Updated: 21 September 2014

Print version

# CEE 772: Instrumental Methods in Environmental Analysis

Lecture #6

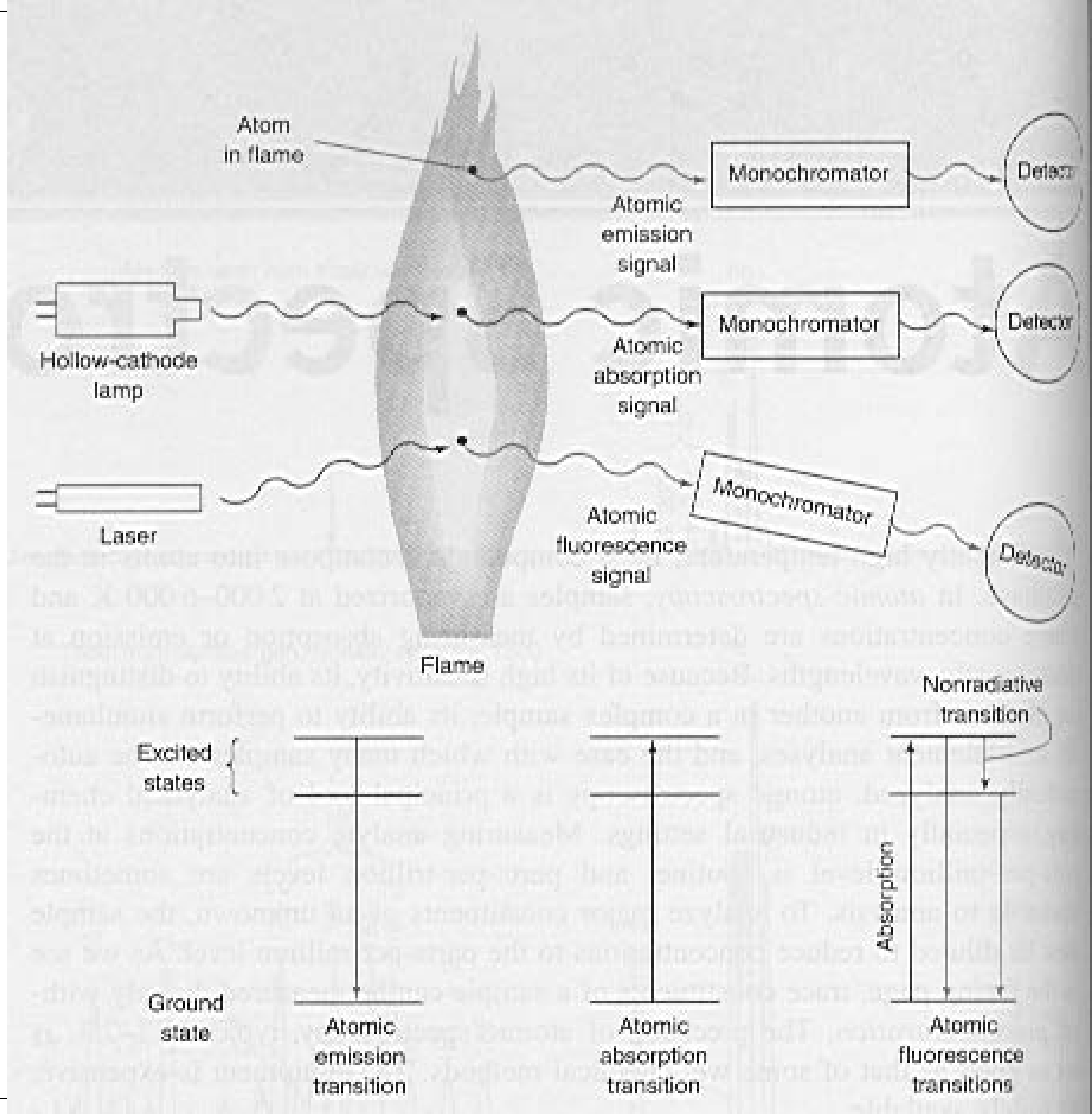
Atomic Spectroscopy: Instrument Design

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

(Harris, Chapt. 22)
(pp.615-635)

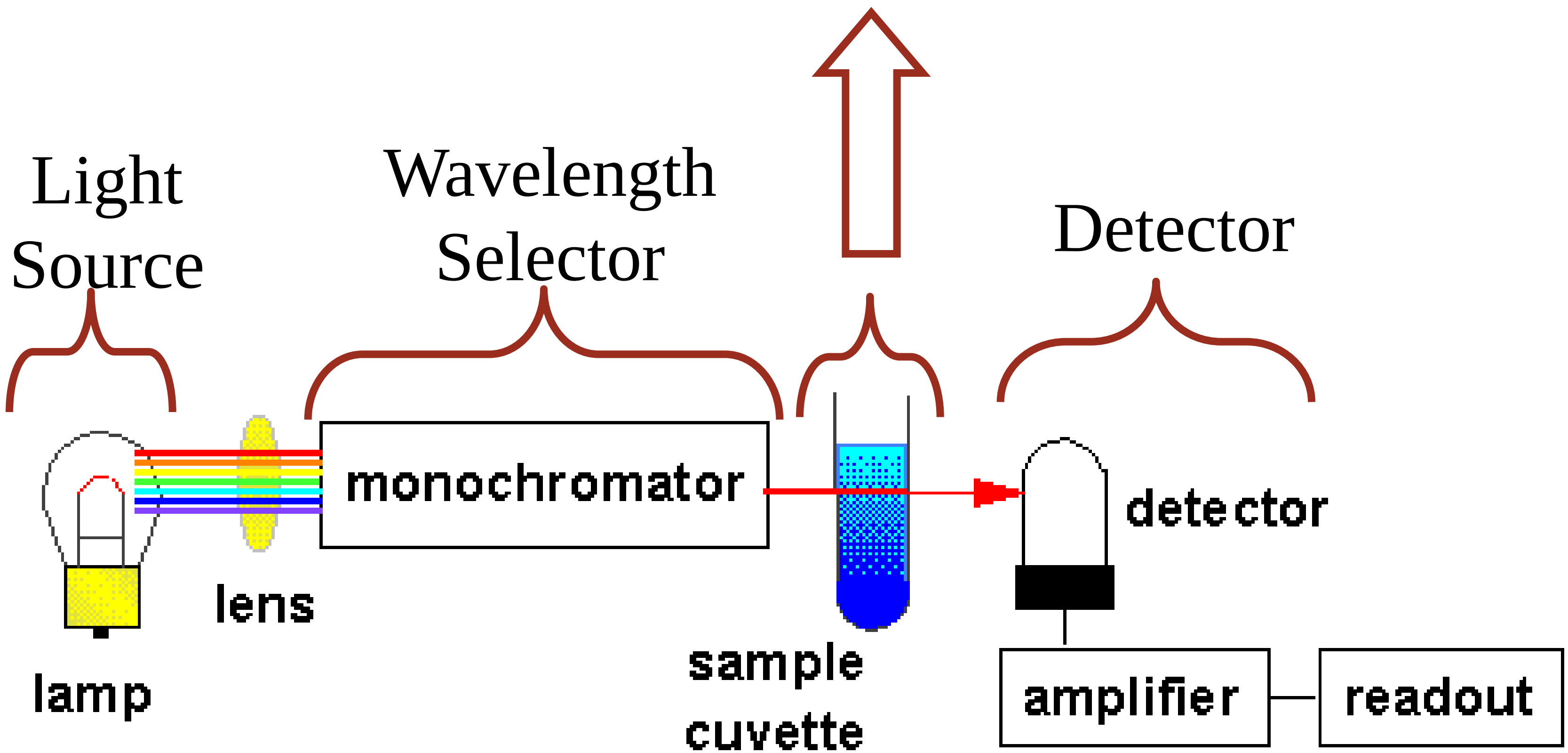
# Atomic Spectrophotometry

- Use
  - Analysis of metals
  - Very sensitive
- Three types
  - Absorption (AAS)
    - Flame and electrothermal (furnace)
  - Emission (AES)
    - Often used with plasma
  - Fluorescence


Atom
in flame
Monochromator
Detector
Atomic
emission
signal
Hollow-cathode
lamp
Monochromator
Detector
Atomic
absorption
signal
Laser
Monochromator
Detector
Atomic
fluorescence
signal
Flame
Excited
states
Ground
state
Atomic
emission
transition
Atomic
absorption
transition
Nonradiative
transition
Absorption
Atomic
fluorescence
transitions

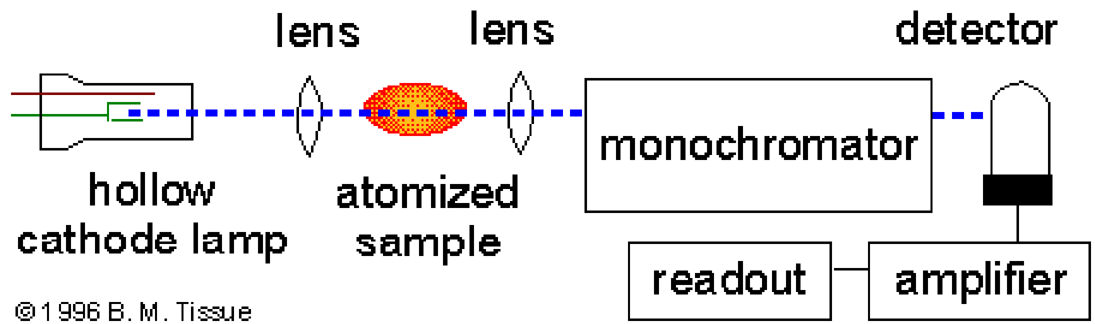
# Atomic Absorption Spectrophotometers

- Sample holder is replaced with an atomizer

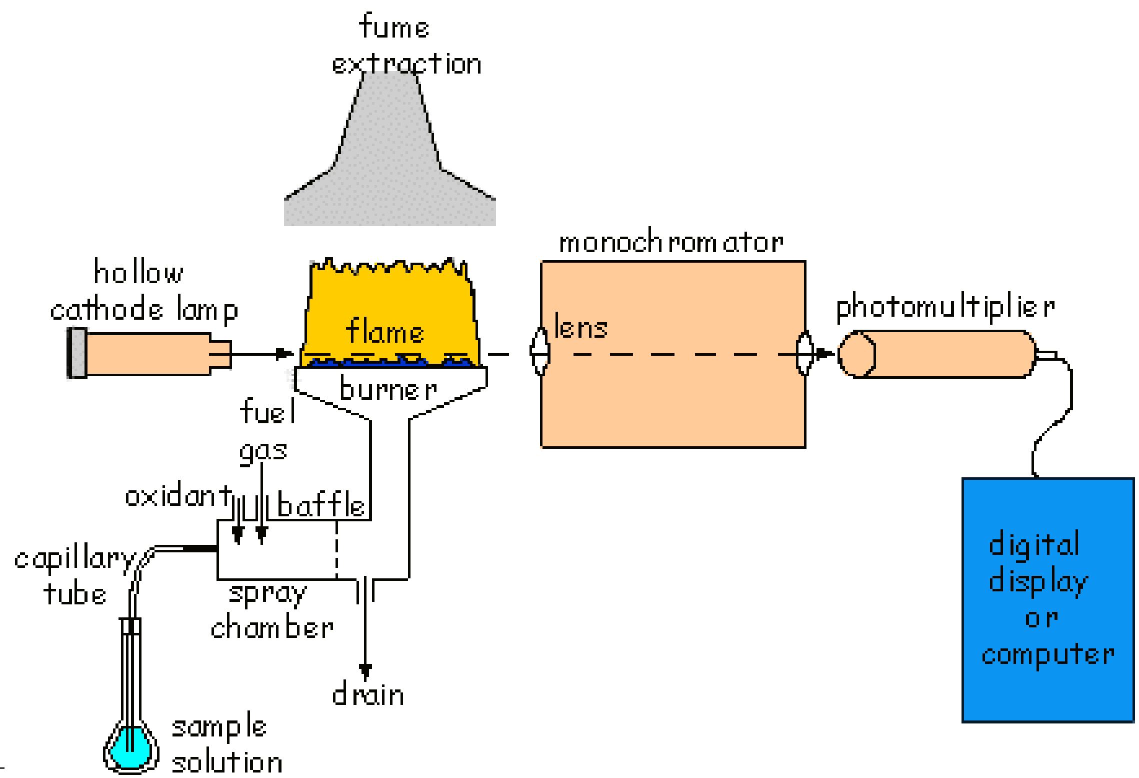


# Atomic Absorption

- General




- Flame



# Possible transitions

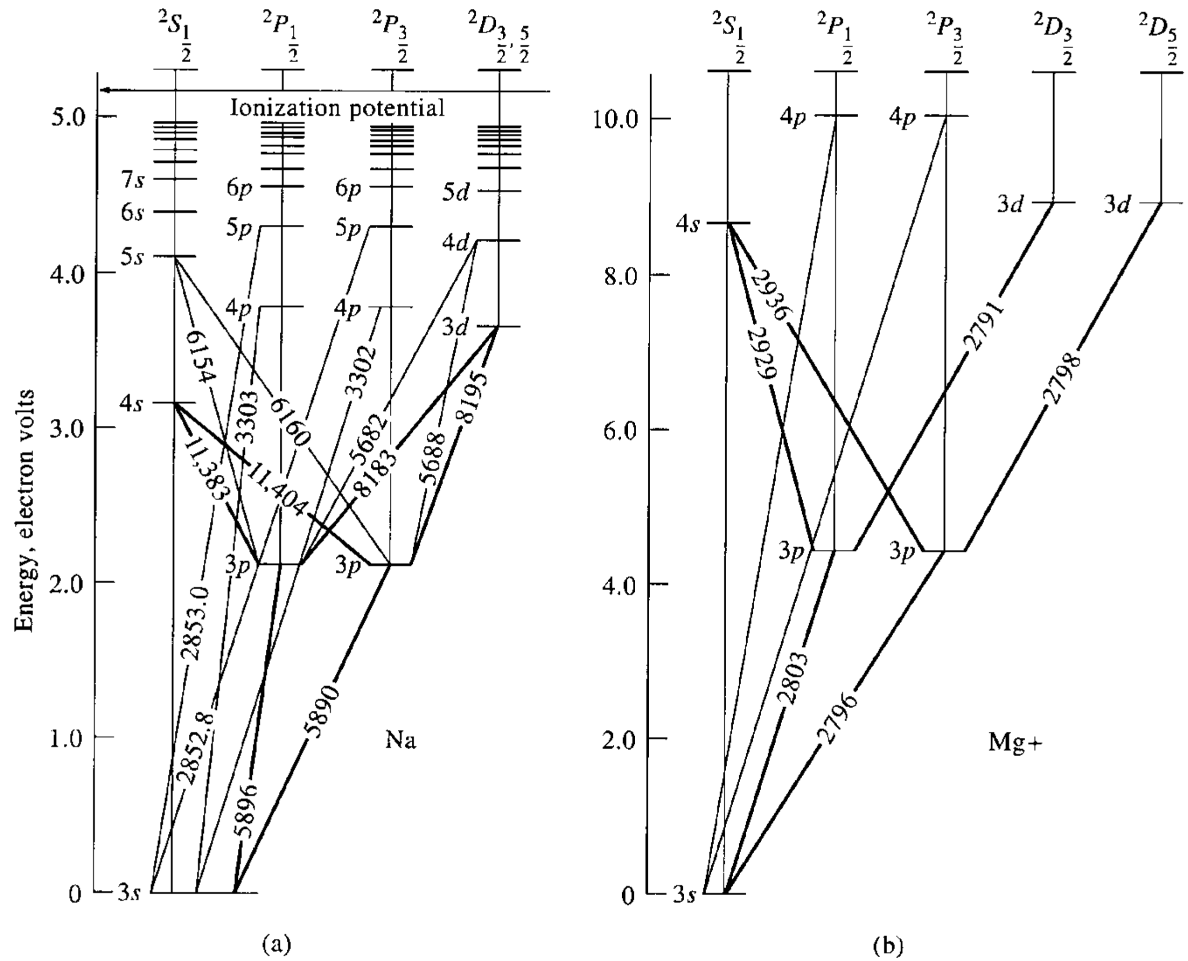
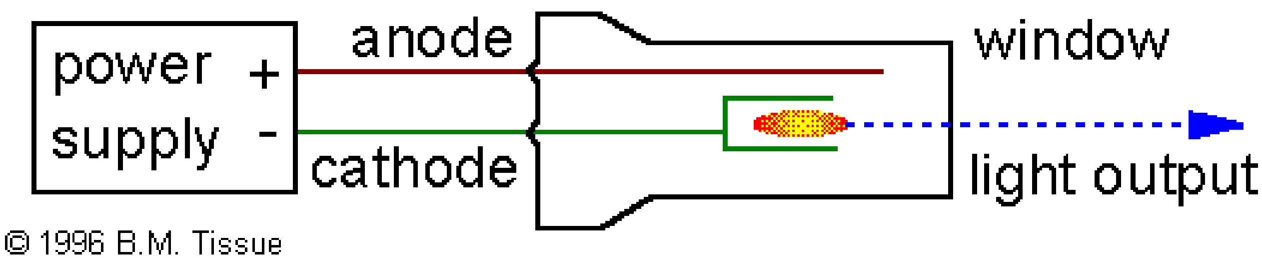
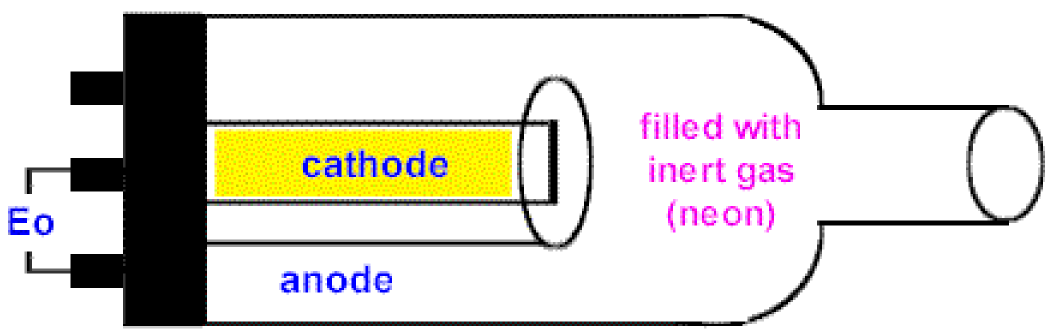



**Figure 8-1** Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

# Light Source

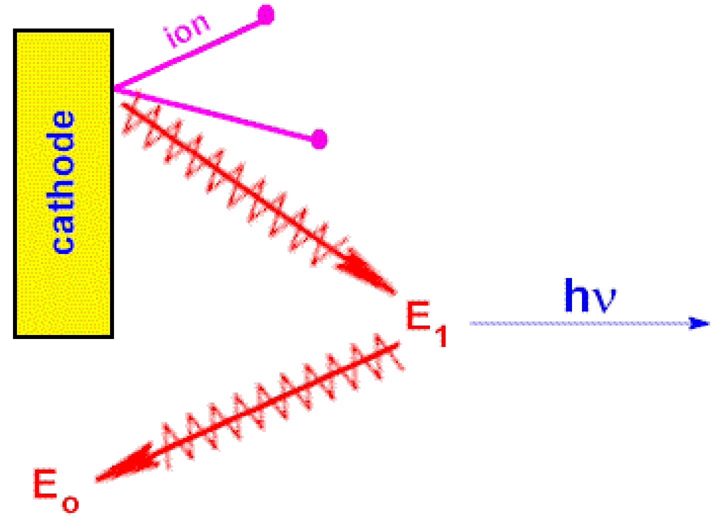
- Hollow Cathode Lamps



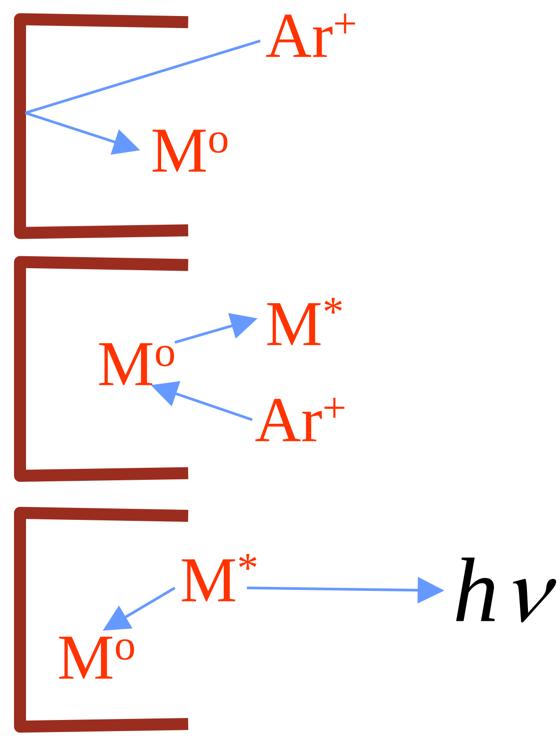




The cathode is covered with the element of interest.

# 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

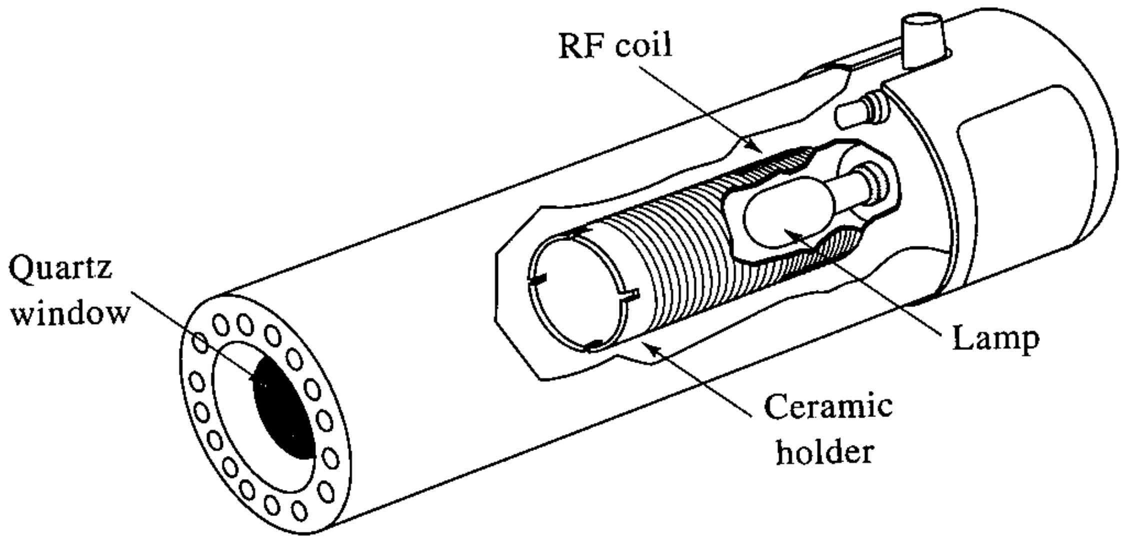


# Hollow Cathode Lamps

- 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

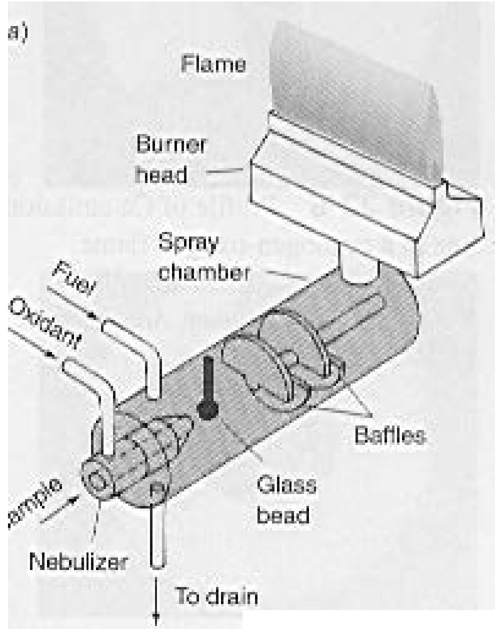
# Electrodeless discharge lamps (EDL)

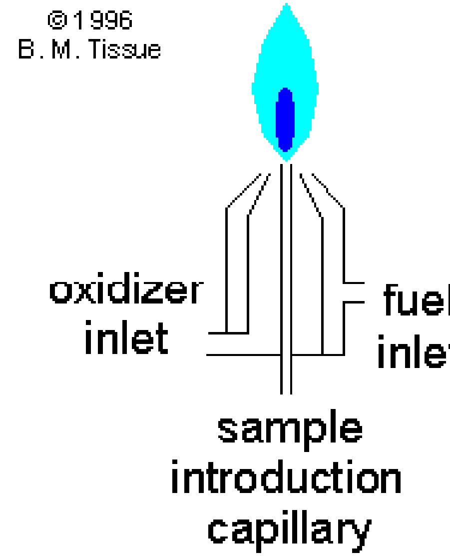
- Features
  - Ratio frequency is applied to a coil
    - Excites elements or its salts inside quartz bulb
  - Requires a special power supply
- Comparison with hollow cathode lamps
  - EDLs are brighter, more intense
    - Give lower MDLs for A
  - EDLs have a longer life
  - EDLs have some probler

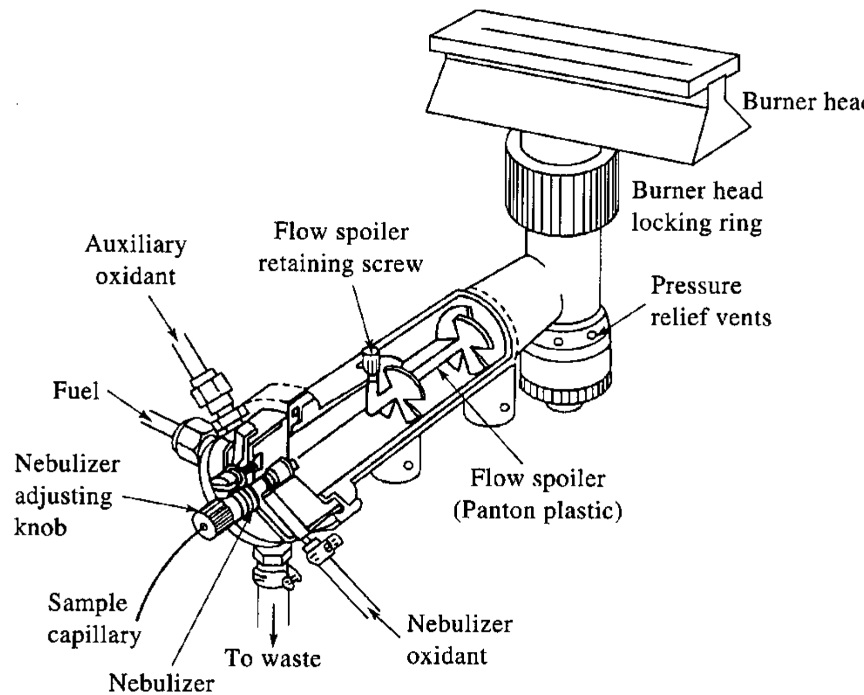


# Flame

- Burner design



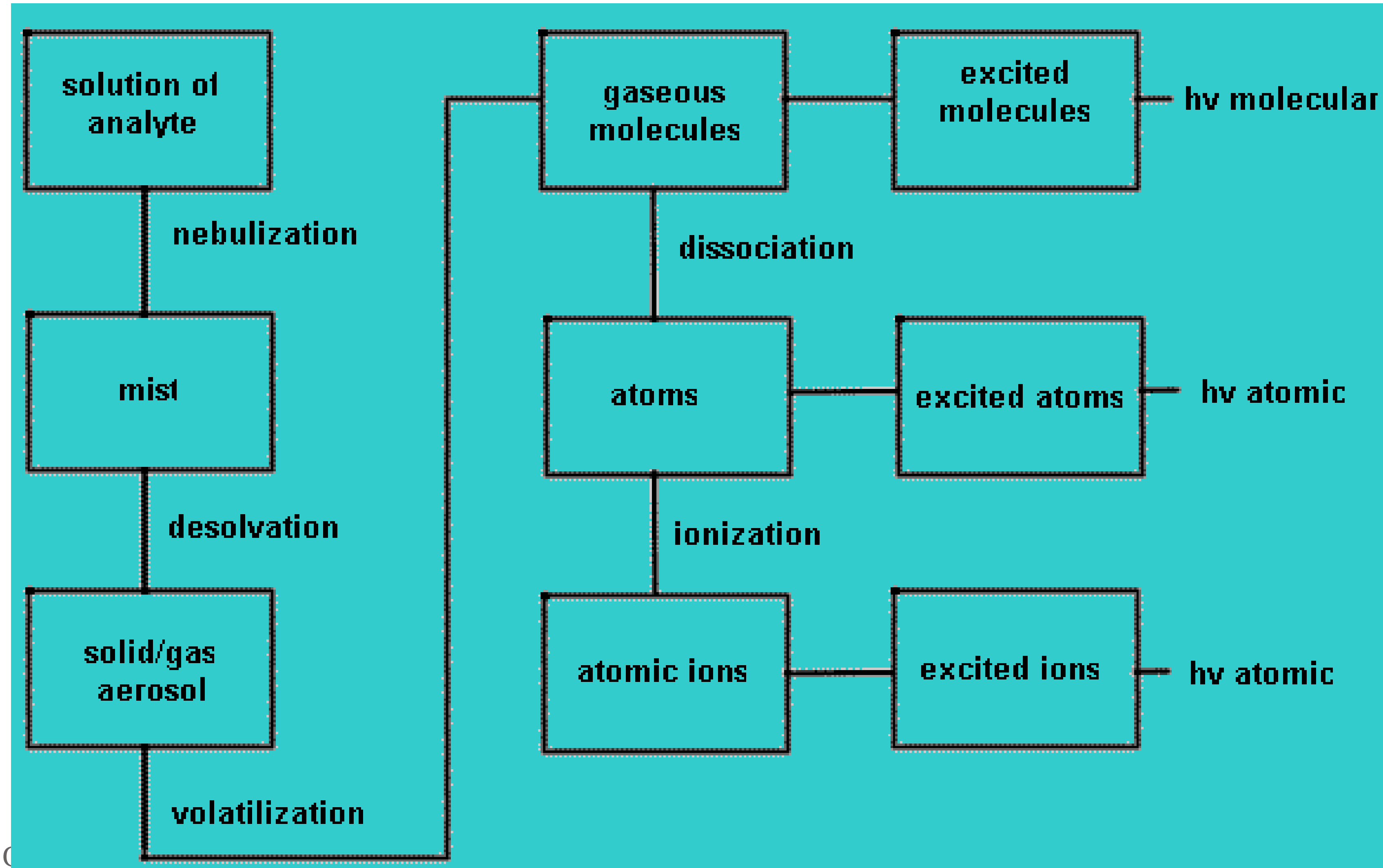



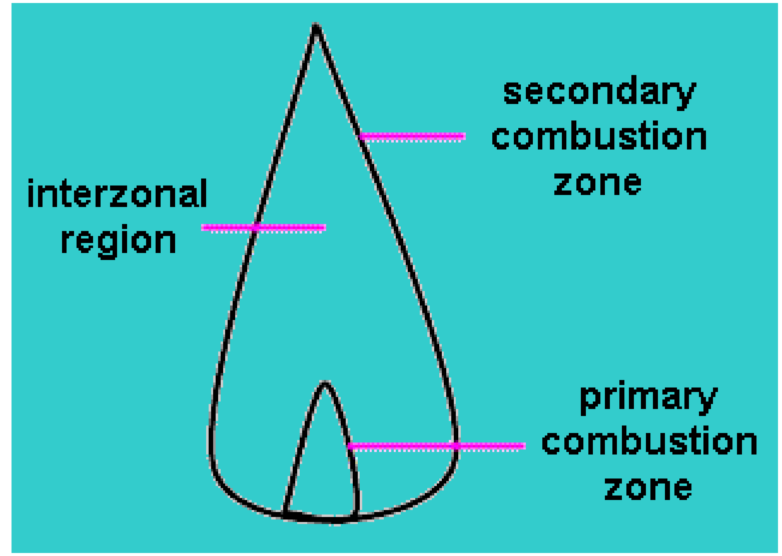

## Temperatures of some common flames

| Fuel | Oxidant | Temperature (K) |
|---|---|---|
| $H_2$ | Air | 2000-2100 |
| $C_2H_2$ | Air | 2100-2400 |
| $H_2$ | $O_2$ | 2600-2700 |
| $C_2H_2$ | $N_2O$ | 2600-2800 |

# Flame AA sample treatment



# Temperature



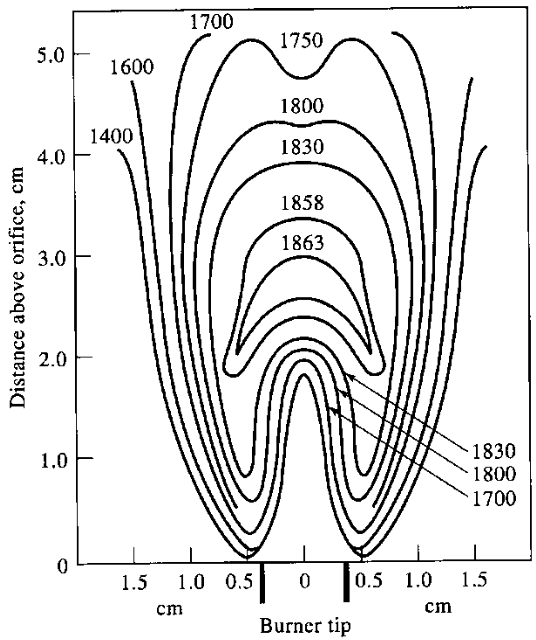




**Figure 9-3** Temperature profiles in °C for a natural

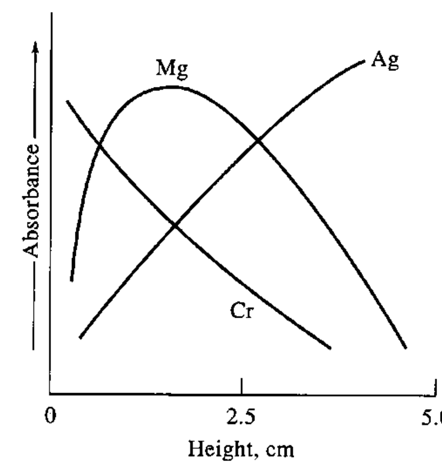
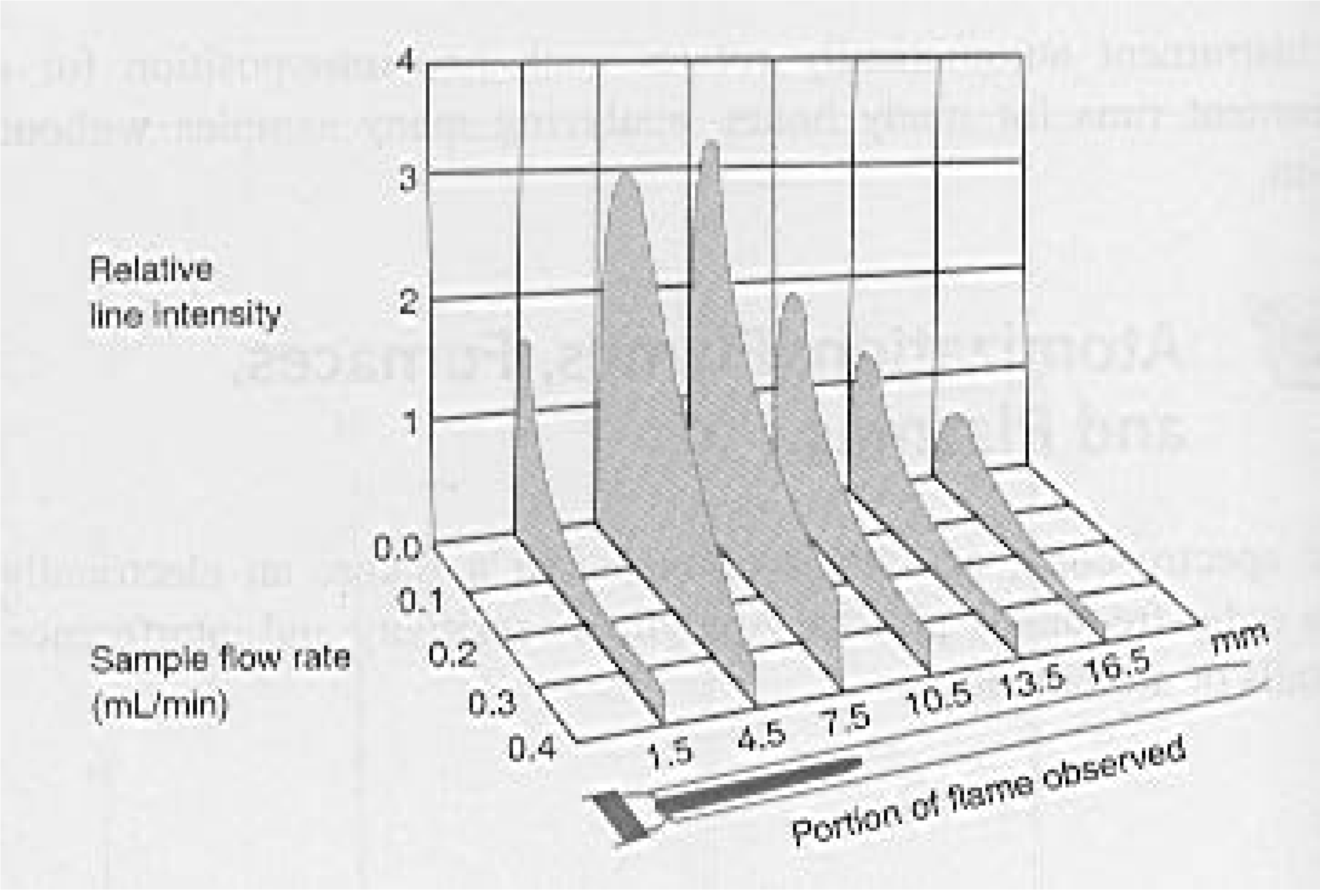
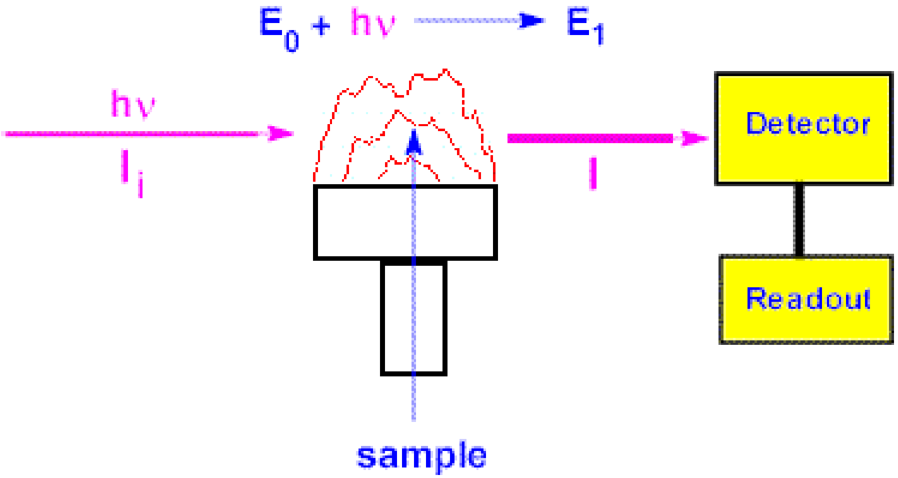


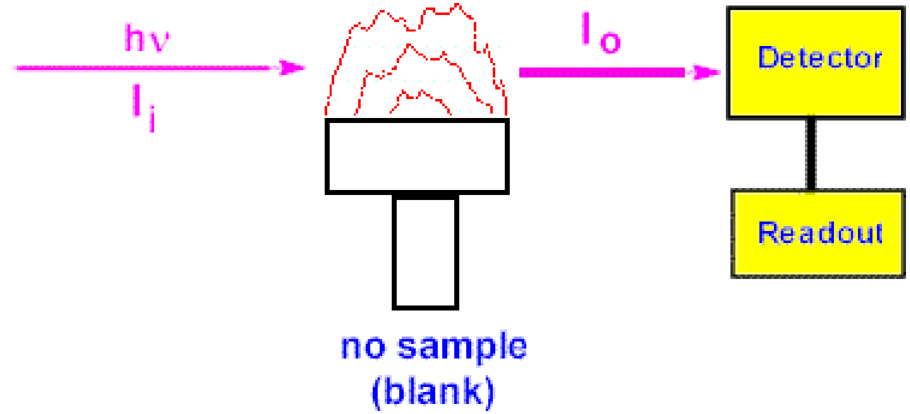

**Figure 9-4** Flame absorbance profile for three elements.

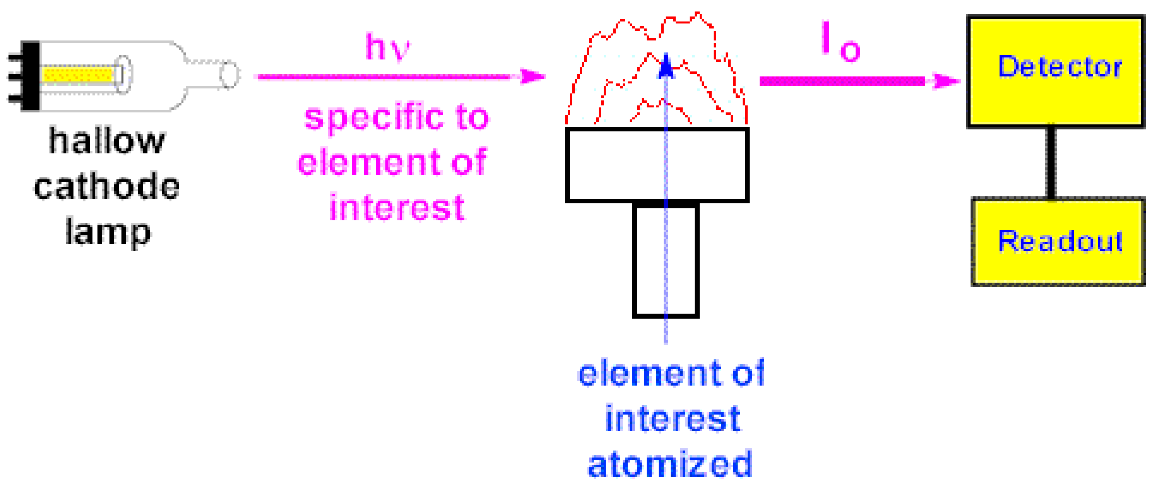
# Impact of flow and position



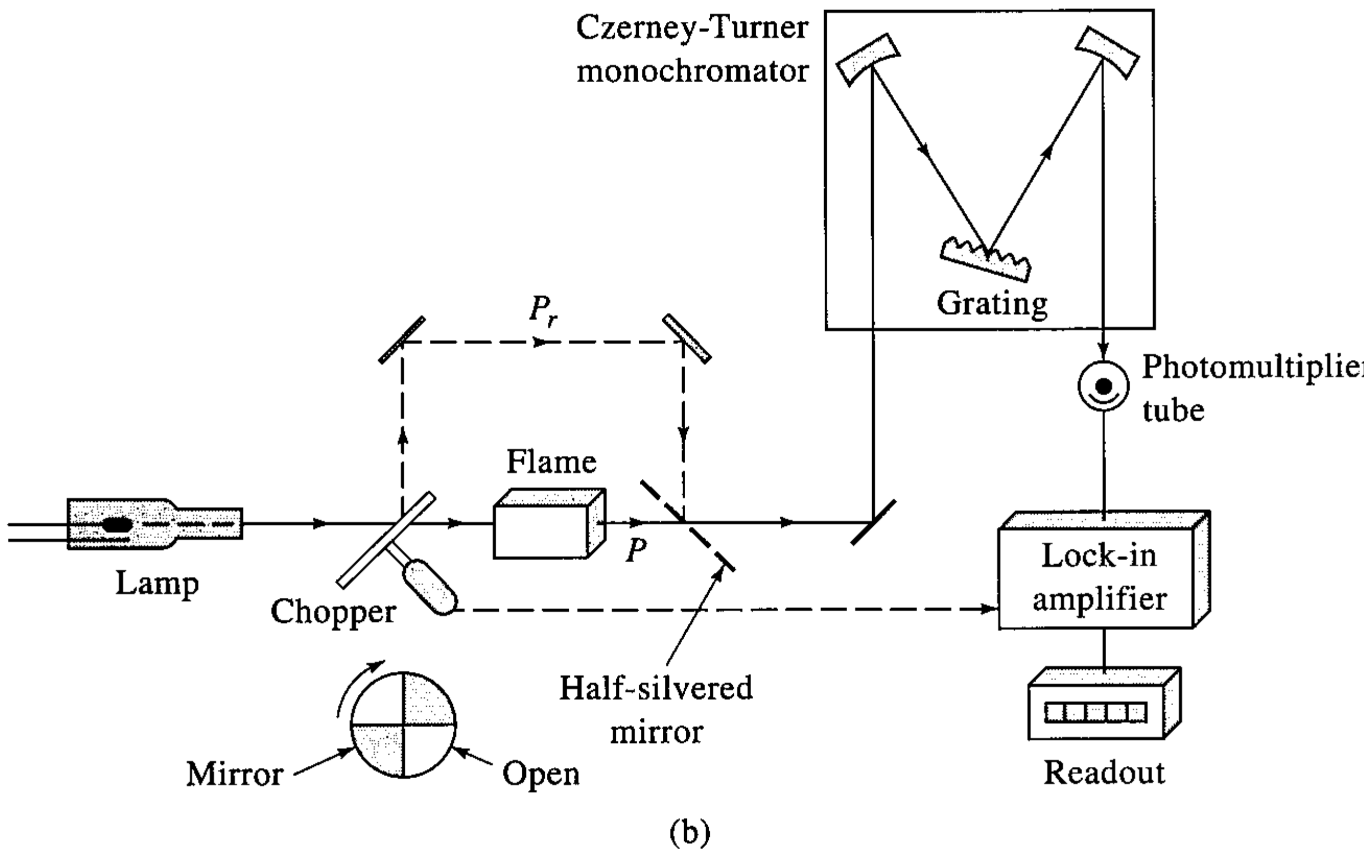



The energy (I) passing out of the flame is the difference between the incoming energy ($I_i$) and the energy absorbed by the sample to raise it to an excited state.



# Instrument Design



# Background Correction

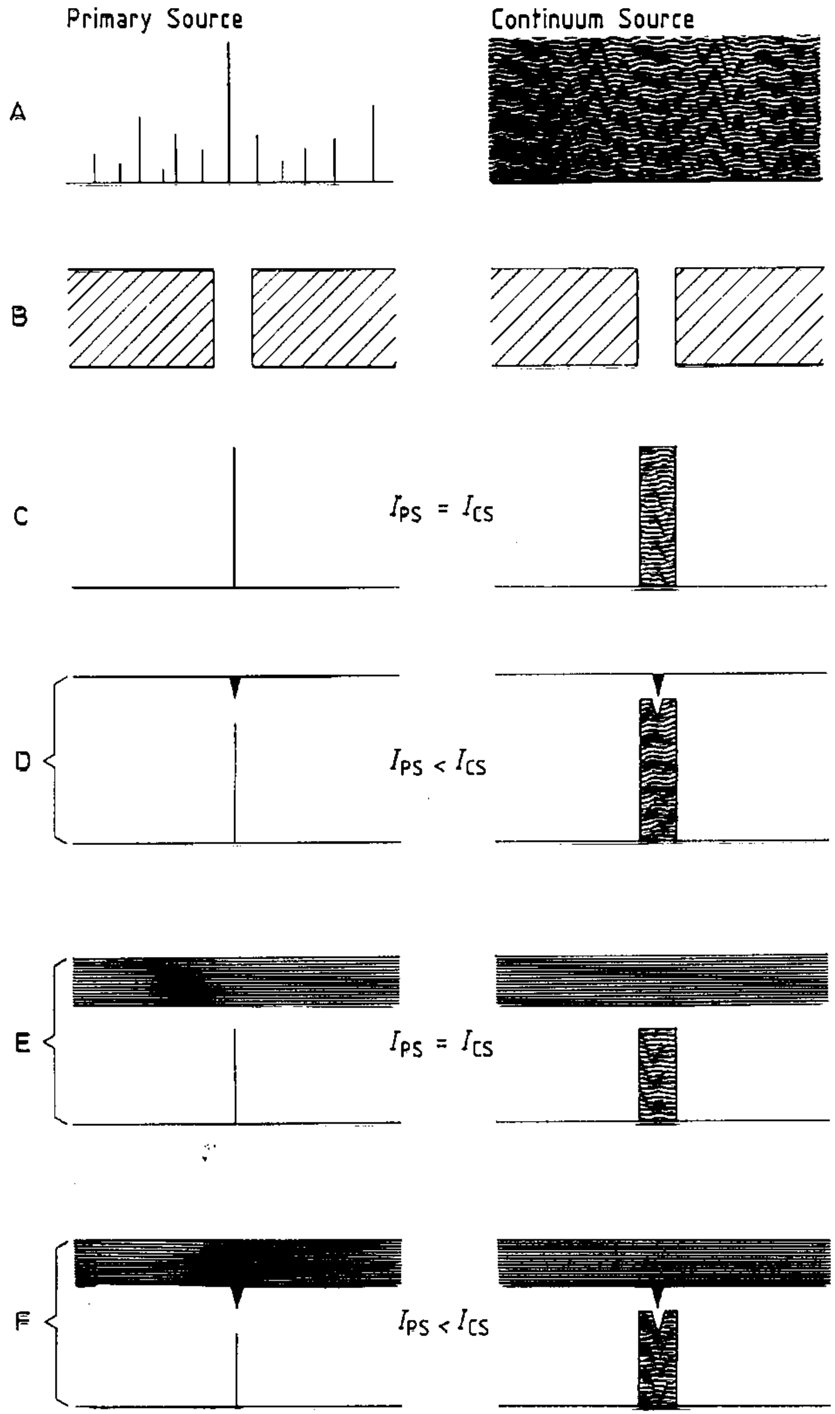



**Figure 77.** Mode of operation of a deuterium background corrector.— **A** The primary source emits a line spectrum while the deuterium lamp emits a continuum. **B** The exit slit of the monochromator isolates the resonance line from the spectrum of the primary source, with a half-intensity width of approximately 0.002 nm, and passes a band of radiation from the deuterium lamp equivalent to the selected bandpass (around 0.2 or 0.7 nm). **C** The radiant intensities of the two sources are equalized within the observed spectral range. **D** For normal atomic absorption by the analyte element, $I_{PS}$ is attenuated by an amount equivalent to its concentration, while $I_{CS}$, in the first approximation, is not attenuated. **E** Broad band background attenuates the intensity of both sources to the same degree. **F** Atomic absorption by the analyte in addition to the background attenuates $I_{PS}$ again by an amount equivalent to its concentration, while $I_{CS}$, in the first approximation, is not further attenuated.

# Bandwidth

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

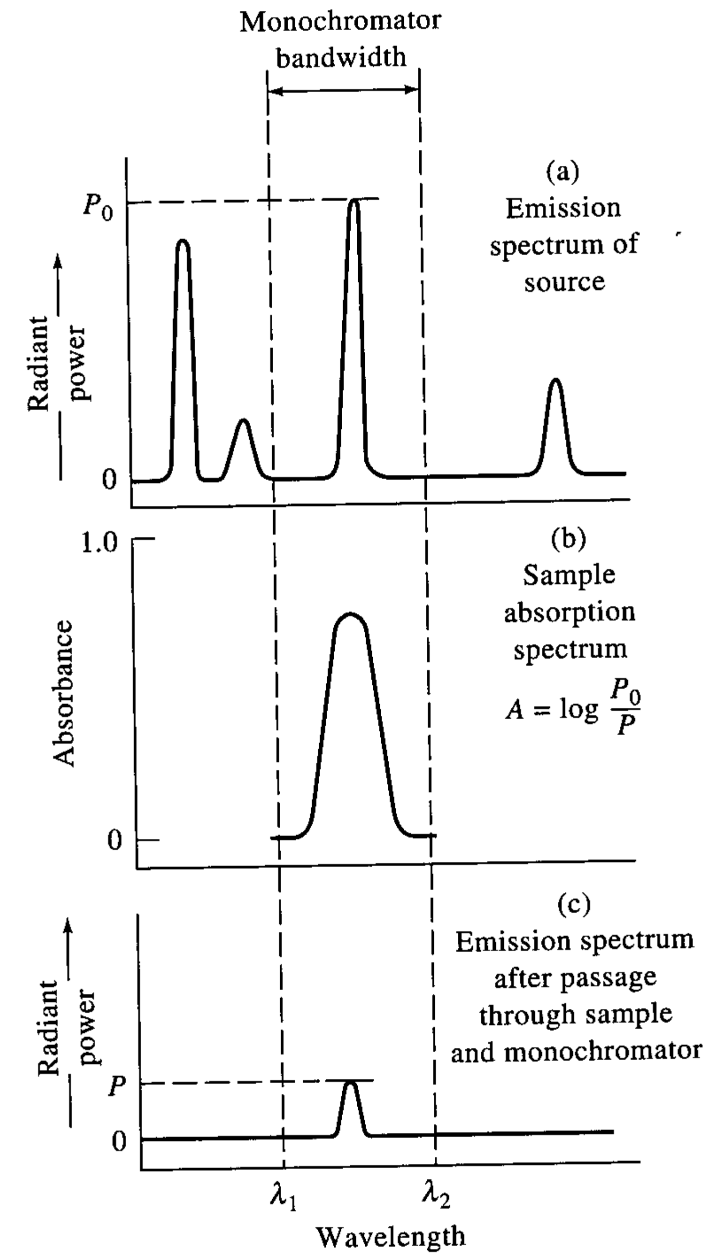
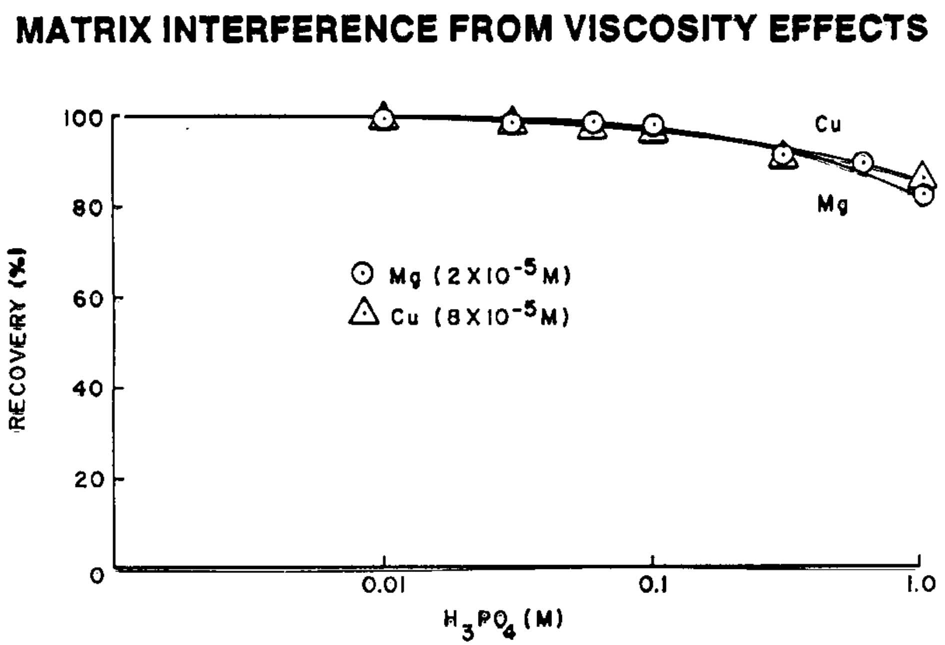



**Figure 9-10** Absorption of a resonance line by atoms.

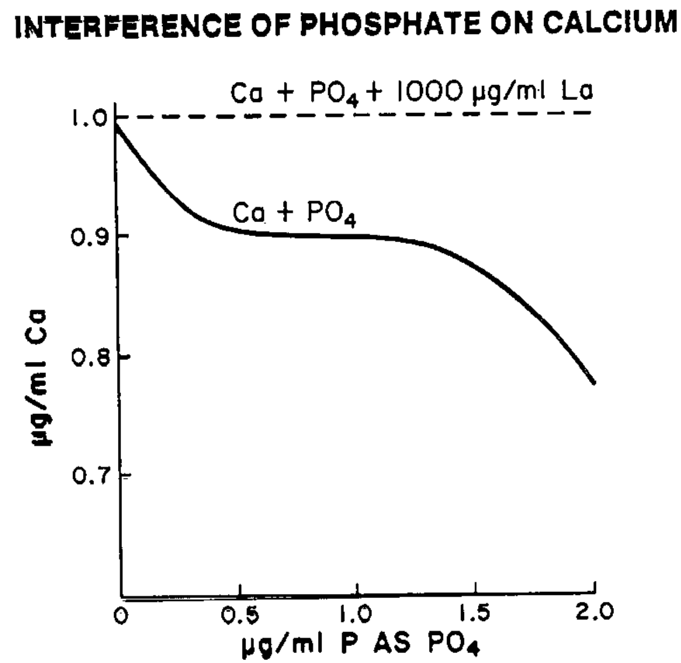
# Matrix Effects 1

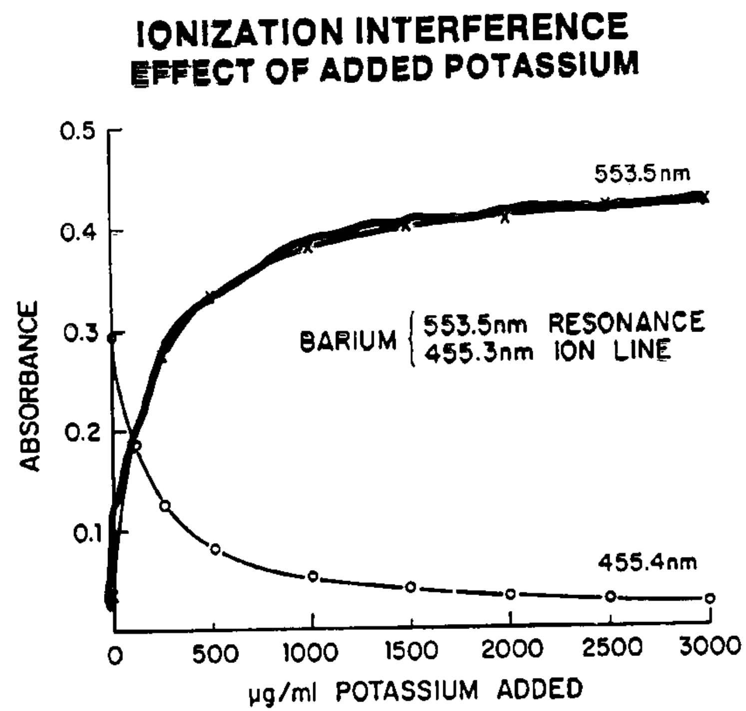
- Viscosity
  - Phosphoric acid example
  - Sulfuric acid vs MeOH



# 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