Atomic Spectrophotometry

- **Use**
  - Analysis of metals
  - Very sensitive

- **Three types**
  - Absorption (AAS)
    - Flame and electrothermal (furnace)
  - Emission (AES)
    - Often used with plasma
  - Fluorescence

---

**Atomic Spectroscopy: Instrument Design**

(Skoog, Chaps. 8 & 9; pp.192-203, 206-227)

(Harris, Chapt. 22)
(pp.615-635)
Atomic Absorption Spectrophotometers

- Sample holder is replaced with an atomizer

Diagram showing the components of an atomic absorption spectrophotometer, including light source, wavelength selector, detector, and other parts.
Atomic Absorption

- General

- Flame

Possible transitions

Figure 8-1: Energy level diagrams for (a) atomic sodium and (b) magnesium(II) ions. Note the similarity in pattern of lines but not in actual wavelengths.
Light Source

- Hollow Cathode Lamps

Components

- Quartz Window
- Cathode (negative)
  - Contains element of interest
- Low pressure chamber
  - With some Ar or Ne
    - (become ionized)

Three steps

- Sputtering
  - Metal atoms are dislodged
- Excitation
  - Through contact with fill gas ions
- Emission
Hollow Cathode Lamps

- Most are single element
- Some multi-element lamps are available
  - More than one metal in the cathode
- Currents are optimized
- Short life
  - Moderate cost ($180-$250)
  - Less suited for volatile elements

Electrodeless discharge lamps (EDL)

- Features
  - Ratio frequency is applied to a coil
    - Excites elements or its salts inside quartz bulb
  - Requires a special power supply
- Comparison with hollow cathode lamps
  - EDLs are brighter, more intense
    - Give lower MDLs for A
  - EDLs have a longer life
  - EDLs have some problem
Flame

- Burner design

**Temperatures of some common flames**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidant</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Air</td>
<td>2000-2100</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>Air</td>
<td>2100-2400</td>
</tr>
<tr>
<td>H₂</td>
<td>O₂</td>
<td>2600-2700</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>N₂O</td>
<td>2600-2800</td>
</tr>
</tbody>
</table>

Flame AA sample treatment
Temperature

Impact of flow and position
The energy $E_0$ passing out of the flame is the difference between the incoming energy $E_1$ and the energy absorbed by the sample to raise it to an excited state.

Instrument Design
Background Correction

- Slit widths are normally recommended with method
- Narrow slit widths
  - May increase linearity
  - May also decrease signal to noise ratio

Bandwidth

- Slit widths are normally recommended with method
- Narrow slit widths
  - May increase linearity
  - May also decrease signal to noise ratio
Matrix Effects 1

- Viscosity
  - Phosphoric acid example
- Sulfuric acid vs MeOH

Matrix Effects 2

- Chemical Interference
  - Formation of Ca$_3$(PO$_4$)$_2$
- Ionization Interferences
  - Ba ionizes readily
  - K ionizes even more easily & elevates electron density in flame
• To next lecture