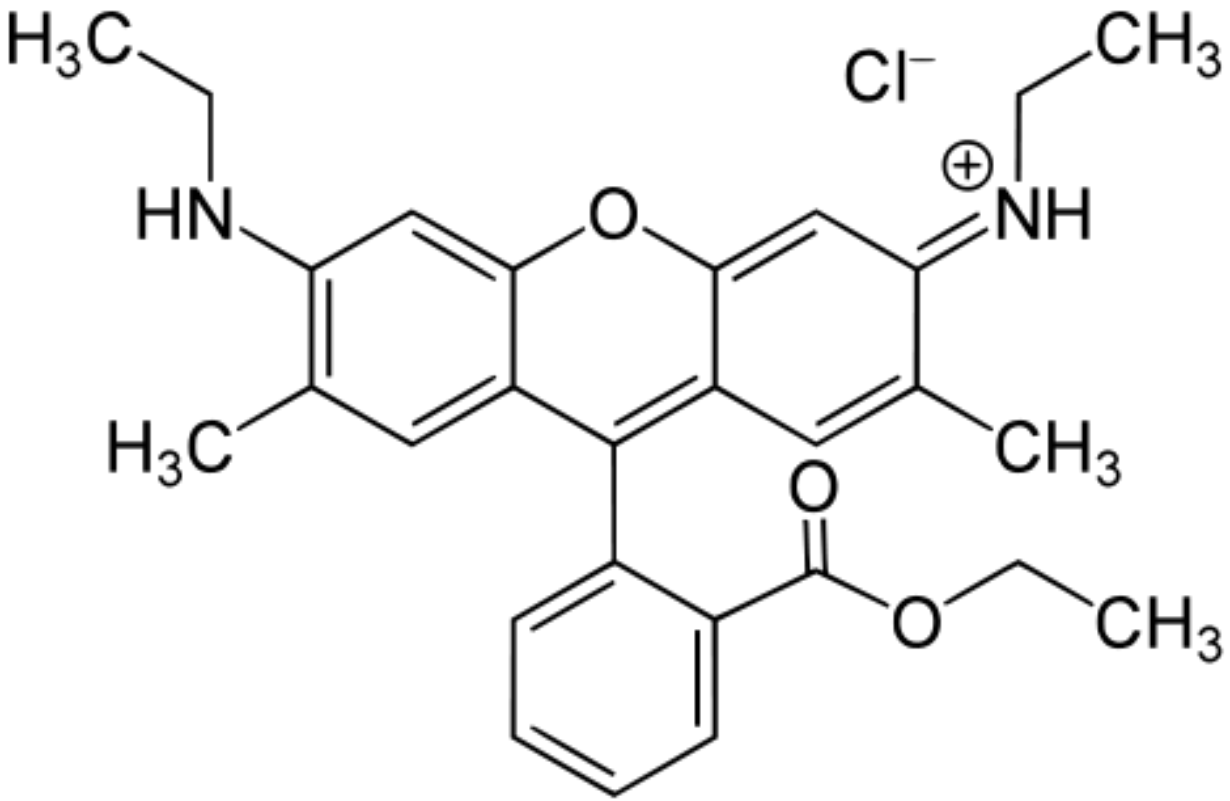

Rhodamine 6G

$\lambda_{max,abs}$ = 530 nm

$\lambda_{max,fluor}$ = 566 nm

Introduction to Molecular Absorption Spectrometry

Read = pp. 336-354 Problems: 13-1,5,8,9,15

$$A = -\log T = \log P_o/P = \varepsilon bC$$

Two air/wall and wall/solution interfaces

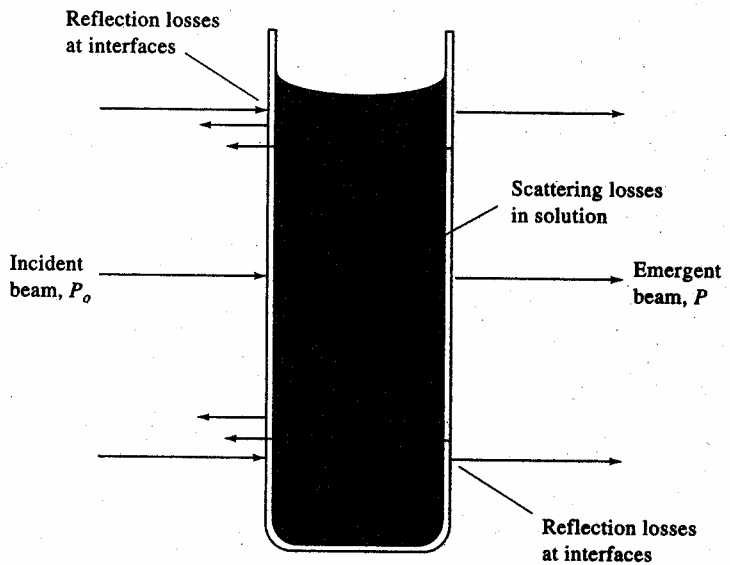

Figure 13-1 Reflection and scattering losses.

Correct for light attenuation by reflection, refraction and scattering!

Quantitative Aspects of Spectroscopic Measurements

- Beer's Law $\boxed{A = \varepsilon b C}$

$$T = \frac{P_{solution}}{P_{solvent}} = \frac{P}{P_o} \qquad A = \log \frac{P_{solvent}}{P_{solution}}$$

- Applies to analyte concentrations < 0.01 M.
- ε depends on refractive index of medium, η.
- Chemical deviations (reactions of analyte).
- Applies only to truly monochromatic light (wavelength selection results in more or less a symmetric band around the central wavelength.

Quantitative Aspects of Spectroscopic Measurements

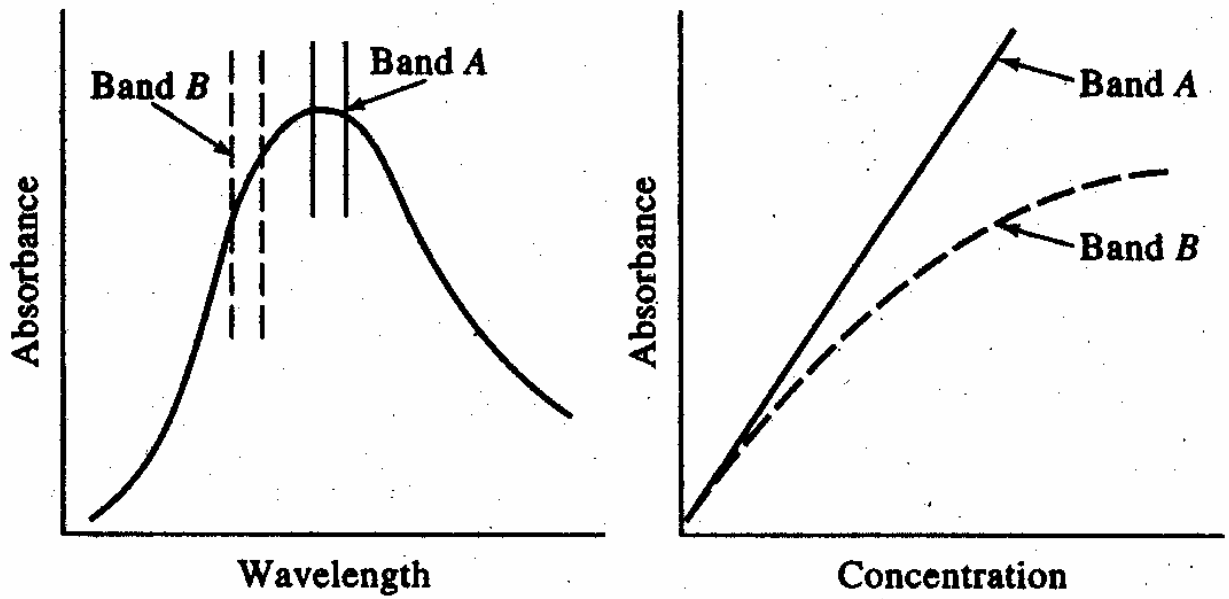

Figure 13-5 The effect of polychromatic radiation upon Beer's law. Band *A* shows little deviation because ϵ does not change greatly throughout the band. Band *B* shows marked deviation because ϵ undergoes significant changes in this region.

Factors Influencing Spectral Resolution

Monochromator ⟶ Grating or prism + focal length + **slit widths**

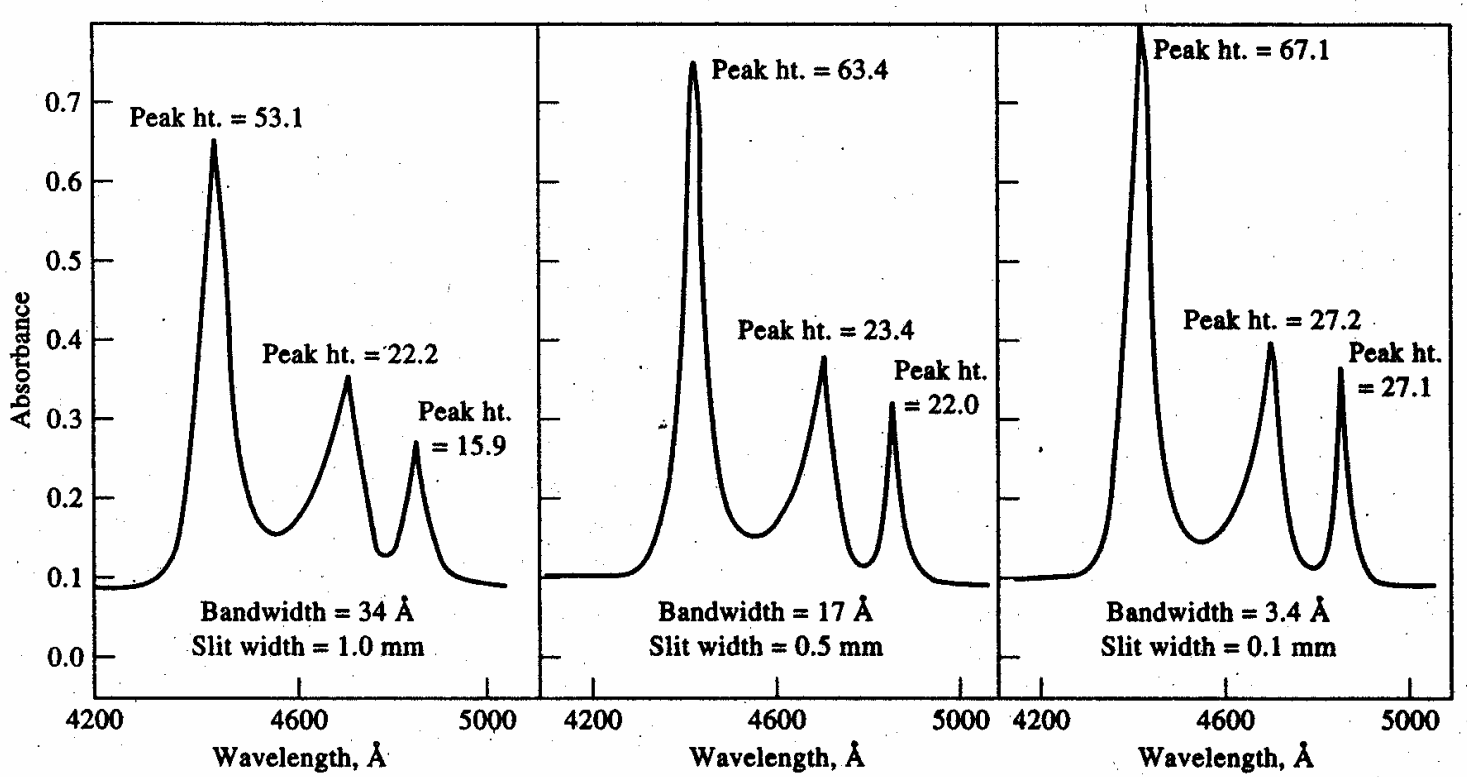

Figure 13-9 Effect of slit width and bandwidth on peak heights. Here, the sample was a solution of praseodymium chloride. *(From* Optimum Spectrophotometer Parameters, Application Report *AR 14-2. Cary Instruments: Monrovia, CA. With permission.)*

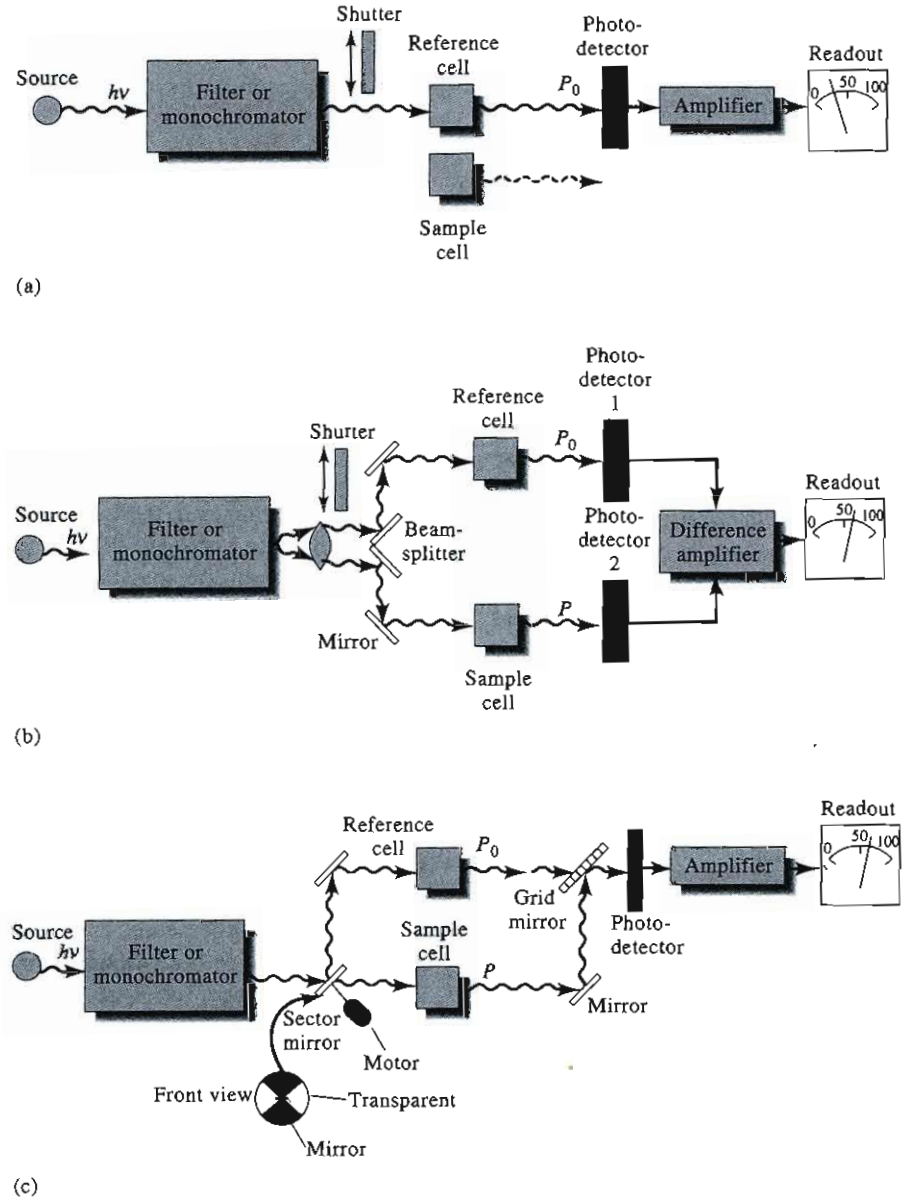

FIGURE 13-13 Instrumental designs for UV-visible photometers or spectrophotometers. In (a), a single-beam instrument is shown. Radiation from the filter or monochromator passes through either the reference cell or the sample cell before striking the photodetector. In (b), a double-beam-in-space instrument is shown. Here, radiation from the filter or monochromator is split into two beams that simultaneously pass through the reference and sample cells before striking two matched photodetectors. In the double-beam-in-time instrument (c), the beam is alternately sent through reference and sample cells before striking a single photodetector. Only a matter of milliseconds separate the beams as they pass through the two cells.

Spectroscopy = use of light to probe the properties of matter….understanding how light interacts with matter.

Spectrophotometry = any technique that uses light to measure chemical concentrations.

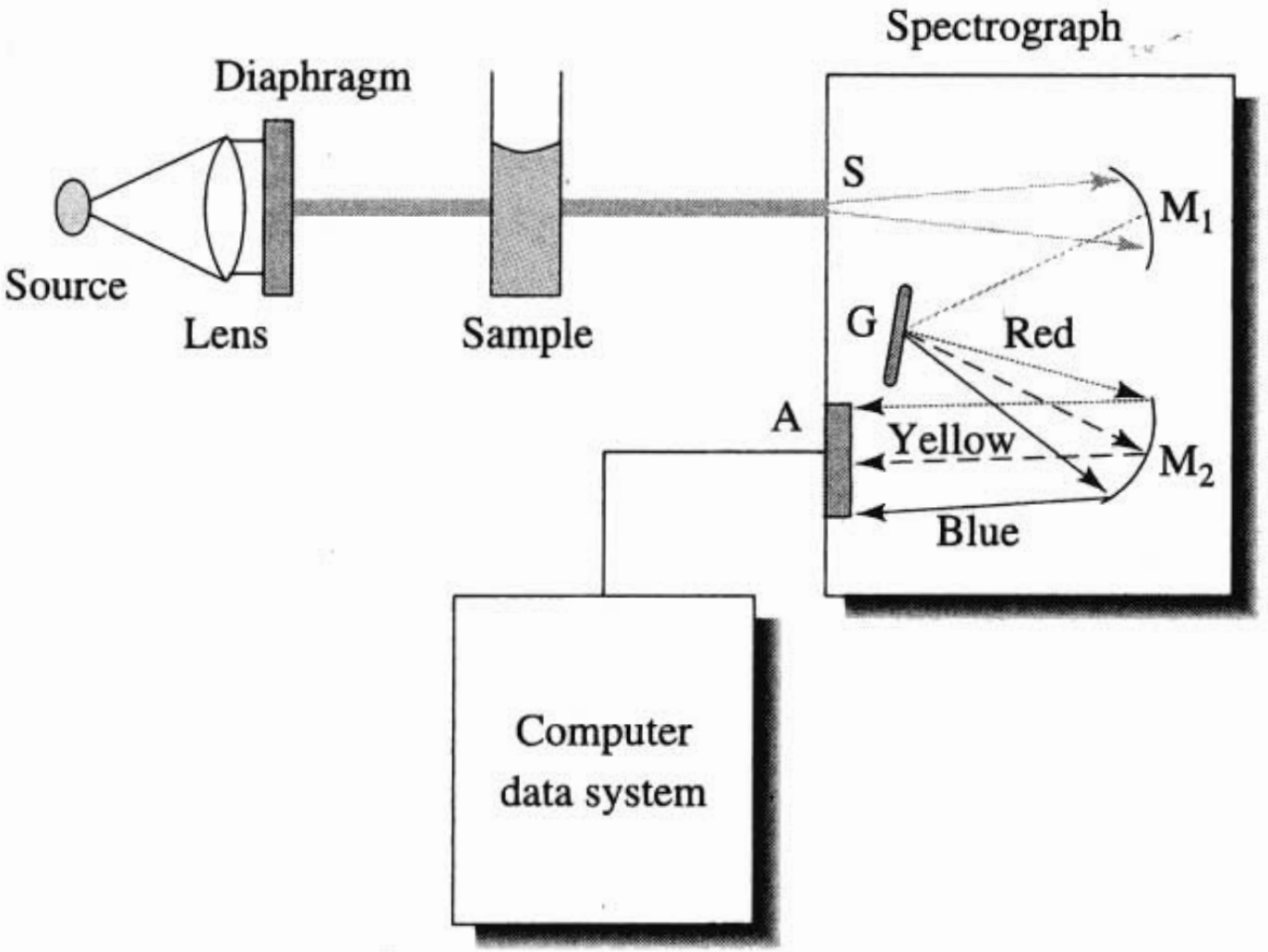

FIGURE 13-14 Diagram of a multichannel spectrometer based on a grating spectrograph with an array detector. Radiation from the tungsten or deuterium source is made parallel and reduced in size by the lens and diaphragm. Radiation transmitted by the sample enters the spectrograph through slit S. Collimating mirror M_1 makes the beam parallel before it strikes the grating G. The grating disperses the radiation into its component wavelengths, which are then focused by focusing mirror M_2 onto the photodiode or CCD array A. The output from the array detector is then processed by the computer data system.

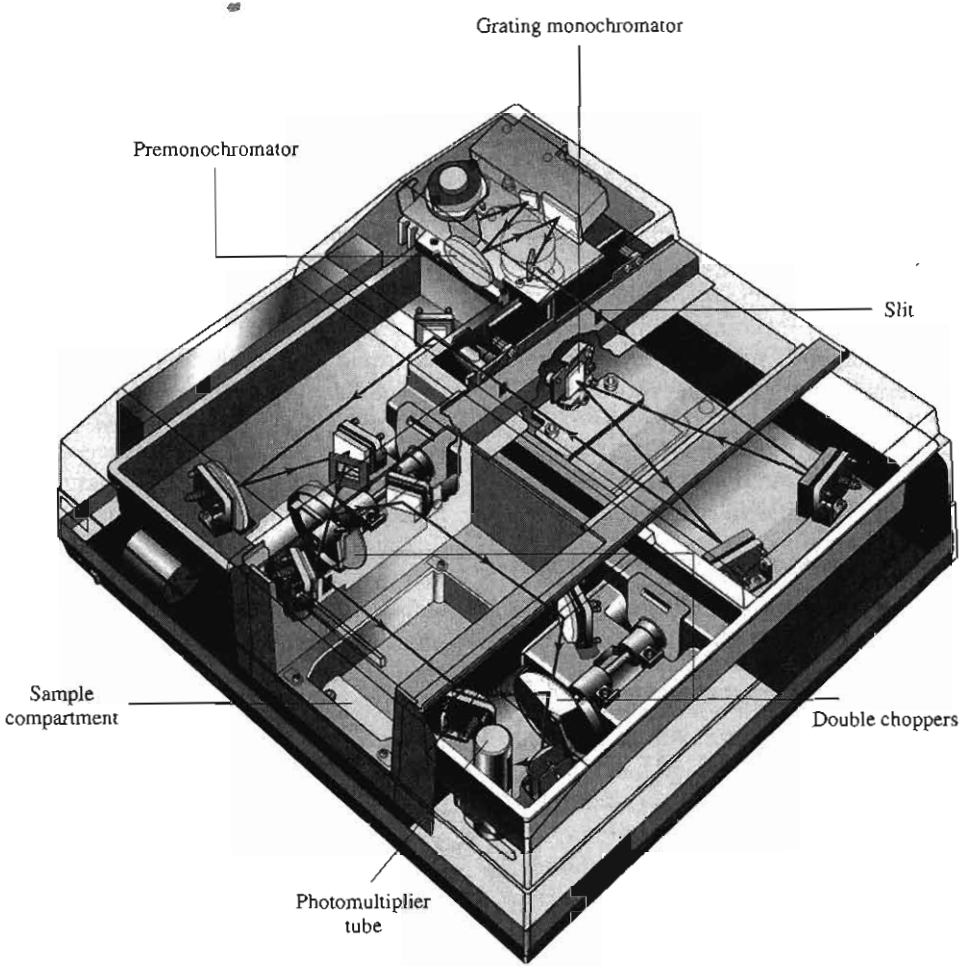

FIGURE 13-23 Optical diagram of the Varian Cary 300 double-dispersing spectrophotometer. The instrument is essentially identical to that shown in Figure 13-22, except that a second monochromator is added immediately after the source. (Varian Inc., Palo Alto, CA.)

Basic Design for a Double-Beam Spectrometer

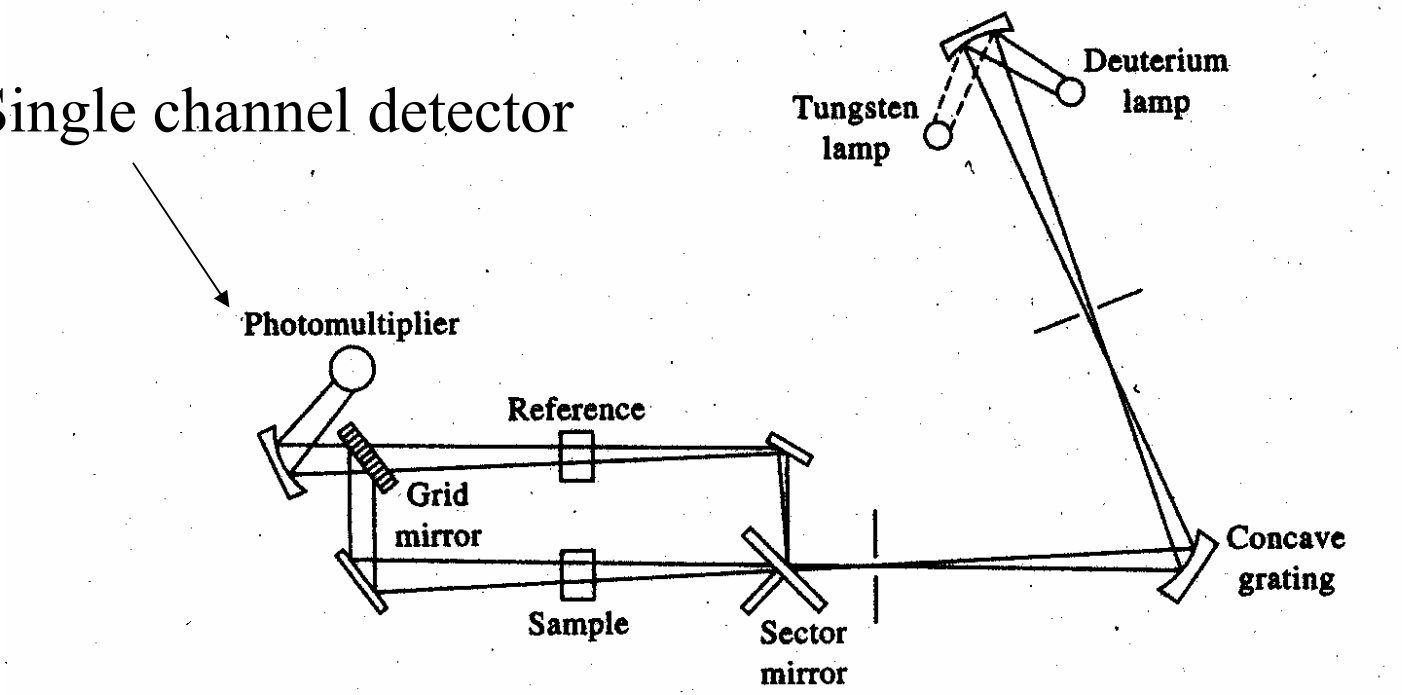

Figure 13-19 Schematic of a typical manual double-beam spectrophotometer for the ultraviolet/visible region.

Source + sample holder + wavelength selector + detector

Basic Design for a Multichannel Spectrometer

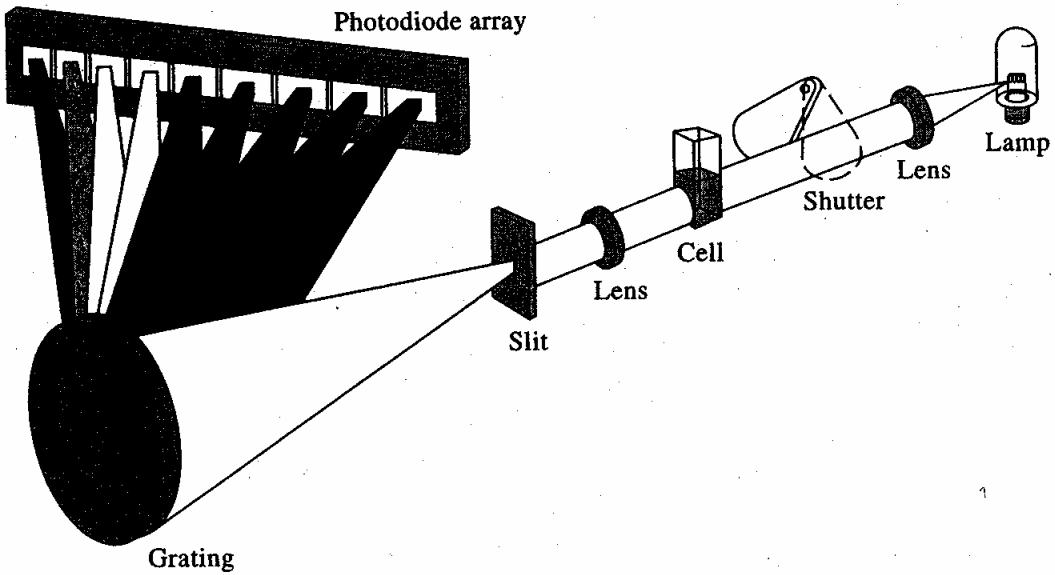

Figure 13-22 A multichannel diode array spectrometer; the HP 8452A. *(Courtesy of Hewlett-Packard Company, Palo Alto, CA.)*

Source + sample holder + wavelength selector + detector.

Key Learning Points

- Wavelength, frequencies and photon energies (key equations)
- How molecules and atoms absorb electromagnetic radiation.
- Atomic energy levels and atomic absorption and emission
- Flames and their function and chemical environment
- Plasmas and their function and chemical environment
- Monochromators, performance criteria and function
- AAS and AES instrument design
- Beer's Law calculations
- Calculations of detection limits and unknown concentrations from standard curves.
- Know how the standard addition and internal standard methods work
- Spectrometers for molecular absorbance in the UV and Vis region
- Fluorometry and instrumentation
- Single and multichannel detectors and how they work.

Getting the Entire Spectrum at Once

- In diode array spectrometers, there is no exit slit. All the dispersed wavelengths that fall on the array are recorded simultaneously.
- Resolution is limited by the size of the diode array but generally is about twice the size of a single element of the array.
- Improved S/N and precision are possible with PDA because of signal averaging (co-adding spectra).
- Improved S/N also because of less flicker noise.
- Useful for measuring chemical kinetics on the msec timescale.

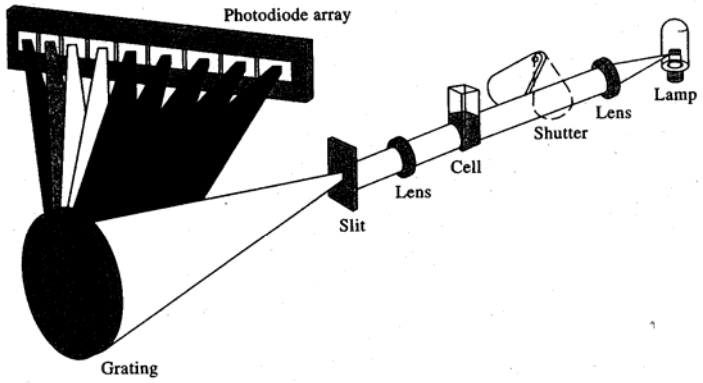

Figure 13-22 A multichannel diode array spectrometer; the HP 8452A. *(Courtesy of Hewlett-Packard Company, Palo Alto, CA.)*

Dispersion Elements

Lenses and mirrors to focus radiation.
Entrance and exist slits to restrict λ.
Dispersion element

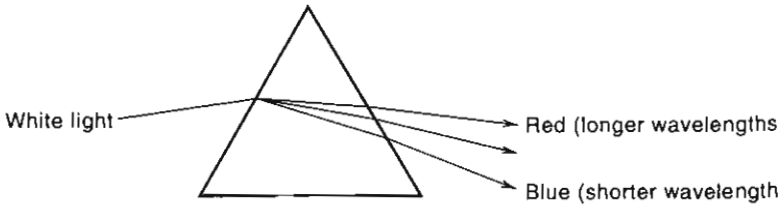

Fig. 16.14. Dispersion of polychromatic light by prism.

UV/Vis = 15,000-20,000 lines/in
IR = 1,500-2,000 lines/in

Good at short wavelengths and poor at longer wavelengths.

Same at all wavelengths

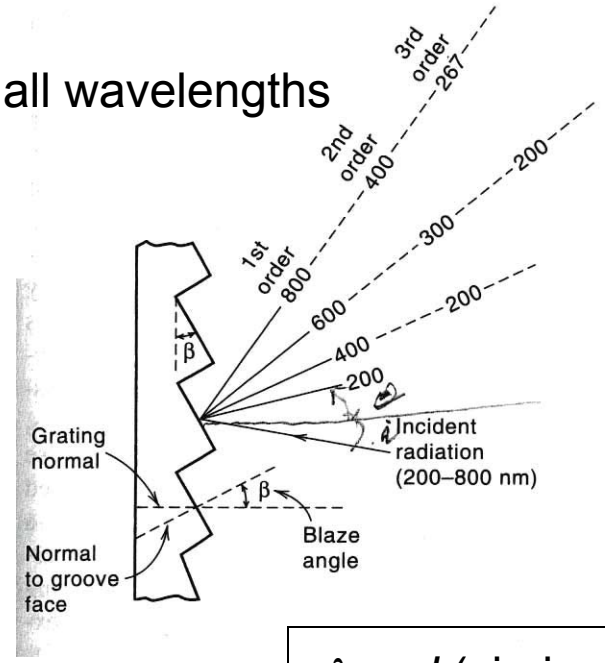

Fig. 16.15. Diffraction of radiation from grating.

1. Spectral purity
2. Dispersion, D^{-1} (nm/mm)
3. Resolving power, $R=\lambda_o/\Delta\lambda = nN$
4. Light gathering power, $f = F/d$

F = focal length
d = collection mirror diameter

$$n\lambda = d\,(\sin i - \sin \theta)$$

e.g., f/2 lens gathers 4x more light than an f/4 lens.

Effective Bandwidth

Radiation passed by the slit is not monochromatic.

$\lambda_{eff} = wD^{-1}\ D^{-1}(nm/mm) = (d \cos r)/nF$

d **= groove spacing**
F **= focal length**
n **= diffraction order**

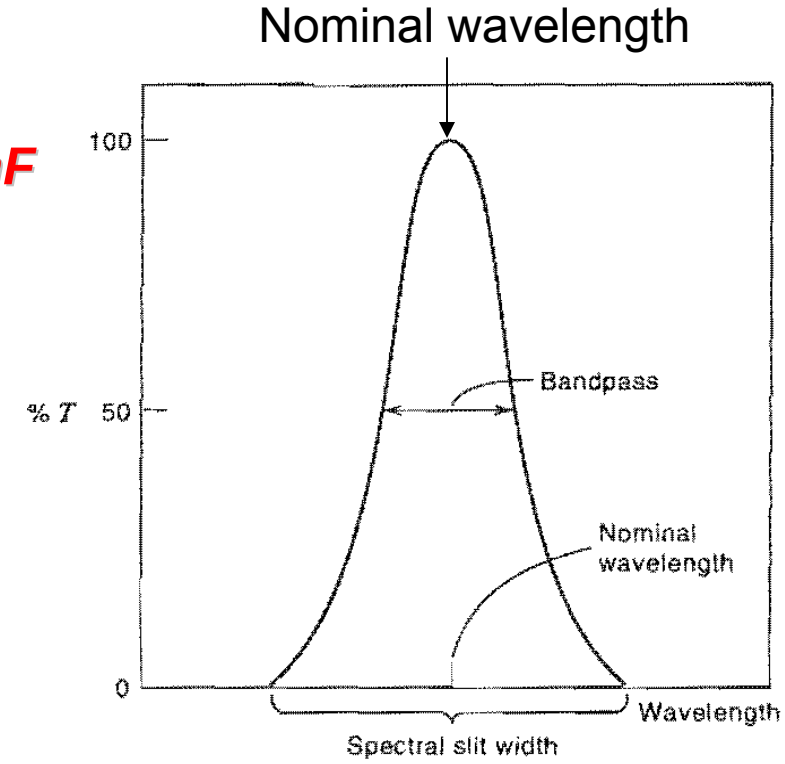

Fig. 16.21. Distribution of wavelengths leaving the slit of monochromator.

Error in Measurement of Transmission

$A = -\log T = \log (1/T) = \log (P_o/P) = \varepsilon bC$

Difficult to precisely measure either very small or very large differences in transmission.

Small errors in measurement of T mean large errors in C determination.

Dilute sample: 10-80% T (0.1-1 AU)

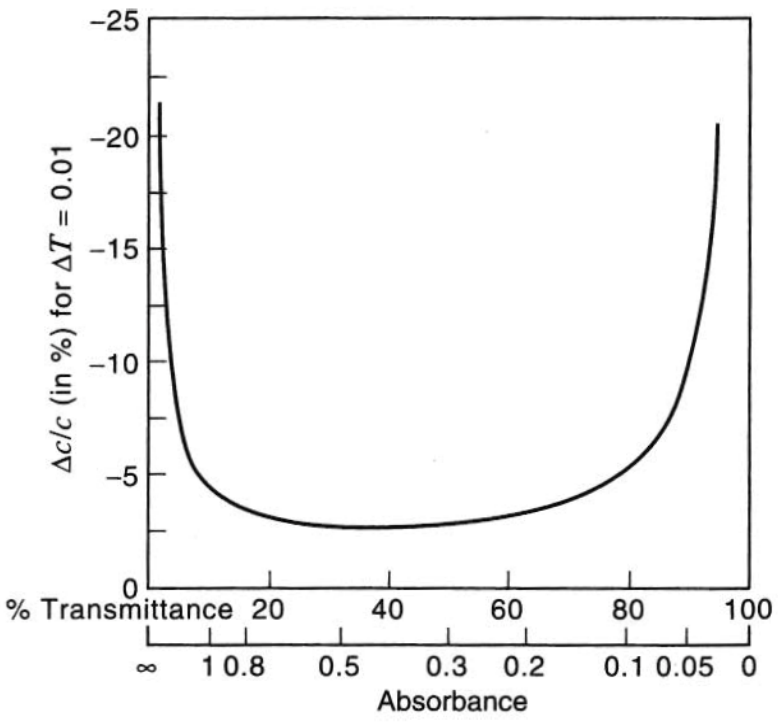

Fig. 16.27. Relative concentration error as function of transmittance for 1% uncertainty in % T.

Chemical Equilibria

$$HA \rightarrow H^+ + A^-$$
$$\lambda_1 \qquad\qquad \lambda_2$$

Isosbestic point = unique wavelength in a two-component system for quantitative determination of total amount of two absorbing species.

(Absorptivity of both species is same at IP)

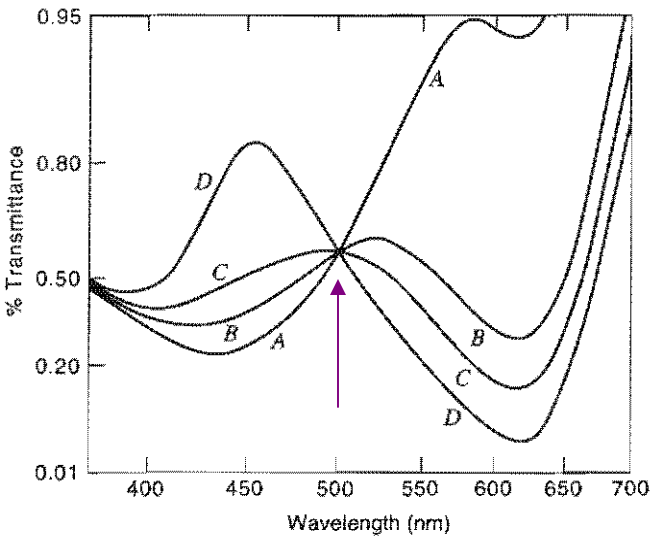

Fig. 16.28. Illustration of isosbestic point of bromthymol blue (501 nm): (*A*) pH 5.45, (*B*) pH 6.95, (*C*) pH 7.50, (*D*) pH 11.60.

Use buffered solutions, constant ionic strength

Isosbestic point is independent of the solution pH. Intensity at this λ would increase with concentration of HA.