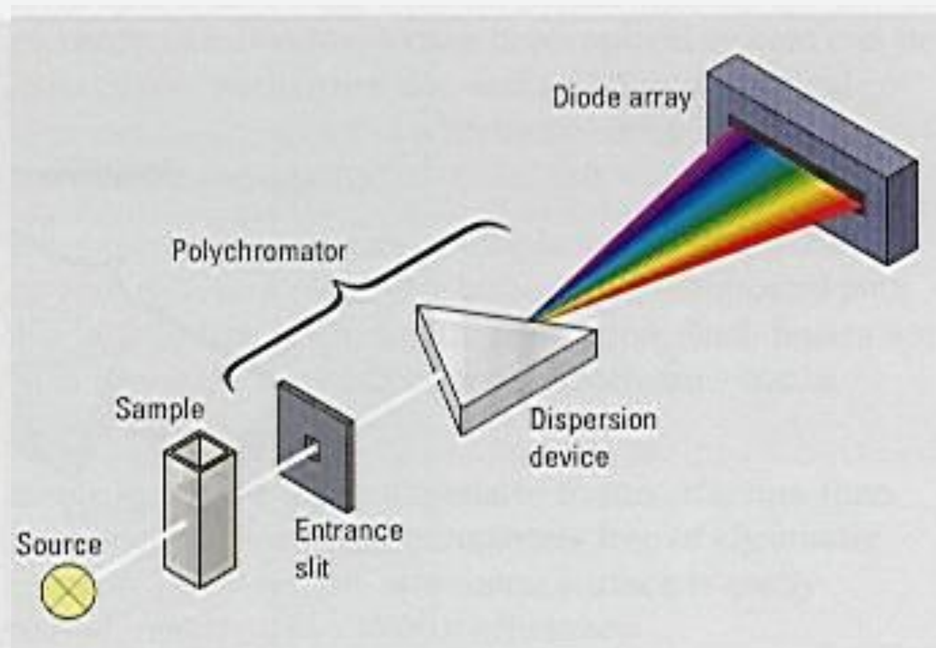


Geometries

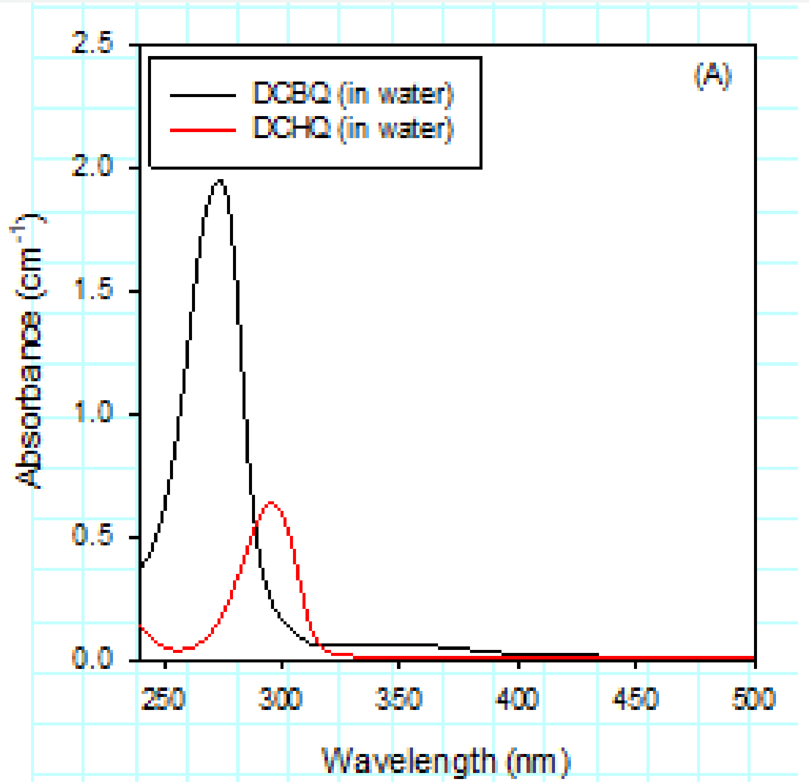


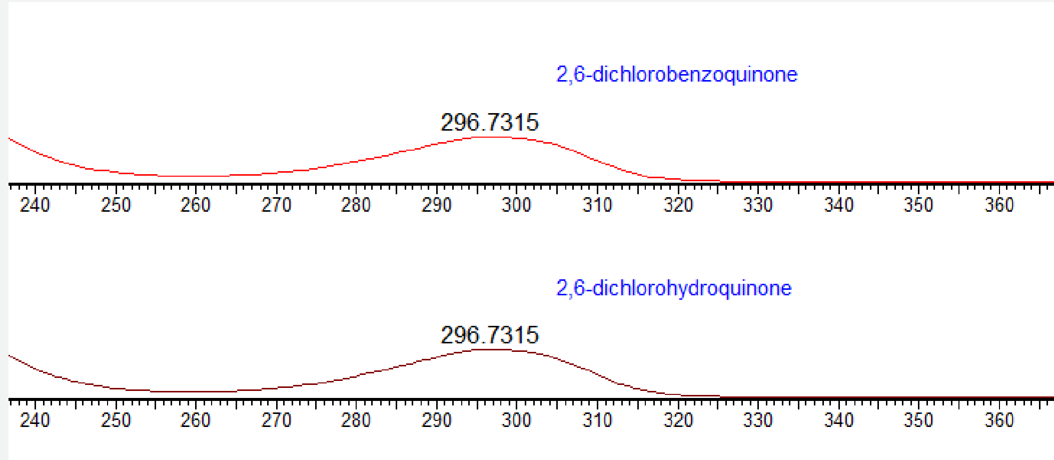


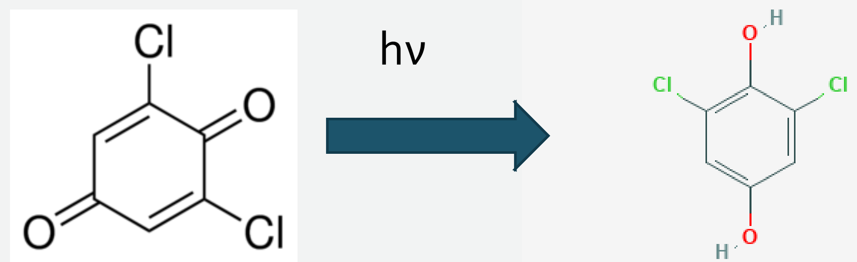
Normal geometry; conventional spectrophotometer



Reversed geometry; photo diode array spectrophotometer


DCBQ (in water)
DCHQ (in water)
(A)
Absorbance (cm-1)
Wavelength (nm)
2.5
2.0
1.5
1.0
0.5
0.0
250
300
350
400
450
500


2,6-dichlorobenzoquinone
296.7315
2,6-dichlorohydroquinone
296.7315
240 250 260 270 280 290 300 310 320 330 340 350 360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DCBQ DCHQ