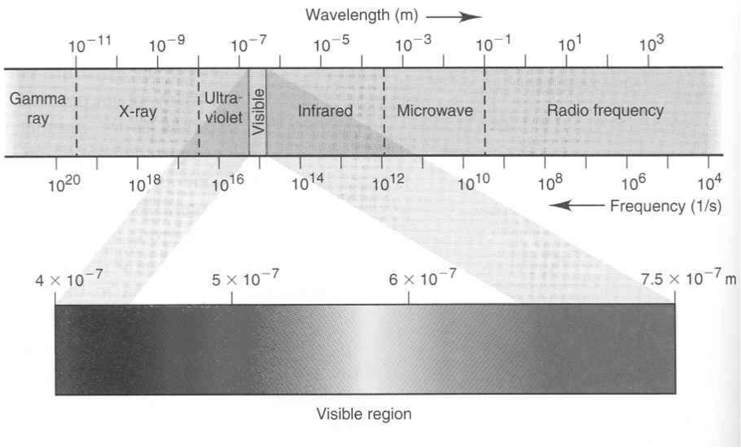
Electromagnetic Spectrum



Source: D. E. Goldberg, *Fundamentals of Chemistry*, 3rd ed., McGraw-Hill, 2001.

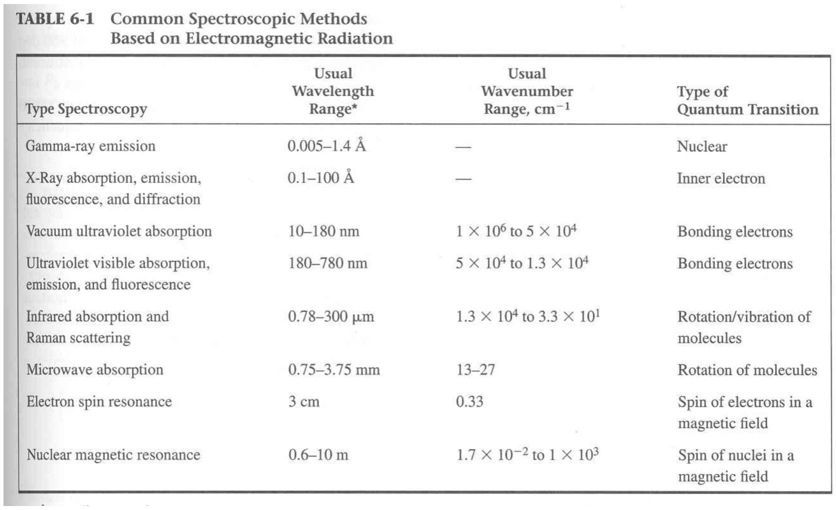


TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	—	Nuclear
X-Ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	—	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 μm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–3.75 mm	13–27	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^3	Spin of nuclei in a magnetic field

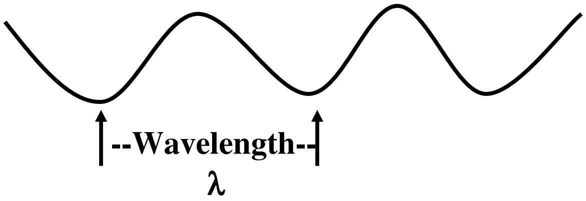
Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Electromagnetic Radiation

Light can exist as:

- **Particles (photons)**
- **Waves**

Waves



Frequency (ν) is the number of waves that pass any given point per second.

Wave Properties

Period (*p*) – the time required for the passage of successive maxima through a fixed point in space.

Frequency (ν) – the number of oscillations of the field that occur per second. Equal to $1/p$. Determined by source and remains invariant regardless of media traversed.

Velocity (*v*) – the rate at which a wave front moves through a medium. Dependent on composition of medium and frequency.

Wave Properties (continued)

Wavelength (λ) – the linear distance between successive maxima or minima of a wave. The wavelength must decrease as radiation passes from a vacuum to some other medium.

Wavenumber (σ) – the number of waves per centimeter.

Energy of Waves

- $v = \nu\lambda$
- **As frequency increases, energy increases.**
  - **As frequency decreases, energy decreases.**
- **As wavelength increases, energy decreases.**
  - **As wavelength decreases, energy increases.**

Wave Properties (continued)

Power (P)– of radiation is the energy of the beam reaching a given area per second.

Intensity (I)– power per unit solid angle. Often used interchangeably with power.

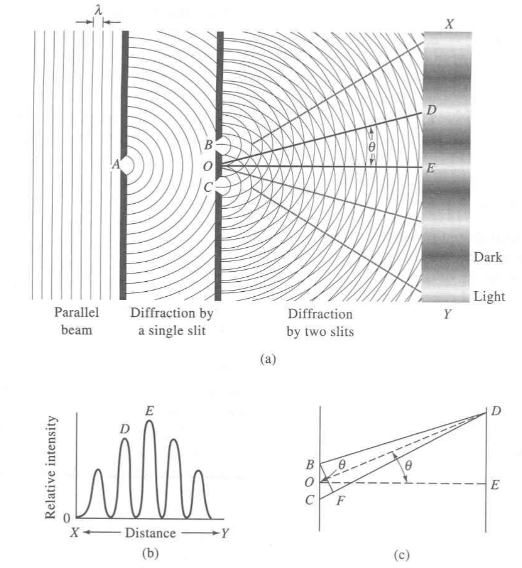
Principle of Superposition

When two or more waves traverse the same space, a displacement occurs which is the sum of the displacements caused by the individual waves.

Constructive vs. Destructive Interference – based on phase difference between waves.

Fourier transform based on fact that any wave motion, regardless of complexity, can be described by a sum of simple sine or cosine terms.

Diffraction – process in which a parallel beam of radiation is bent as it passes a sharp barrier or through a narrow opening. A consequence of interference.



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

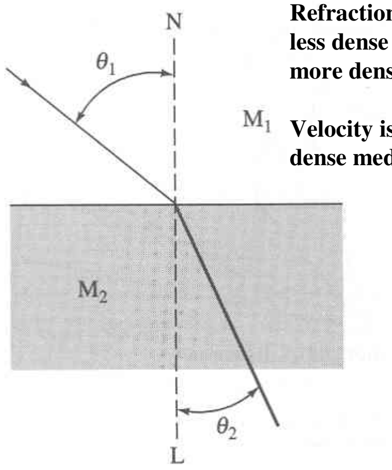
Refraction of Radiation

Refractive Index: $n_i = c/v_i$
where c is the speed of light in a vacuum

Dispersion – the variation of refractive index of a substance with frequency or wavelength.

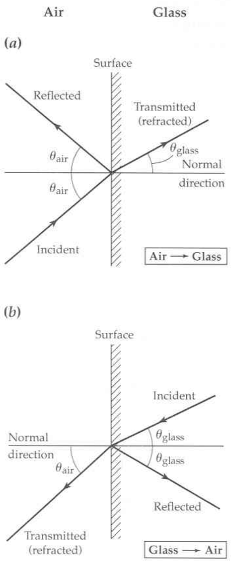
Normal Dispersion – gradual increase in refractive index with increasing frequency (or decreasing wavelength).

Anomalous Dispersion – sharp change in refractive index is observed. Always occurs at frequencies that correspond to the natural harmonic frequency associated with some part of the molecule, atom, or ion of a substance. At these frequencies, permanent energy transfer from the radiation to the substance occurs and absorption of the radiation is observed.



Refraction of light from less dense medium into more dense medium.

Velocity is lower in more dense medium.



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.

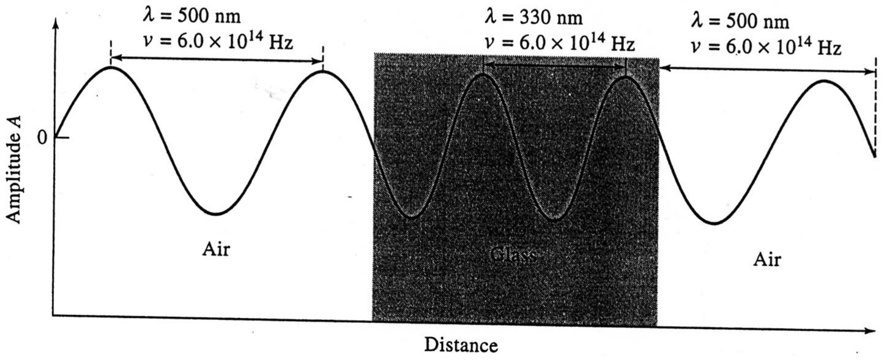


Figure 6-2 Effect of change of medium on a monochromatic beam of radiation.

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Scattering of Radiation

Rayleigh Scattering – scattering by molecules or aggregates of molecules with dimensions significantly smaller than the wavelength of radiation. Intensity related to wavelength, dimensions of scattering particles, and polarizability.

Raman Scattering – part of the scattered radiation suffers from quantized frequency changes as a result of vibrational energy transitions occurring in a molecule as a consequence of the polarization process.

Absorption of Radiation

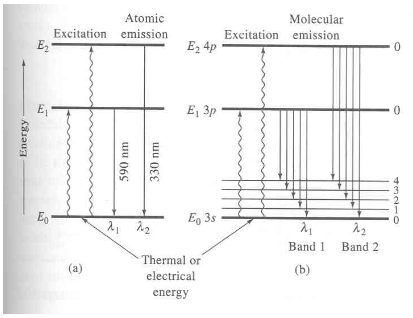
Selective removal of certain frequencies by transfer of energy to atoms or molecules.

Particles promoted from lower-energy (ground) states to higher-energy (excited) states.

Energy of exciting photon must exactly match the energy difference between the ground state and one of the excited states of the absorbing species.

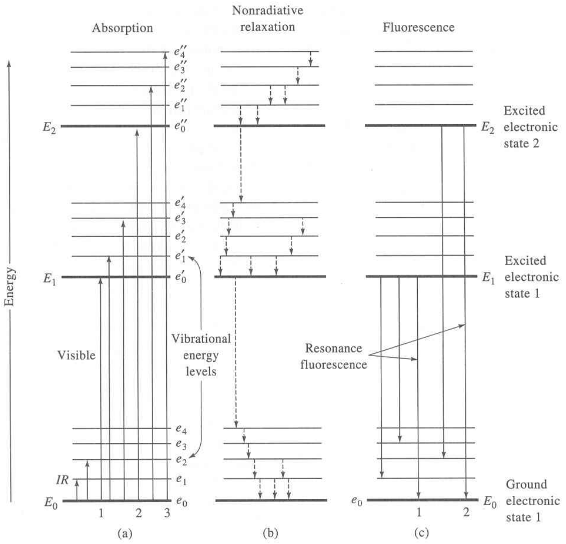
Emission of Radiation

Electromagnetic radiation is produced when excited particles return to lower-energy levels or the ground state.



Energy-level diagrams showing emission from atoms (left) and molecules (right).

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.



Energy-level diagram of molecular fluorescence

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Optical Spectroscopy Methods

- **Absorption**
- **Emission**
- **Luminescence**
- **Scattering**

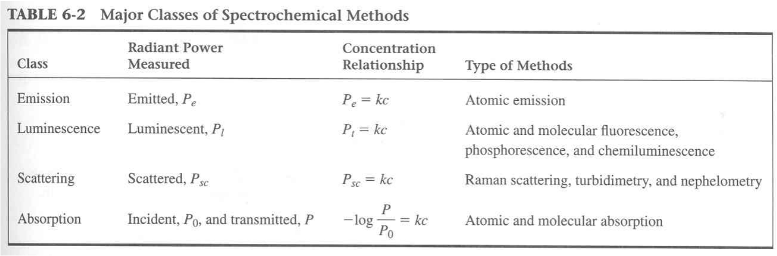


TABLE 6-2 Major Classes of Spectrochemical Methods

Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, P_e	$P_e = kc$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Scattering	Scattered, P_{sc}	$P_{sc} = kc$	Raman scattering, turbidimetry, and nephelometry
Absorption	Incident, P_0, and transmitted, P	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

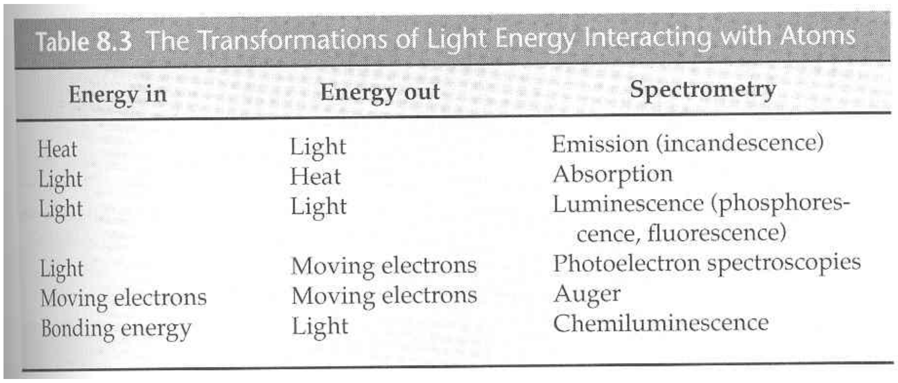


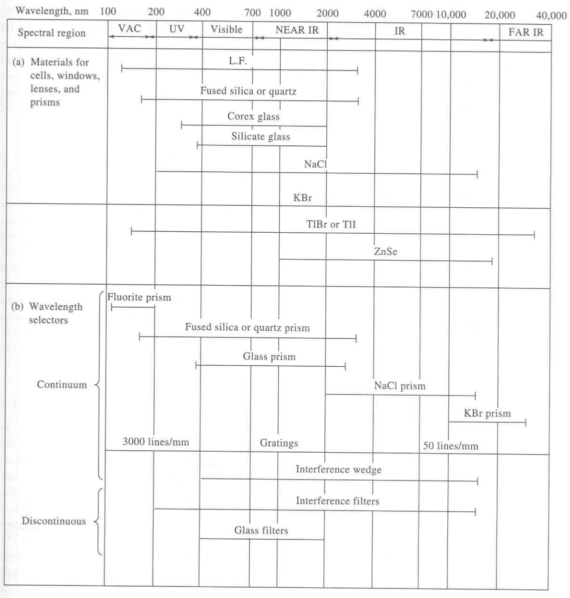
Table 8.3 The Transformations of Light Energy Interacting with Atoms

Energy in	Energy out	Spectrometry
Heat	Light	Emission (incandescence)
Light	Heat	Absorption
Light	Light	Luminescence (phosphorescence, fluorescence)
Light	Moving electrons	Photoelectron spectroscopies
Moving electrons	Moving electrons	Auger
Bonding energy	Light	Chemiluminescence

Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.

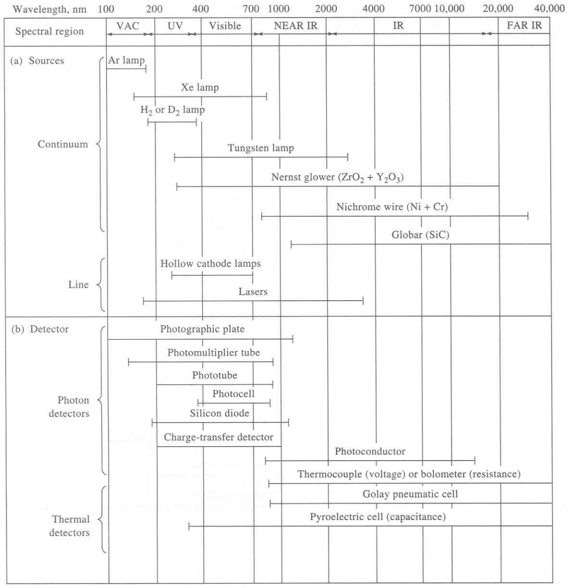
Components of Spectroscopic Instruments

- **Stable source of radiant energy**
  In emission spectroscopy, sample is radiation source
- **Transparent container to hold sample**
- **Device to isolate restricted region of spectrum for measurement**
- **Radiation detector or transducer**
- **Signal processor**



Materials and wavelength selectors for spectroscopic instruments.

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.



Sources and detectors for spectroscopic instruments

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

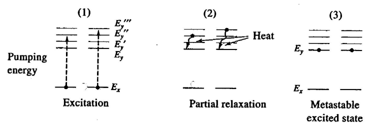
Radiation Sources

Sufficient power
Suitable stability

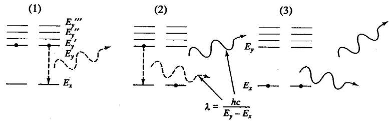
Types:

- **Continuous sources – *e.g.*, lamps used for absorption**
- **Line sources – *e.g.*, vapor lamps used in AA**
- **Lasers (<u>l</u>ight <u>a</u>mplification by <u>s</u>timulated <u>e</u>mission of <u>r</u>adiation)**

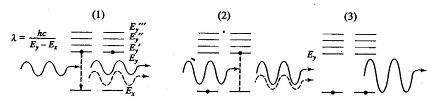
Lasers:



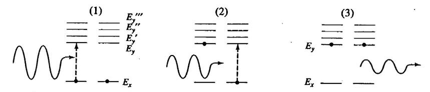
(a) Pumping (excitation by electrical, radiant, or chemical energy)



(b) Spontaneous emission



(c) Stimulated emission



(d) Absorption

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Wavelength Selectors

Filters

Monochromators
  - **Grating – usually used**
  - **Prism**

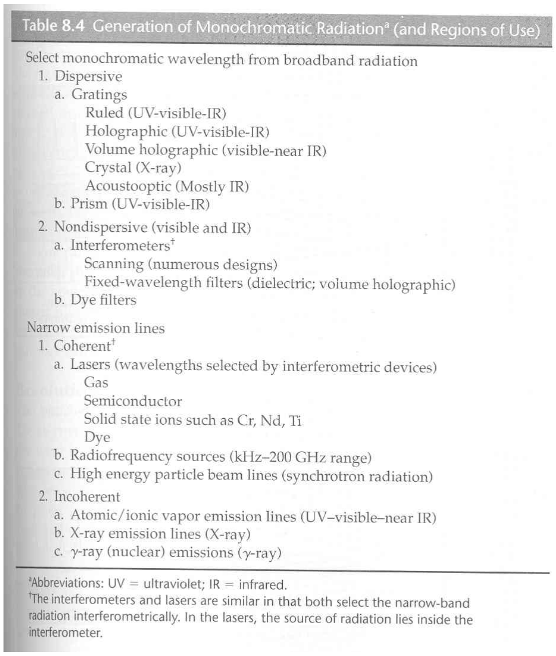


Table 8.4 Generation of Monochromatic Radiation[a] (and Regions of Use)

Select monochromatic wavelength from broadband radiation
- 1. Dispersive
  - a. Gratings
    - Ruled (UV-visible-IR)
    - Holographic (UV-visible-IR)
    - Volume holographic (visible-near IR)
    - Crystal (X-ray)
    - Acoustooptic (Mostly IR)
  - b. Prism (UV-visible-IR)
- 2. Nondispersive (visible and IR)
  - a. Interferometers[†]
    - Scanning (numerous designs)
    - Fixed-wavelength filters (dielectric; volume holographic)
  - b. Dye filters

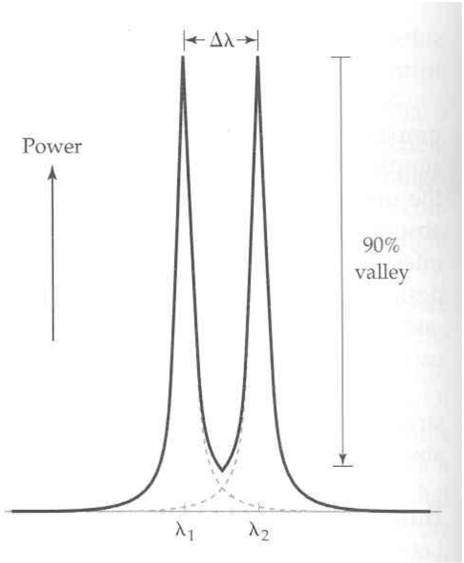
Narrow emission lines
- 1. Coherent[†]
  - a. Lasers (wavelengths selected by interferometric devices)
    - Gas
    - Semiconductor
    - Solid state ions such as Cr, Nd, Ti
    - Dye
  - b. Radiofrequency sources (kHz–200 GHz range)
  - c. High energy particle beam lines (synchrotron radiation)
- 2. Incoherent
  - a. Atomic/ionic vapor emission lines (UV–visible–near IR)
  - b. X-ray emission lines (X-ray)
  - c. γ-ray (nuclear) emissions (γ-ray)

---

[a] Abbreviations: UV = ultraviolet; IR = infrared.

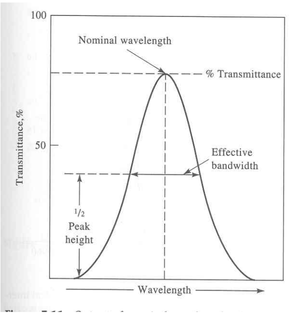
[†] The interferometers and lasers are similar in that both select the narrow-band radiation interferometrically. In the lasers, the source of radiation lies inside the interferometer.

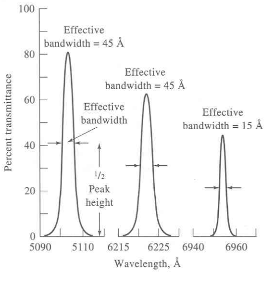
Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.



Resolution is the separation of wavelengths in a spectrum.

Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.

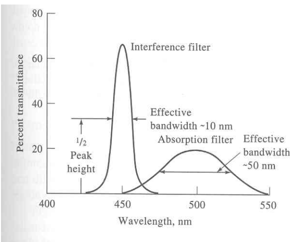




(Left) Output of typical wavelength selector.

(Middle) Transmission characteristics of typical interference filters.

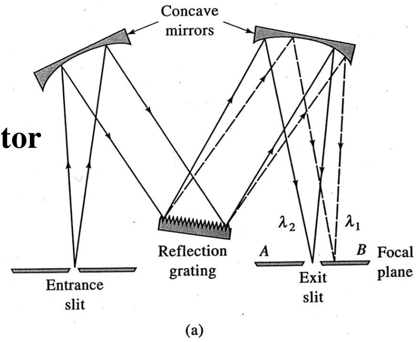
(Right) Effective bandwidths of interference and absorption filters.



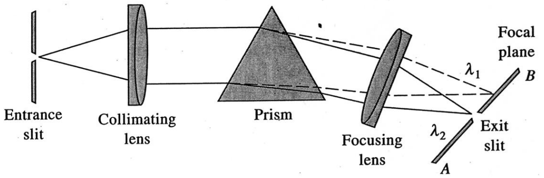
Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Monochromators

Czerney-Turner Grating Monochromator

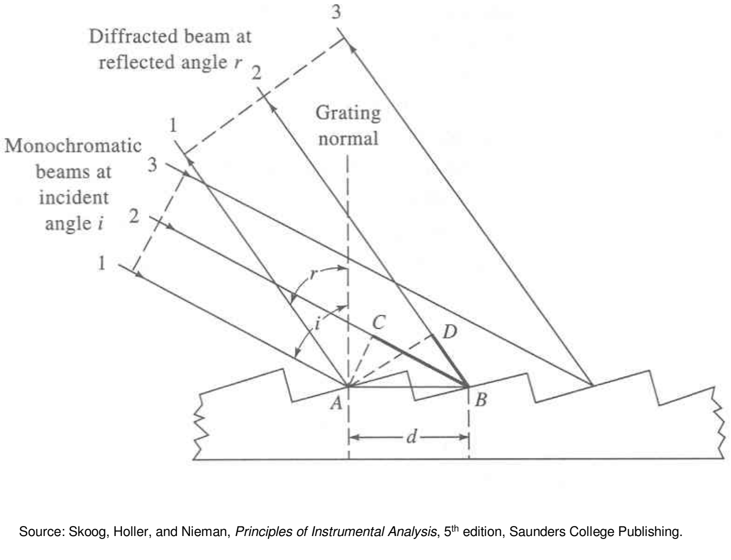


Bunsen Prism Monochromator



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Diffraction from an Echellette-type grating.



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Advantages of Grating Monochromators

Wavelength independence of dispersion.

Fixed dispersion makes it easy to scan an entire spectrum at constant bandwidth after initial adjustment of slitwidth.

Better dispersion for same size of dispersing element.

Can disperse radiation in far UV and infrared regions where absorption prevents use of prisms.

Disadvantages of Grating Monochromators

Produce great amounts of stray radiation.

Produce more high-order spectra.

- **Both of these disadvantages can be minimized with filters.**

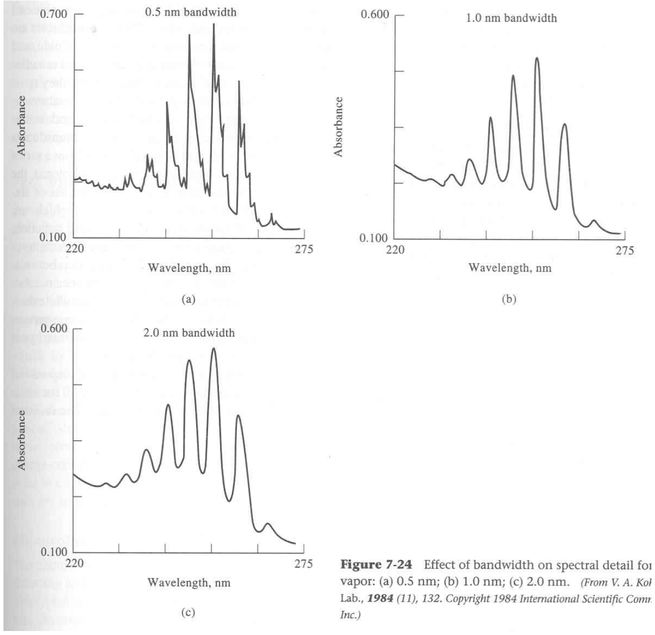


Figure 7-24 Effect of bandwidth on spectral detail fo
vapor: (a) 0.5 nm; (b) 1.0 nm; (c) 2.0 nm. *(From V. A. Kol*
Lab., ***1984*** *(11), 132. Copyright 1984 International Scientific Com*
Inc.)

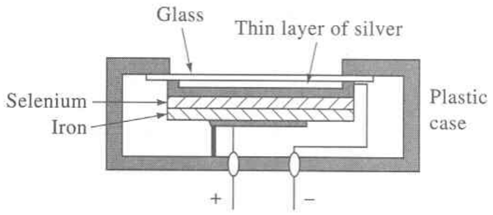
Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Types of Photon Detectors

Photovoltaic Cells (or Barrier-Layer Cells) – the radiant energy generates a current at the interface of a semiconductor layer and a metal.

Phototubes – radiation causes emission of electrons from a photosensitive solid surface.

Photomultiplier Tubes – contain a photoemissive surface as well as several additional surfaces that emit a cascade of electrons when struck by electrons from the photosensitive area.



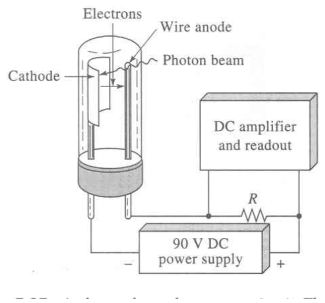
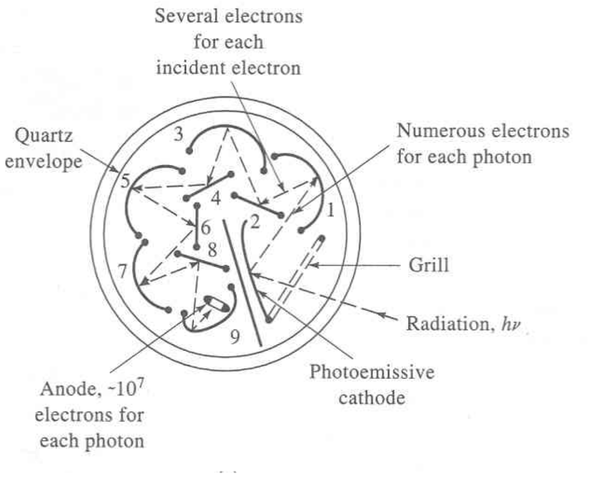


Diagram of barrier-layer cell (top) and phototube (bottom).

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Cross-section of Photomultiplier Tube



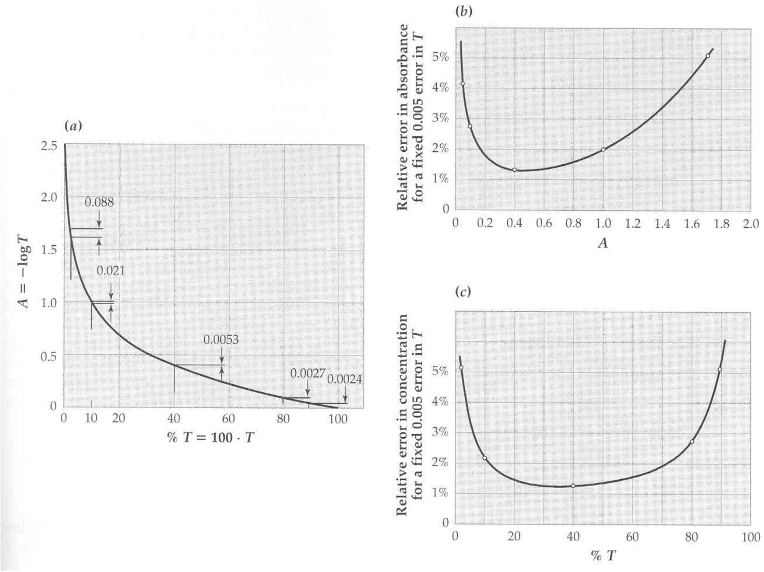
Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Types of Photon Detectors (continued)

Photoconductivity Detectors – absorption of radiation by a semiconductor produces electrons and holes, thus leading to enhanced conductivity.

Silicon Photodiodes – Protons increase the conductance across a reversed-biased pn junction. Used as diode array detectors to observe the entire spectrum simultaneously.

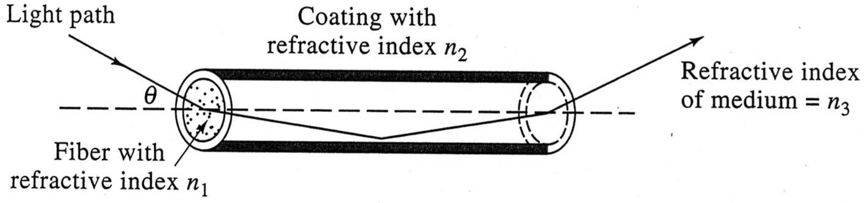
Error in transmittance, absorbance, and concentration.



Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.

Fiber Optics

- **Good for transmission of light over long distances**
- **Flexible**



Numerical aperture = $n_3 \sin\theta = \sqrt{n_1^2 + n_2^2}$

$n_1 > n_2 > n_3$

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Frequency Domain Spectroscopy – radiant power data are recorded as a function of frequency (or wavelength).

Time Domain Spectroscopy – concerned with changes in radiant power with time. Achieved by Fourier transform.

Advantages of Fourier Transform Spectroscopy

Fellgett Advantage – all of the resolution elements for a spectrum are measured simultaneously, thus reducing the time required to derive a spectrum at any given signal-to-noise ratio.

Jacquinot Advantage – the large energy throughput of interferometric instruments (which have few optical elements and no slits to attenuate radiation.

High wavelength precision, making signal averaging feasible.

Ease and convenience that data can be computer-manipulated.