Skoog – Chapter 7
Components of Optical Instruments

- General Design of Optical Instruments
- Sources of Radiation
- Wavelength Selectors
- Sample Containers
- Radiation Transducers (Detectors)
- Signal Processors and Readouts
- Fiber Optics

Ultraviolet – Visible – Infrared Instrumentation

- Focus our attention on measurements in the UV-vis region of the EM spectrum
- Good instrumentation available
- Very widely used techniques
- Longstanding and proven methods
- IR instrumentation will be considered from time to time particularly when there are similarities to UV-vis

Absorption measurements require:

1) source of radiation

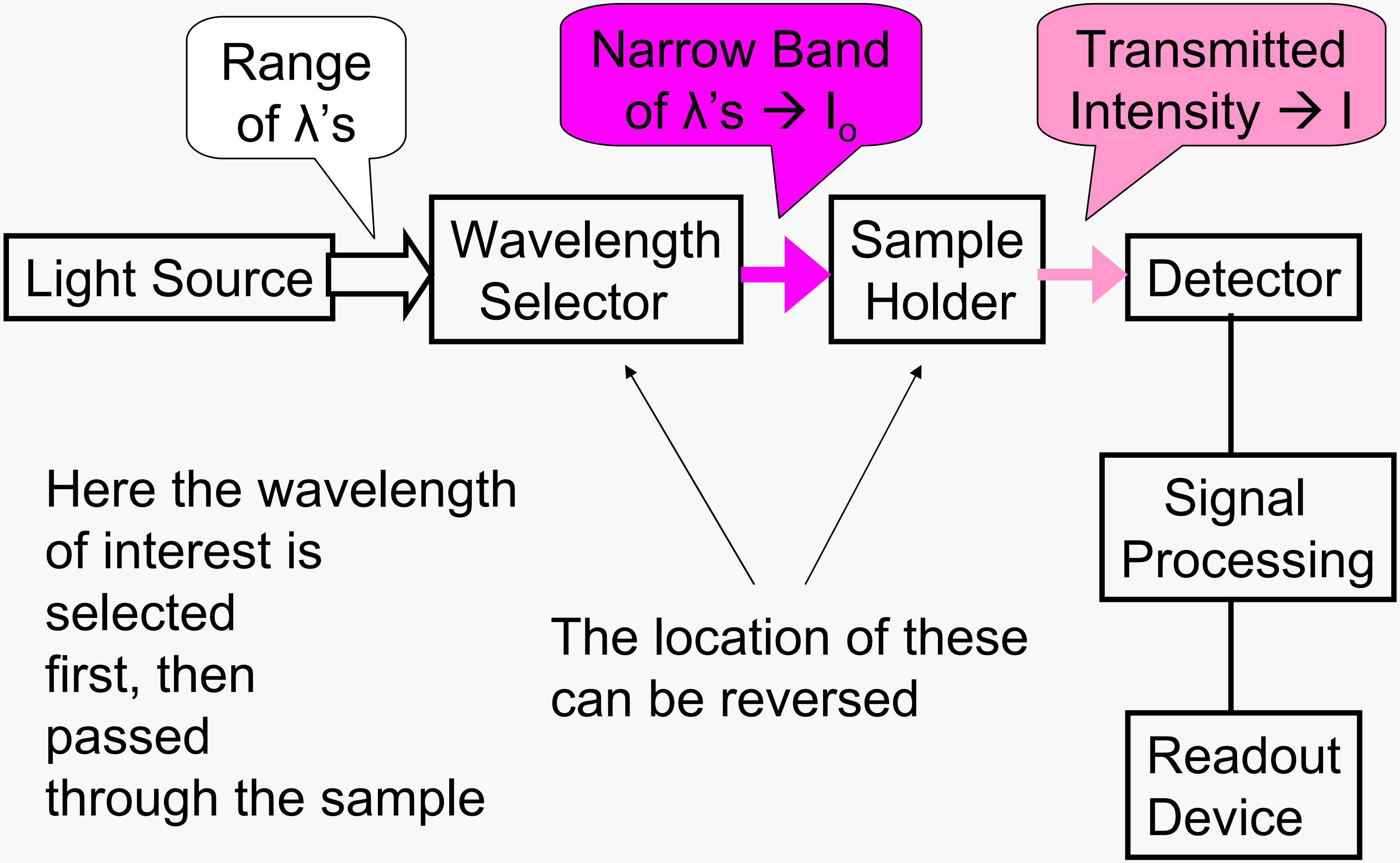
2) device for dispersing radiation into component wavelengths

3) a means of putting sample into the optical path, i.e., cell

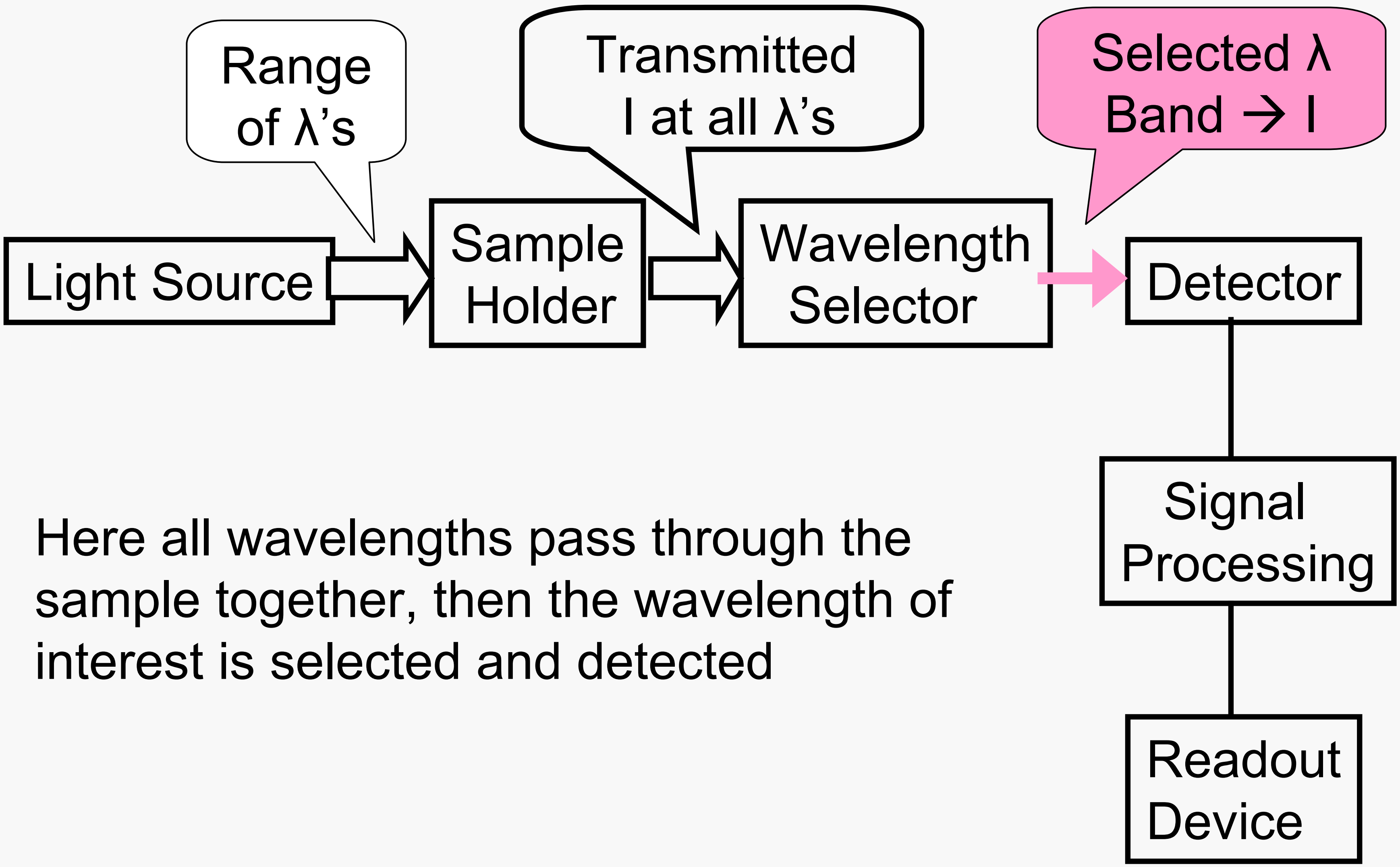
4) Detector to convert the EM to an electrical signal

5) readout device or circuitry, i.e., meter, computer, recorder, integrator, etc.

Block diagram of instrument for absorption



Block diagram of instrument for absorption

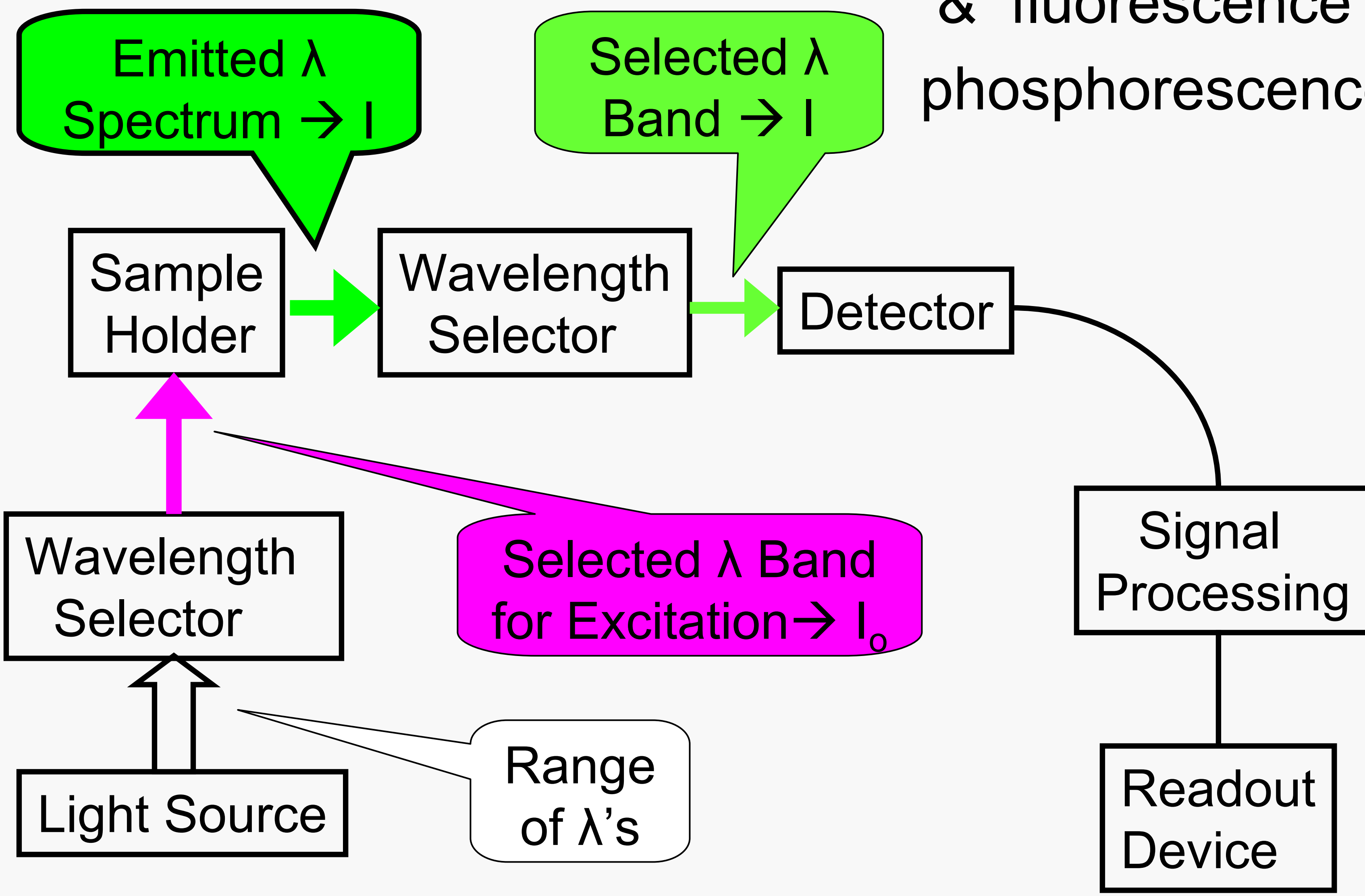


Here all wavelengths pass through the sample together, then the wavelength of interest is selected and detected

Emission measurements require:

1) means of exciting emission i.e., way of populating upper energy level which spontaneously emits
2) device for dispersing radiation into component wavelengths
3) a means of putting sample into the optical path, i.e., cell
4) Detector to convert the EM to an electrical signal
5) readout device or circuitry, i.e., meter, computer, recorder, integrator, etc.

Block diagram of instrument for emission i.e.,
& fluorescence
phosphorescence



- The requirements for the various components used in different instruments change with the type of spectroscopy as well as for different kinds of measurements within a type of spectroscopy
- We will consider the components separately then combine them to make the overall instrument
- And finally look at the measurements with regard to theory and practice

Sources – important characteristics

1) Spectral distribution i.e., intensity vs. λ
   (continuum vs. line sources)
2) Intensity
3) Stability – short term fluctuations
   (noise), long term drift
4) Cost
5) Lifetime
6) Geometry – match to dispersion device

I) CONTINUUM SOURCES

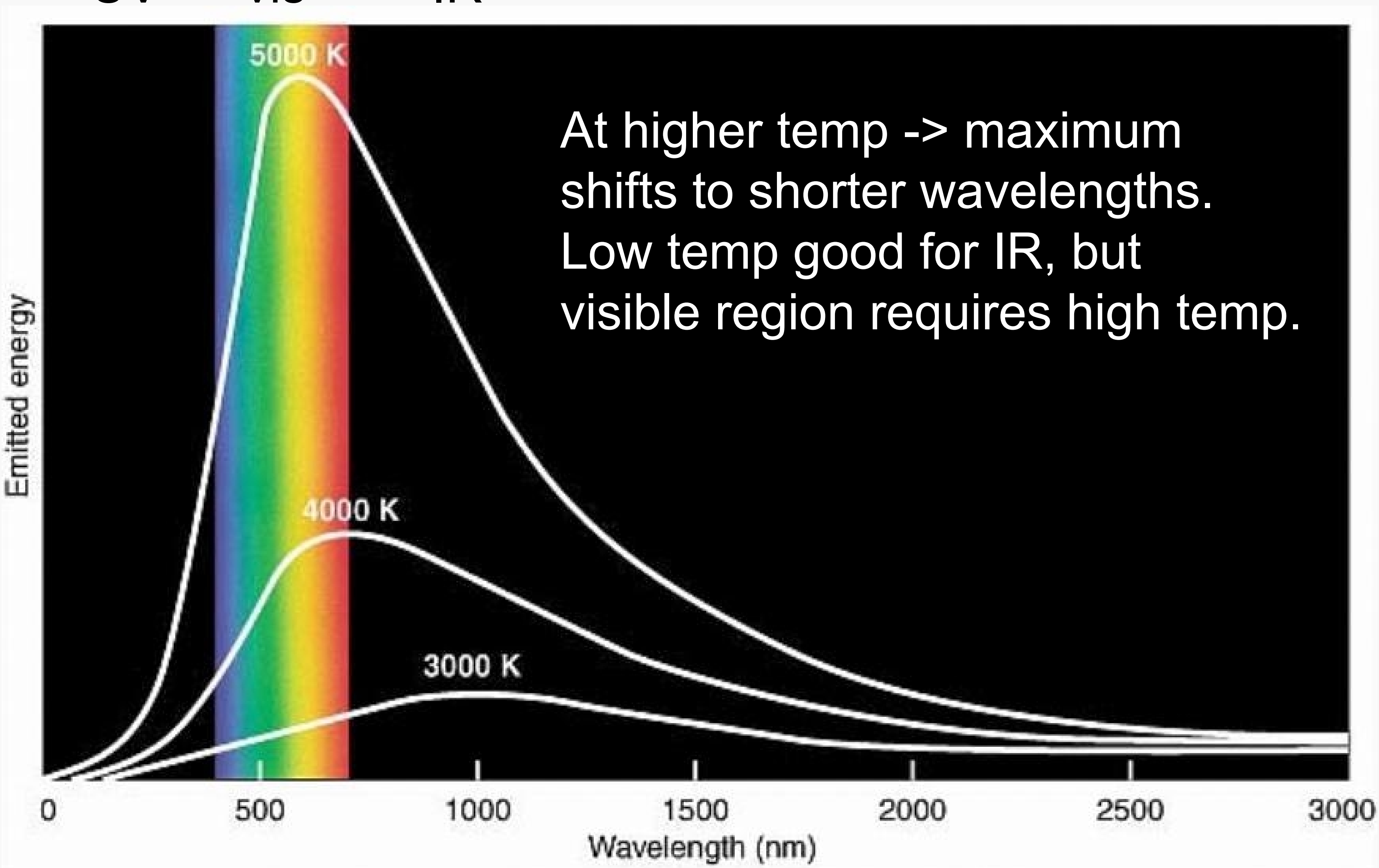
1) **Thermal radiation** (incandescence) – heated solid emits radiation close to the theoretical "Black Body" radiation i.e., perfect emitter, perfect absorber

Behavior of Black Body

- Total power ~ T^4 therefore need constant temperature for stability when using incandescent sources
- Spectral distribution follows Planck's radiation law

Spectral Distribution Curves of a Tungsten (Black Body) Lamp

UV vis IR



IR Region thermal sources (Black Body) are:

a) Nernst Glower – fused mixture of ZrO_2, Y_2O_3, and ThO_2 normally operated at 1900 ^oC – better for shorter IR λ's (near IR)

b) Globar – silicon carbide normally operated at 1200 to 1400 ^oC – better at longer IR λ's (doesn't approach Black Body)

c) Incandescent Wire – e.g., nichrome wire – cheapest way

- All operated at relatively low temperature.
- Good for IR and give some visible emission.
- Operated in air so will burn up if temp goes too high

Advantages

- Nernst Glower – low power consumption, operates in air, long lifetime
- Globar – more stable than Nernst Glower, requires more power & must be cooled. Long lifetime, but resistance changes with use

Visible Region sources are:

a) <u>Glass enclosed Tungsten (W) filament</u> - normally operated at ~3000 ^oK with inert atmosphere to prevent oxidation. Useful from 350 nm to 2000 nm, below 350 nm glass envelope absorbs & emission weak

b) <u>Tungsten-Halogen lamps</u> - can be operated as high as 3500 ^oK. More intense (high flux). Function of halogen is to form volatile tungsten-halide which redeposits W on filament, i.e., keeps filament from burning out. Requires quartz envelope to withstand high temps (which also transmits down to shorter wavelengths). Fingerprints are a problem – also car headlights

2) **Gas Discharge Lamps** – two electrodes with a current between them in a gas filled tube. Excitation results from electrons moving through gas. Electrons collide with gas → excitation → emission

At high pressure → "smearing" of energy levels → spectrum approaches continuum

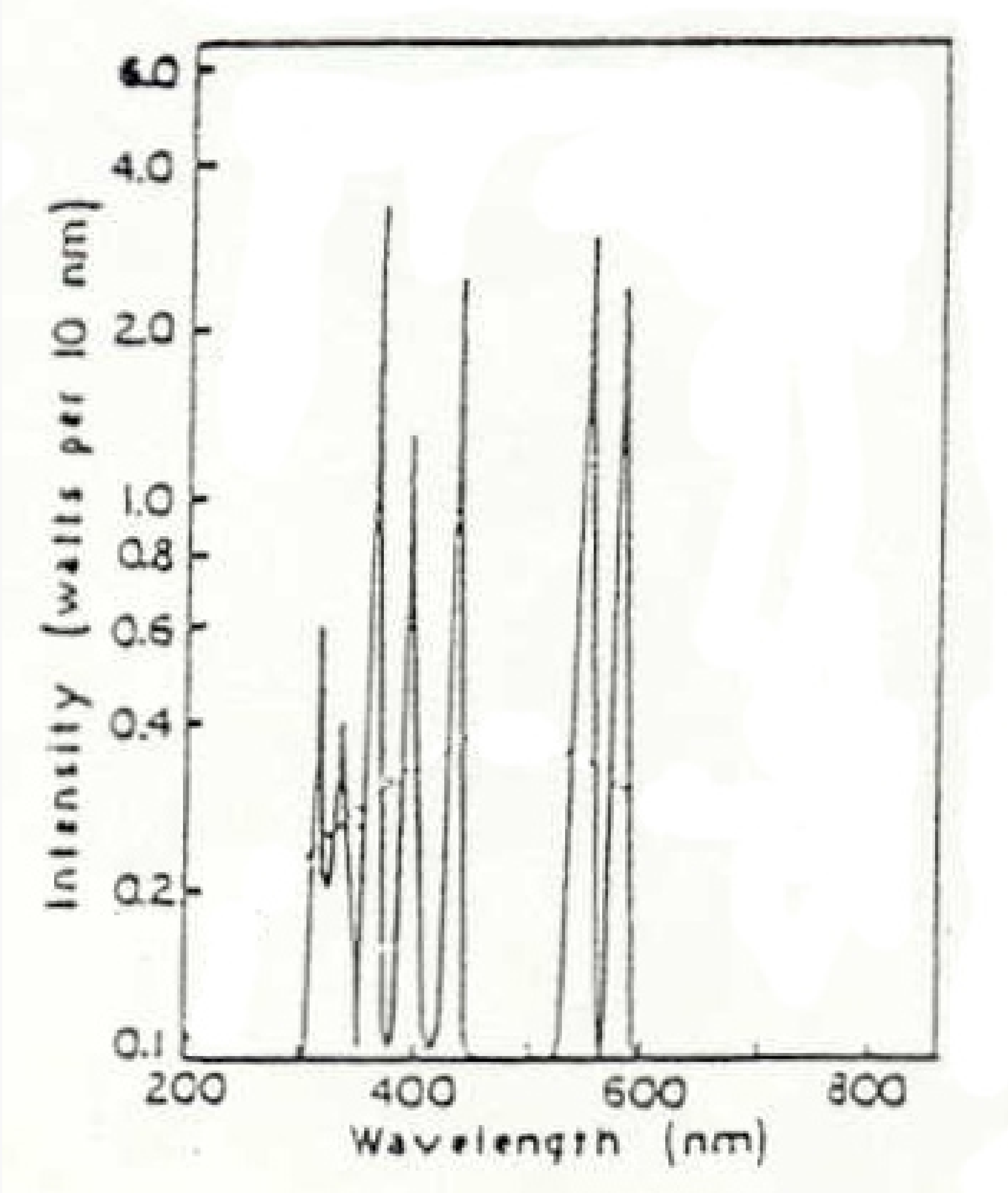
The higher the pressure, the greater the probability that any given molecule or atom will be perturbed by its neighbor at the moment of emission.

a) <u>Hydrogen Lamp</u>

- most common source for UV absorption measurements

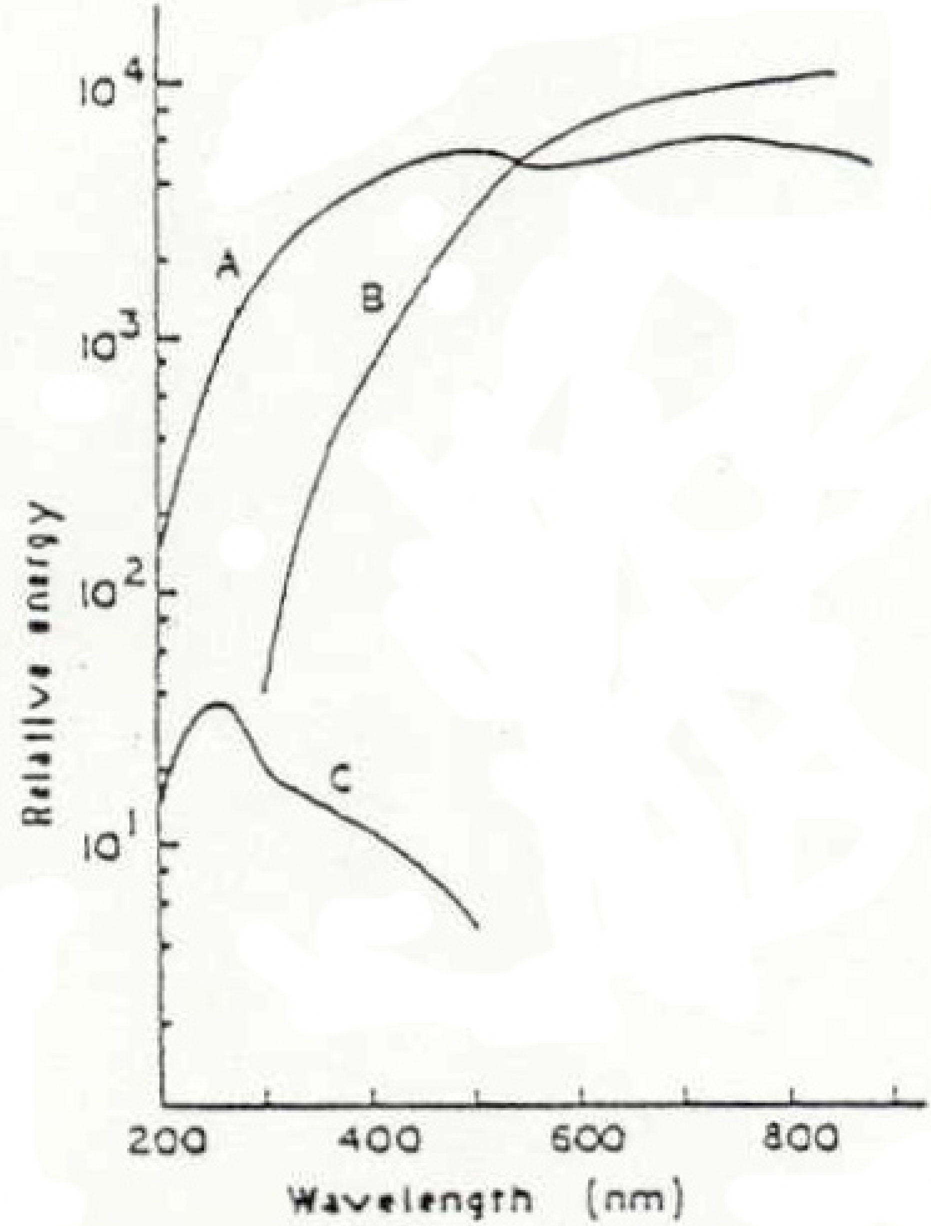
H_2 emission is from 180 nm to 370 nm limited by jacket

Line spectrum from →
100 watt Hydrogen Lamp at low pressure in Pyrex



b) <u>Deuterium Lamp</u> – same λ distribution as H_2 but with higher intensity (3 to 5 times) - D_2 is a heavier molecule & moves slower so there is less loss of energy by collisions

High pressure D_2 → with quartz jacket

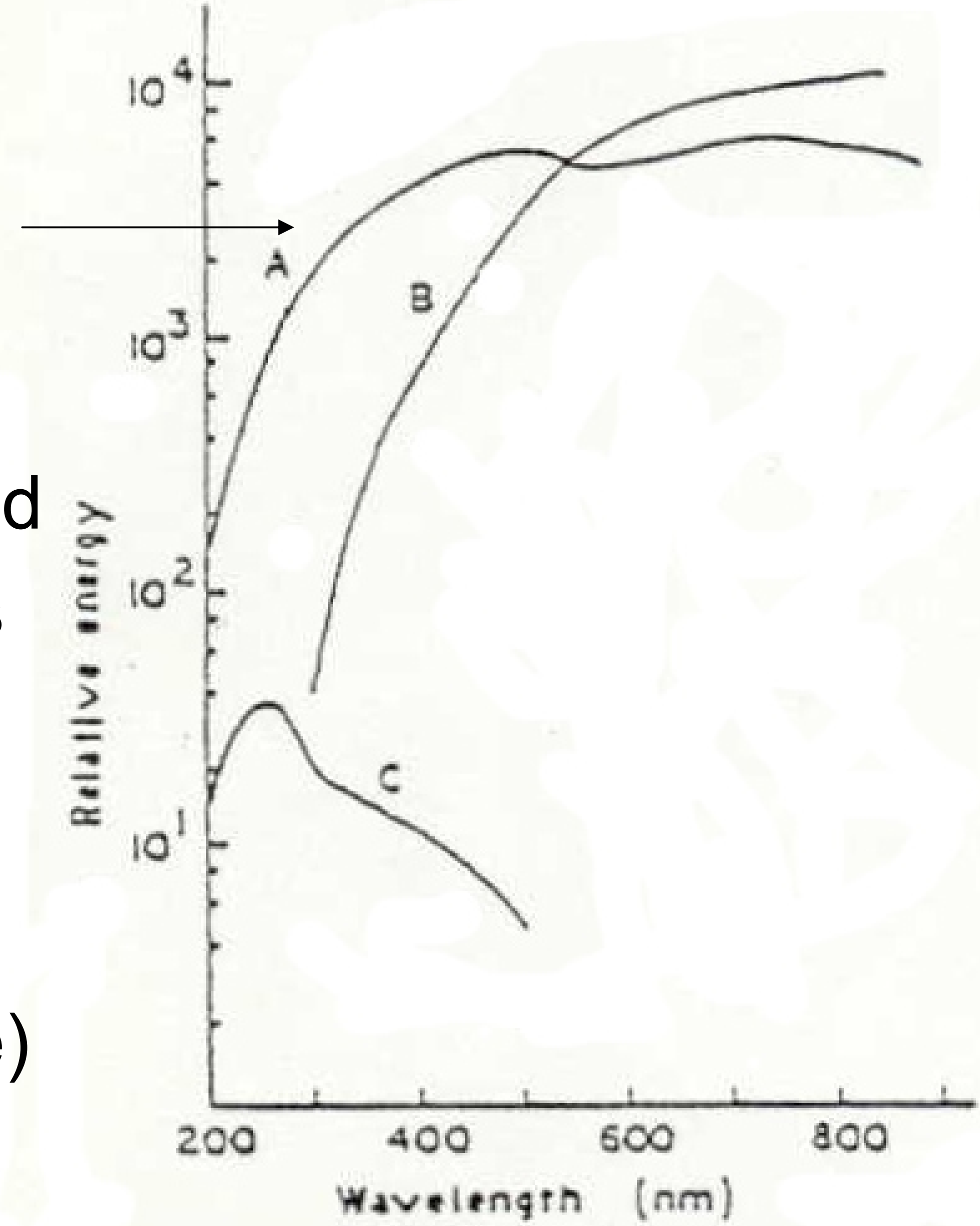


Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

For higher intensity

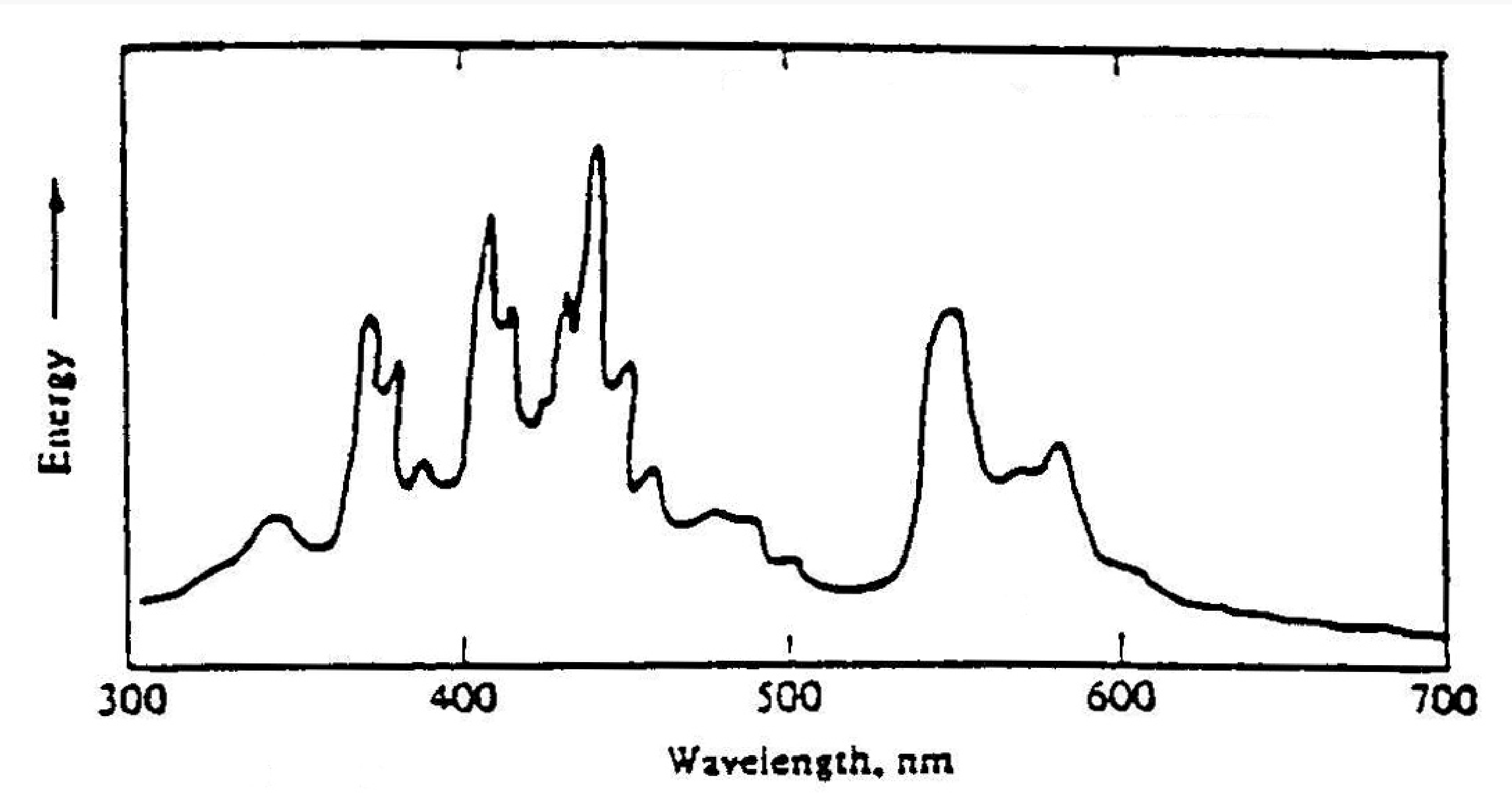
c) <u>Xenon Lamp</u> – Xe at high pressure (10-20 atm)

- high pressure needed to get lots of collisions for broadening leading to continuum
- short life relatively
- arc wander (stabilize)
- need jolt to start
- output = f(time)



Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

d) High Pressure Mercury Lamp – can't completely eliminate bands associated with particular electronic transitions even at very high pressures (e.g., 100 atm)



- For UV-vis absorption spectrophotometry usually use H_2 for UV and tungsten for visible region (switching mid scan)
- Sometimes use D_2 instead of H_2
- For fluorescence spectrophotometry use xenon arc lamp in scanning instruments
- Can use He below 200 nm
- Hg at low pressure is used in fixed wavelength (non scanning) fluorometers
- Can use mixture of Hg and Xe

II) LINE SOURCES

1) **<u>Gas (Vapor) Discharge Lamps</u>** at low pressure (i.e., few torr) – minimize collisional interaction so get line spectrum

   - most common are Hg and Na

   - often used for λ calibration

   - Hg pen lamp

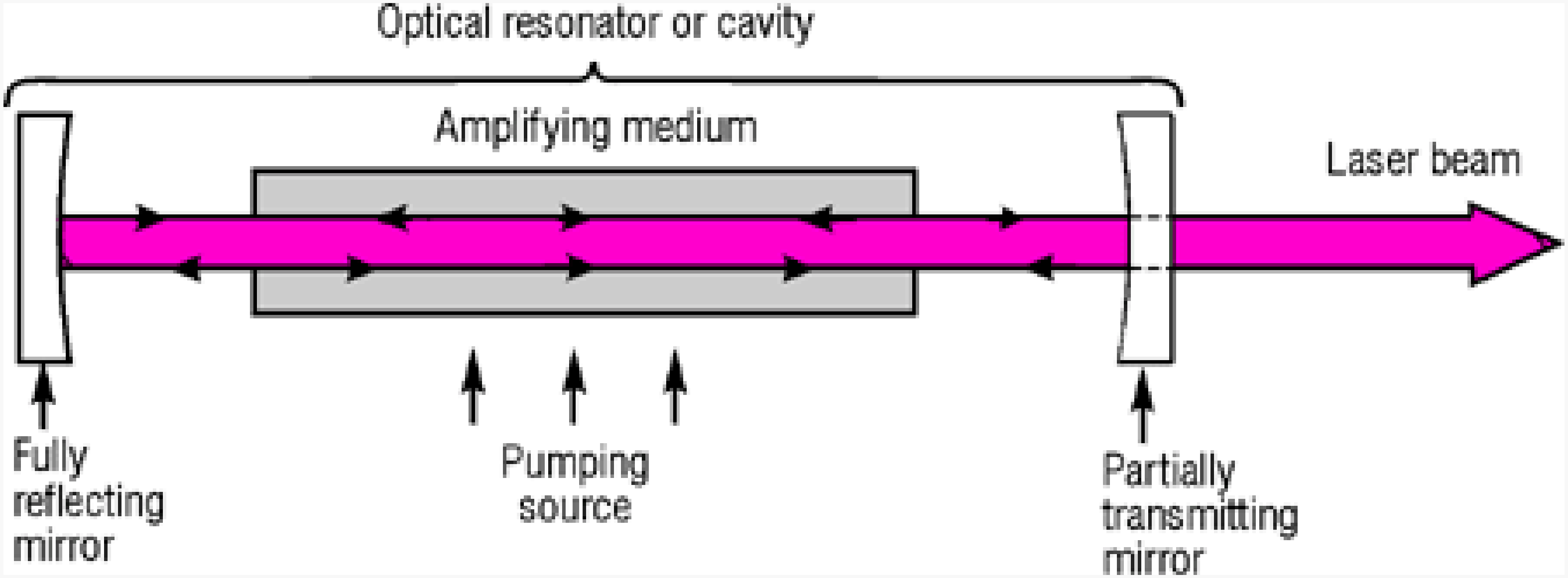
   - fluorescent lights are another example

   - also used UV detectors for HPLC

2) **<u>Hollow Cathode Lamps (HCL)</u>** – for AA

3) **<u>Electrodeless Discharge Lamps (EDL)</u>** - AA

4) **<u>Lasers (Light Amplification by Stimulated Emission of Radiation)</u>** – start with material that will exhibit stimulated emission and populate upper states typically using another light source



Stimulated Emission – photon strikes excited state causing it to emit a burst of photons

Pumping source used to populate upper states can be flashlamp, another laser or electrical

Often use prism to select pumping wavelength

Advantages of lasers

1) Intense
2) Monochromatic – very narrow band
3) Coherent – all radiation at same phase angle

4) Directional – full intensity emitted as beam

Limitations of lasers

1) High cost in many cases
2) Wavelength range is somewhat limited
3) Many operate in pulsed mode – some are continuous wave (CW)

Pulsed mode lasers are not always problematic as light sources, can use pulse frequency with gated detection

Types of Lasers:

1) **Solid State Lasers**

a) Ruby laser – Al_2O_3 + Cr(III) - 694.3 nm pumped with Xe arc flashlamp – pulsed (can be continuous)

b) Nd/YAG laser – yittrium aluminum garnet + Nd - 1064 nm

2) **Gas Lasers**

a) Neutral atom – He-Ne – 632.8 nm continuous

b) Ion lasers – Ar^+ or Kr^+ 514.5 nm

c) <u>Molecular lasers</u> – CO_2 (10,000 nm = 1000 cm^{-1}) or N_2 (337.1 nm) pulsed

d) <u>Eximer lasers</u> – inert gas + fluorine creates eximers ArF^+ (193 nm), KrF^+ (248 nm), XeF^+ (351) pulsed

3) **<u>Dye Lasers</u>** – tunable over 20 – 50 nm many dyes available for wide range of λ's

4) **<u>Semiconductor Diode Lasers</u>** – wide range of λ's available, continuous

Wavelength Selection

Three main approaches:

1) Block off unwanted radiation – optical filters

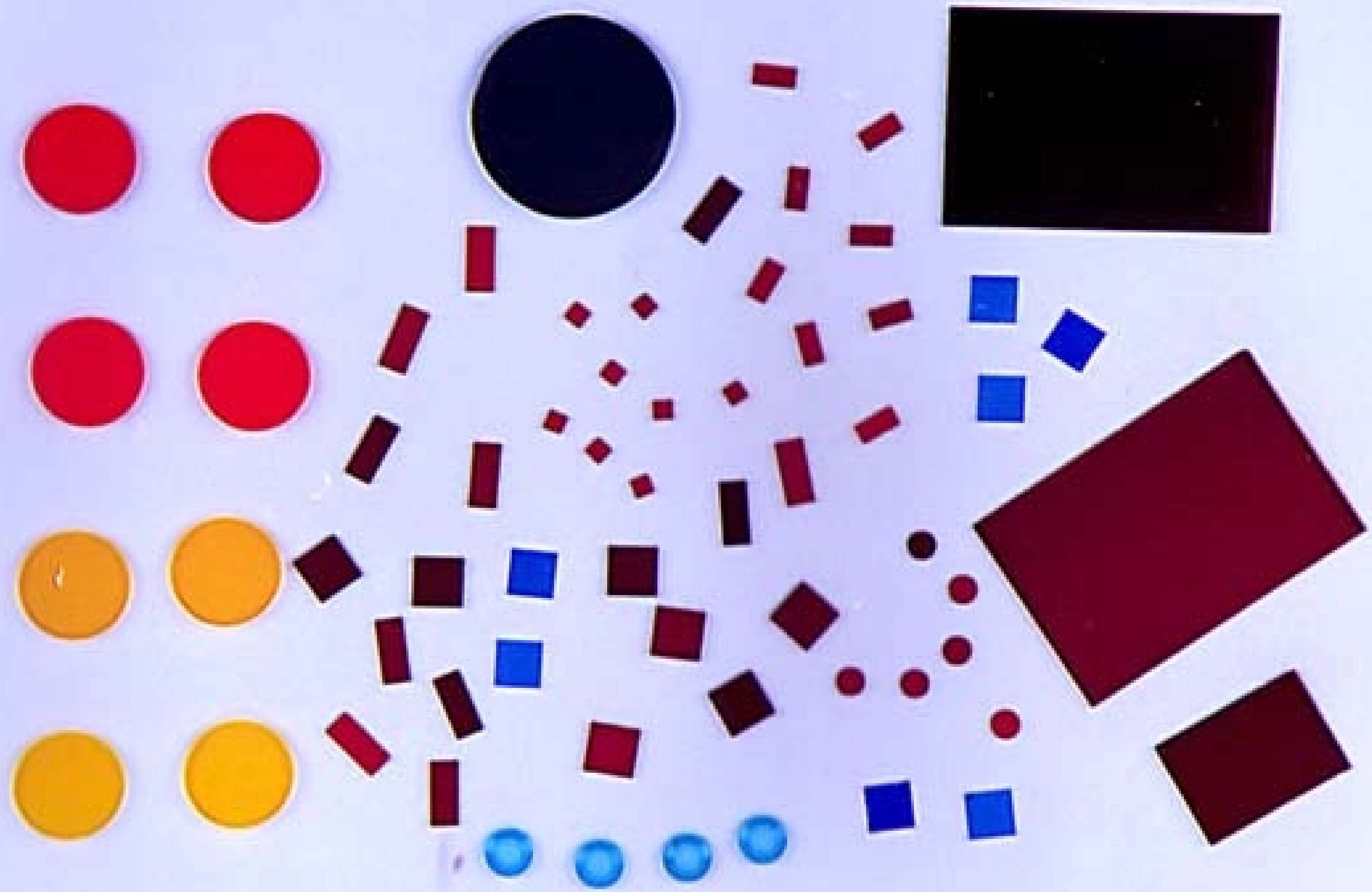
2) Disperse radiation & select desired band – monochromator

3) Modulate wavelengths at different frequencies - interferometer

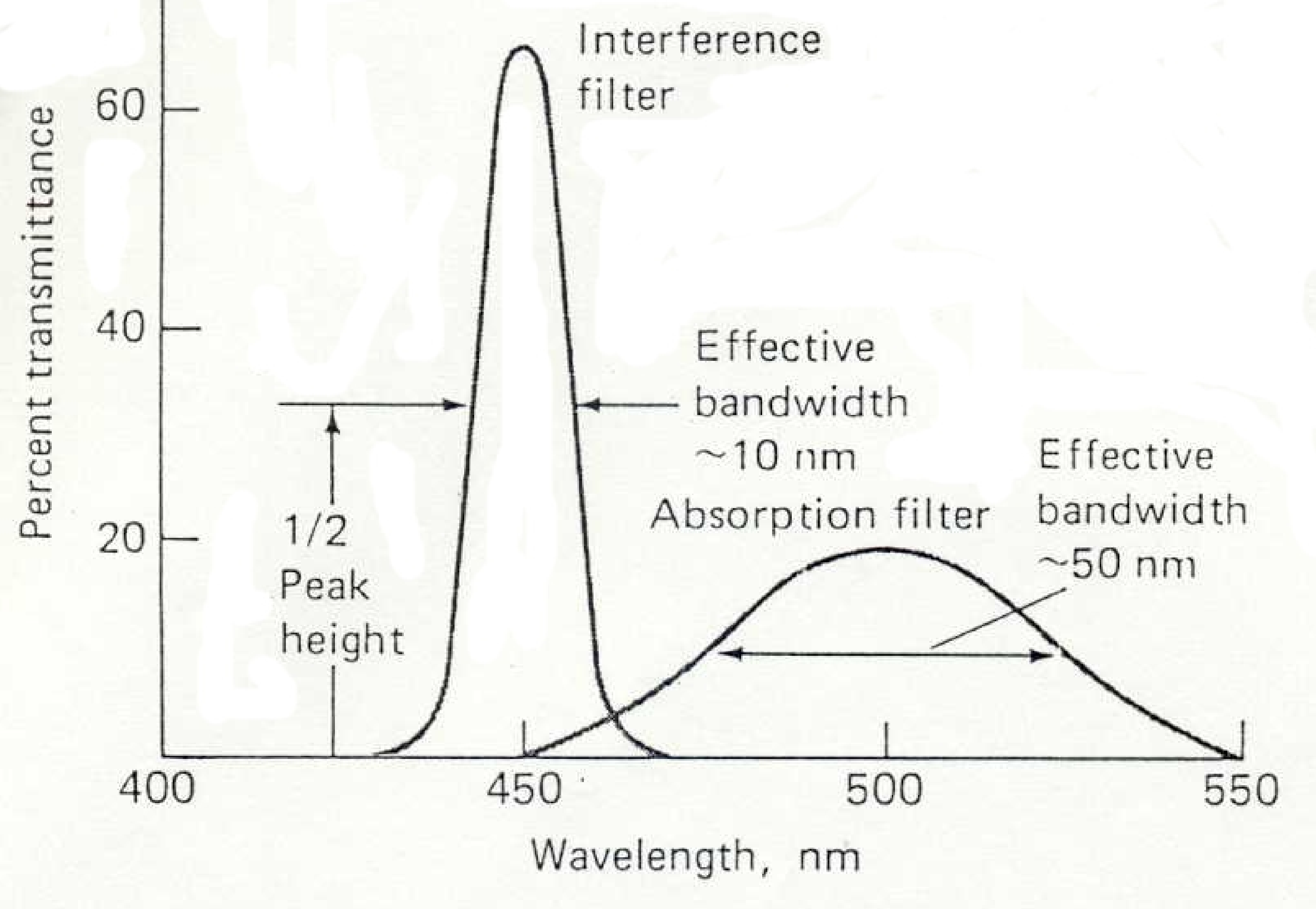
FILTERS

1) **<u>Absorption</u>** – colored glass, colored film, colored solutions – cheapest way

Assortment of Glass & Quartz Optical Filters



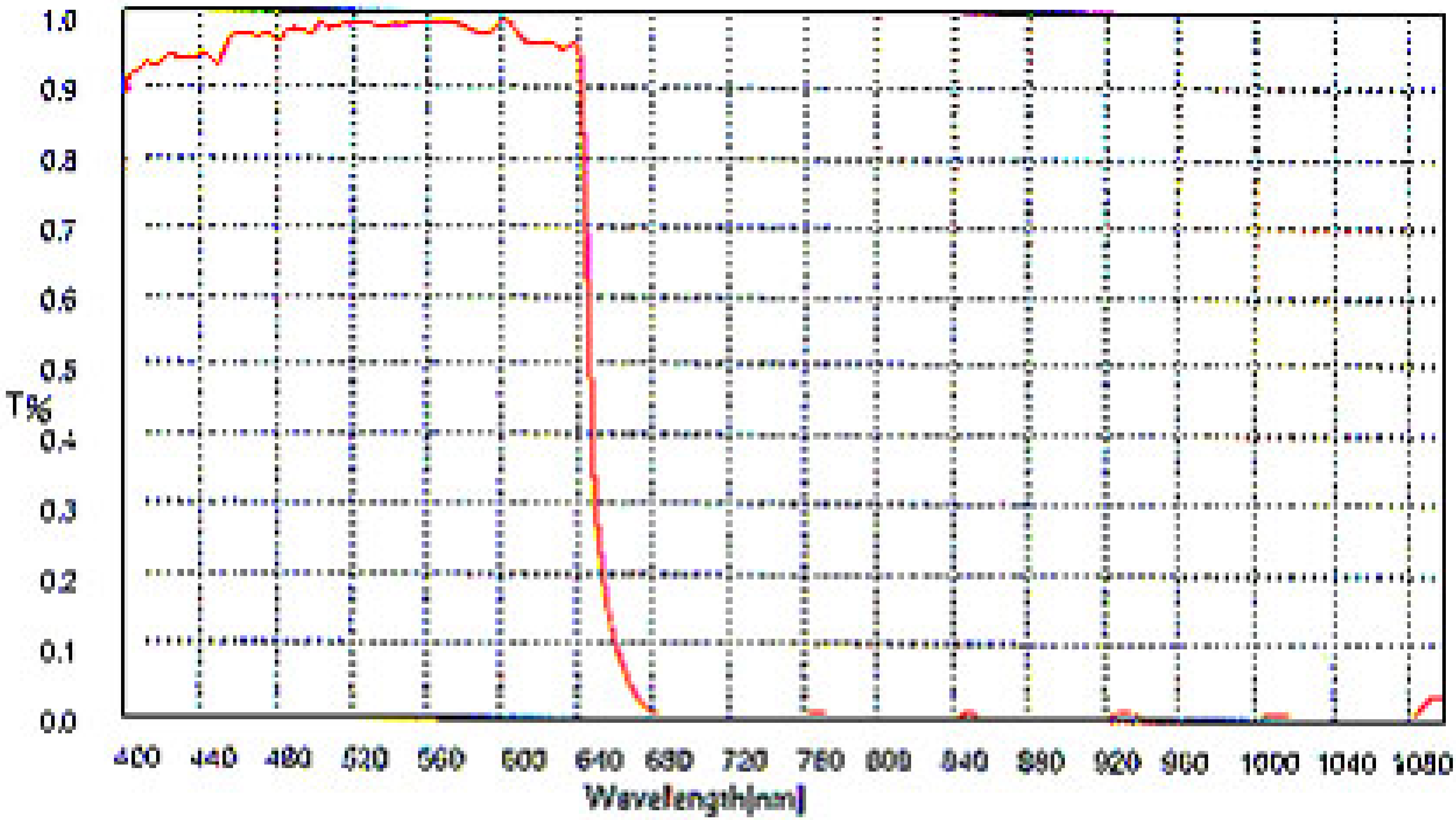
Transmittance Curves for Optical Filters



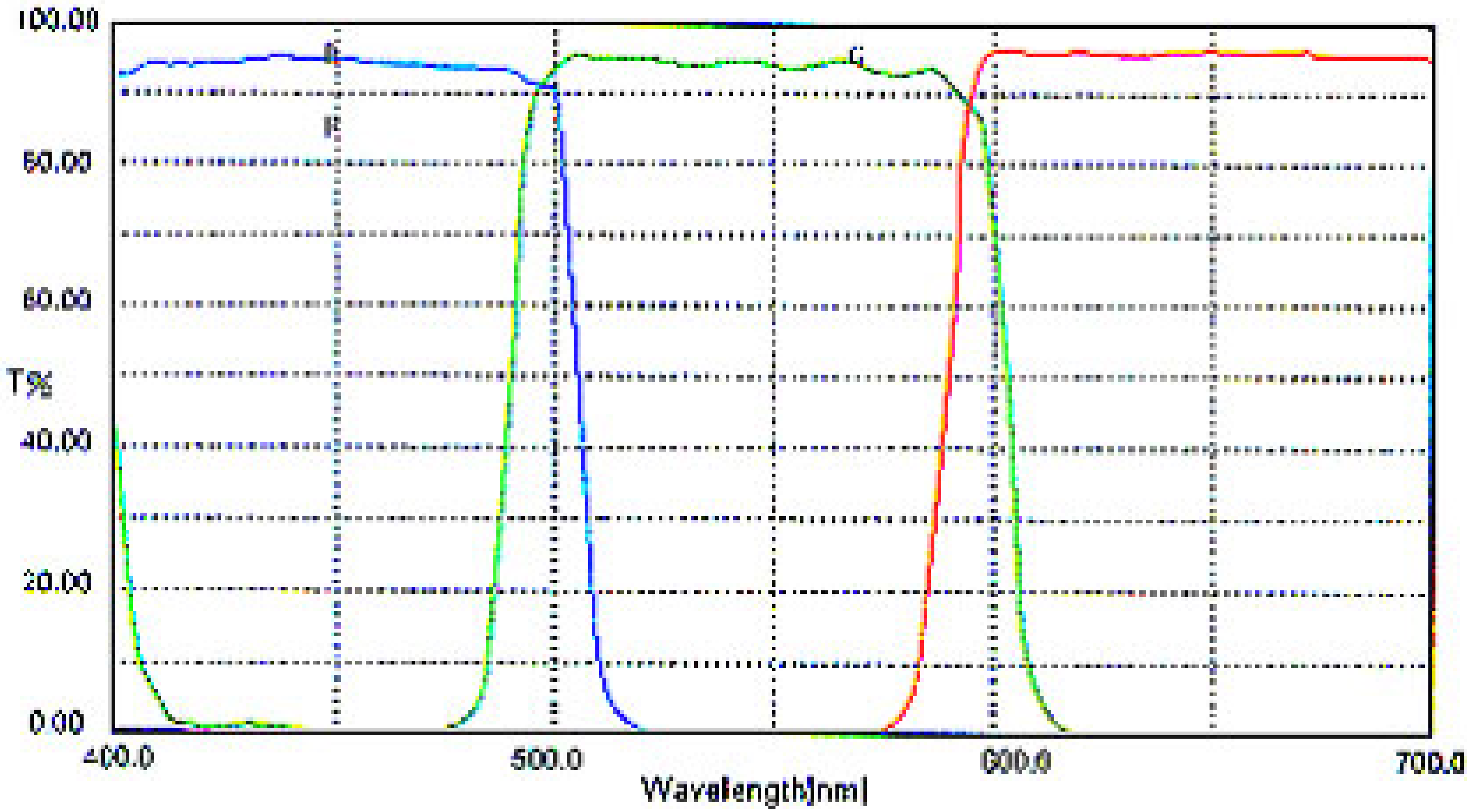
- Absorption filters are also known as bandpass filters
- Usually exhibit low peak transmittance
- Typically have a broad peak profile
- Can use two or more absorption filters together to produce desired transmittance characteristics
- Generic filters are 2 x 2 inch glass or quartz
- Relatively inexpensive

Cut-off filters or sharp-cut filters are also available such as the 650 nm cut-off filter shown here

Cut-on filters have reverse profile

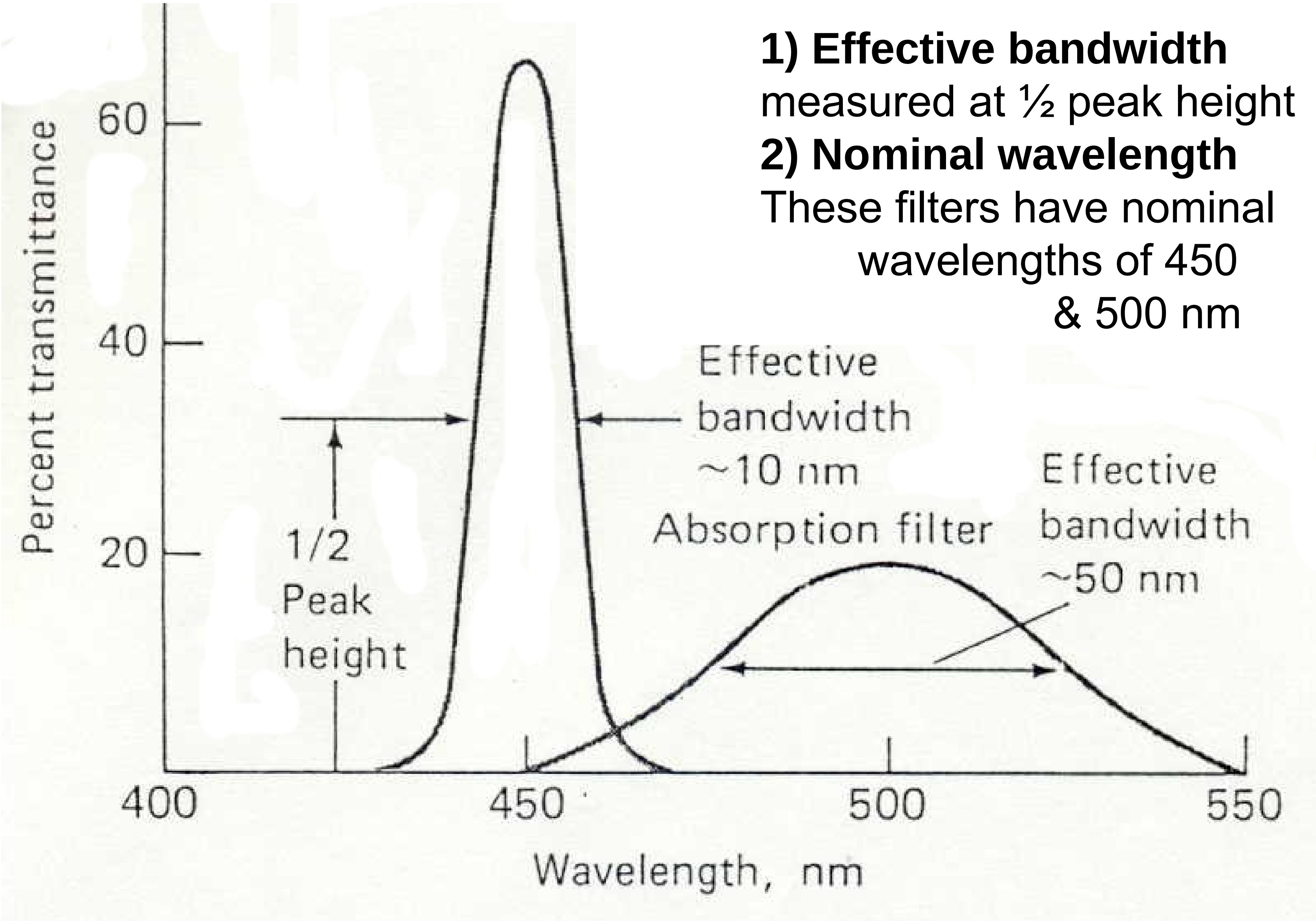


Combining two appropriate cut-off filters produces a bandpass filter. The example shown here comes from 3 filters producing bands at 500 & 600 nm.

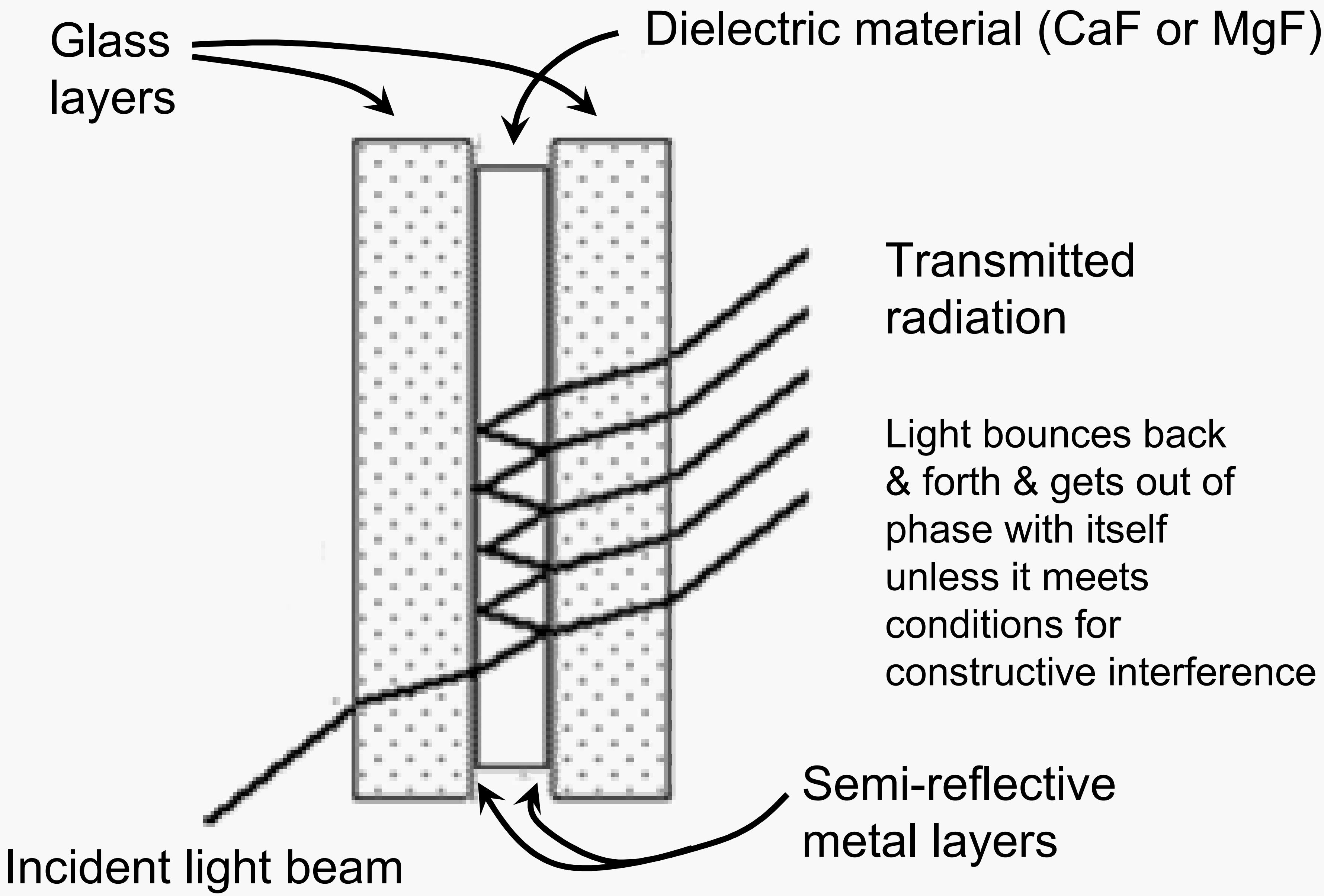


Two terms associated with optical filters are:

1) Effective bandwidth
measured at ½ peak height
2) Nominal wavelength
These filters have nominal wavelengths of 450 & 500 nm



2) **Interference filters** – usually Fabrey-Perot type



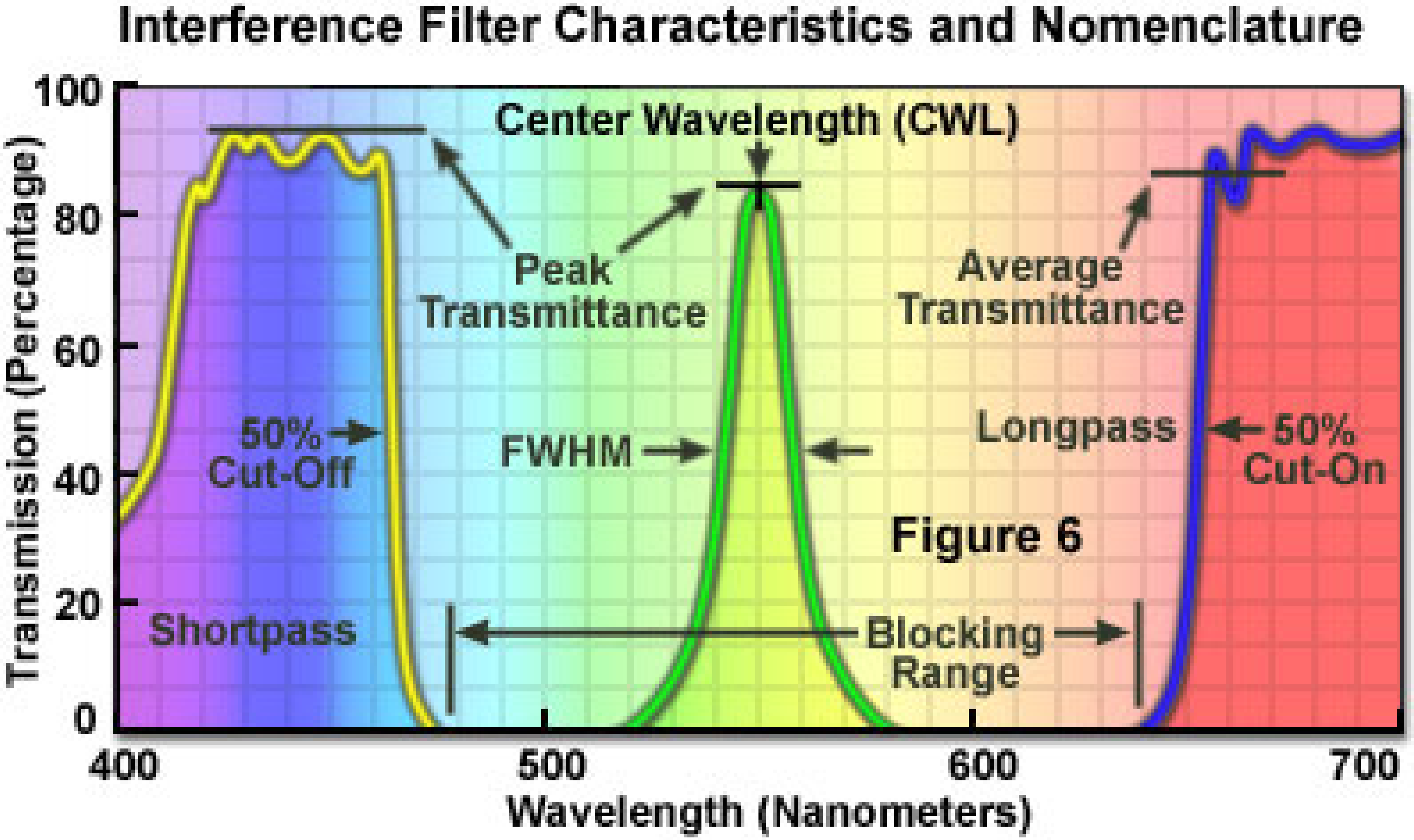
Condition for constructive interference

$$2d = \frac{m\lambda}{\eta}$$

- order of interference (m)
- distance between semi-reflective layers (d)
- refractive index of dielectric (η)

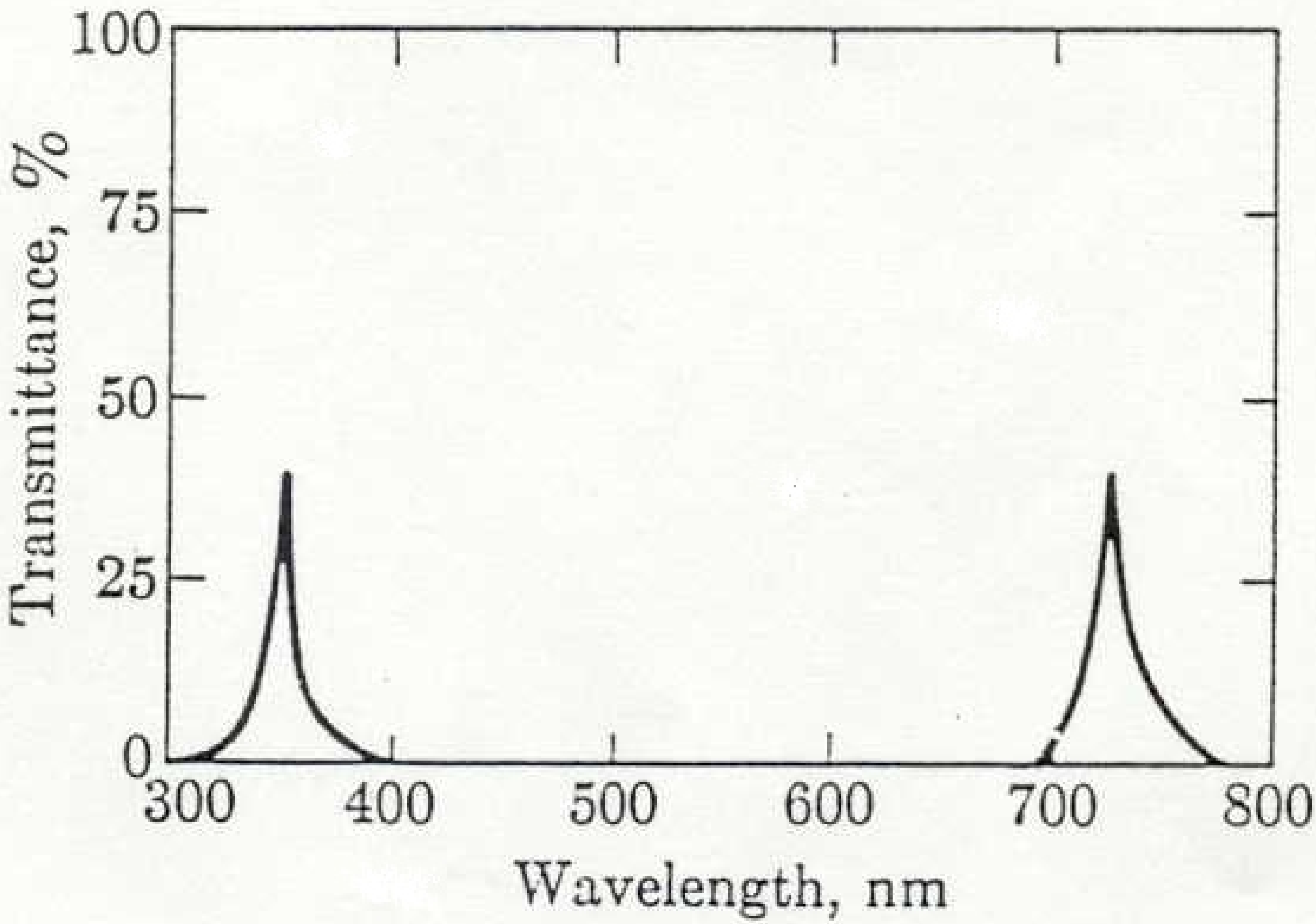
If distance (d) is multiple (m) of wavelength (λ) then it won't be interfered with

Concept of Order – constructive & destructive interference causes waves with different phase angles to be eliminated except if they are multiples of each other

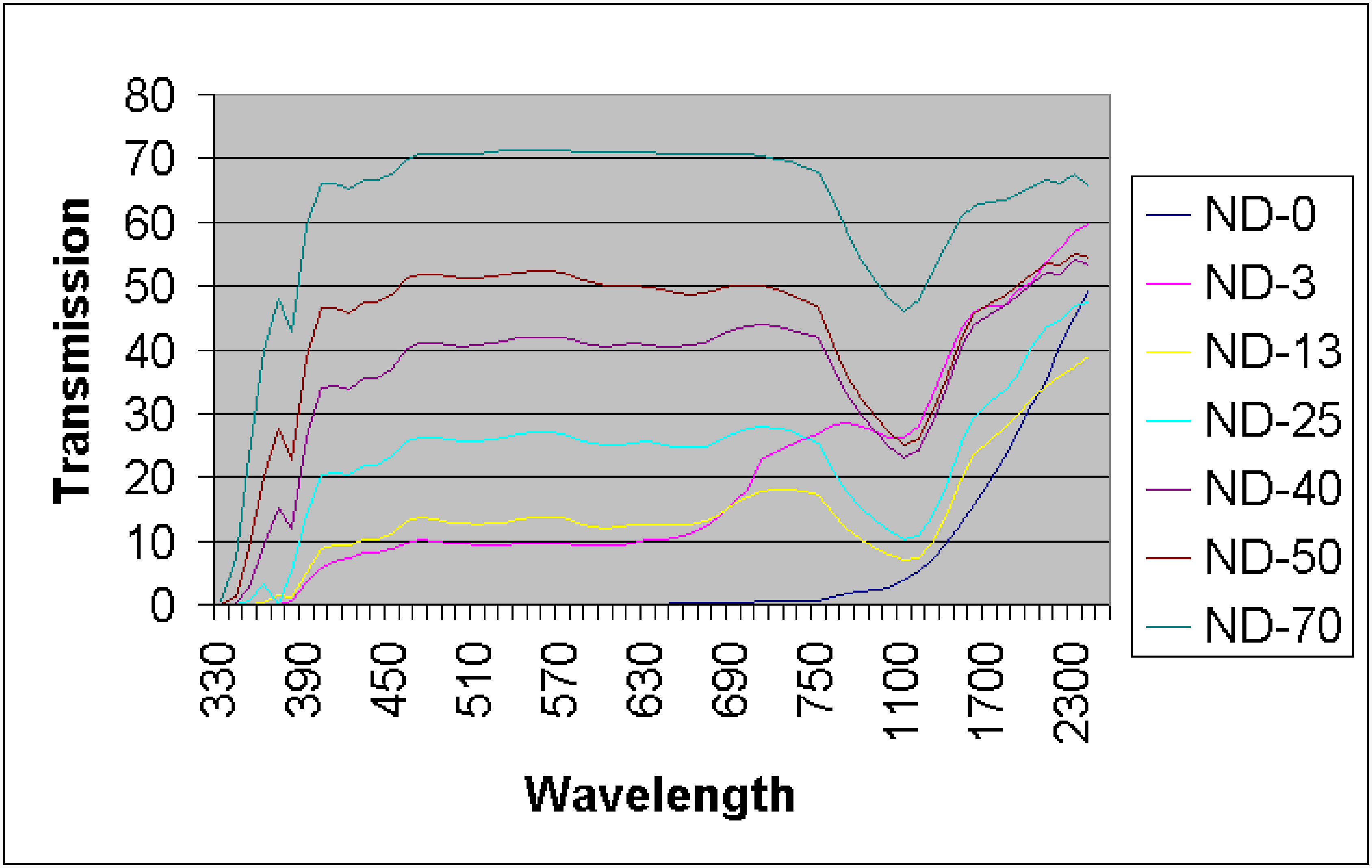


FWHM – full width at half maximum

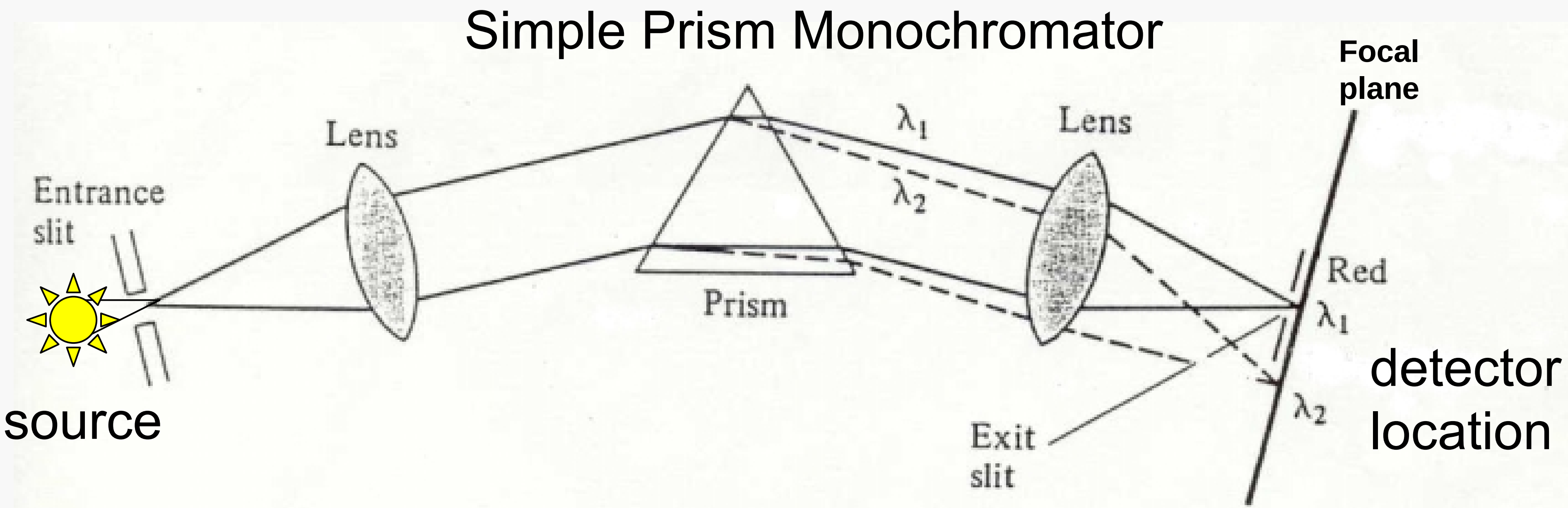
Transmittance vs. wavelength for typical Fabrey-Perot Interference filter showing first and second order λ's (m = 1 & m = 2)



3) <u>Neutral density filters</u> – reduces intensity without any λ discrimination



II) MONOCHROMATORS



Entrance slit allows source radiation to illuminate the first lens which collimates the light spreading it across the face of the **prism**. Prism disperses radiation into component wavelengths and the second lens focuses the spectrum at the **focal plane**. An **exit slit** selects the band of radiation to reach the detector. Dispersing element can be a **prism** or a **diffraction grating**. Focusing elements can be **lenses** or **mirrors**.

- Optical Materials – need optically transparent materials for lenses, prisms & sample cells
- In visible region – can use glass down to 350 nm
- In the UV region – quartz is material of choice
- In the IR region – NaCl, KBr, etc. The heavier the atoms of the salt, the farther into the IR region (i.e., longer λ) before significant absorption occurs

Problem – sensitivity to moisture