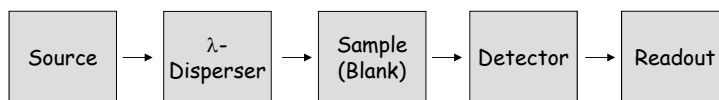


Spectroscopy in the UV and Visible: Instrumentation

- “Typical” UV-VIS instrument



- 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 **are not**) useful for all wavelength ranges.
 - Composition, construction limit components to finite useful wavelength ranges

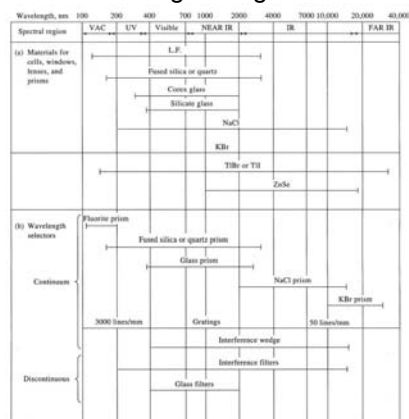


Figure 7-2 (a) Construction materials and (b) wavelength selectors for spectroscopic instruments.

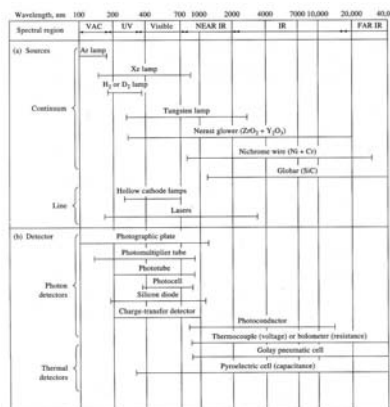
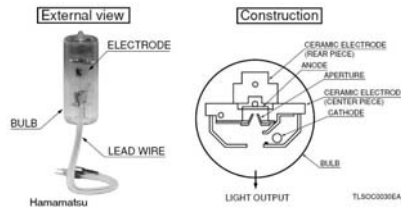


Figure 7-3 (a) Sources and (b) detectors for spectroscopic instruments.

UV-Vis Sources

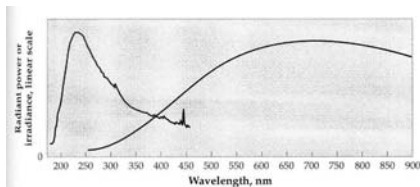
- Typically *continuum* sources
- UV Range: Hydrogen and Deuterium arc lamps
 - Electrical excitation at low pressure (<0.5 torr) , low voltage (~40V DC)
 - Forms molecular excited state that undergoes dissociation and photoemission

$$D_2 + E_e \rightarrow D_2^* \rightarrow D' + D'' + \text{photon}$$
 - Energy of photon depends on energies of D' and D''
 - Provides continuum from ~160-380 nm

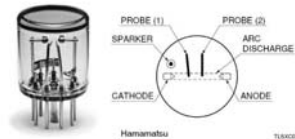


UV-Vis Sources

- 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)

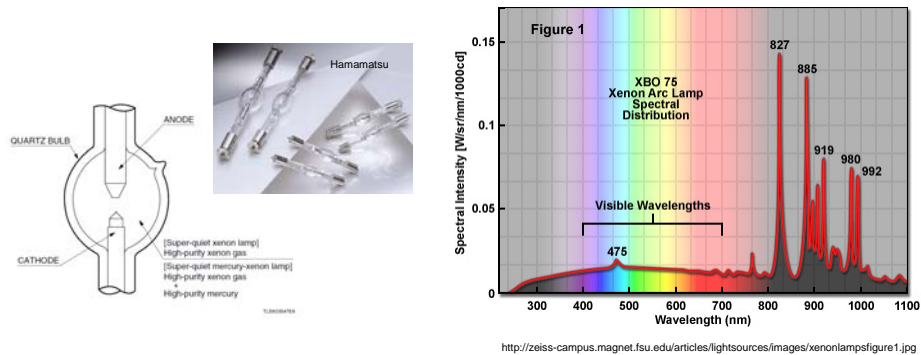


◀ FIGURE 8B.2 Radiant-power spectrum of a deuterium arc lamp (left) and an incandescent source with a temperature of 4200 K, such as a tungsten filament lamp (right).



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



Line Sources in the UV and Vis

- 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 redeposition of metal atoms onto electrodes - recycling
 - Need to avoid excessively high potentials
 - Line broadening (Doppler)
 - Self-absorption
 - Need separate lamp for each element

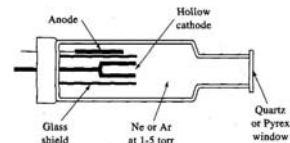


Figure 9-11 Schematic cross section of a hollow cathode lamp.

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 from 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

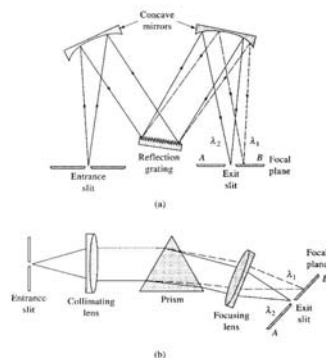
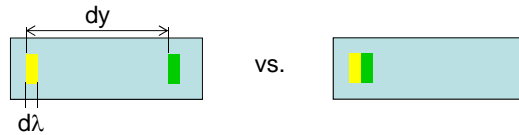


Figure 7-16 Two types of monochromators: (a) Czerny-Turner grating monochromator and (b) Bunsen prism monochromator. (In both instances, $\lambda_1 > \lambda_2$.)

Wavelength Dispersion and Selection

- Why slits?
- Device disperses wavelengths in space. Quantified by:
 - Linear Dispersion, $D = dy/d\lambda$ 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

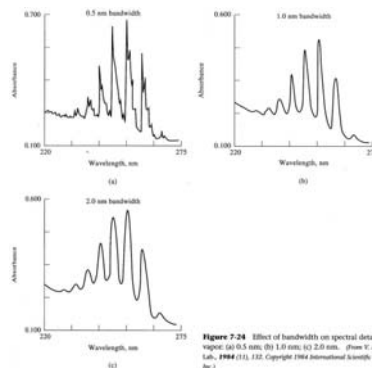


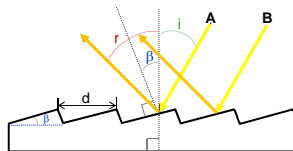
Figure 7-24 Effect of bandwidth on spectral detail for benzene: (a) 0.5 nm; (b) 1.0 nm; (c) 2.0 nm. (From K. A. Braker, *Analyt. Lab.*, 1994 (11), 132. Copyright 1994 International Scientific Communications Inc.)

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 grooves 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

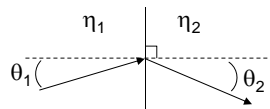
$$n\lambda = d(\sin i + \sin r)$$

Wavelength Dispersion: Gratings

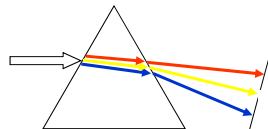
- See an overlap of orders at a given i and r
- Example: 1500 line/mm grating, $i = 12.0^\circ$, $r = -30.0^\circ$
- Characteristics
 - Angular Dispersion: wavelength dependence of reflection
 - Linear Dispersion: “spread” in wavelength along focal plane
 - Resolving Power: ability to separate wavelengths

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”



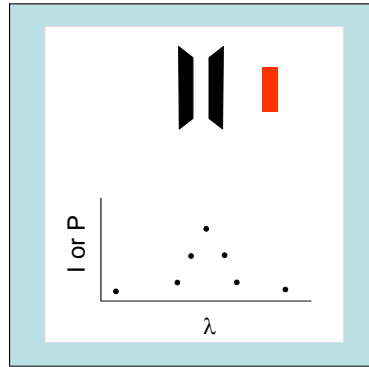
- Snell's Law: $\eta_1 \sin \theta_1 = \eta_2 \sin \theta_2$
- For prisms, there are two interfaces to consider.
- Angles of refraction depend on refractive index and construction of prism



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

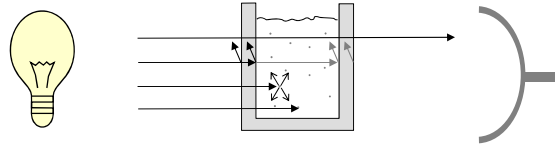
Monochromator Output

- 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

- **Phototube:**

- Incident photon causes release of an electron
- Photocurrent $\propto P_{\text{light}}$
- Not best for low-light scenarios

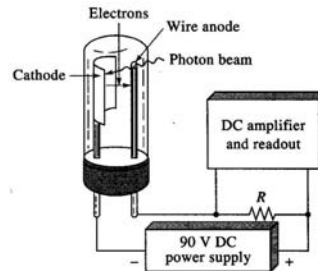
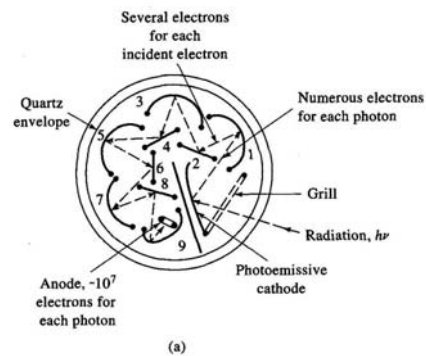


Figure 7-27 A phototube and accessory circuit. The photocurrent induced by the radiation causes a potential drop across R , which is then amplified to drive a meter or recorder.

Detectors for UV-VIS

- **Photomultiplier:**

- 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 \rightarrow current
 - Current $\propto P_{\text{light}}$
 - 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

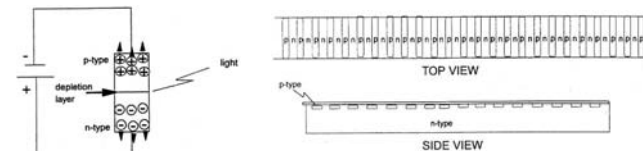


Figure 5.24 A PDA. The top view shows the face that the light would fall on. The side view shows that the p-type elements are embedded in a continuous layer of n-type semiconductor. (From Brown, used with permission.)

Detectors for UV-VIS

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

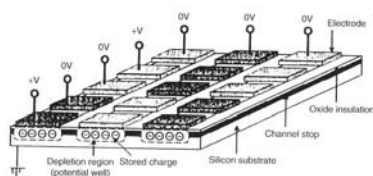
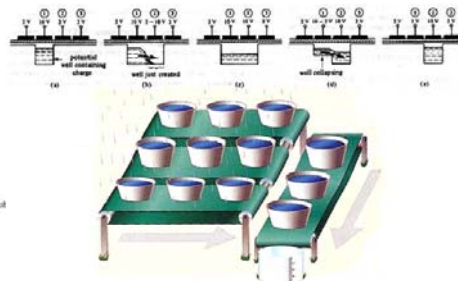
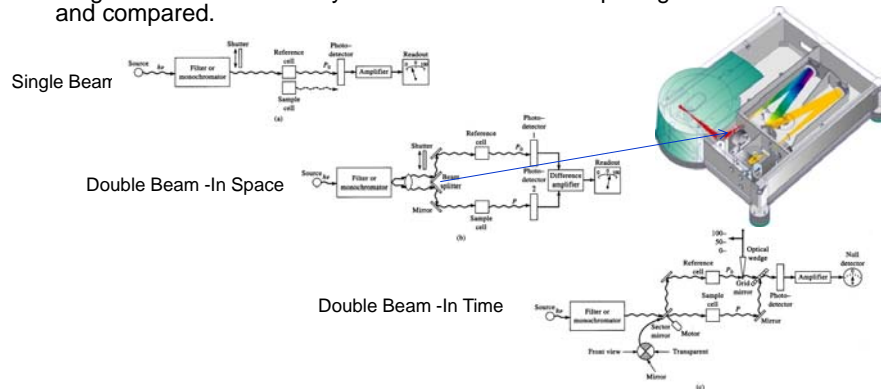


Figure 7.19 Schematic of a CCD. In this CCD, three electrodes define a pixel. [Courtesy of Jai Yuen, Inc., Horiba Group, Edison, NJ (www.jhoriba.com).]



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.



- 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!

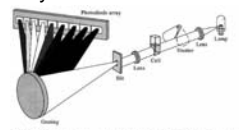


Figure 43-22 A multichannel device (see text), the SP 8452A. Courtesy of Thermo Nicolet Instrument Co. (1)

- 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

