Spectrometers:
Sources → Monochromators → Detectors
Overview of a “Simple” Spectrophotometer (not really so simple)

- The typical spectrophotometer is made up of a complex arrangement of mirrors (collimators), lenses, slits, etc.
- By comparison, the spectrophotometer based on the photodiode array detector (PDA) provides an elegant solution to UV/VIS absorption measurements; however, it typically suffers from poor resolution (0.5 nm for PDA vs. 0.05 nm).
- PDA’s are conventionally used as “real-time” detectors for compounds with chromophoric species, i.e., where compounds absorb in the region of UV/VIS.
- Significantly more on PDA’s later.
Typical Spectrophotometers

- Every spectrophotometer is made up of essentially the same hardware.
- Splitting the beam (dotted lines) into a reference cell following wavelength selection is often used with more sophisticated UV/VIS spectrophotometers.
Component Overview of UV/VIS Spectrophotometers

- **Sources**
  - Low pressure *hydrogen* or *dueterium discharge tubes* (UV)
  - Xe lamp
  - Tungsten lamp (VIS)
  - LASER (not for UV/VIS - *fluorescence*) (later)

- **Wavelength selection**
  - Filters
  - Monochromators
    - Prisms
    - Gratings
    - Slits

- **Transducers**
  - Phototubes
  - Photomultiplier Tubes
  - Multichannel Photon Transducers
    - Photodiode Arrays
    - Charge Transfer Devices
    - Charge Injection Devices
    - Charge coupled Devices
    - Thermal Transducers (*infrared radiation*) (later)
The frequency of radiation does not change in traversing a medium; however, the velocity does (p118 SHN). This forms the basis of describing refractive index (p124 SHN). Note that as a beam of radiation (say 450 nm) traverses a medium there is a loss of velocity, but that it does not result in permanent energy transfer.

Consider the following table. Some common sources and their associated energies are presented for comparative purposes.

\[ E = \frac{hc}{\lambda} = hv \]

<table>
<thead>
<tr>
<th>Sources</th>
<th>Wavelength (nm)</th>
<th>Energy (J)</th>
<th>Energy (eV)</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Frequency (Hz or s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>3</td>
<td>6.62E-17</td>
<td>413</td>
<td>3.33E+06</td>
<td>1.0E+17</td>
</tr>
<tr>
<td>Vacuum UV</td>
<td>30</td>
<td>6.62E-18</td>
<td>41</td>
<td>3.33E+05</td>
<td>1.0E+16</td>
</tr>
<tr>
<td>UV</td>
<td>200</td>
<td>9.93E-19</td>
<td>6.2</td>
<td>5.00E+04</td>
<td>1.5E+15</td>
</tr>
<tr>
<td>VIS</td>
<td>600</td>
<td>3.31E-19</td>
<td>2.1</td>
<td>1.67E+04</td>
<td>5.0E+14</td>
</tr>
<tr>
<td>IR</td>
<td>3000</td>
<td>6.62E-20</td>
<td>0.41</td>
<td>3.33E+03</td>
<td>1.0E+14</td>
</tr>
<tr>
<td>microwave</td>
<td>30000</td>
<td>6.62E-21</td>
<td>0.041</td>
<td>3.33E+02</td>
<td>1.0E+13</td>
</tr>
</tbody>
</table>
UV/VIS Considerations

- Molecules may be thermolabile and could breakdown upon prolonged exposure to the incident radiation, from white light (broad band) exposure (sample heating).
- Incident radiation *can* be intense white light (broad band) provided the sample exposure time is minimal (<1s). This is the concept used in spectrophotometers based on PDA detectors (later).
- Monochromators permit selected wavelengths to pass through the sample, which if you think about it significantly reduces the possibility of “heating” the sample during absorbance measurement at that wavelength. Also, since UV/VIS spectrophotometers are generally *not* based on multi-channel detectors, we have to coordinate the detector response with a specific incoming wavelength (e.g., a photomultiplier cannot discriminate between $\lambda=300$ and $\lambda=500$ nm).
- Target analytes may be part of a suspension of particles. As such, we have to concern ourselves with light scattering. This also presents limitations based on system noise (later).
  - If $\lambda >>$ particle diameter - Rayleigh scattering
  - If $\lambda <<$ particle diameter - colloidal appearance
Sources

- The following diagram provides an overview of a simple spectrophotometer.
- We are interested at this time at the source of radiation, which is in this example a tungsten lamp.
- Why is there a lens positioned in front of the slit?

FIGURE 7-17  (a) The Spectronic 20 spectrophotometer. (b) Its optical diagram. (Courtesy of Milton Roy Company, Analytical Products Division, Rochester, NY.)
The typical wavelength ranges studied are:

- 160-375 nm (H₂/D₂ discharge tubes). UV lamps based on Hg are also common.
- 350-2500 nm as the most common output regions for Tungsten lamps. The efficiency of a W lamp output below 300 nm is low, and as such a UV lamp is thereby also required to provide reliable radiation at the higher energy levels.
- \( E_{\text{out}} \sim (\text{Voltage})^4 \). For this reason, V has to be extremely stable.
- W/halogen lamps (W/I) - extremely efficient, also produces UV

High intensity outputs don’t provide an advantage to quantitative determinations (recall measuring difference in absorption of specific wavelengths). These outputs are quite useful for high resolution work where narrow slit widths are used (more on slit widths later).

**Figure 13-11** Output from a deuterium lamp.

**Figure 14.13** Intensity of radiation as a function of wavelength for a typical tungsten bulb at 3000 K.
Interim Summary

- So, we now have a source of broad band UV/VIS radiation. Unless a multichannel detector is used in the instrument, we will need to select specific wavelengths.
- Consider the following diagram:

![Diagram of UV/VIS spectrophotometer](image)

**FIGURE 7-17** (a) The Spectronic 20 spectrophotometer. (b) Its optical diagram. (Courtesy of Milton Roy Company, Analytical Products Division, Rochester, NY.)
Wavelength Selectors
Skoog Holler Nieman Chapter 7 p154

• A narrow band of radiation incident on a sample is required to ensure both sensitivity and selectivity of absorption measurements. In particular, narrow bands are required with linear systems (such as a monochromator on an axis) to ensure linearity of response as a function of (sample) [analyte].

• Filters
  – Interference filters
  – Interference wedges
  – Absorption filters

• Monochromators
  – Prism monochromators
  – Grating monochromators
  – The echellette (and echelle) grating
  – Concave gratings
  – Holographic gratings

• Slits
  – Important part of a monochromator
**Filters**  
*Skoog Holler Nieman Chapter 7 p155*

**Interference Filters (and wedges)**

- These filters rely on optical interference (destructive wave addition) to provide narrow bands of radiation.
- The dielectric layer thickness determines the $\lambda$ of transmitted radiation. (Wedge - $t$ varies.)

$$\lambda = \frac{2 \cdot t \cdot \eta}{n}$$

where:
- $t$ is the dielectric thickness
- $\eta$ is refractive index of dielectric
- $n$ is the order of interference
- $\lambda$ is the transmitted wavelength at $\theta = 0^\circ$

**Absorption Filters**

- Here we are talking about coloured glass or a dye that absorbs the wavelength we wish to reject.
- Bandwidths are extremely large (30 to 250 nm) (see next page).
- Combining two absorption filters of different $\lambda_{\text{max}}$ can yield a bandpass filter.

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**Figure 7-12** (a) Schematic cross section of an interference filter. Note that the drawing is not to scale and that the three central bands are much narrower than shown. (b) Schematic to show the conditions for constructive interference.

**Figure 7-15** Comparison of various types of filters for visible radiation.
Comparison Between Interference and Absorption Filters
Skoog Holler Nieman Chapter 7 p155

• Basically, the interference filter can provide superior bandwidth definition over an absorption filter:

![Effective bandwidths for two types of filters.]

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

• It is noteworthy to recognize that the greater the bandwidth definition the lower the %transmittance through that filter.
The monochromator is vital in its role to vary the energy of radiation incident on a sample - thus providing a spectral scan. The concept is straightforward - focus the dispersed radiation onto an exit slit. That radiation is then incident on the sample.

Two basic types of monochromators:
- Prism
- Grating (reflective processes)

One must be aware of the fact that prisms do not provide a linear dispersion of radiation, whereas a grating does:

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**Figure 7-17** Dispersion for three types of monochromators. The points A and B on the scale in (c) correspond to the points shown in Figure 7-16.
• The “Bunsen prism monochromator”. Note that $\lambda_1 > \lambda_2$.
• This “unit” is comprised of a number of elements.
  – Entrance slit
  – Collimating lens (to disperse the incoming “white” radiation into parallel streams)
  – A prism, on which the incoming radiation is dispersed at both surfaces
  – Another lens, this time to focus the collimated beam to a rectangular points along the focal plane
  – A exit slit which can be narrowed or enlarged as required, depending on required resolution (later on slits).
• Note that all wavelength elements are present on the focal plane; however, only those selected to exit the “unit” are positioned at the exit slit.
• Prisms are sometimes used in line with a grating (later).
A Czerney-Turner grating monochromator. Note that $\lambda_1 > \lambda_2$.

- This “unit” is comprised of a number of elements
  - Entrance slit
  - A concave mirror to “spread out” the incoming radiation to a width that will maximize the amount of radiation incident on the grating
  - A reflective grating which disperses the incoming radiation depending on incident angle and reflective angle
  - Another concave mirror, this time to
  - A exit slit which can be narrowed or enlarged as required, depending on required resolution (later on slits); however, for a reflective grating, the slit widths can remain essentially constant.
Czerny-Turner Mounting