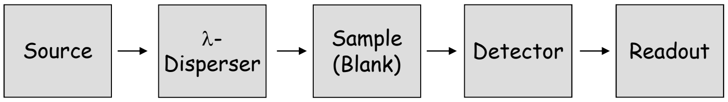
Spectroscopy in the UV and Visible: Instrumentation

- **“Typical” UV-VIS instrument**



Source → λ-Disperser → Sample (Blank) → Detector → Readout

- Monitor the relative response of the sample signal to the blank

$$\text{Transmittance} = T = \frac{P}{P_0} = \frac{S}{B}$$

Spectroscopy in the UV and Visible: Instrumentation

- Components may not (at typically **<u>are not</u>**) useful for all wavelength ranges.
  - Composition, construction limit components to finite useful wavelength ranges

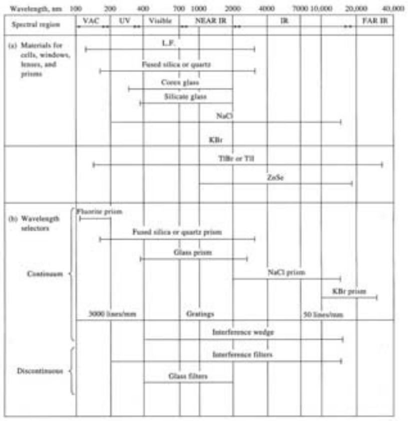


Figure 7-2 (a) Construction materials and (b) wavelength selectors for spectroscopic instruments.

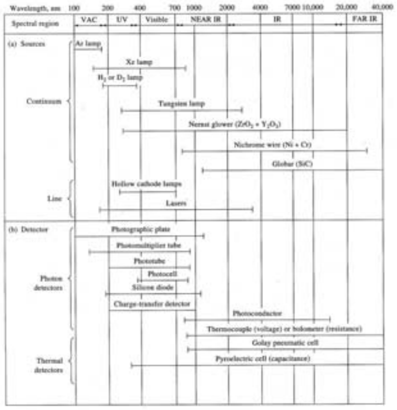


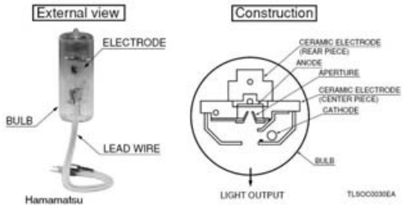
Figure 7-3 (a) Sources and (b) detectors for spectroscopic instruments.

UV-Vis Sources

- Typically *continuum* sources
- UV Range: Hydrogen and Deuterium arc lamps
  - Electrical excitation at low pressure (<0.5 torr) , low voltage (~40V DC)
  - Forms molecular excited state that undergoes dissociation and photoemission

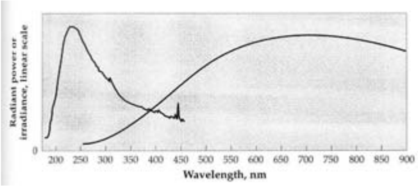
$$D_2 + E_e \rightarrow D_2^* \rightarrow D' + D'' + \text{photon}$$

  - Energy of photon depends on energies of D' and D"
  - Provides continuum from ~160-380 nm

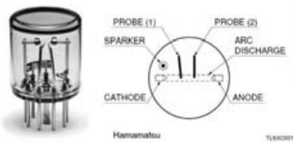


UV-Vis Sources

- Visible Range: Tungsten Filament Lamps
  - Resistively heated wire - "blackbody" radiation
  - Emits from ~350-3000 nm (Fig 6-18)
  - ~15% of radiation falls in the visible @3000K
  - (Also Xe arc lamps - 200-1000 nm)

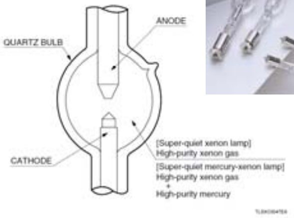


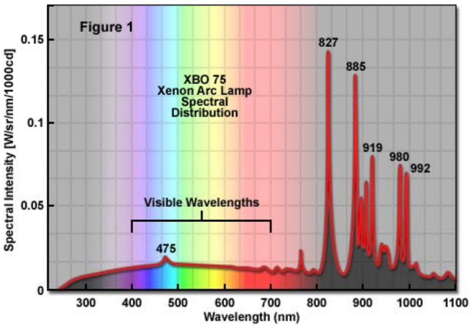
◀ FIGURE 8B.2
Radiant-power spectrum of a deuterium arc lamp (left) and an incandescent source with a temperature of 4200 K, such as a tungsten filament lamp (right).



UV-Vis Sources

- Emmison Spanning UV-VIS: Xe arc lamps
  - High pressure Xenon gas (several atm)
  - Emit from ~200-1000 nm (Xe line spectra in IR)
  - High voltage initiation, low voltage to maintain plasma
  - Generate significant heat, need external cooling





http://zeiss-campus.magnet.fsu.edu/articles/lightsources/images/xenonlampsfigure1.jpg

Line Sources in the UV and Vis

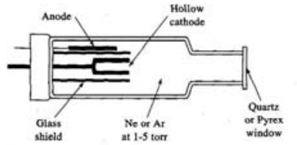


Figure 9-11 Schematic cross section of a hollow cathode lamp.

- Hollow Cathode Lamp
  - Cathode is coated with atom of interest
  - Tube is filled with Ar or Ne
  - High voltage ionizes gas, charged ions are accelerated toward electrodes
    - Produces sputtering of atoms (ground and excited)
    - Excited atoms emit light at atomic lines
  - Design of HCL results in redepostion of metal atoms onto electrodes - recycling
  - Need to avoid excessively high potentials
    - Line broadening (Doppler)
    - Self-absorption
  - Need separate lamp for each element

Wavelength Dispersion and Selection

- Why disperse the beam at all?
- Why disperse prior to sample?
  - Decomposition
  - Fluorescence
- See http://www.horiba.com/us/en/scientific/products/optics-tutorial/ for a great online optics reference.

Wavelength Dispersion and Selection

- Most instruments use a *monochromator* to separate light form the source into discrete wavelength segments
- Components:
  - Entrance slit
  - Collimating/focusing device - mirror or lens, ***nonideal***
  - Dispersing device -filter, grating or prism
  - Collimating/focusing device - mirror or lens
  - Exit slit

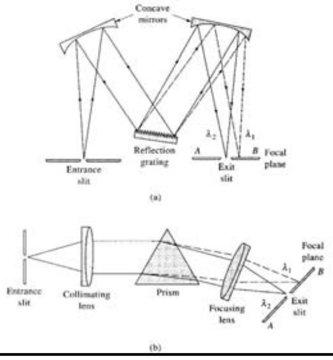
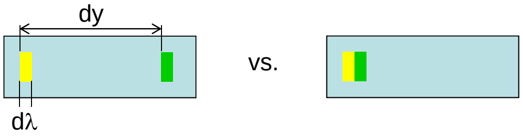


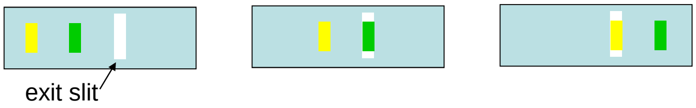
Figure 7-16 Two types of monochromators: (a) Czerney-Turner grating monochromator and (b) Bunsen prism monochromator. (In both instances, $\lambda_1 > \lambda_2$.)

Wavelength Dispersion and Selection

- Why slits?
- Device disperses wavelengths in space. Quantified by:
  - **Linear Dispersion, D = dy/dλ and**
  - **Reciprocal Linear Dispersion, D^{-1} = 1/D**



- By scanning the dispersed beam across a slit, a small fraction of wavelengths are allowed to pass to the sample.



Wavelength Dispersion and Selection

- How much of the beam is allowed to “fit”?
  - Ideally, exit and entrance slits are the same size
  - Dispersing element produces slit-sized images of portions of the beam
  - These slit-sized images are passed across the exit slit. What is the response?
  - Bandwidth = wD^{-1}
    - Size of spectral slice
  - Impact on spectral detail

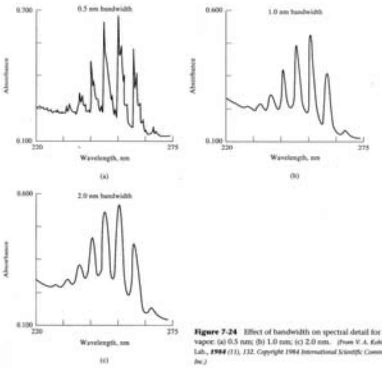


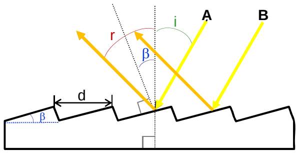
Figure 7-24 Effect of bandwidth on spectral detail for benzene vapor: (a) 0.5 nm; (b) 1.0 nm; (c) 2.0 nm. *(From V. A. Kohler, Amer. Lab.,* ***1984*** *(11), 132. Copyright 1984 International Scientific Communications Inc.)*

Optical Elements and Wavelength Dispersion

- Optical components are not ideal
  - Lenses: *Chromatic aberration* because refractive index changes with wavelength
    - focal length changes with wavelength
  - Mirrors: *Reflective losses.* Lenses and inefficiencies in mirrors contribute to ~4% loss per element.
- Dispersive Elements: Filters
  - Construction determines what fixed range of wavelengths will be allowed to pass.
  - Interference Filters:
    - “sandwich” containing reflective material and dielectric layer.
    - Only wavelengths that result in in-phase reflections: Depends on thickness and dielectric
  - Absorption Filters:
    - “colored” plates
    - Light that is not absorbed by the filter is transmitted
    - Often used in combination

Wavelength Dispersion: Gratings

- Reflection Gratings: Optically flat reflective surface with series of parallel groves of equal spacing. (60- 6000 grooves/mm)
    - Ruled vs. Holographic



- Consider a monochromatic wavefront:
  - Points A and B have same wavelength, frequency, velocity…
  - Initially wavefront contains coincident light: Constructive interference
  - In order for constructive interference to result after grating, A and B must travel a fixed number of wavelengths ($n\lambda$)
    - Otherwise destructive interference
  - Can solve geometrically: Grating Equation

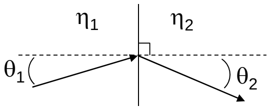
$$n\lambda = d(\sin i + \sin r)$$

Wavelength Dispersion: Gratings

- See an overlap of orders at a given i and r
- Example: 1500 line/mm grating, i = 12.0º, r = -30.0º
- Characteristics
  - Angular Dispersion: wavelength dependence of reflection
  - Linear Dispersion: “spread” in wavelength along focal plane
  - Resolving Power: ability to separate wavelengths

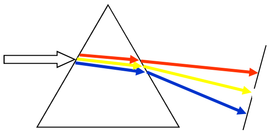
Wavelength Dispersion: Prisms

- Based on the fact that refractive index is wavelength dependent
- When light crosses the interface between materials of different η, it is “bent”



- Snell's Law: $\eta_1 \sin\theta_1 = \eta_2 \sin\theta_2$

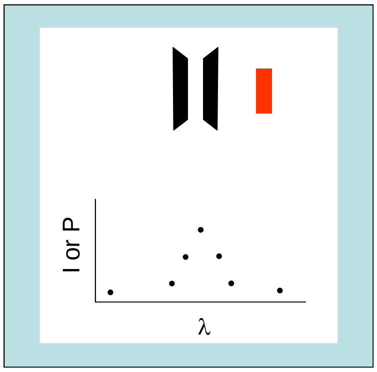
- For prisms, there are two interfaces to consider.
- Angles of refraction depend on refractive index and construction of prism



- Since each λ “sees” a different η, varying angles result

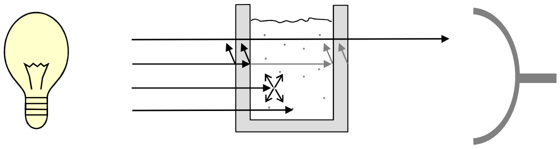
Monochromator Output

- What happens as a band of wavelengths moves across slit?



- Bandpass, Bandwidth, Effective Bandwidth

Sample Considerations



- Several possible fates for photon
  - Reflection
  - Scattering
  - Absorption

- Choose cell and sample composition carefully.
- “Match”

Detectors for UV-VIS

- Photon Transducers: Covert photon energy to electrical signal (current, voltage, etc.)
- **Detectors based on *photoelectric effect:***
  Phototubes, Photomultiplier tubes
- **<u>Phototube:</u>**
  - Incident photon causes release of an electron
  - Photocurrent $\propto P_{light}$
  - Not best for low-light scenarios

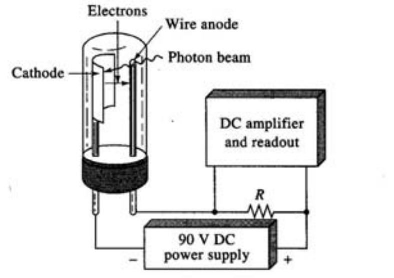
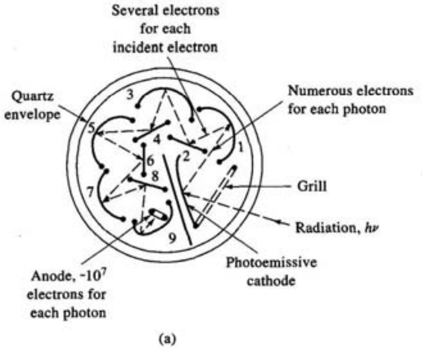


Figure 7-27 A phototube and accessory circuit. The photocurrent induced by the radiation causes a potential drop across *R,* which is then amplified to drive a meter or recorder.

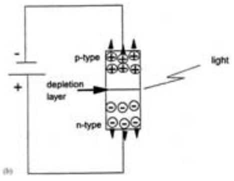
Detectors for UV-VIS

- **<u>Photomultiplier:</u>**
  - Ejected photoelectron strikes *dynode*, secondary e^- released
  - Voltage accelerates e^- to next dynode and so on
    - big voltage divider
  - Result is large charge packet hitting anode
    - High Gain



Detectors for UV-VIS

- **Semiconductor-based detectors**
  - Photodiodes, Photodiode arrays, CCD, CID
- **Photodiodes and Photodiode Arrays:**
  - Reverse biased junction
  - Photons produce e^-- hole pairs → current
  - Current $\propto P_{light}$
    - less sensitive than PMTs
  - Photodiode Arrays: PDA
    - Assembly of individual photodiodes on a chip
    - Each diode can be addressed individually
    - Experiment is set up so that monochromator disperses light across PDA, with a small # of diodes per wavelength
    - allow simultaneous collection of all wavelengths



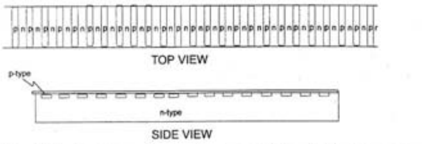


Figure 5.24 A PDA. The top view shows the face that the light would fall on. The side view shows that the p-type elements are embedded in a continuous layer of n-type semiconductor. (From Brown, used with permission.)

Detectors for UV-VIS

- Charge transfer devices (CCD, CID)
  - two- or three-dimensional arrays
  - allow integration of accumulated charge - better sensitivity

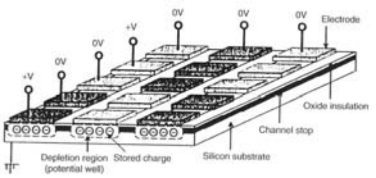
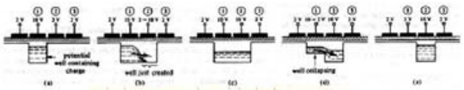


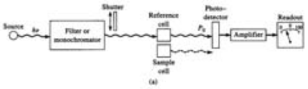
Figure 7.19 Schematic of a CCD. In this CCD, three electrodes define a pixel. [Courtesy of Joh Yvon, Inc., Horiba Group, Edison, NJ (www.jyhoriba.com).]

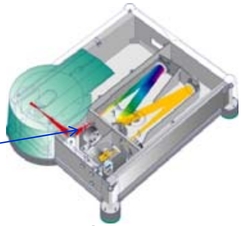


Instrument Assemblies

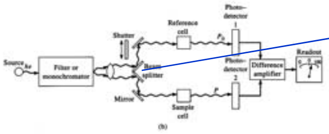
- Single wavelength: Photometers (filter-based)
- Multiple Wavelength Capability, Two classes: Single- (scanning) and Multi-channel
- Single channel: defined by how reference and sample signals are taken and compared.

Single Beam

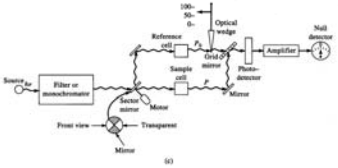




Double Beam -In Space



Double Beam -In Time



- Advantages and disadvantages of single vs. double beam

Instrument Assemblies

- Multichannel Devices: Array-based (typically)
  - Collect P for all wavelengths simultaneously
  - Need single detector for each wavelength - Array!

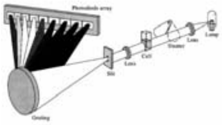


Figure 13-22 A multichannel diode array spectrometer, the HP 8452A. (Courtesy of Hewlett-Packard Company, Palo Alto, CA.)

  - No mechanical movement of monochromator
  - Software stores blank response.
    - Digitally ratioed to sample response to produce spectrum.
  - Advantages
    - Fast response
    - Fewer mechanical parts
  - Disadvantages
    - Wavelength resolution depends on monochromator and size of array (physical size and # of elements)
    - $$$

- **Our instruments:**
  - **Milton Roy (PDA), Ocean Optics (CCD)**
  - **Cary 50 (Scanning)**

HPLC Detector

- Same Parts
  - A. Source
  - B. Slit
  - C. Grating
  - D. Beamsplitter
  - E. “Cell”
  - F. Detectors