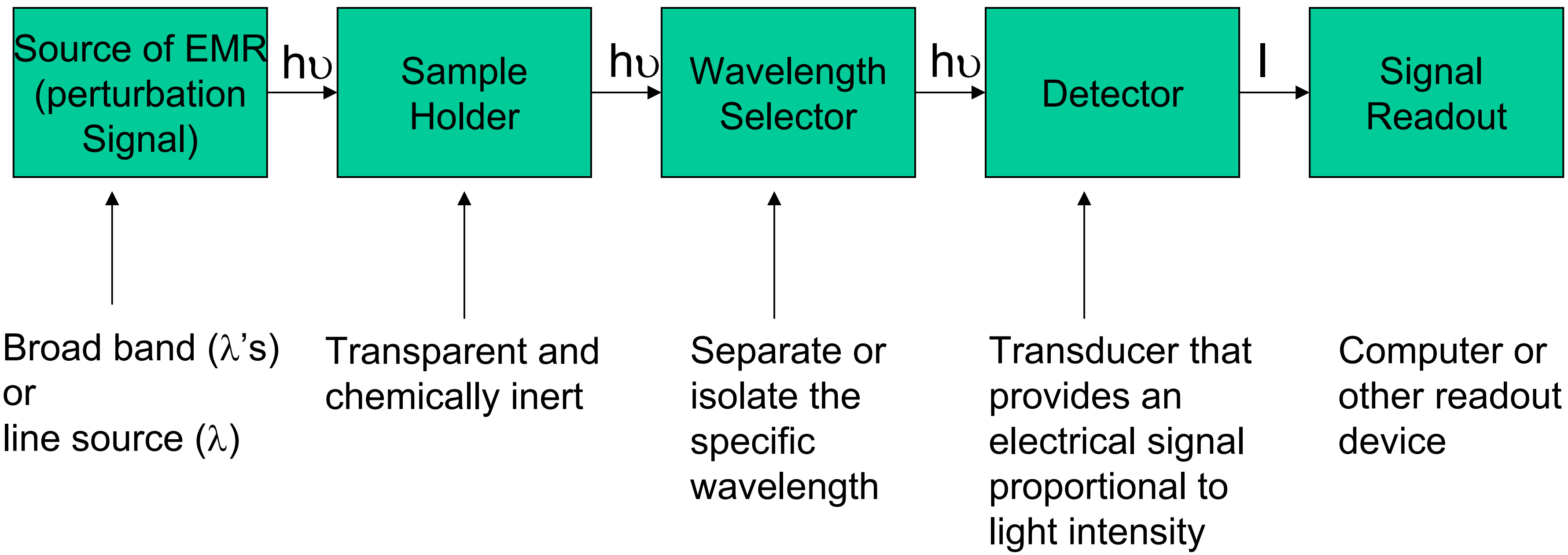
Chapter 7 – Components of Optical Instruments

Read pp. 164-173; 180-190; 191-200

Problems: 1,2,3,6,16,19

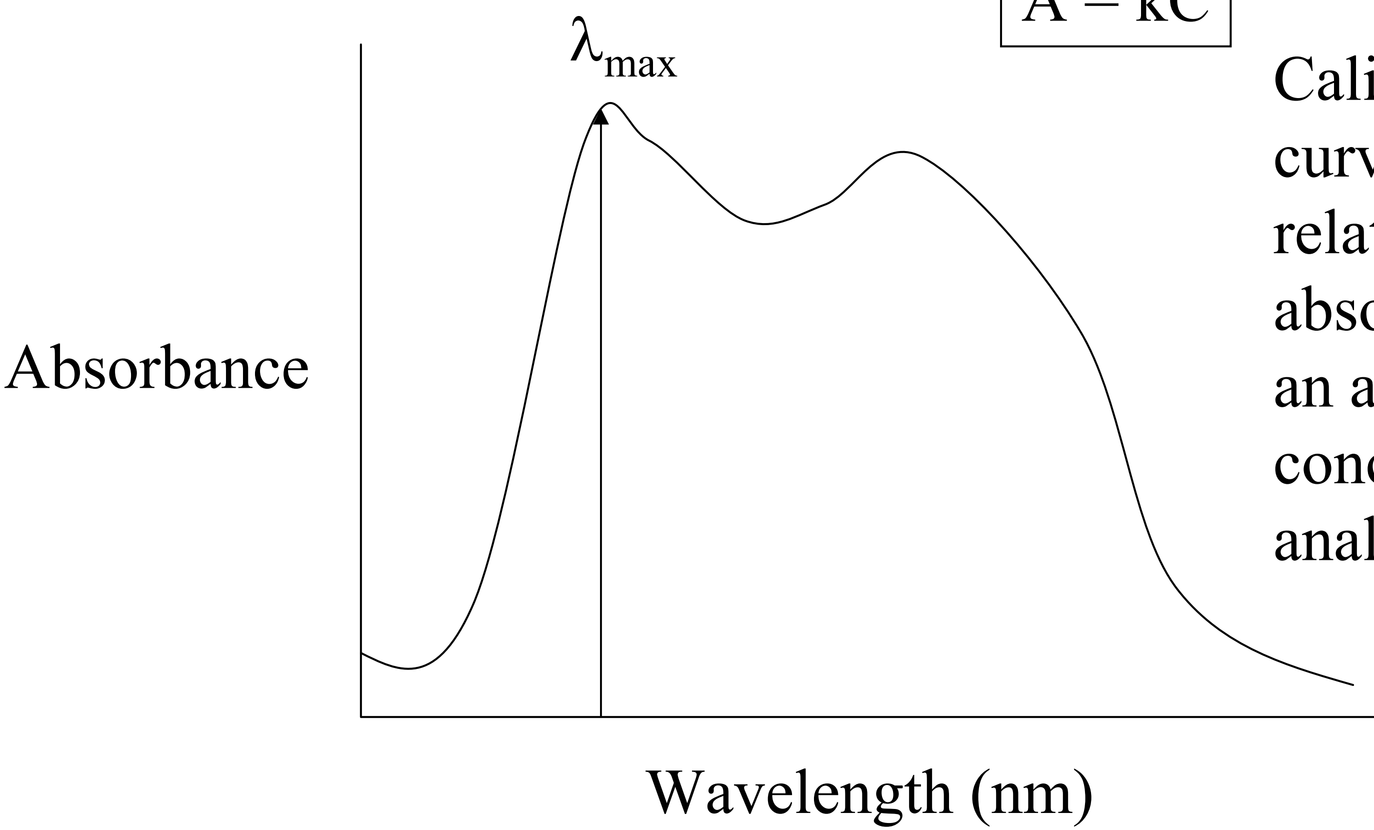
Configuration of an instrument for an ***absorption*** measurement.



Remember: All light intensity loss must be due to *absorbance* by the analyte. Therefore, two measurements are always necessary: one with the analyte present and a background (without the analyte).

What Does the Output Look Like in a Spectrometric Measurement?

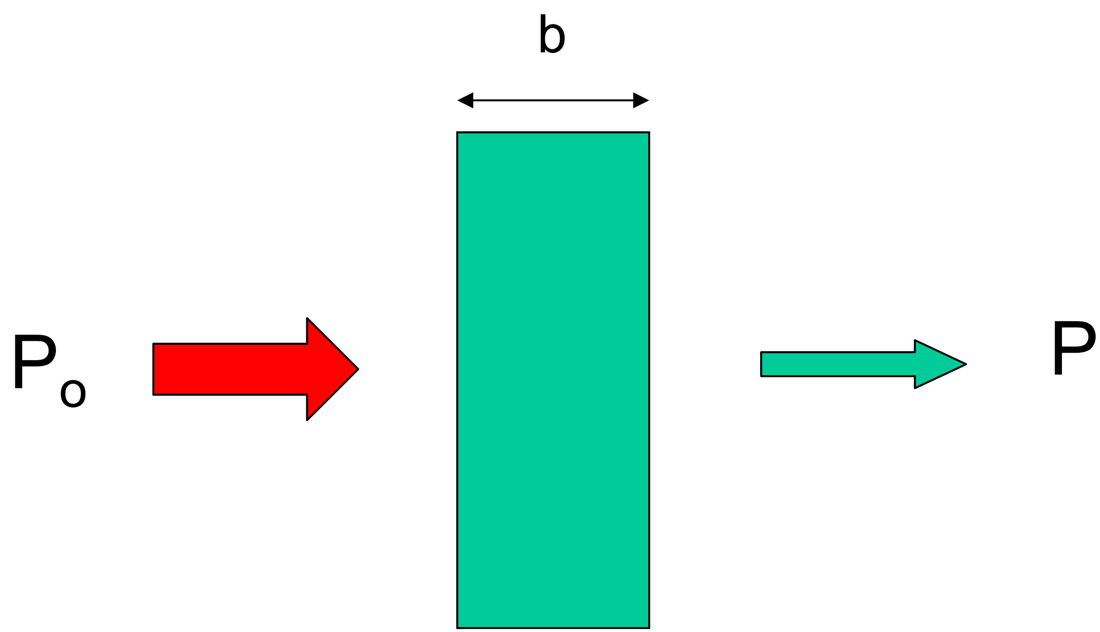
$A = kC$



Calibration curve needed to relate absorbance to an actual concentration of analyte.

The instrument scans the wavelength (or energy) from one value to another, and records the light intensity change at the detector.

The Absorbance Measurement



Absorbing solution
of concentration, C

$$A(\lambda) = \varepsilon(\lambda)bC = \log P_0/P$$

ε= molar extinction coefficient, L mol^{-1} cm^{-1}

b = path length, cm   C = concentration of analyte, mol L^{-1}

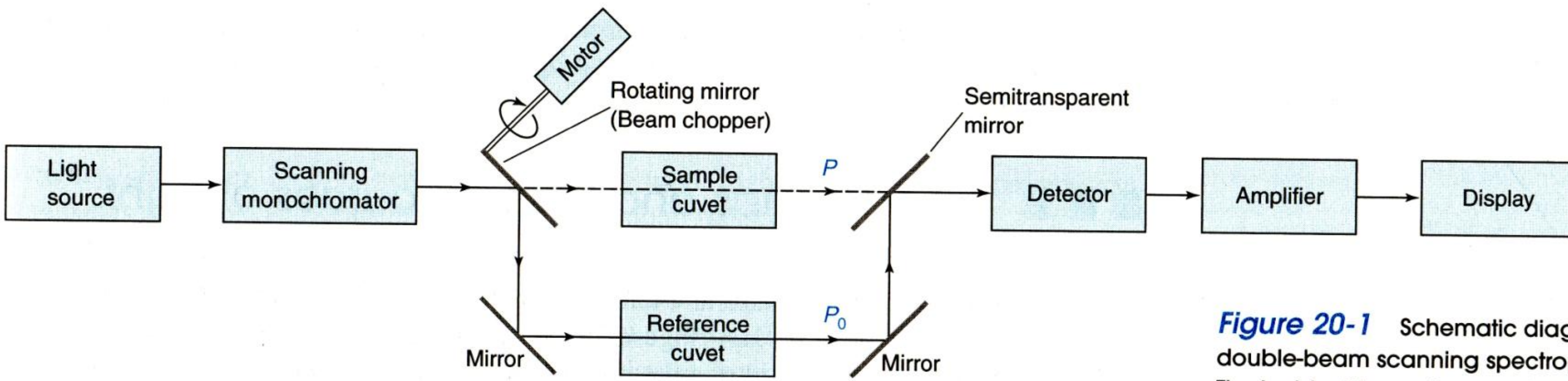


Figure 20-1 Schematic diagram of a double-beam scanning spectrophotometer. The incident beam is passed alternately through the sample and reference cuvets by the rotating beam chopper.

absorbance as a function of time, as in a kinetics experiment, because both the source intensity and the detector response slowly drift.

Sources of Electromagnetic Radiation

- Broad band or continuum sources

  Xe lamp (180 – 800 nm)

  W lamp (300 – 2000 nm)

Variable intensity over the entire range of wavelengths.

- Line sources

  Hollow cathode lamps (atomic spectroscopy)

  Lasers (light amplification by stimulated emission of radiation)

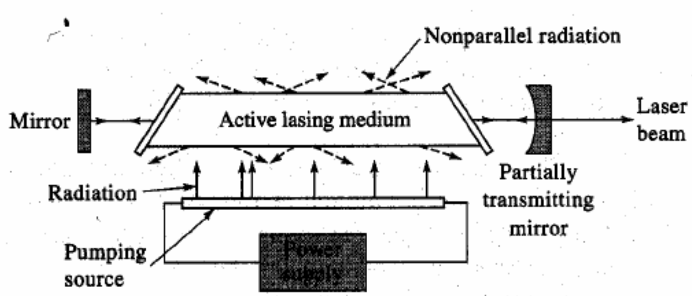


Figure 7-4 Schematic representation of a typical laser source.

How Does a Laser Function?

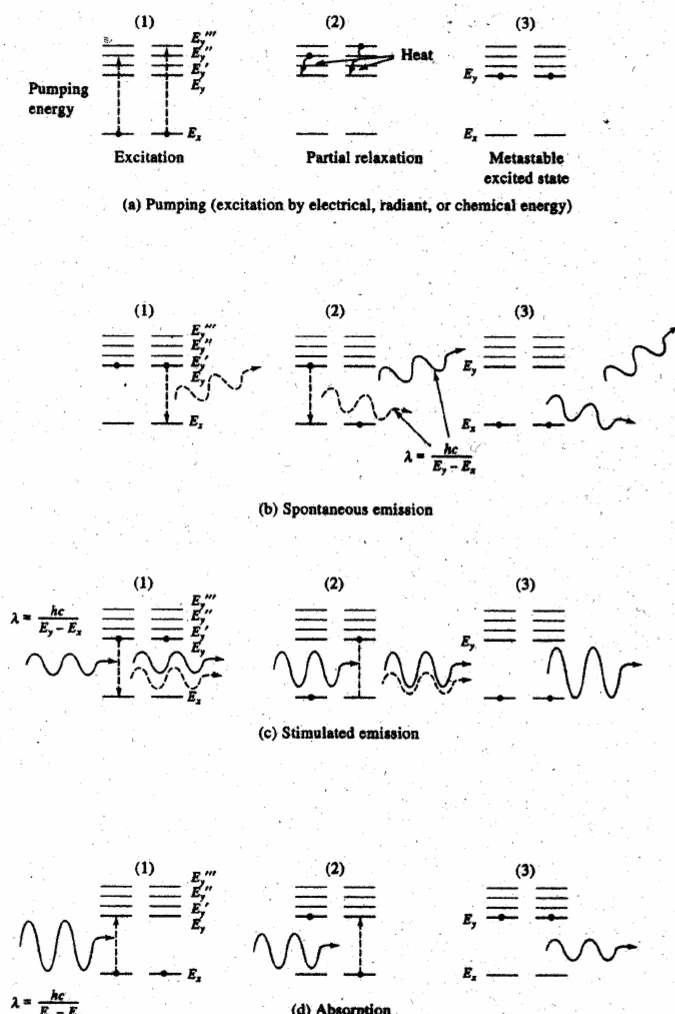


Figure 7-5 Four processes important in laser action: (a) pumping (excitation by electrical, radiant, or chemical energy), (b) spontaneous emission, (c) stimulated emission, and (d) absorption.

Pumping or net excitation
$N_{ex} >> N_{gs}$

Spontaneous emission
(light release or emission)

Stimulated emission

Absorption

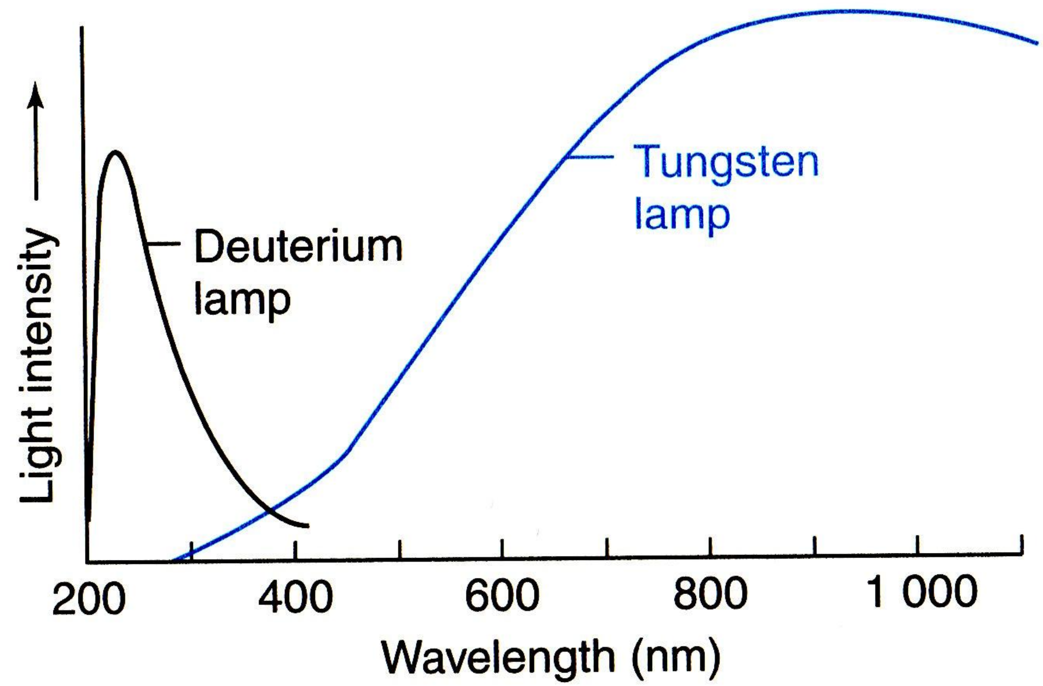


Figure 20-3 Intensity of a tungsten filament at 3 200 K and a deuterium arc lamp.

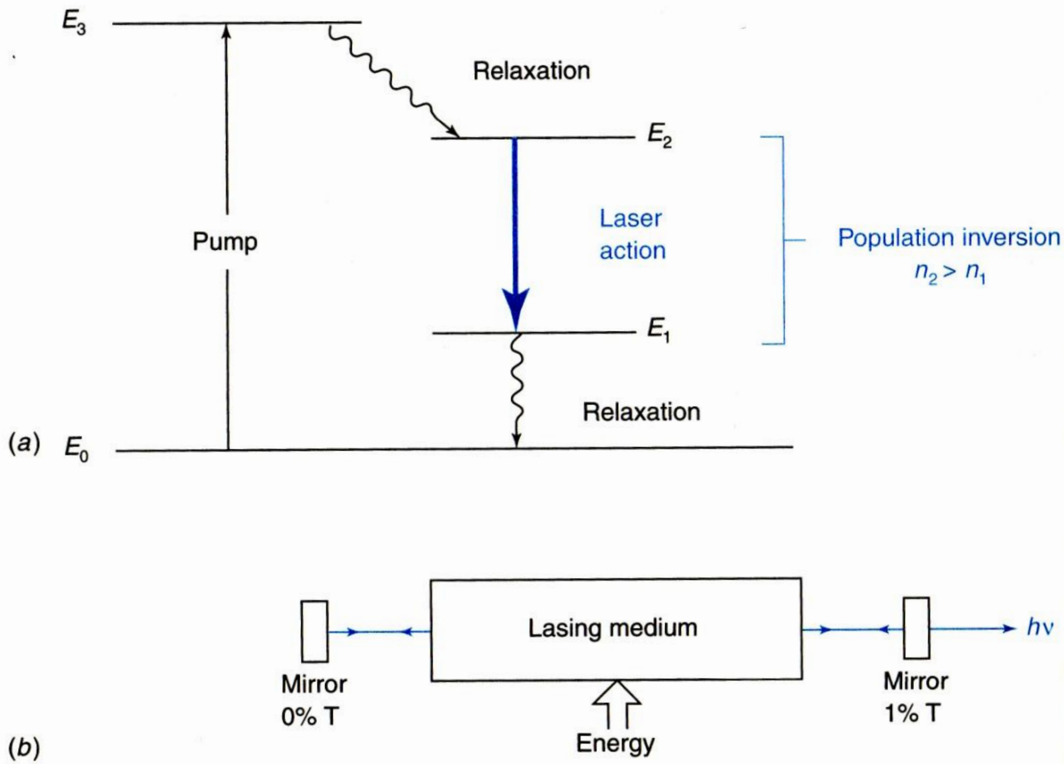


Figure 20-4 (*a*) Energy-level diagram illustrating the principle of operation of a laser. (*b*) Basic components of a laser. The population inversion is created in the lasing medium. Pump energy might be derived from intense lamps or an electric discharge.

Laser Light Sources

- High intensity or output power
- Monochromatic (one wavelength)
- Coherent (superposition of waves – all waves in-phase with one another)
- Excellent spatial and temporal resolution

- Gas, solid or liquid media are possible.

- N_2 = 337 nm, Ar = 514 nm, Nd:YAG = 1064 nm, dyes = (400-1000 nm).

Wavelength Selectors

- Filters (bandpass or rejection)

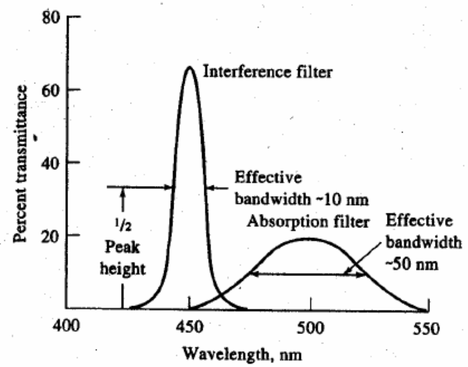


Figure 7-14 Effective bandwidths for two types of filters.

Cheap but low resolution wavelength selectors

- Monochromator

Expensive but high resolution wavelength selectors

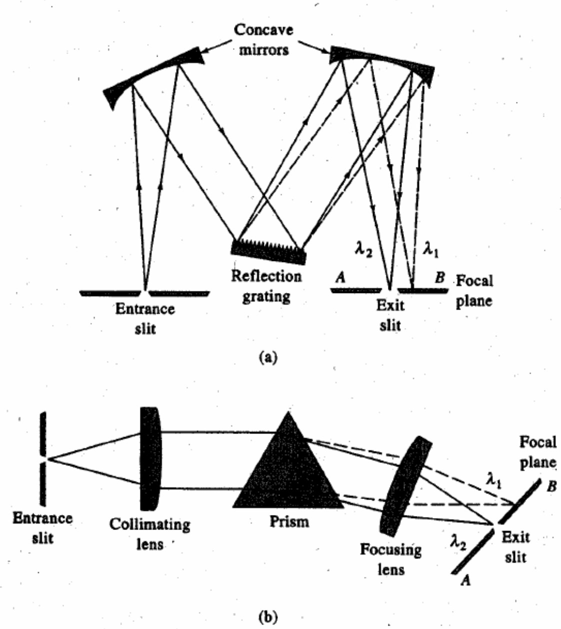


Figure 7-16 Two types of monochromators: (a) Czerney-Turner grating monochromator and (b) Bunsen prism monochromator. (In both instances, $\lambda_1 > \lambda_2$.)

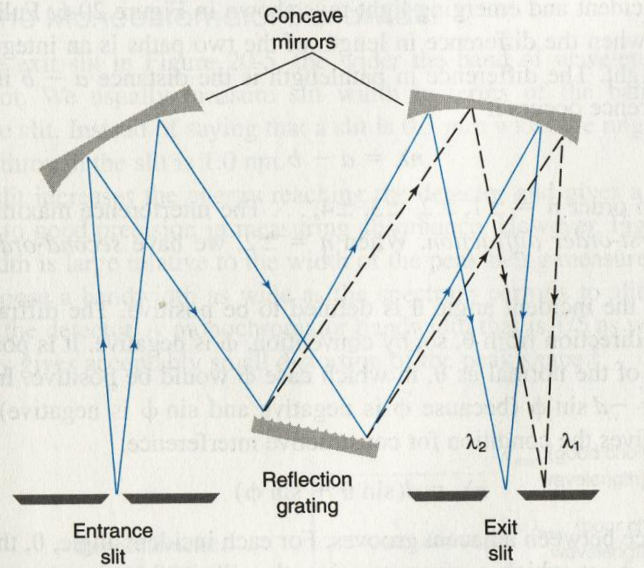


Figure 20-5 Czerny-Turner grating monochromator.

The reflection grating in Figure 20-6 is ruled with a series of closely spaced, parallel grooves with a repeat distance *d*. The grating is coated with aluminum to make it reflective. A thin protective layer of silica (SiO_2) on top of the aluminum protects the metal surface from oxidizing, which would reduce its reflectivity. When light is reflected from the grating, each groove behaves as a source of radiation. When adjacent light rays are in phase, they

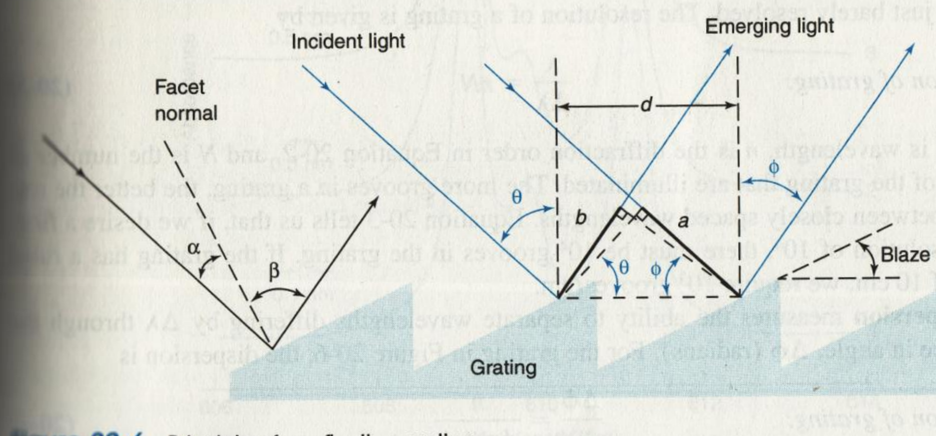


Figure 20-6 Principle of a reflection grating.

Performance Criteria for Monochromators

- Linear dispersion, D

$$D = \frac{dy}{d\lambda} = \frac{Fdr}{d\lambda}$$

- Resolving power

$$R = \frac{\lambda}{\Delta\lambda}$$

- Light gathering power (1-10)

Lower the number, the better the light gathering power

$$f = \frac{F}{d}$$

- Stray light rejection

Detectors or Transducers

- Devices that record intensity changes in the incident light and convert these intensity changes to a proportional electrical signal.
- I_{ph} ~ light intensity $S = kP + k_d$
- Single channel or multichannel types.
- Sensitivity, stability, dark current, can it respond to more than one wavelength simultaneously, etc.
- Phototubes, photodiodes vs. photomultiplier tubes vs. charge transfer devices (CCD's).

Types of Detectors

Single Channel

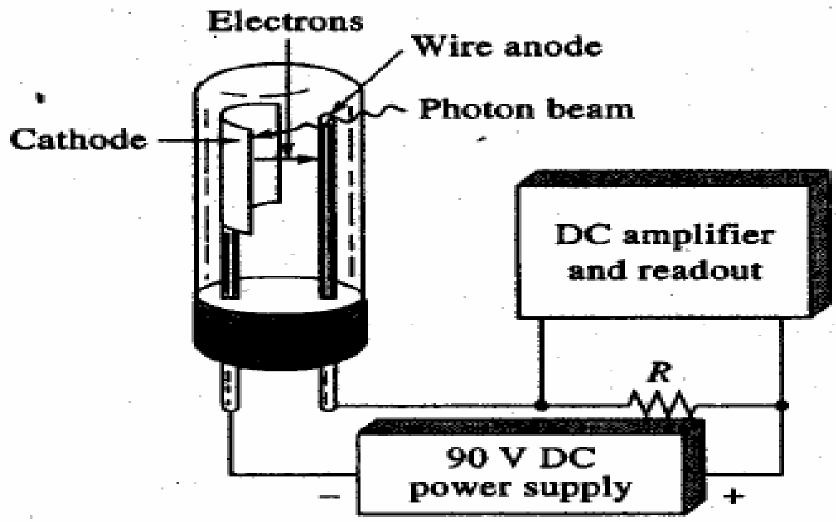


Figure 7-27 A phototube and accessory circuit. The photocurrent induced by the radiation causes a potential drop across *R*, which is then amplified to drive a meter or recorder.

I_{ph} (photocurrent) = kP (radiant power)

Types of Detectors

Single Channel

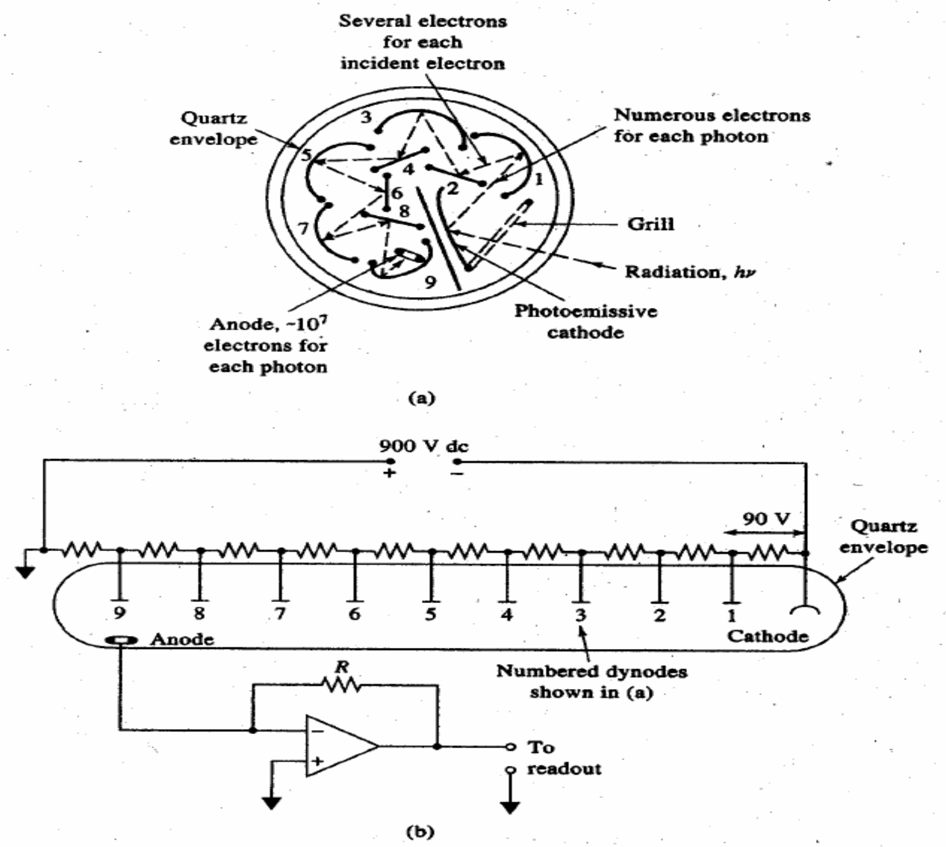
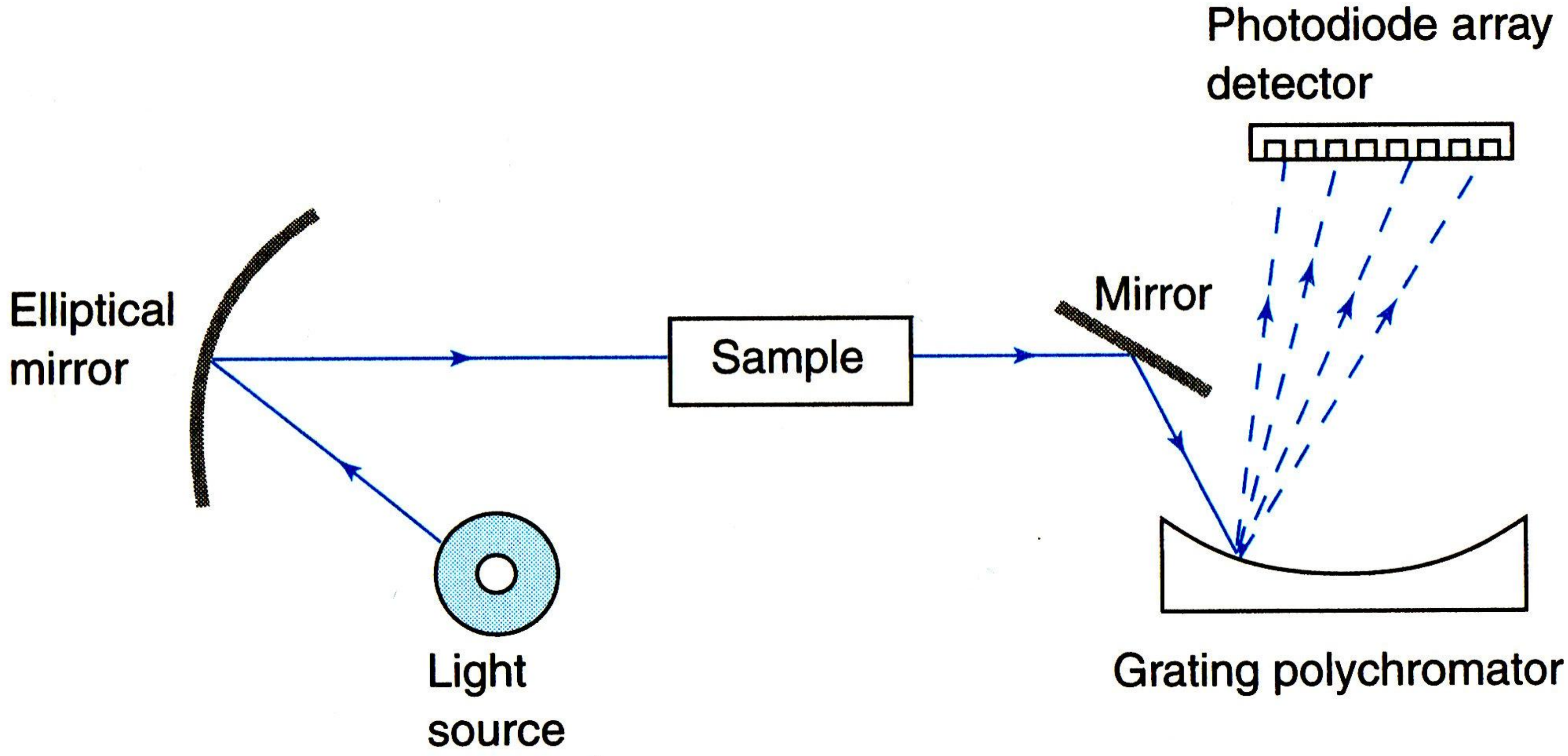


Figure 7-29 Photomultiplier tube: (a) cross-section of the tube and (b) electrical circuit.

I_{ph} (photocurrent) = kP (radiant power - amplified)

Multichannel Detector (Multiple Wavelengths Simultaneously)



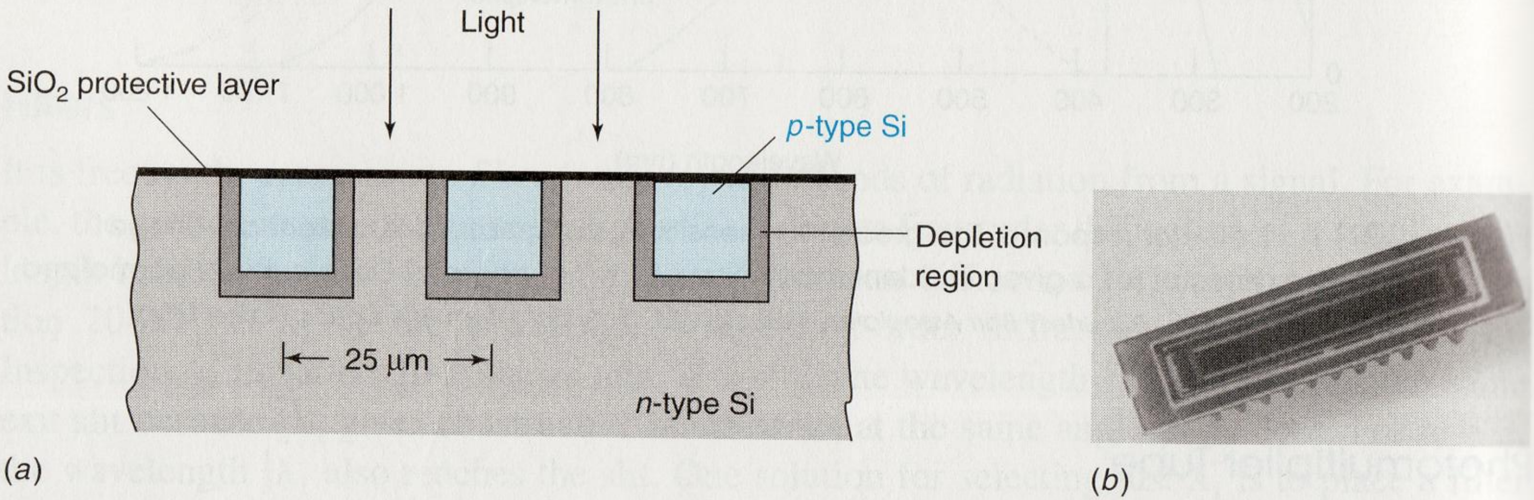


Figure 20-13 (*a*) Schematic cross-sectional view of photodiode array. (*b*) Photograph of array with 1 024 elements, each 25 μm wide and 2.5 mm high. The central black rectangle is the photosensitive area. The entire chip is 5 cm in length. *[Courtesy Oriel Corporation, Stratford, CT.]*

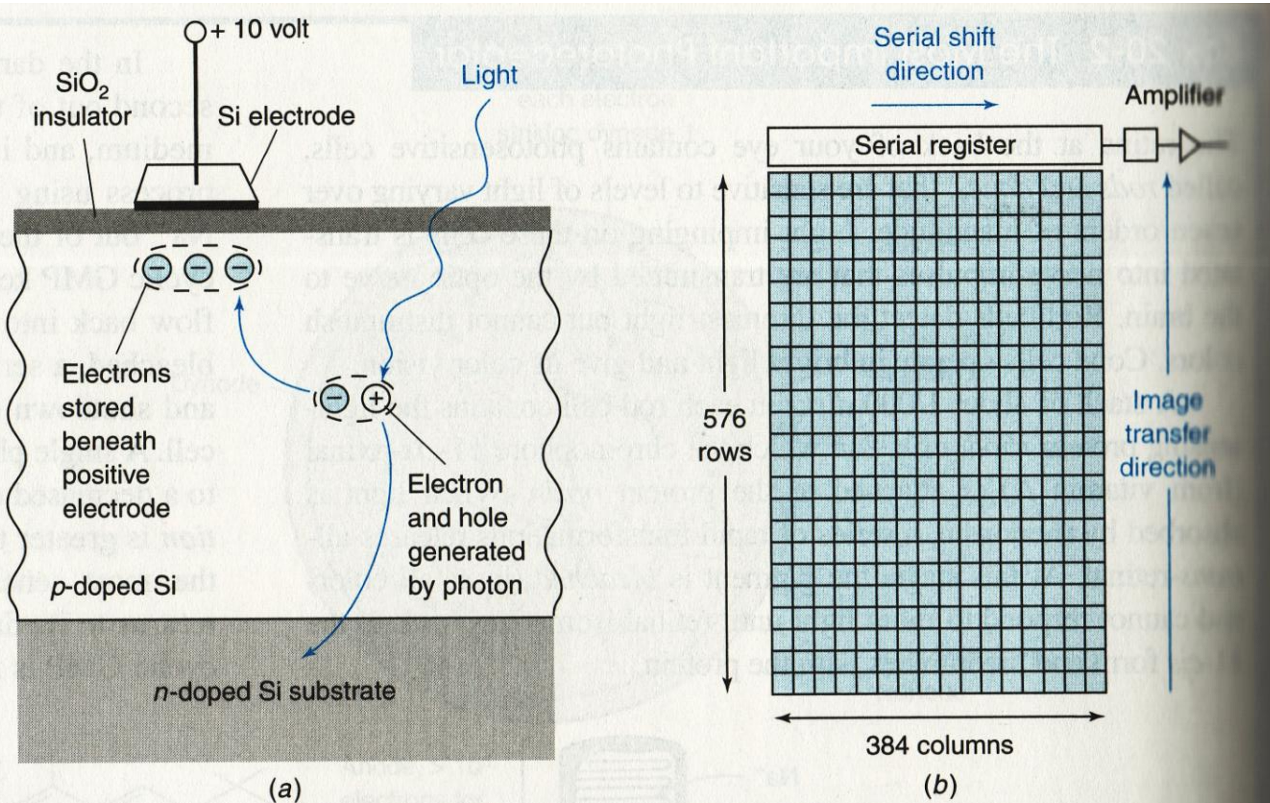


Figure 20-15 Schematic representation of a charge coupled device. (*a*) Cross-sectional view, indicating charge generation and storage in each pixel. (*b*) Top view, showing two-dimensional nature of an array. An actual array is about the size of a postage stamp.