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Print version

CEE 772: Instrumental Methods in Environmental Analysis

Lecture #6

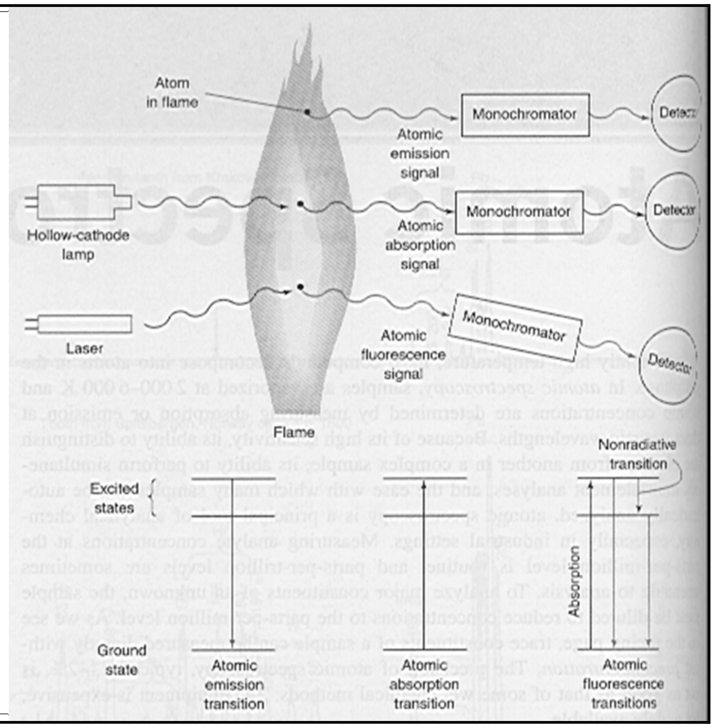
Atomic Spectroscopy: Instrument Design

(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



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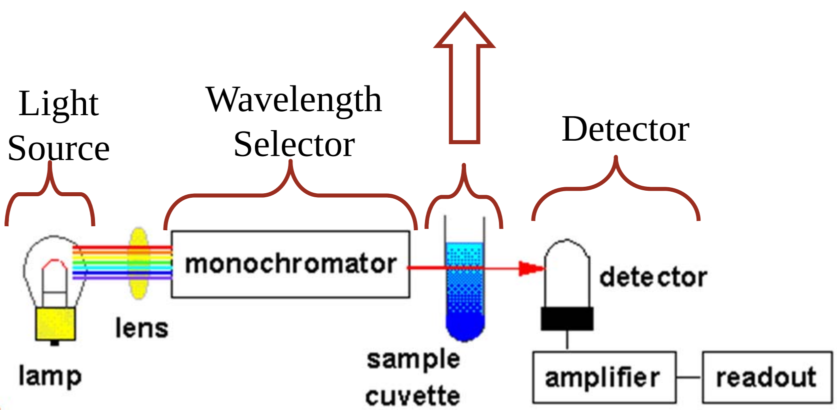
Atomic Absorption Spectrophotometers

- Sample holder is replaced with an atomizer



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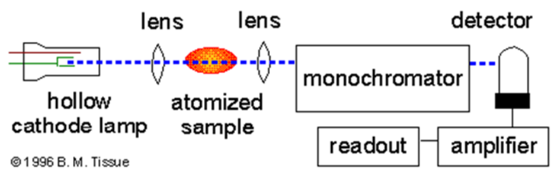
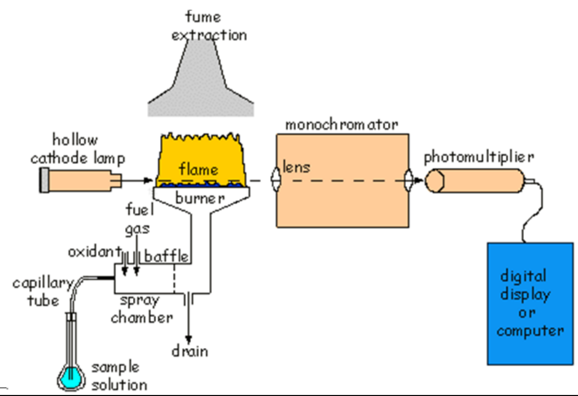
Atomic Absorption

- General



- Flame



Possible transitions

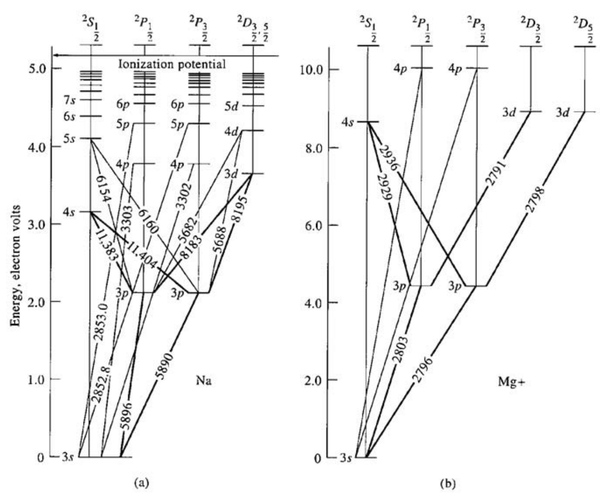


Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

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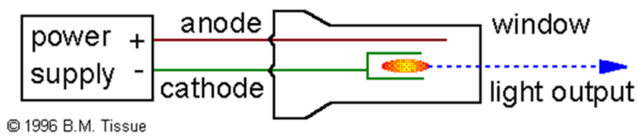
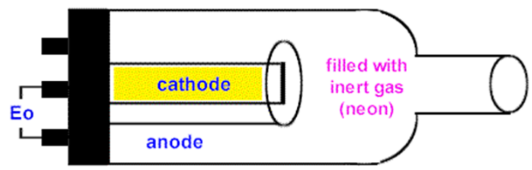
Light Source

- Hollow Cathode Lamps





The cathode is covered with the element of interest.

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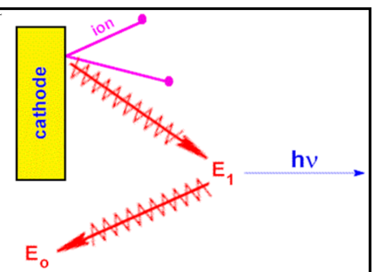
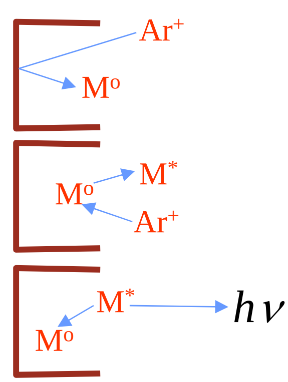
Hollow Cathode Lamps



- 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



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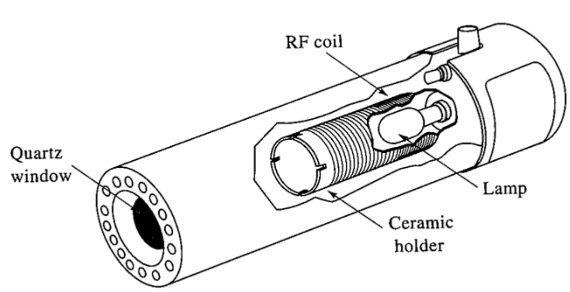
Hollow Cathode Lamps

- 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

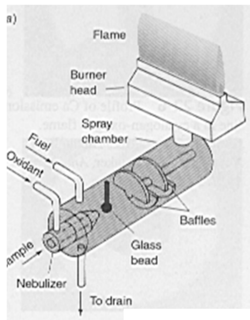
Electrodeless discharge lamps (EDL)

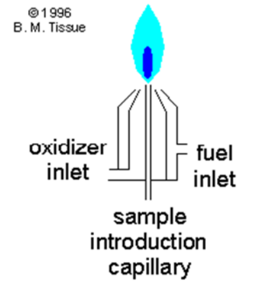
- Features
  - Ratio frequency is applied to a coil
    - Excites elements or its salts inside quartz bulb
  - Requires a special power supply
- Comparison with hollow cathode lamps
  - EDLs are brighter, more intense
    - Give lower MDLs for A:
  - EDLs have a longer life
  - EDLs have some problen



Flame

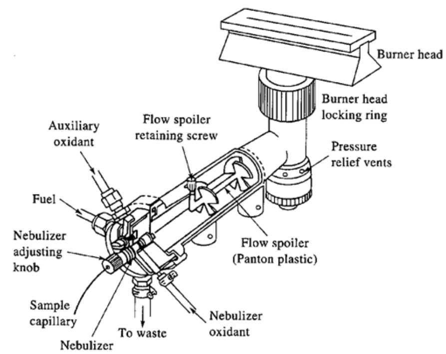
- Burner design





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



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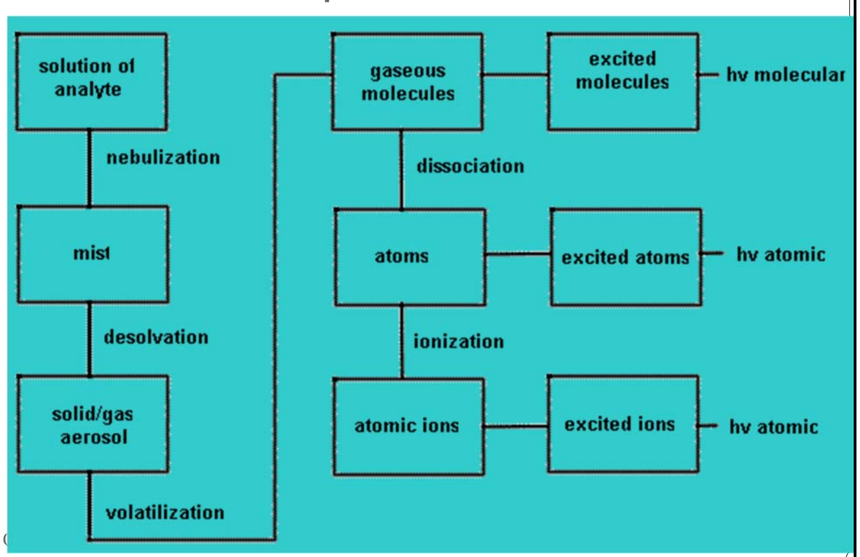
Flame AA sample treatment



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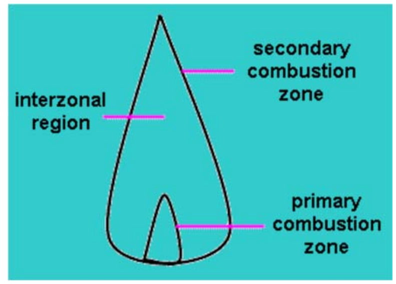
Temperature



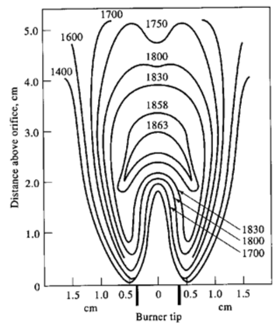


Figure 9-3 Temperature profiles in °C for a natural

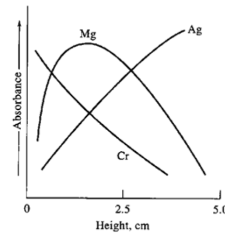
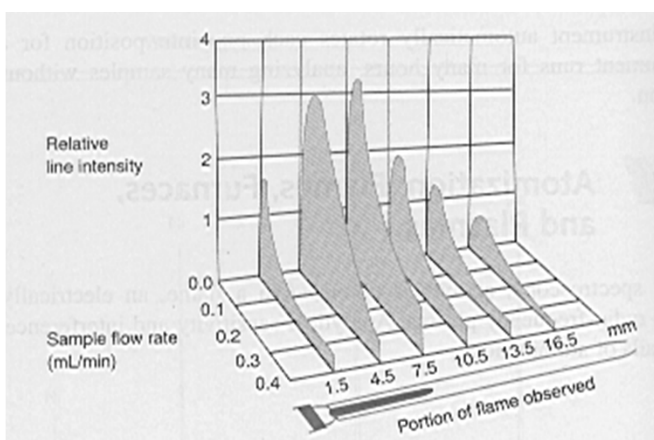
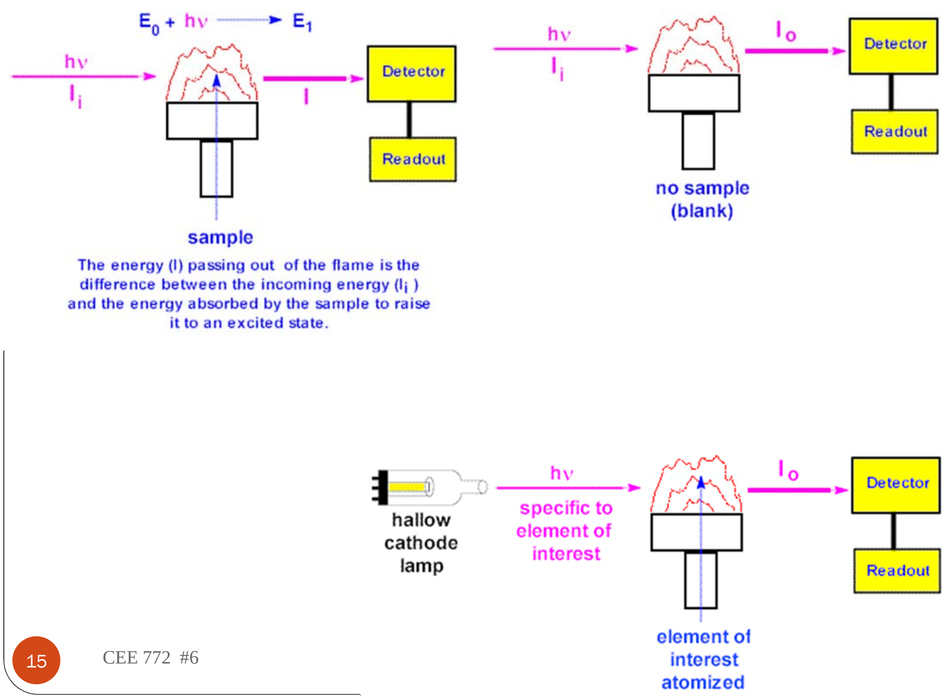


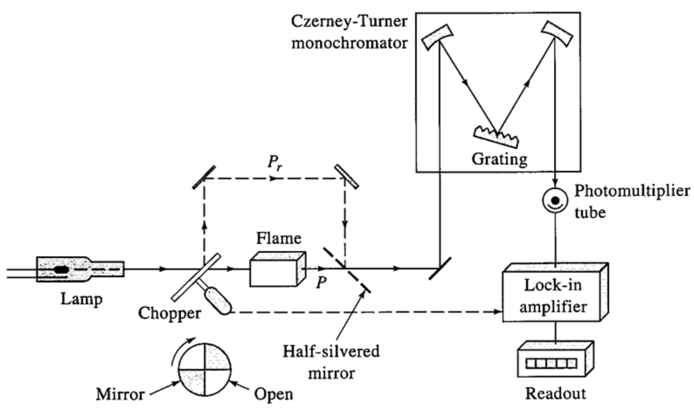
Figure 9-4 Flame absorbance profile for three elements.

Impact of flow and position





Instrument Design



(b)

Background Correction

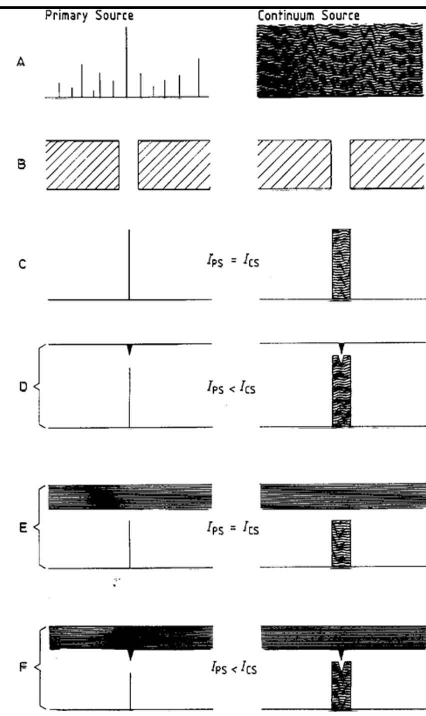


Figure 77. Mode of operation of a deuterium background corrector.— **A** The primary source emits a line spectrum while the deuterium lamp emits a continuum. **B** The exit slit of the monochromator isolates the resonance line from the spectrum of the primary source, with a half-intensity width of approximately 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

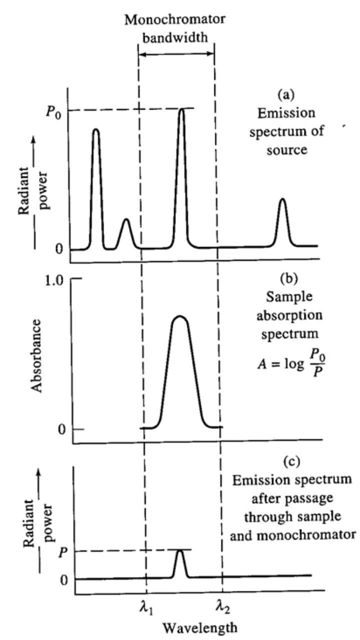
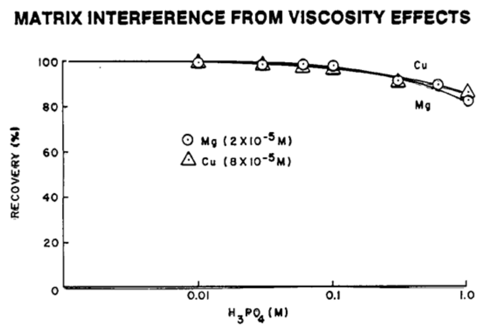


Figure 9-10 Absorption of a resonance line by atoms.

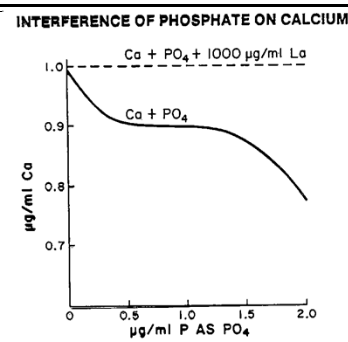
Matrix Effects 1

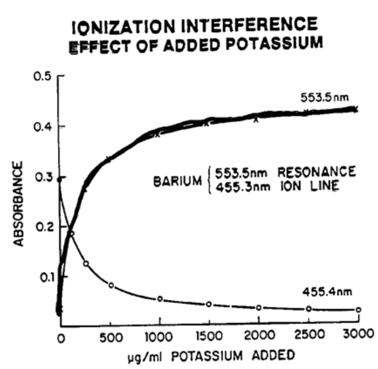
- Viscosity
  - Phosphoric acid example
  - Sulfuric acid vs MeOH



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