

**Chapter 18 – Fundamentals of
Spectrophotometry (cont'd)**
AND
Chapter 20 - Spectrophotometers

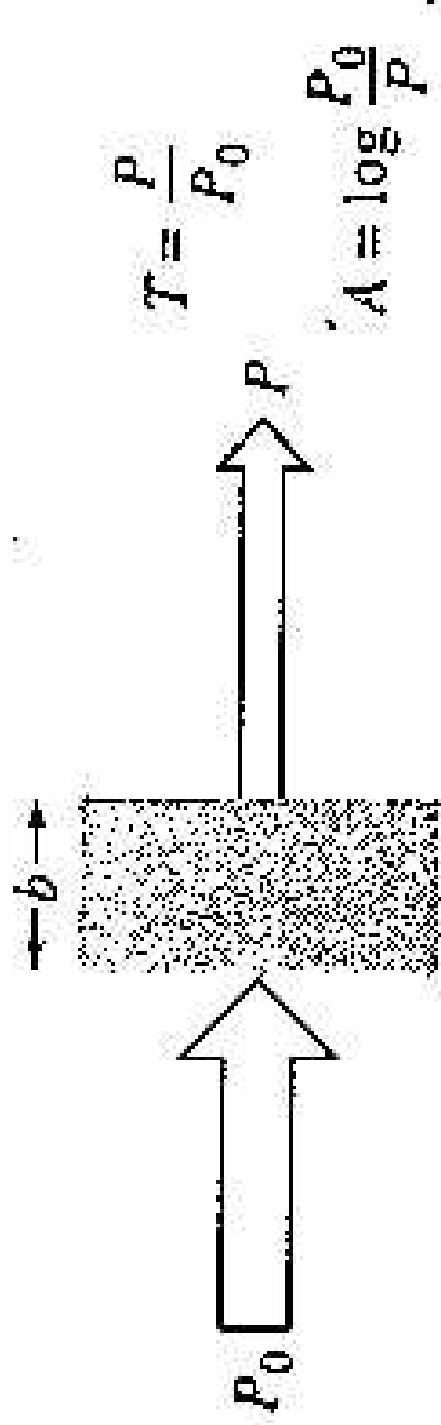
Homework for Chapter 20 –

Due Monday, April 13

Problems 20-1, 20-3, 20-4, 20-6, 20-9, 20-27

Note: We will talk about some applications of spectrophotometry in class, but will not have any homework assigned from Chapt. 19.

Absorption of Light



Absorbing
solution of
concentration c

Absorption Methods, Transmittance

$$T = P/P_o$$

where

$T \Rightarrow$ transmittance

$P \Rightarrow$ power of transmitted
radiation

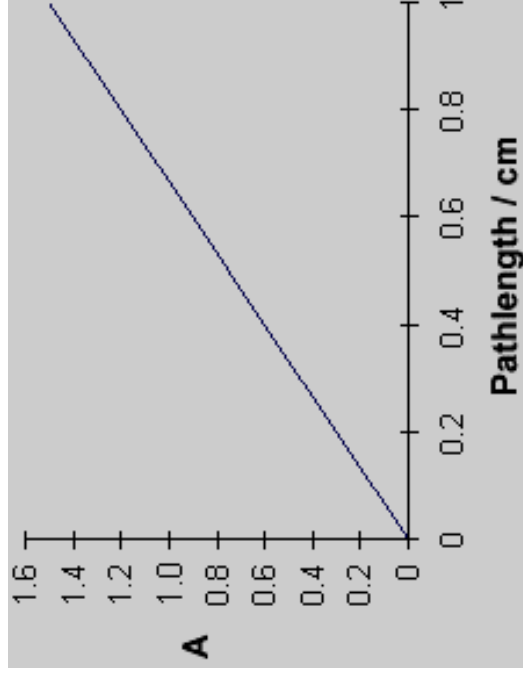
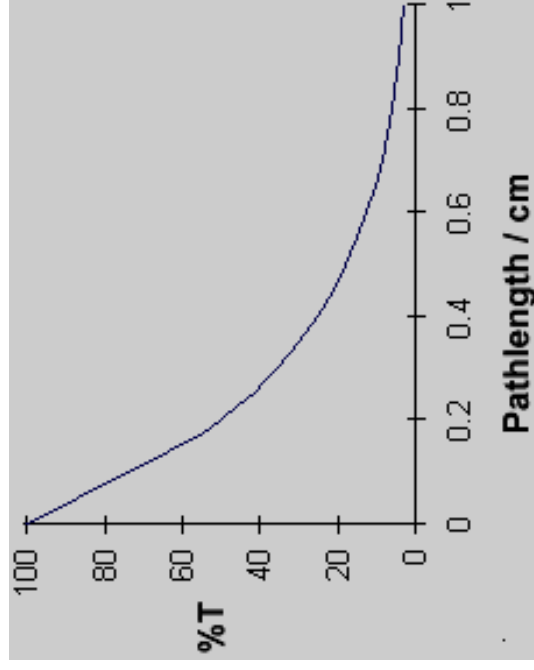
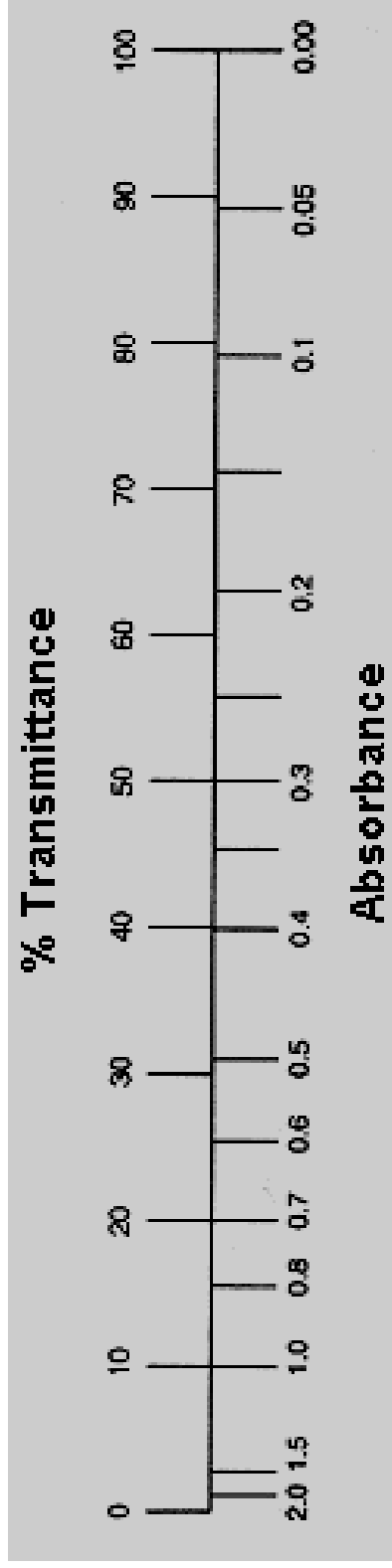
$P_o \Rightarrow$ power of incident
radiation

$$\%T = (P/P_o) * 100$$

where $\%T \Rightarrow$ percent transmittance

Absorbance and transmittance

$$\text{Absorbance} \Rightarrow A = -\log_{10} T = -\log_{10} (P/P_0)$$



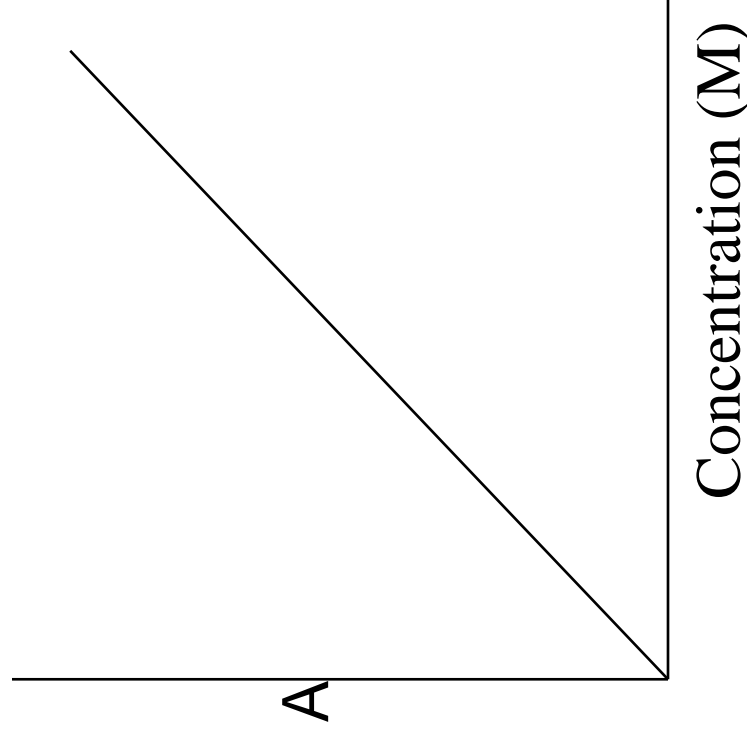
Absorption Methods, Beer's Law

$$A = \epsilon bc$$

$b \Rightarrow$ path length (cm)

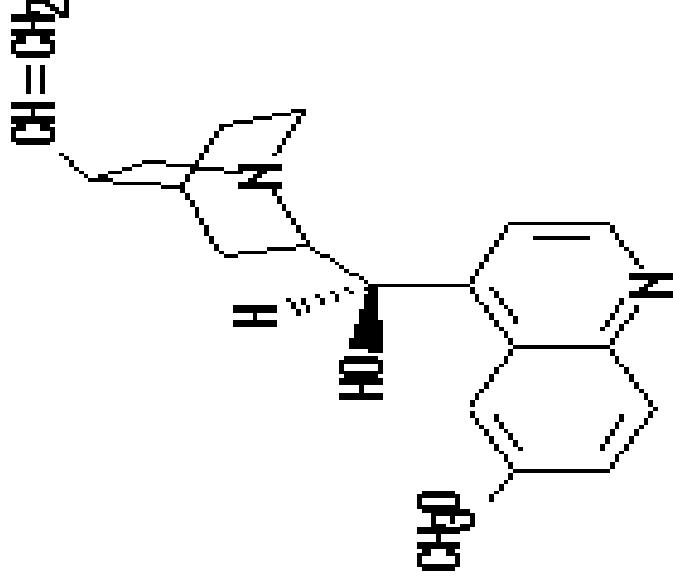
$c \Rightarrow$ concentration (M)

$\epsilon \Rightarrow$ molar absorptivity
($M^{-1} \text{cm}^{-1}$)



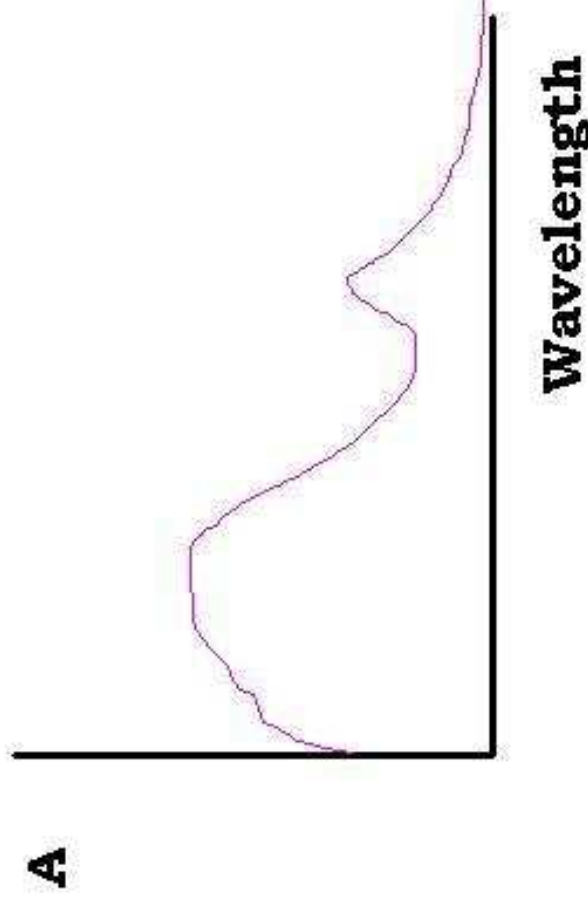
A “chromophore”

- A chromophore is a part of a molecule (functional group, ring structure, etc.) that is responsible for the absorption of light
- Examples: C=O in acetone; aromatic ring in xylene



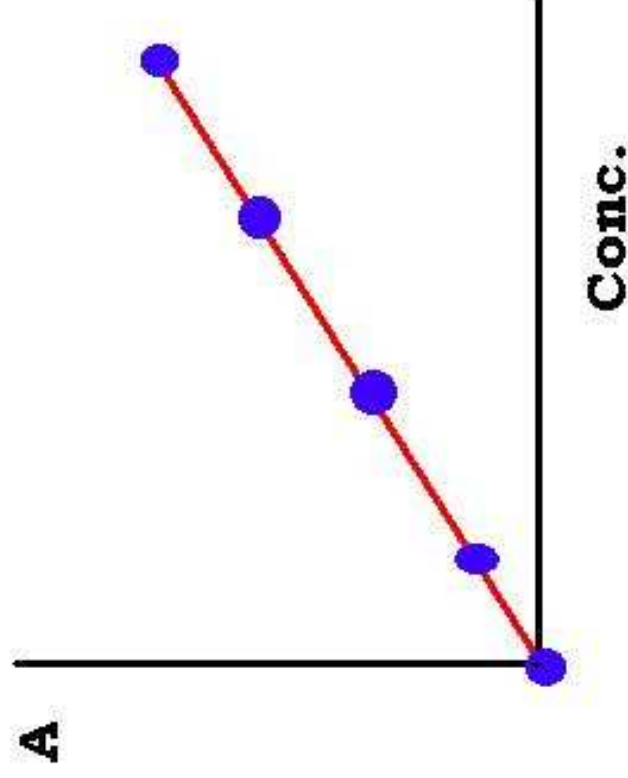
Beer's Law

$$A = \epsilon bc$$



The absorption spectrum
A vs. λ
 ϵ specific to each energy (λ)

Beer's Law calibration plot

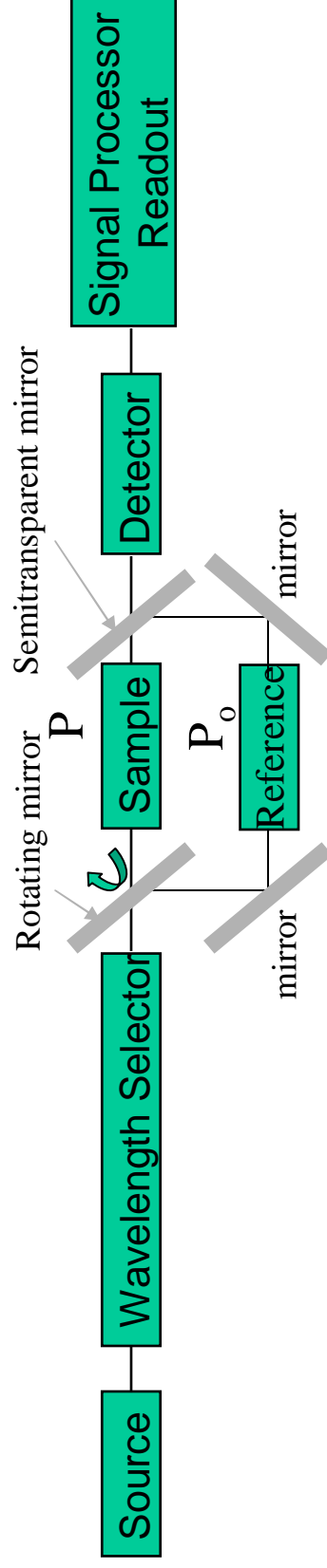


$$A = \epsilon bc$$

A vs. c

ϵ and b constants

Components of Optical Instruments



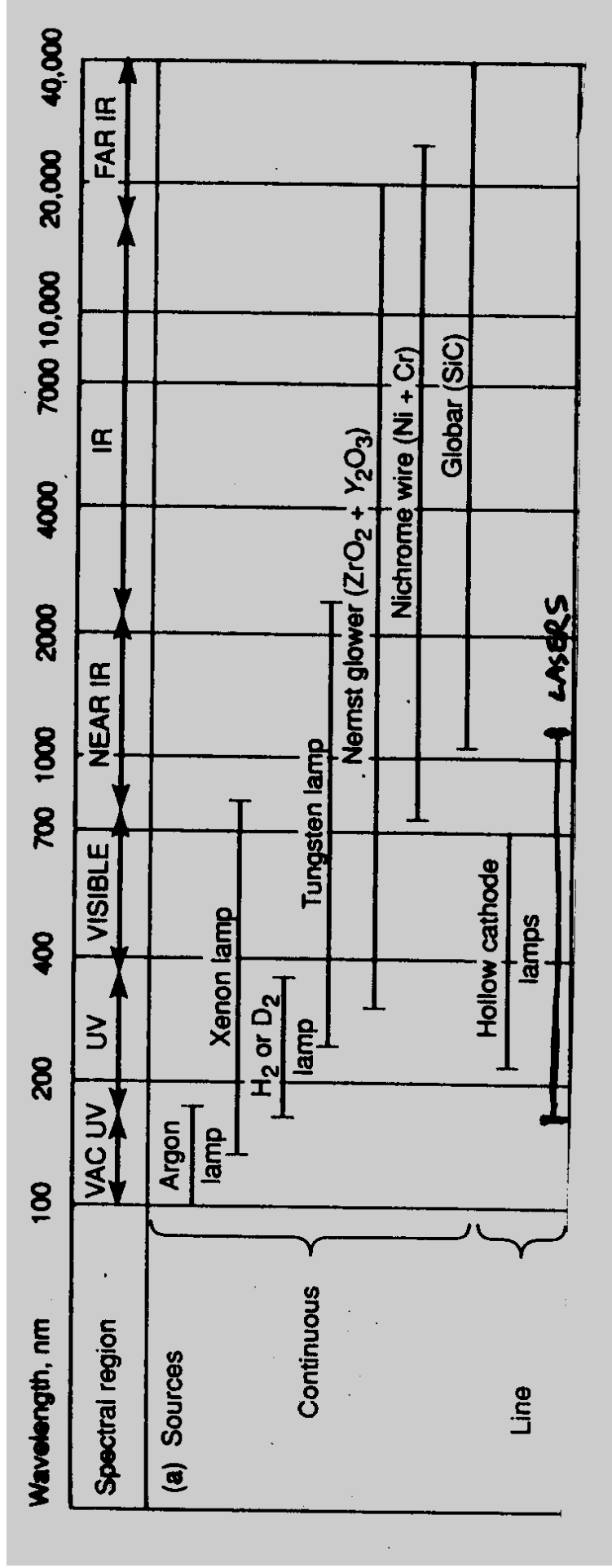
Absorption Spectrometer

Emission Flame Photometer

Flame Atomic Absorption Spectrometer

Fluorescence and/or Scattering Spectrometer

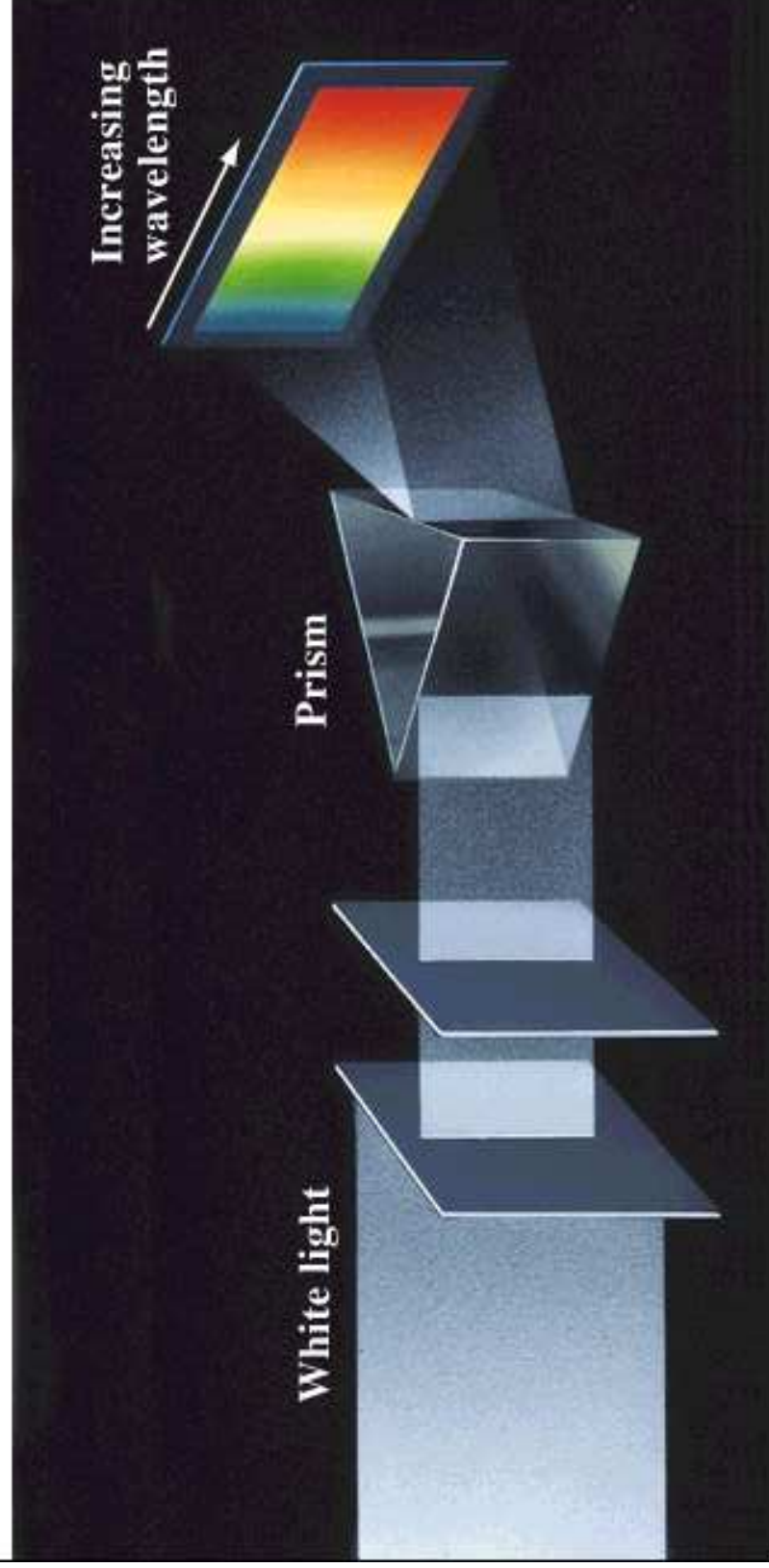
Light sources



Examples of Sources

- Deuterium lamp - good source for UV continuum radiation - widely used in UV spectrophotometers
- Tungsten filament lamp - Good source of continuum radiation in the 330- 2000 nm range; common in visible, near-IR colorimeters, spectrophotometers. Stable light output with regulated power supply. Similar to regular light-bulb but run at 3000 K.
- Heated metal and ceramic filaments used for the “mid-IR”, which is $\sim 500\text{-}4000\text{ cm}^{-1}$ (A warm object is an efficient IR source). Common source for IR spectroscopy is called a Nernst Glower, globar, or a nichrome wire.

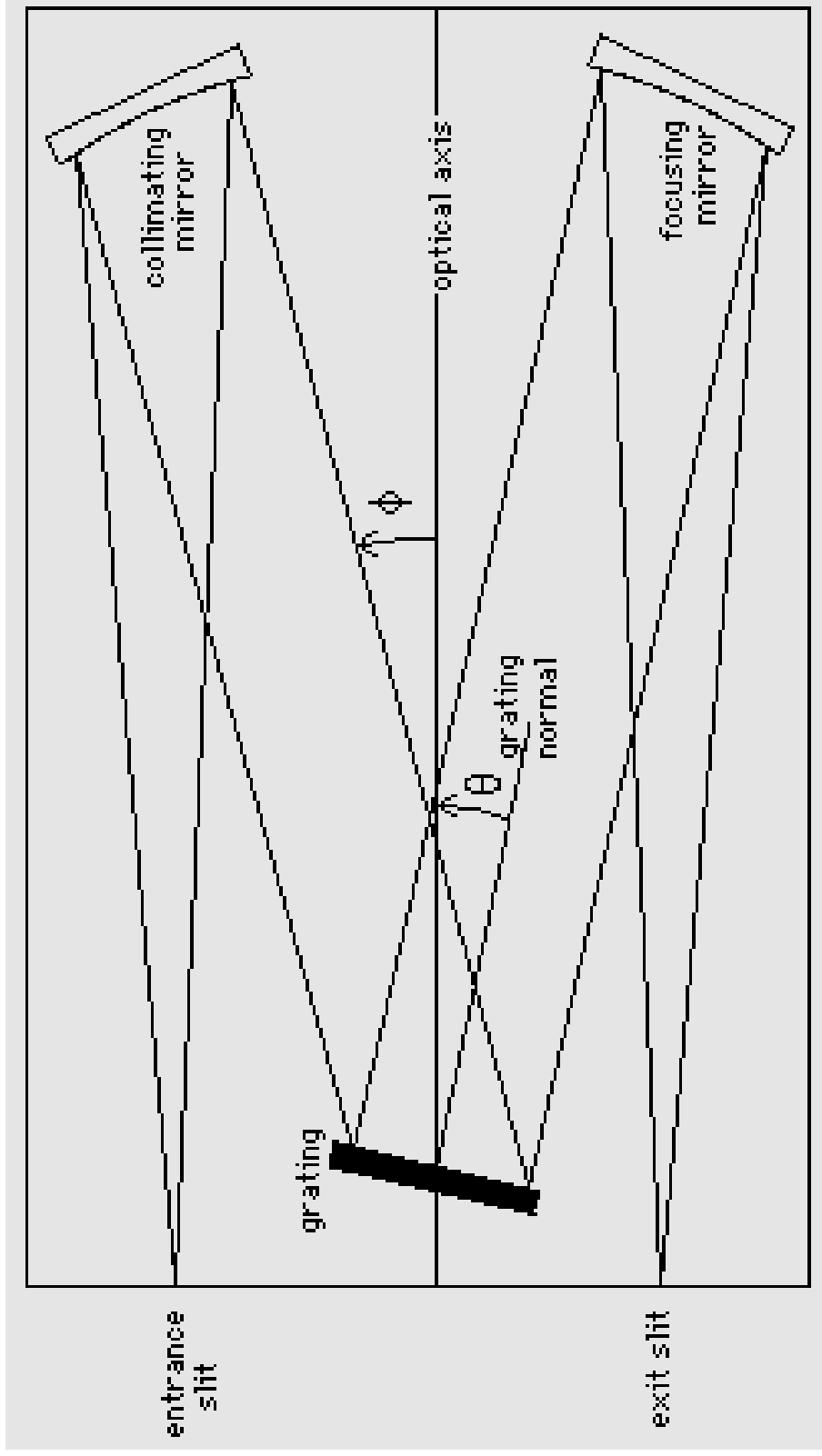
Purpose of monochromator: Separation of multi- λ light into individual λ 's



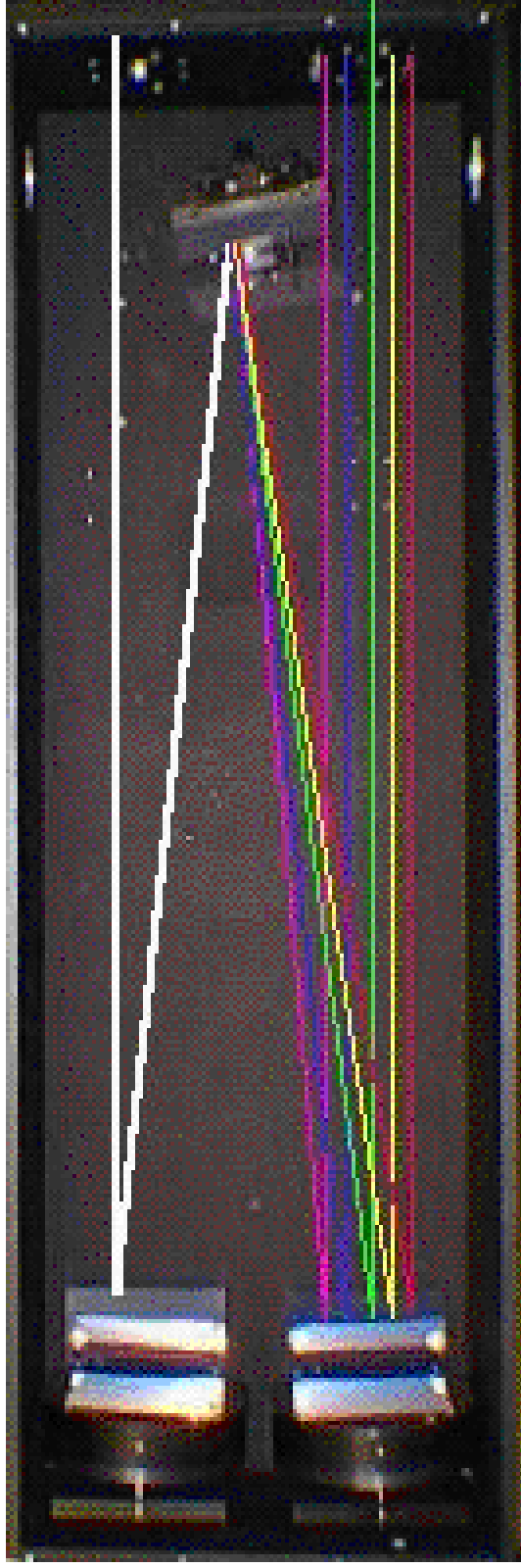
Monochromators

Components:

entrance slit, collimating element (lens or mirror), prism or grating as dispersing element, focusing element (lens or mirror), exit slit

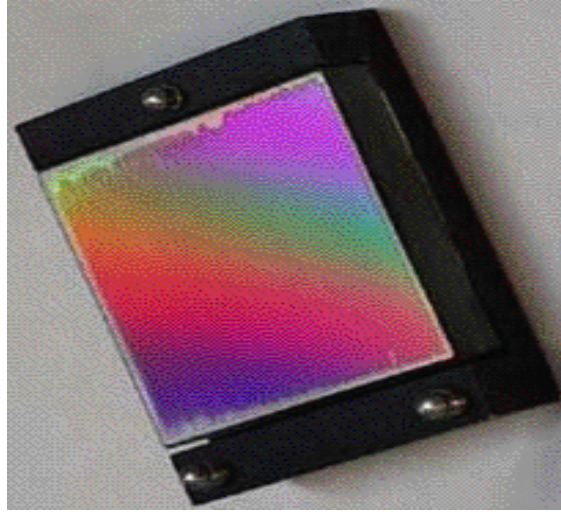


monochromator



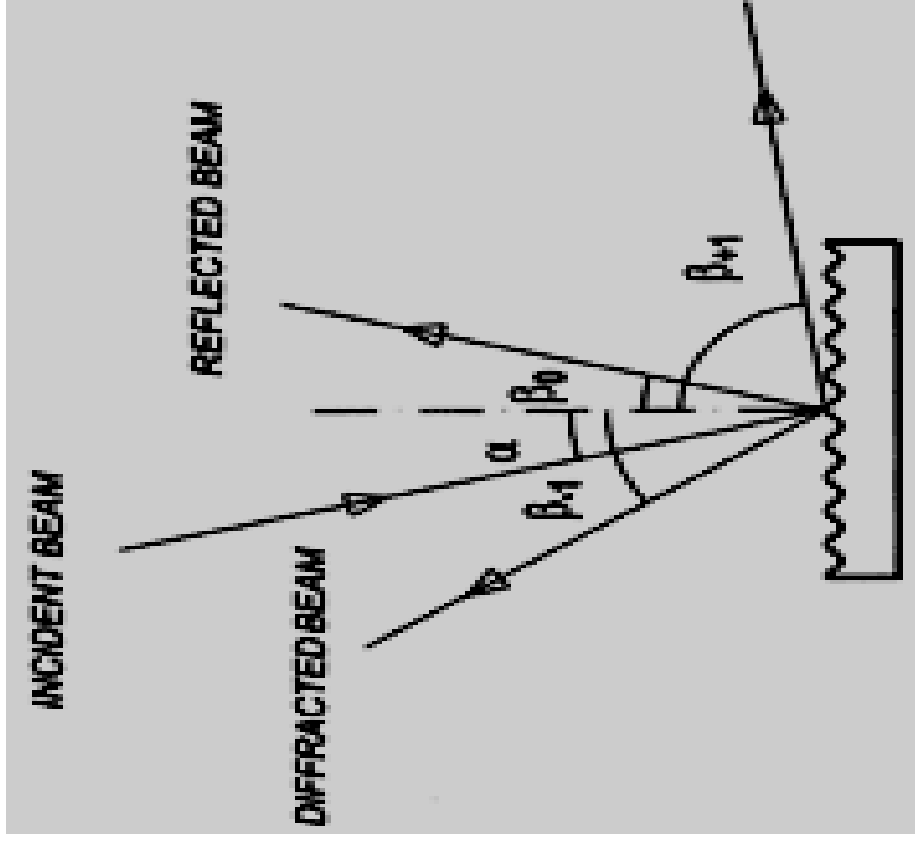
<http://www.chem.hope.edu/~polik/labtour/monochromator-inside.html>

An important use of diffraction is
in producing monochromatic light
from “white” light sources



How do gratings work?

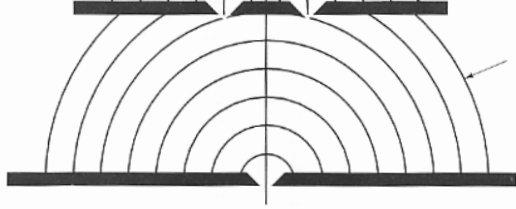
- The incident beam is diffracted in a manner given by Equation (1)
- The grooves act like multiple apertures providing the diffraction patterns (constructive & destructive interference)
- The term “m” is referred to as the **order** of the diffraction
- Dispersion increases with order but intensity diminishes



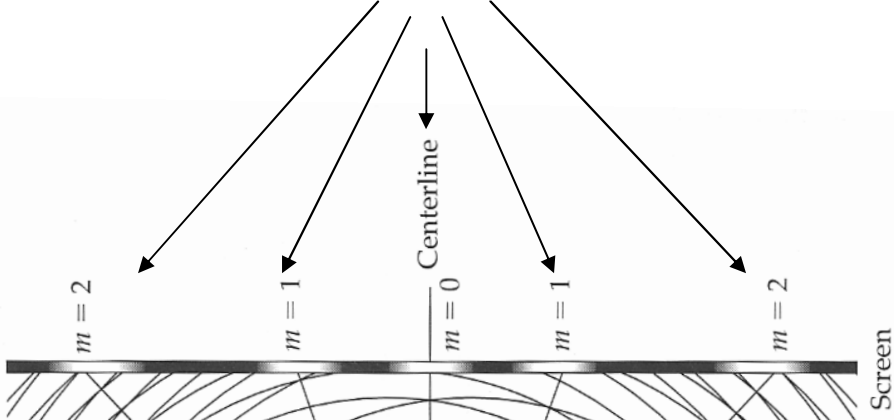
$$\sin\alpha + \sin\beta_m = -m\lambda/d$$

(a)

Coherent
light
Two-slit
diffraction



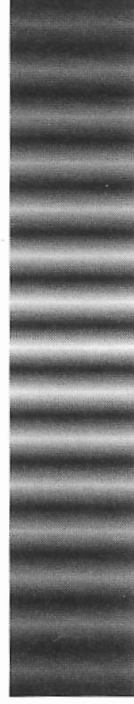
Wave
maxima



m: order

- where constructive interference occurs
- observe as bright spots (below)

(b)



Centerline

Sample Containers

Ultra-Violet

- quartz

Visible

- quartz
- glass

Infrared

- NaCl
- AgCl
- KBr

Criteria for Sample Containers

- Transparent to excitation light
- Compatible with samples
- Rugged

Types of Detectors

UV-Visible

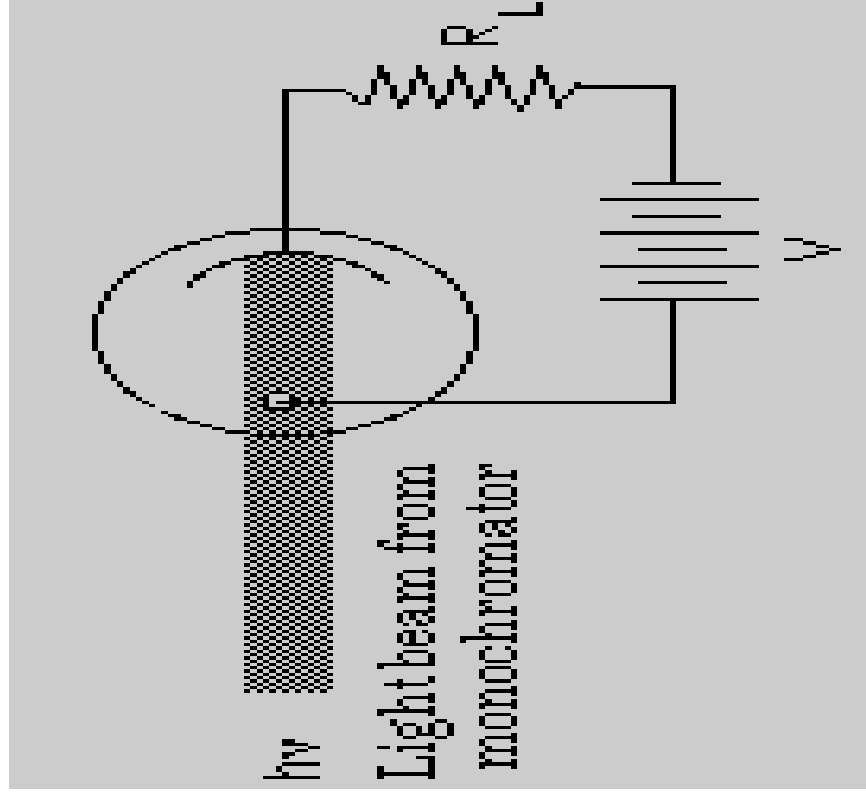
- Photon Detectors
- Vacuum Phototubes
- Photomultiplier Tubes
- Photodiodes
- Linear Photodiode arrays
- Charge-Transfer (Charge Coupled Device, CCD)

Infrared

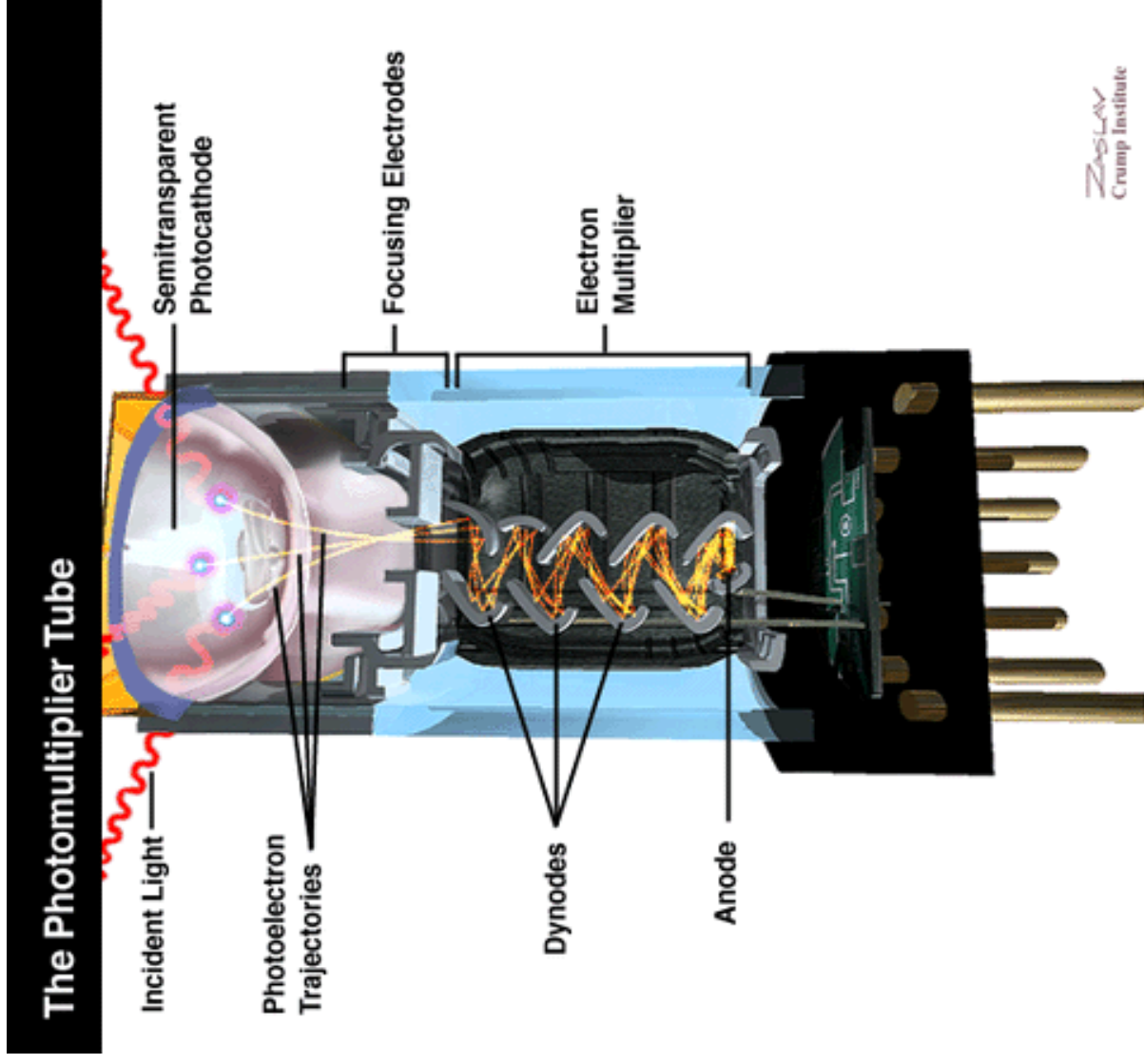
- Heat Detectors

Photoelectric effect based detectors: phototubes

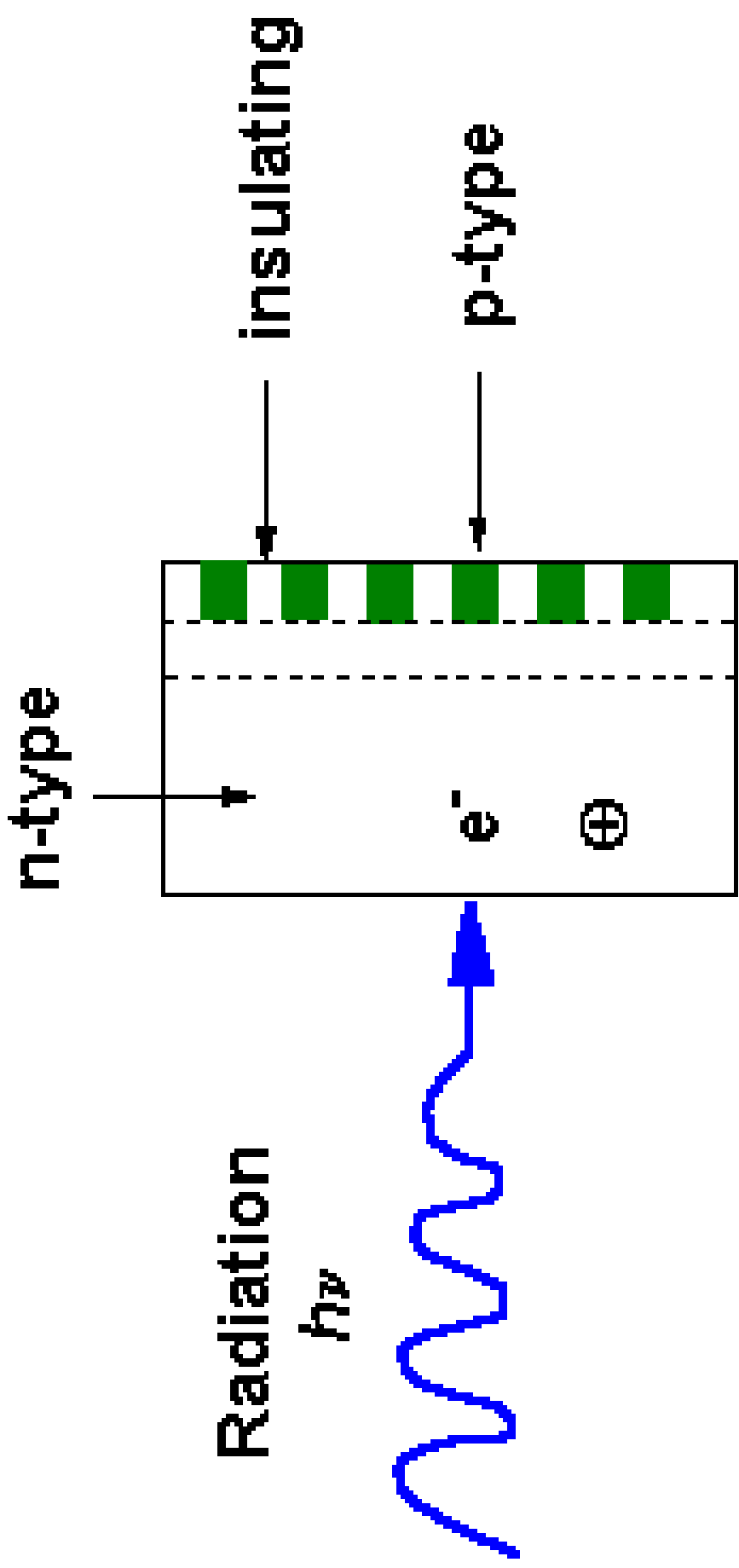
- Phototubes are used for high light intensity applications
- Photons produce photoelectrons; the “photocurrent” is proportional to intensity



- **Photomultiplier tubes** are used for low light intensity and “photon counting” applications
- Photons strike primary electrode, emits e⁻; these electrons strike successive secondary surfaces, finally producing a large “pulse” of electrons



Semiconductor-base Detectors (Photodiodes and CCD's)



Detectors for IR

- Heat detectors
 - thermocouple
 - Ferroelectric
- Semiconductor-based detectors (like HgCdTe)
 - Low bandgap semiconductors
 - Must be cooled for good quantum efficiency, low noise