Visible Spectroscopy

Chem 304 Unit 4A

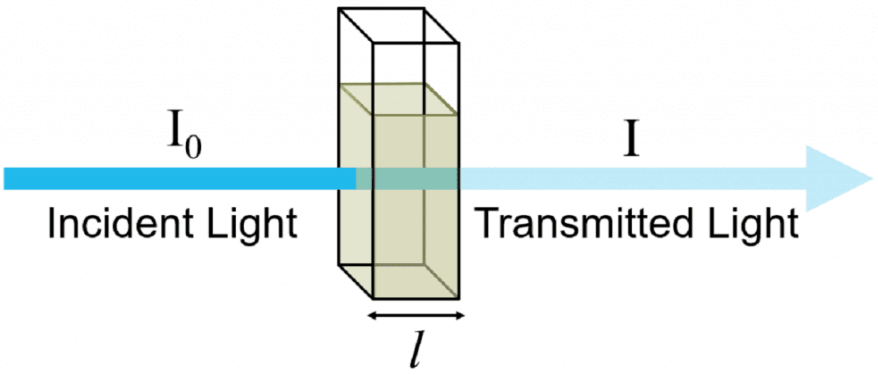
- Spectroscopy is study of interaction between electromagnetic radiation (light) and matter.
- Matter can absorb, scatter, emit, reflect, refract, split and combine photons of different wavelength.
- Visible spectroscopy is concerned with absorption of visible radiation (400-700 nm).
- Visible spectroscopy is useful for both, qualitative and quantitative analysis.
- All spectroscopic methods depend on Beer's law (also called Beer-Lambert's law) for quantitative analysis.

Beer–Lambert law relates the attenuation (=reduction) of electromagnetic radiation intensity $\log_{10}(I_o/I)$ to the concentration of a single attenuating species (c), the optical path length through the sample (b or l) and absorptivity of the species (a_λ, a, ε_λ or ε, called **molar absorptivity** or **molar extinction coefficient**) at a particular wavelength (λ, generally λ_{max}, where attenuation is maximum).

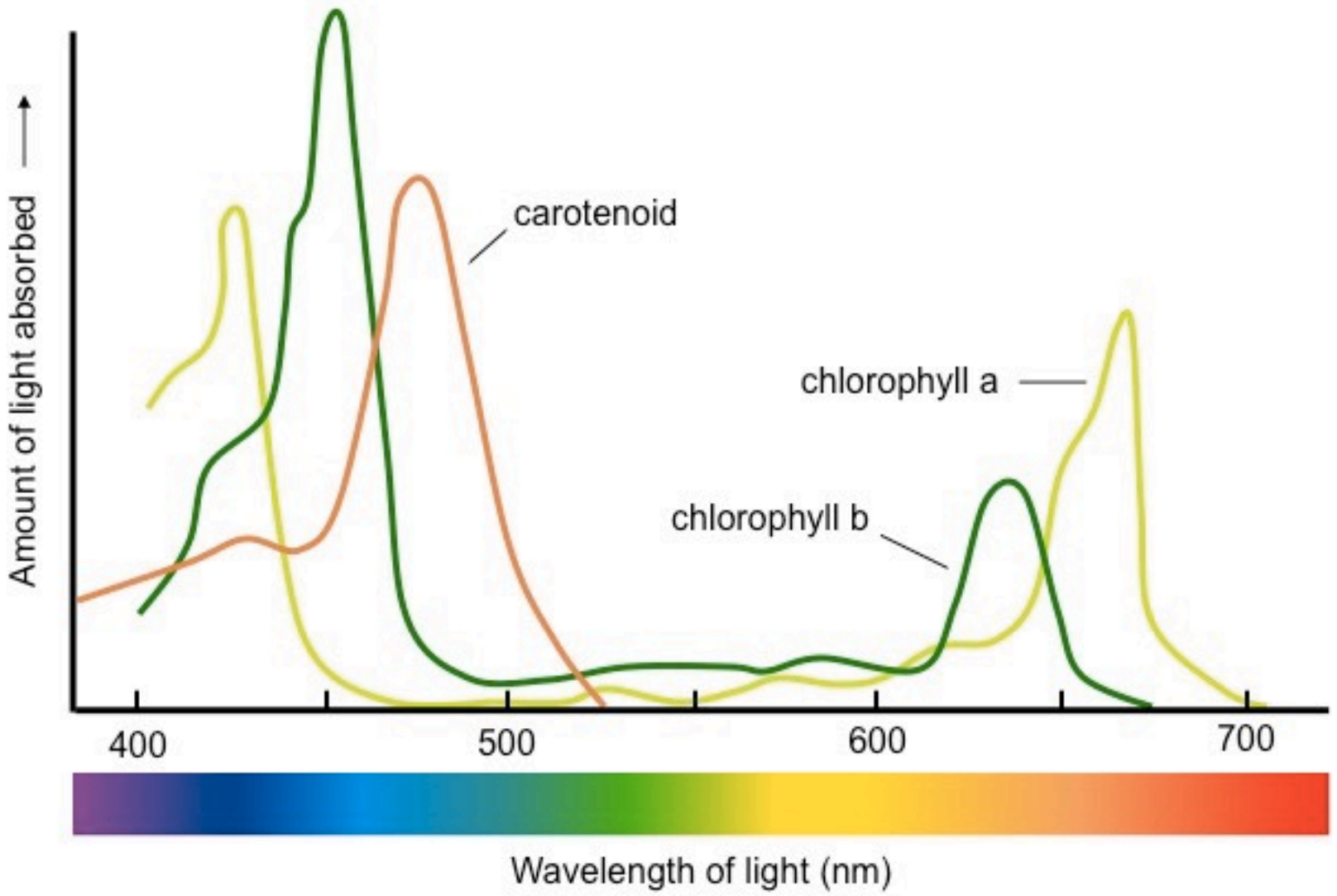
$$\log_{10}(I_o/I) = a_\lambda bc \text{ or simply } \mathbf{A = abc}$$

Term A is absorbance, $\mathbf{A = \log_{10}(I_o/I)}$

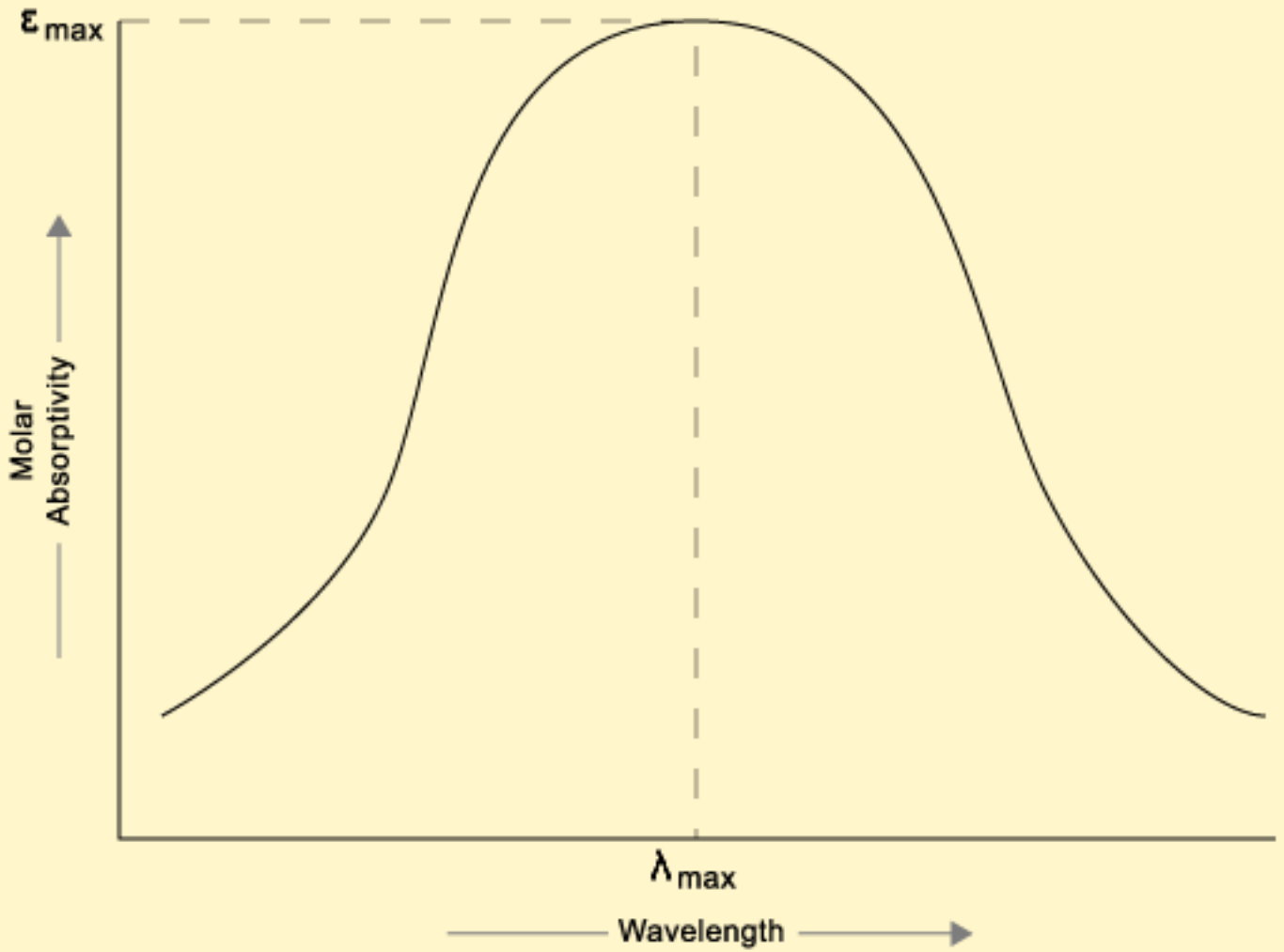
Where, I_o is original intensity of light and I is intensity of transmitted light.



Example of Visible Spectrum



λ_{max} and ε_{max}



Derivation of Beer-Lambert law

Lambert found attenuation of light depends on thickness of sample (b).

$$\log_{10}(I_o/I) \propto b \Rightarrow A = k_1 b$$

Beer found attenuation of light depends on concentration of light absorbing species (c)

$$\log_{10}(I_o/I) \propto c \Rightarrow A = k_2 c$$

(k_1 & k_2 are proportionality constants)

Combining both, $\mathbf{\log_{10}(I_o/I) = A = abc}$, where $a = k_1 k_2$.

$\mathbf{I = I_o 10^{-abc}}$ is equivalent form of Beer-Lambert law.

Further, if Intensity is measured in %, $\mathbf{A = 2 - \log_{10}(I)}$

Example 1: If absorbance is 1, what fraction of light was absorbed?

We know, $\mathbf{A = 2 - \log_{10}(I)}$, ∴ log(I) = 1, ∴ I = 10%.

But I is intensity of transmitted light.

Thus, 90% light was absorbed.

The fraction of light absorbed is 0.9

Example 2: If $\epsilon = 8400\ M^{-1}cm^{-1}$, path length is 1 cm and A=0.70, calculate concentration.

A = abc = ϵbc

thus c = A/ab

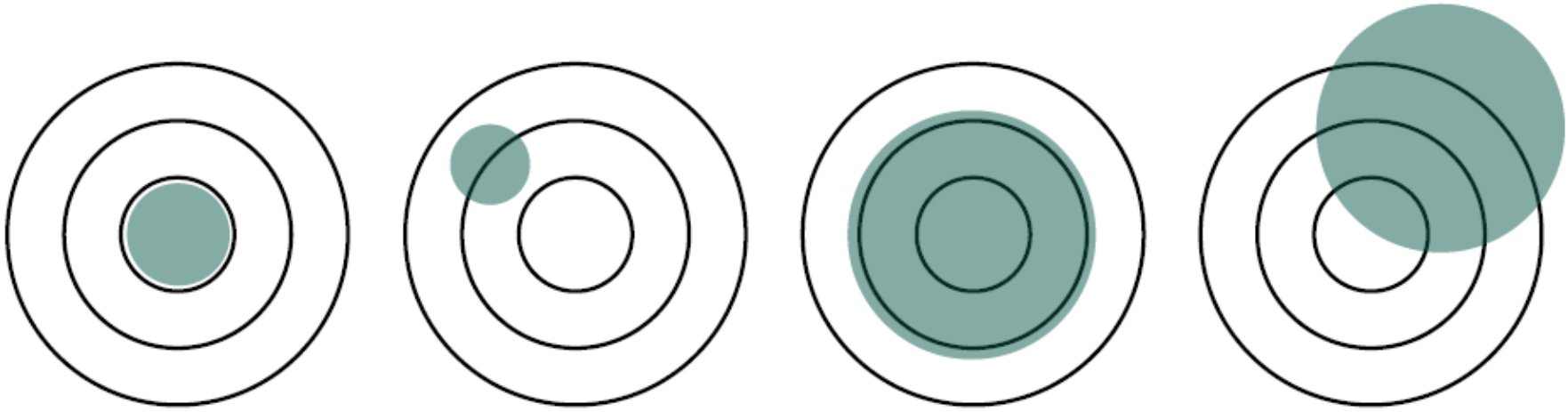
c = 0.70/(8400 x 1)

$c = 8.33 \times 10^{-5}$ mol/L is the answer.

Limitations of the Beer-Lambert law

1. Deviations in absorptivity coefficients at *high concentrations (>0.01M)*
2. Scattering of light due to particulates in the sample.
3. Fluorescence or phosphorescence of the sample.
4. Changes in refractive index at high analyte concentration.
5. Shifts in chemical equilibria as a function of concentration, solvent, matrix etc.
6. Non-monochromatic radiation, stray light and other instrumental limitations.

Photometric Precision and Accuracy



High Precision
High Accuracy

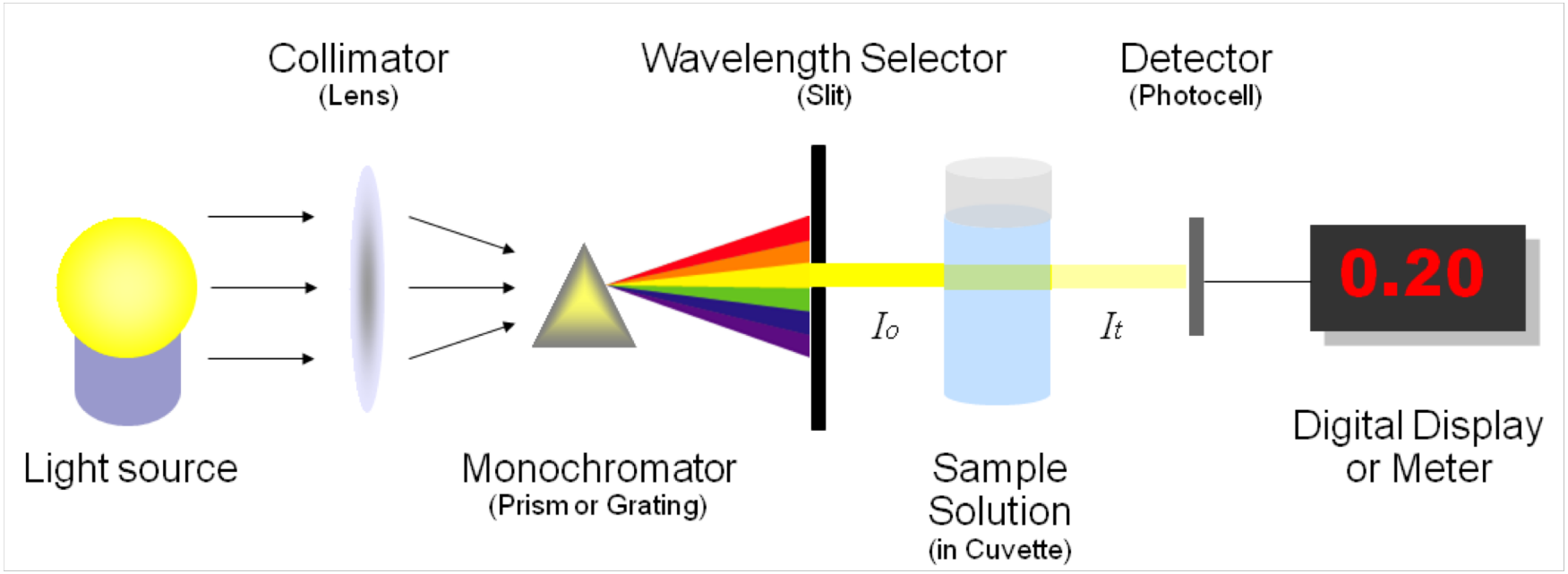
High Precision
Low Accuracy

Low Precision
High Accuracy

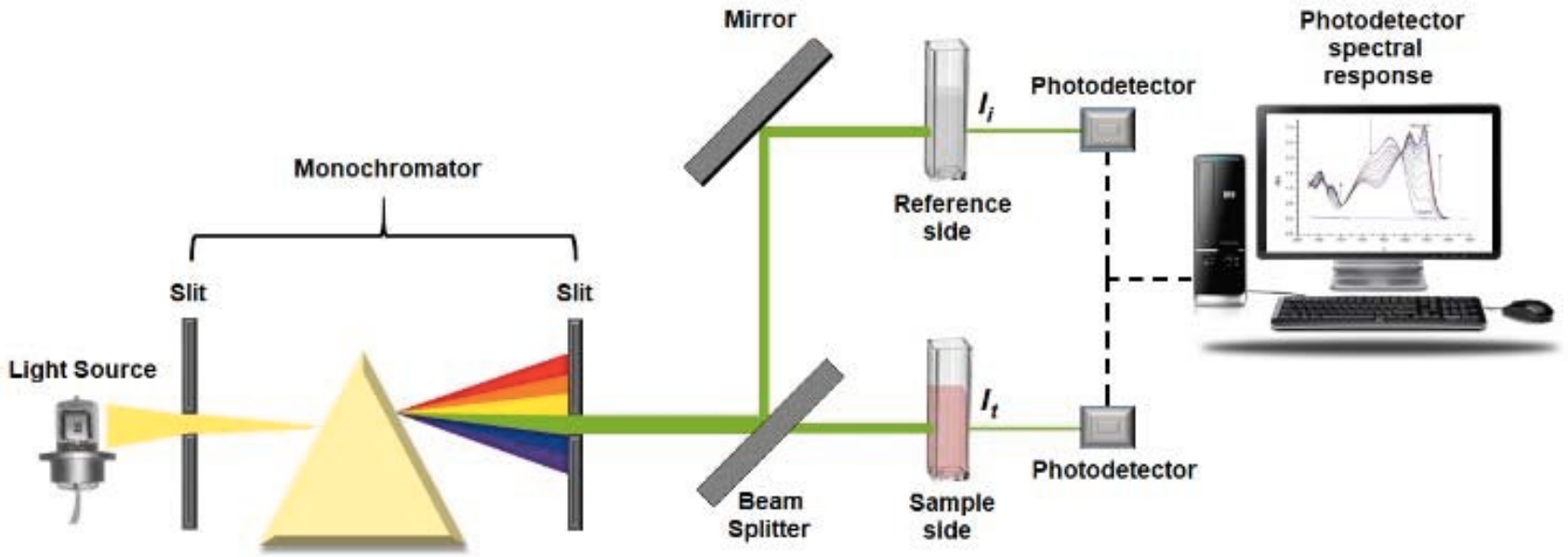
Low Precision
Low Accuracy

Precision depends upon limitations of Instrumental setup, while Accuracy depends upon calibration and limitations of Lambert-Beer's Law

Single Beam Spectrophotometer

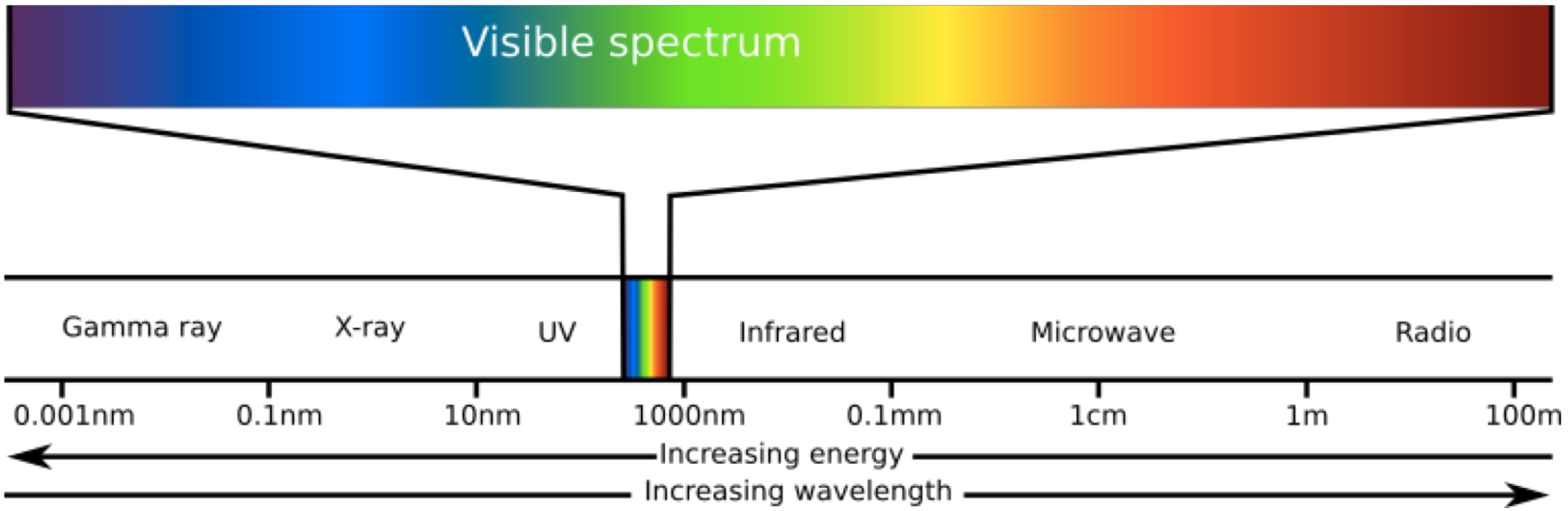


Double Beam Spectrophotometer



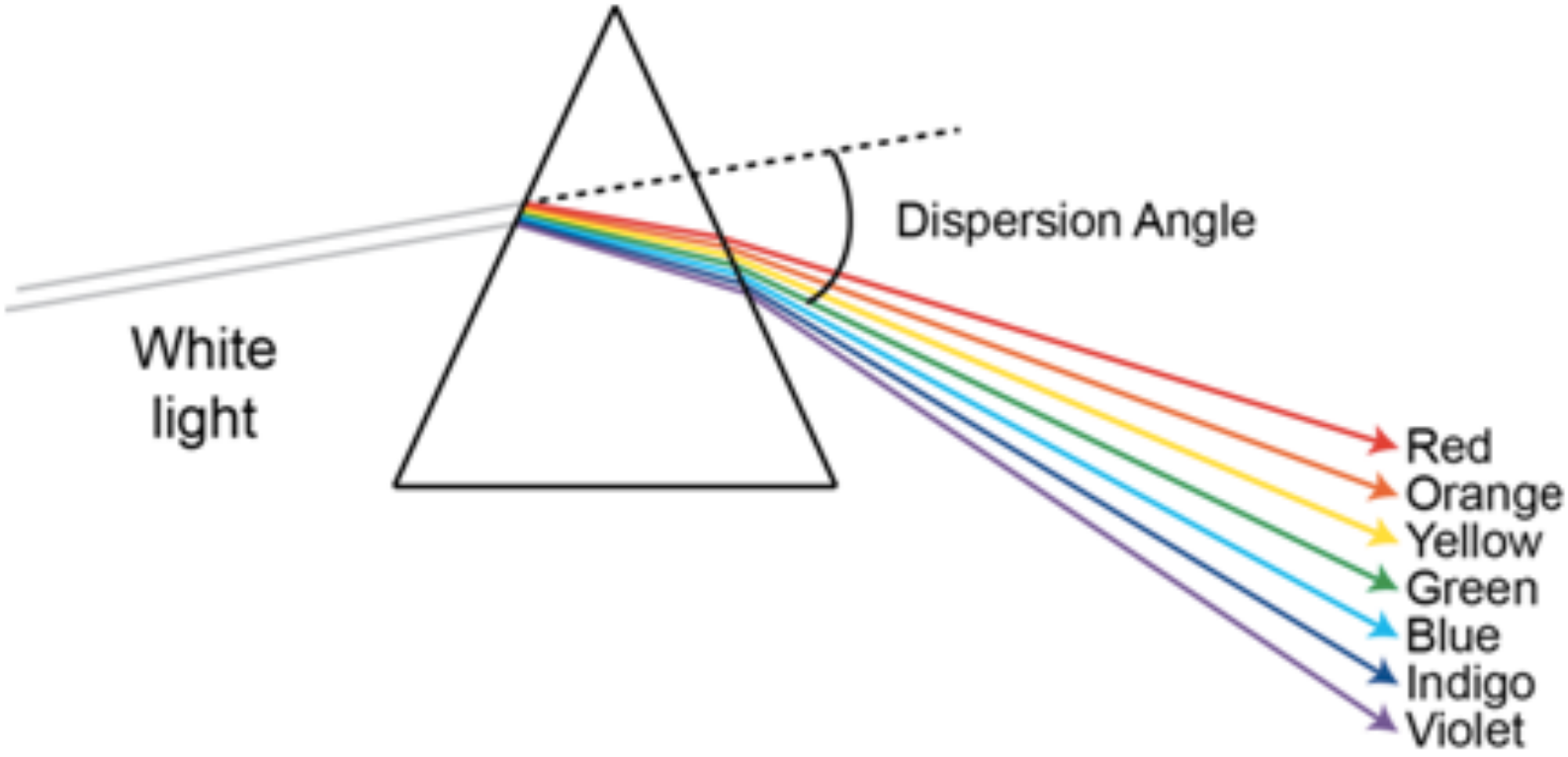
Sources

1. For UV : Deuterium Lamp (200-400nm) and Xenon Arc (200-1000nm)
2. For Visible : Tungsten Lamp (350-2500nm)
3. For UV, Visible, IR : Monochromatic LEDs



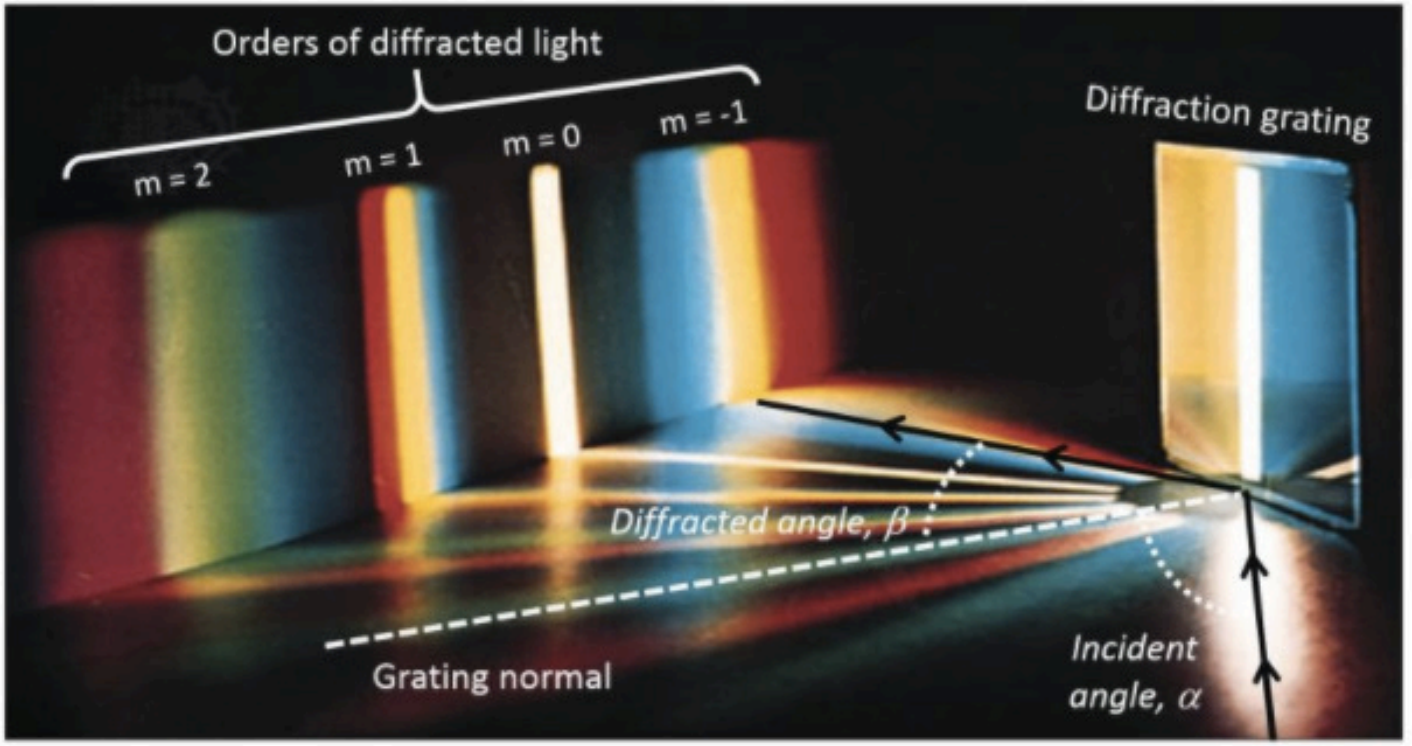
Wavelength Selectors (Monochromators)

1. Prism (spread 50nm)



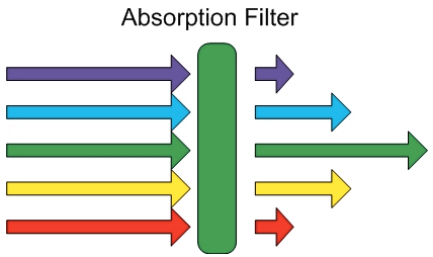
Wavelength Selectors (Monochromators)

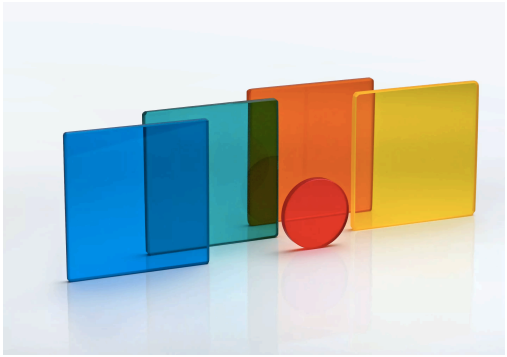
2. Grating (spread 5-25nm)
    a. Diffraction/Reflection b. Holographic

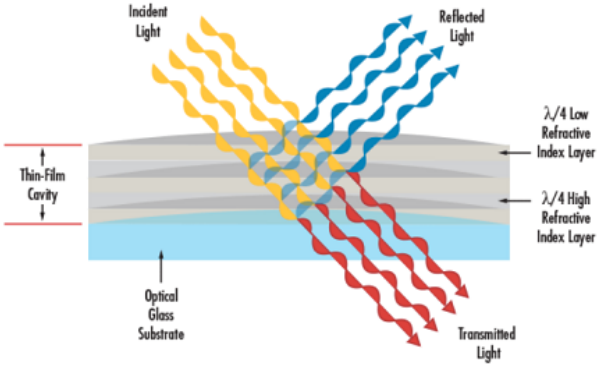


Wavelength Selectors

3. Filters
    a. Glass (spread 150nm)
    b. Gelatin (spread 25-50nm)
    c. Interferometric (spread 15nm)







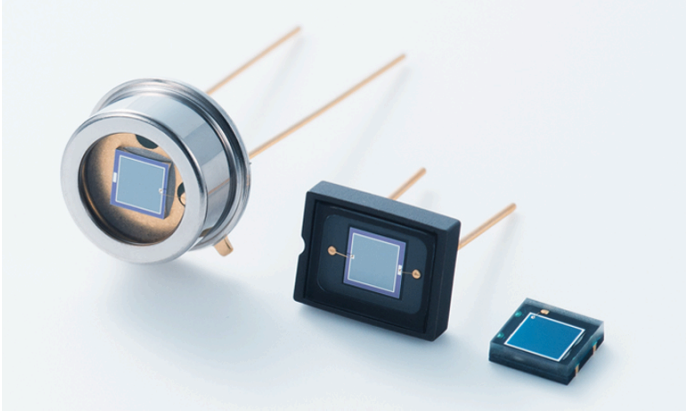
Sample Holders

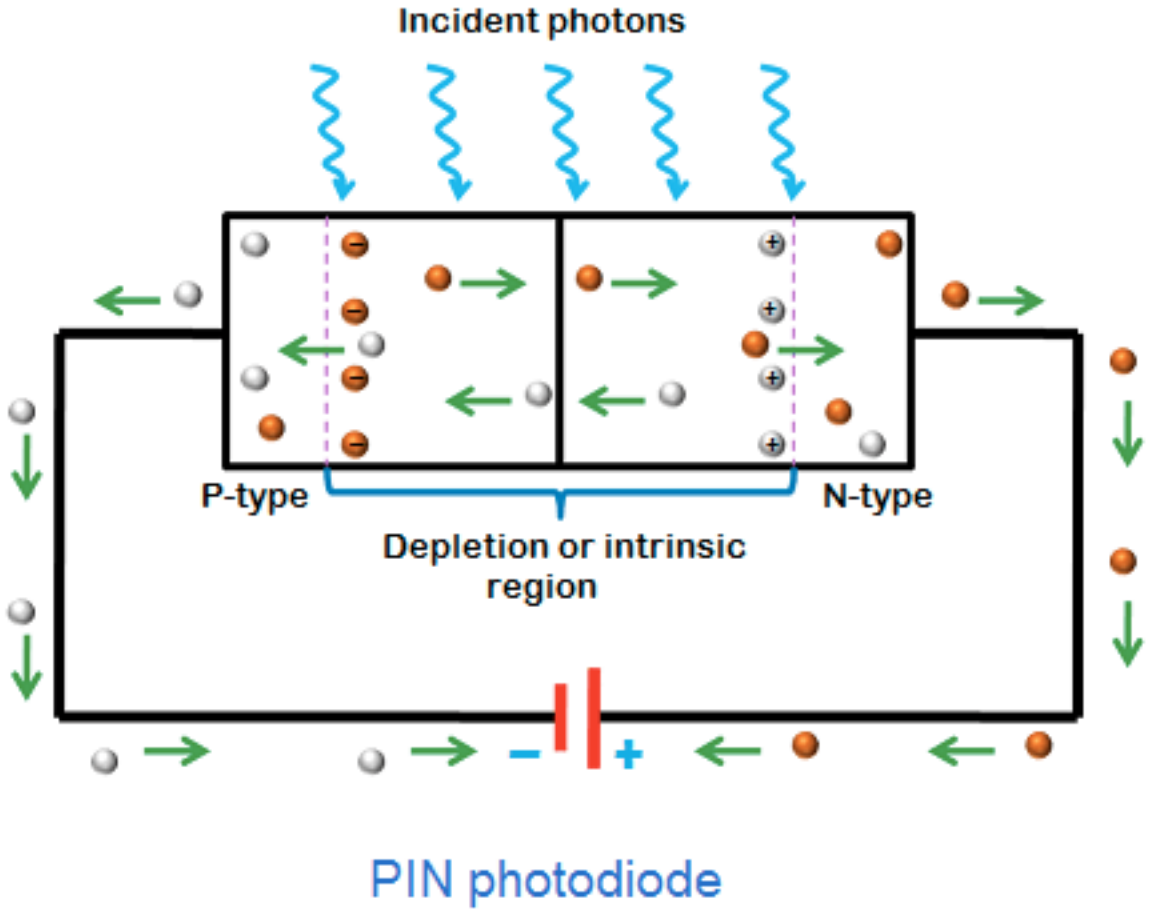
Sample Holders (Cuvette) should not absorb light.

a. Glass (For Visible)
b. Quarts (For UV)
c. KBr, CsBr (for IR)

Detectors

1. Photo Cells

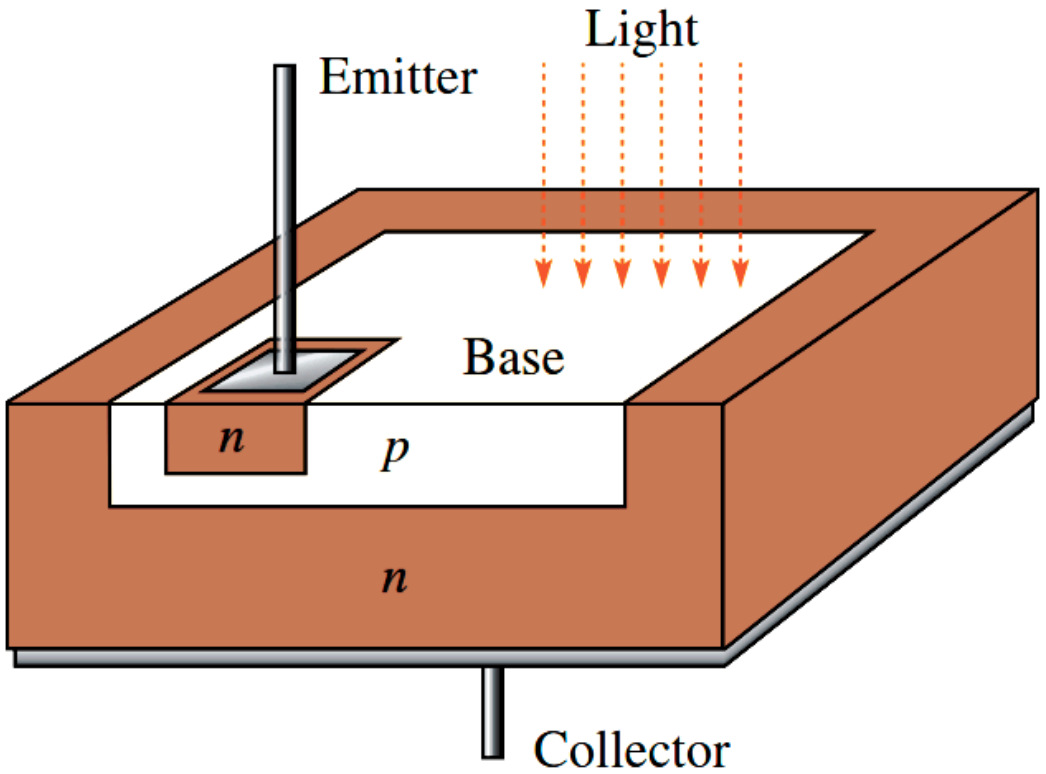




PIN photodiode

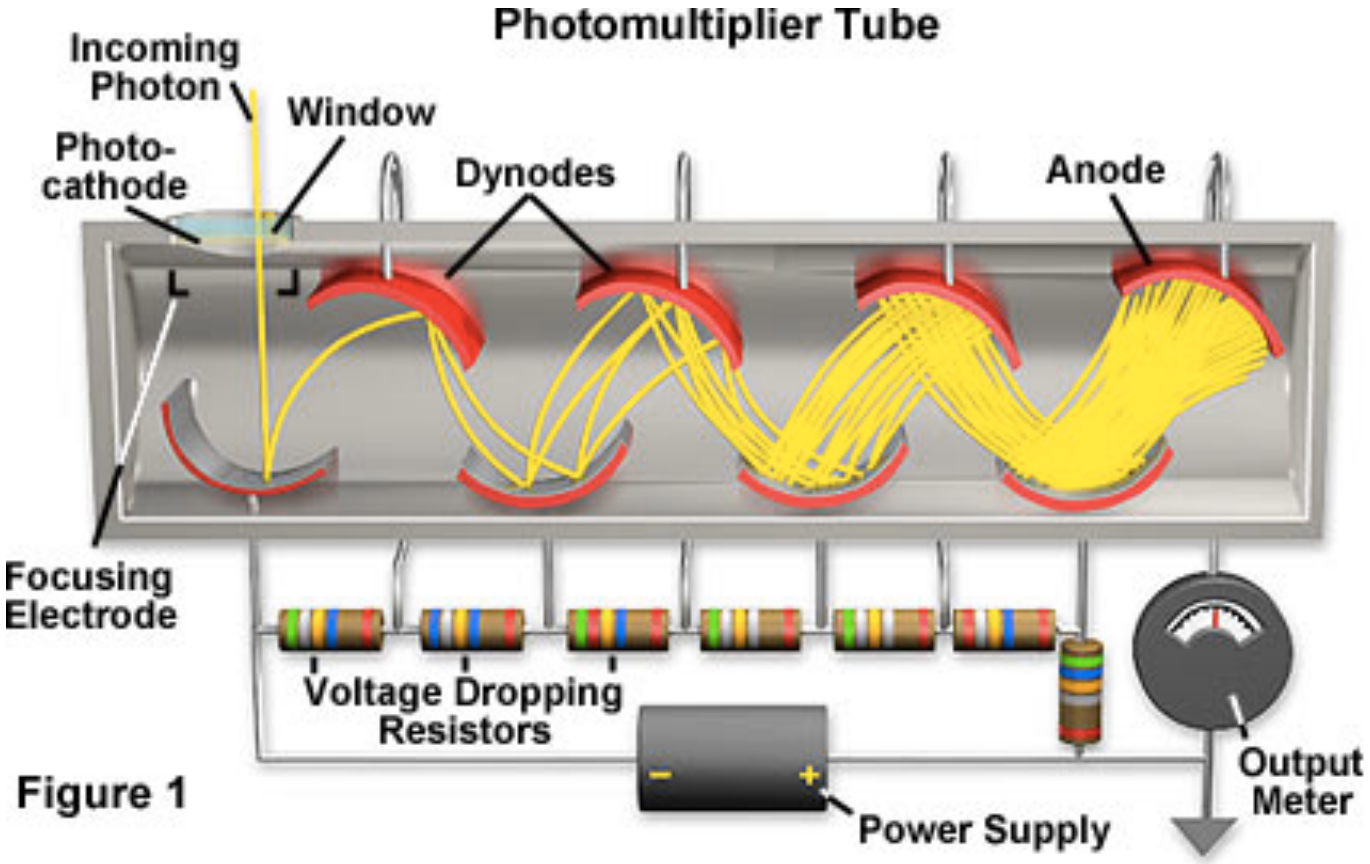
Detectors

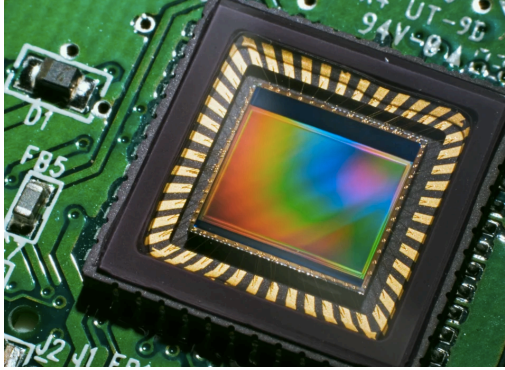
2. Phototransistors



Detectors

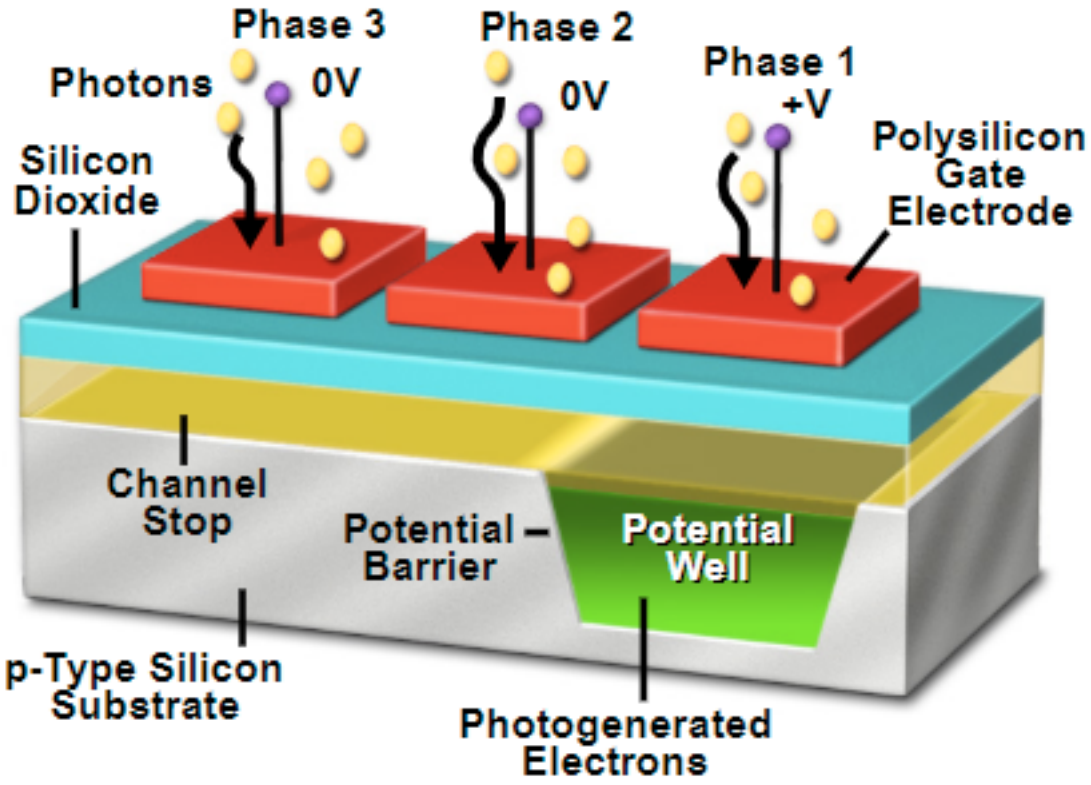
3. Photo Multipliers





Detectors

4. CCD (Charge Coupled Devices)



Your questions are always welcome.

The more you ask, the more you learn.