

Chemistry 4631

Instrumental Analysis

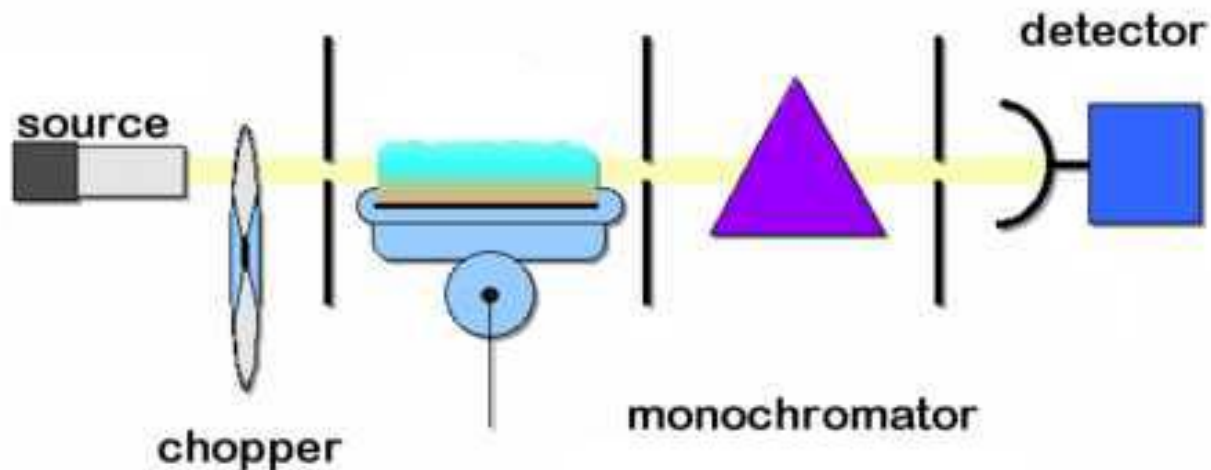
Lecture 16



Optical Atomic Spectrometry

Atomic absorption equipment

In its simplest form, an AA resembles a single beam spectrophotometer.



Optical Atomic Spectrometry

Instrumentation

Radiation sources

Hollow cathode lamp

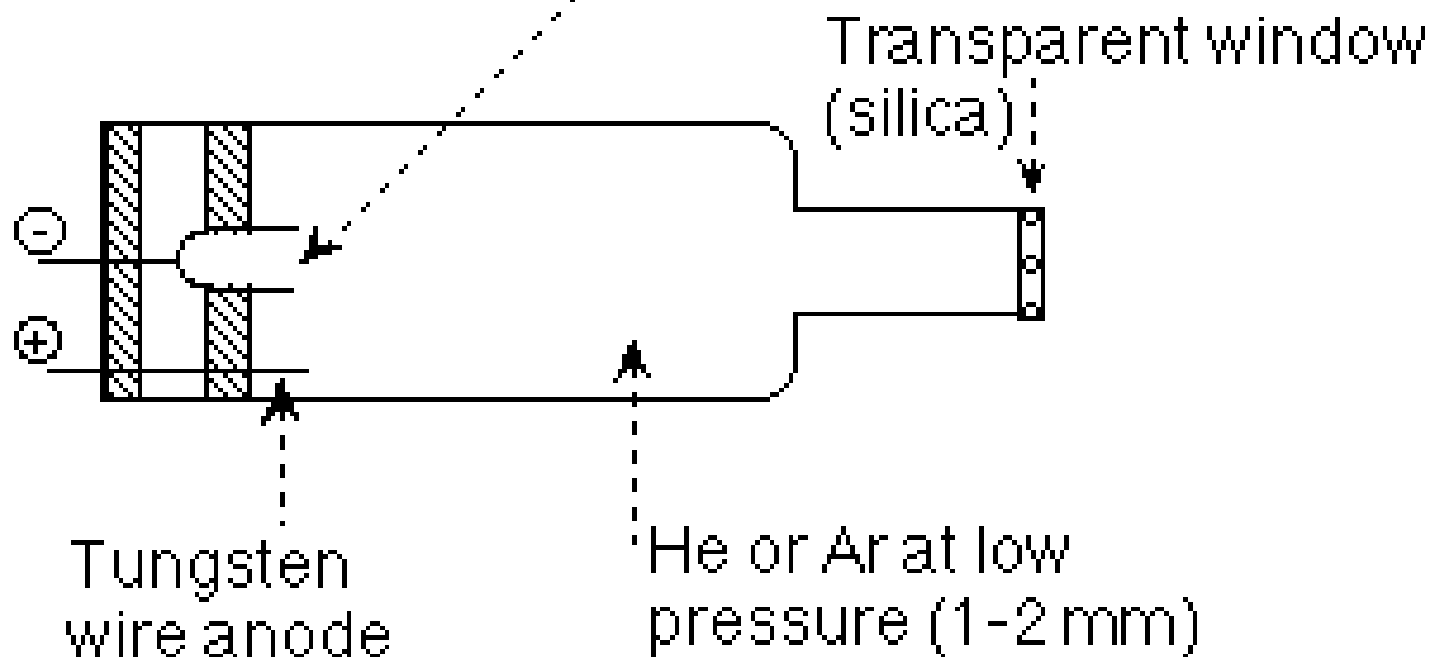
Most common source

Consist of W anode and a cathode sealed in a glass tube filled with Ne or Ar.

Optical Atomic Spectrometry

Hollow cathode lamp

Hollow cylinder cathode coated with element same as analyte



Optical Atomic Spectrometry

Radiation sources

Hollow cathode lamp

A potential of 300 V is applied across the electrodes and generates a current of 5-15 mA, ionizing the inert gas.

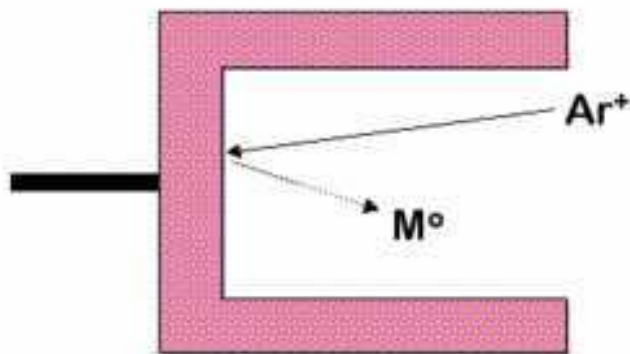
The ionize gas strikes the cathode surface with enough kinetic energy to sputter the metal from the surface.

The sputtered metal atoms are excited and emit characteristic radiation as they return to ground state.

Optical Atomic Spectrometry

Hollow cathode lamp

The lamp is filled with an inert gas like argon or neon. When a potential is applied, it causes the gas to become excited and it is driven towards the cathode.

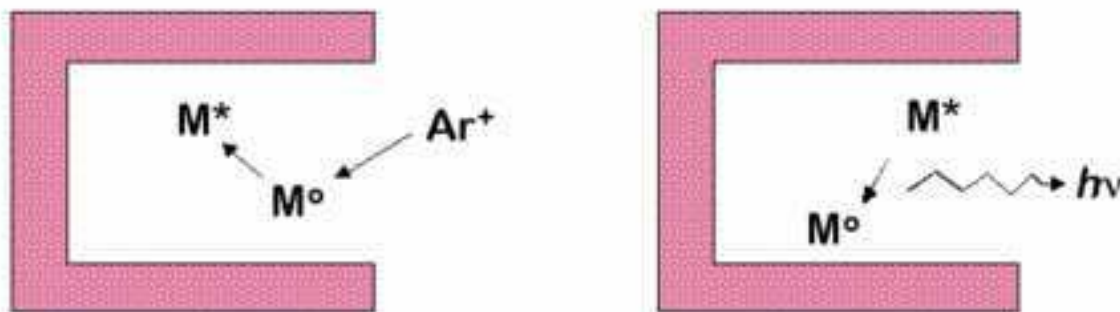


Metal atoms are then sputtered off the surface of the cathode.

Optical Atomic Spectrometry

Hollow cathode lamp

Repeated bombardment of the metal atom by the gas causes it to be excited. It ultimately relaxes, producing specific atomic emission lines.



Optical Atomic Spectrometry

Radiation sources

Electroless Discharge Lamps (EDLs)

Constructed from a sealed quartz tube containing small quantity of inert gas and metal.

A field of radio-frequency or microwave radiation is applied and ionizes the inert gas which excited the metal atoms that emit a spectrum.

Available for ~ 15 elements

Optical Atomic Spectrometry

Electroless Discharge Lamps (EDLs)

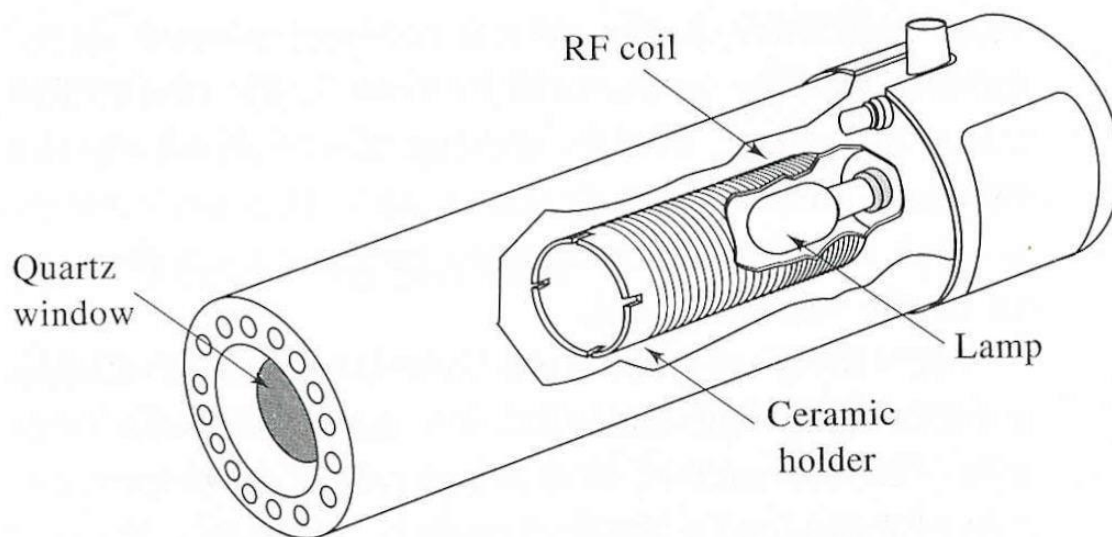


Figure 9-12 Cutaway of electrodeless discharge lamp. (From W. B. Barnett, J. W. Vollmer, and S. M. DeNuzzo, *At. Absorption Newsletter*, 1976, 15, 33. With permission.)

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Optical Atomic Spectrometry

Radiation sources

Source Modulation

For AAS need to remove interferences caused by emission of radiation by the flame.

The monochromator removes much of this radiation, except radiation corresponding to the λ of the monochromator setting.

Optical Atomic Spectrometry

Radiation sources

Source Modulation

To eliminate these effects need to modulate the output of the source so the intensity fluctuates at a constant frequency.

The detector then receives two signals

- alternating one from the source
- continuous one from the flame

To accomplish this use a simple chopper or modulate the frequency of the source.

Optical Atomic Spectrometry

Atomization (Flames)

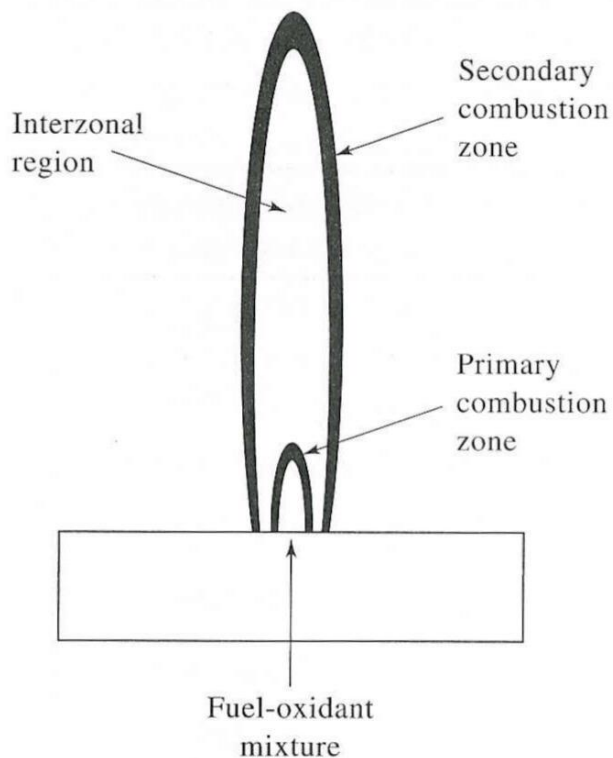


Figure 9-2 Regions in a flame.

Optical Atomic Spectrometry

Flame Profile

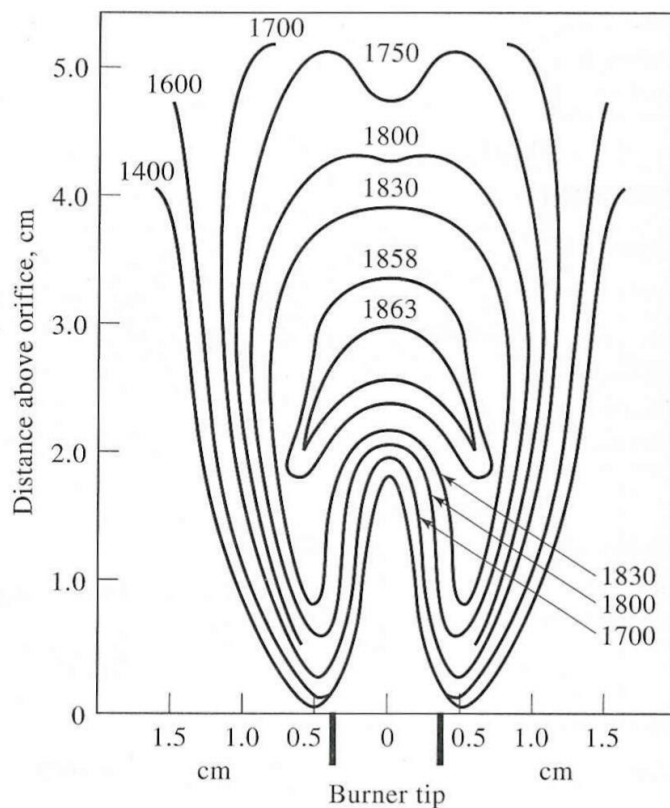


Figure 9-3 Temperature profiles in °C for a natural gas/air flame. (From B. Lewis and G. vanElbe, *J. Chem. Phys.*, 1943, 11, 94. With permission.)

Optical Atomic Spectrometry

“Cookbooks”

Element	Analysis line wavelength (nm)	Absorption sensitivity	Flame type
Cs	852.11	10	Air-C ₂ H ₂
Cu	324.75 327.40 217.89 218.17 222.57	10 4.7 1.2 1.0 0.6	Air-C ₂ H ₂
Dy	404.59 421.17 418.68	10 8.9 8.0	N ₂ O-C ₂ H ₂
Er	400.79 415.11 386.28	10 5.9 5.5	N ₂ O-C ₂ H ₂
Eu	459.40 462.72 466.19	10 8.7 7	N ₂ O-C ₂ H ₂
Fe	248.33 271.90 371.99 385.99	10 2.7 0.9 0.6	Air-C ₂ H ₂

Optical Atomic Spectrometry

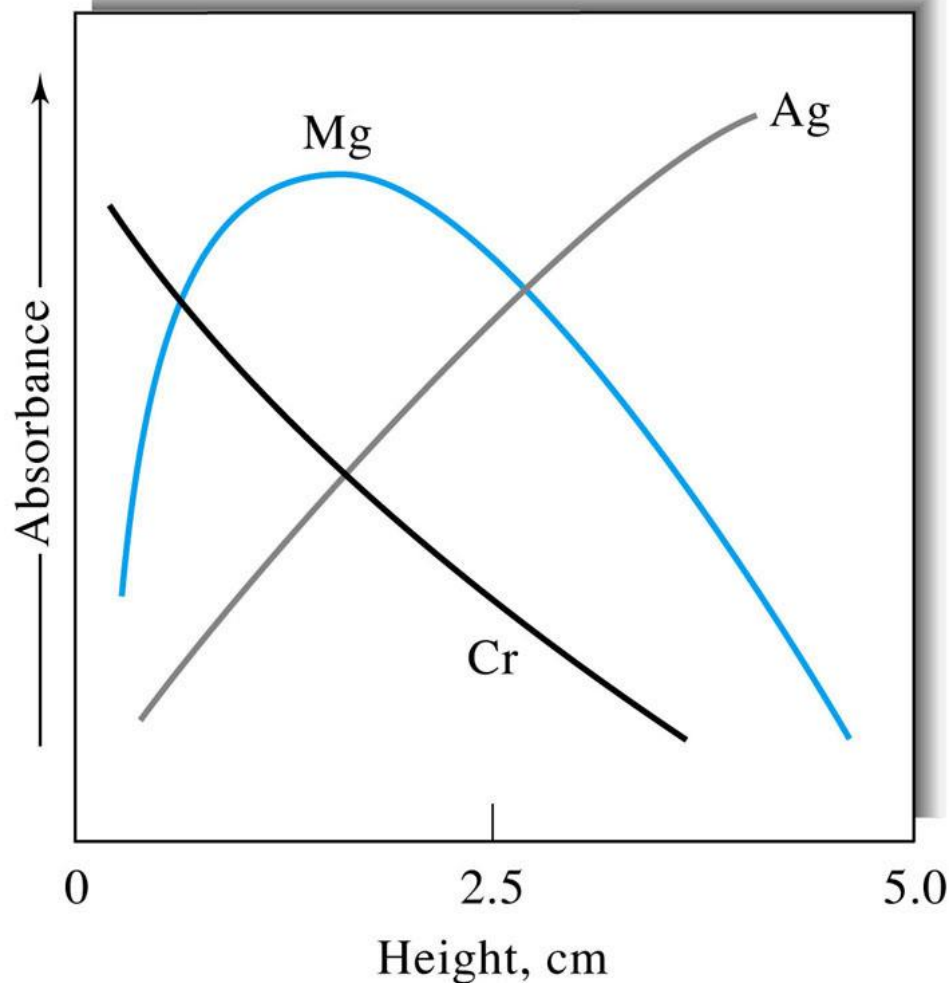
TABLE 9-1 Properties of Flames

Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, cm s⁻¹
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

Optical Atomic Spectrometry

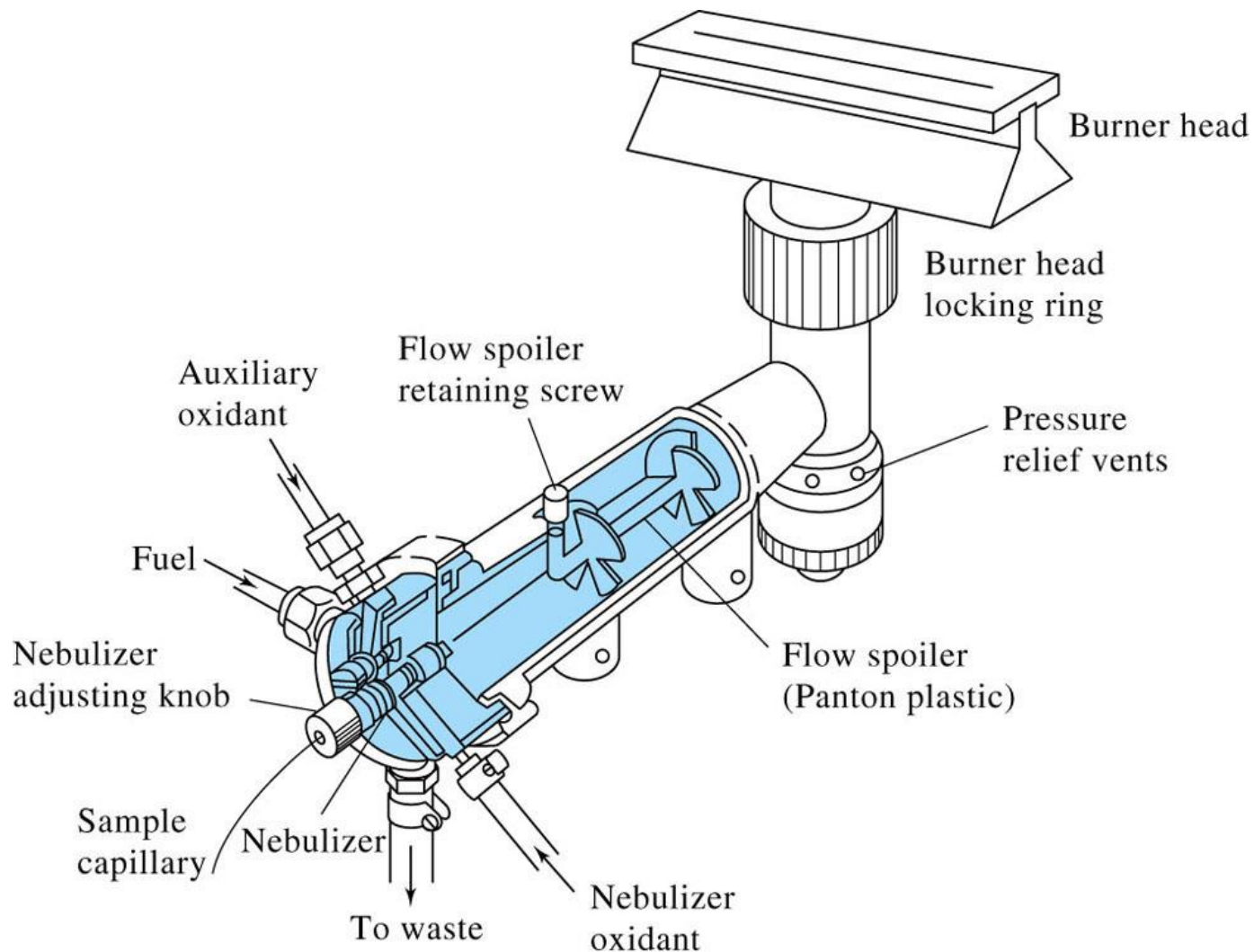
Flame Absorbance

Absorption profile
for different elements



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Optical Atomic Spectrometry



Optical Atomic Spectrometry

Electrothermal Atomization

- **First on the market in 1970's**
- **Sensitivity enhanced over flame atomization**

Optical Atomic Spectrometry

Electrothermal Atomization

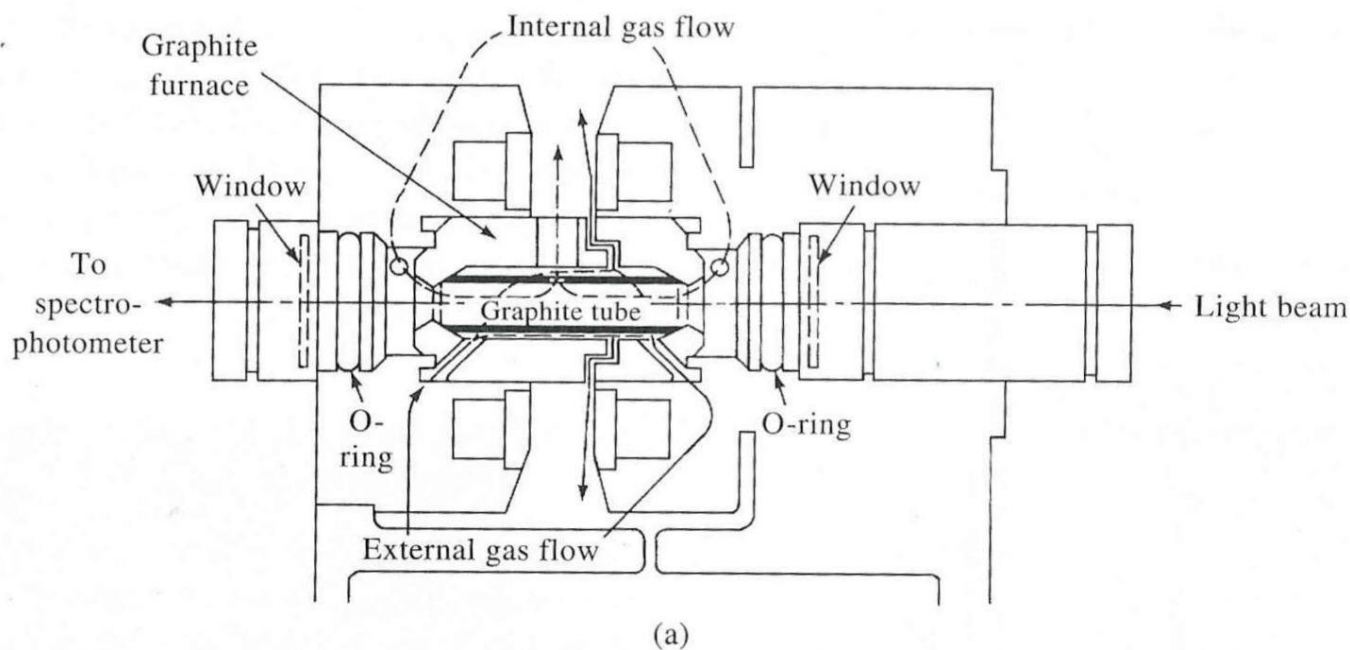


Figure 9-6 (a) Cross-sectional view of a graphite furnace. (Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.) (b) The L'vov platform and its position in the graphite furnace. (Reprinted with permission from W. Slavin, *Anal. Chem.*, 1982, 54, 689A. Copyright 1982 American Chemical Society.)

Optical Atomic Spectrometry

Electrothermal Atomization

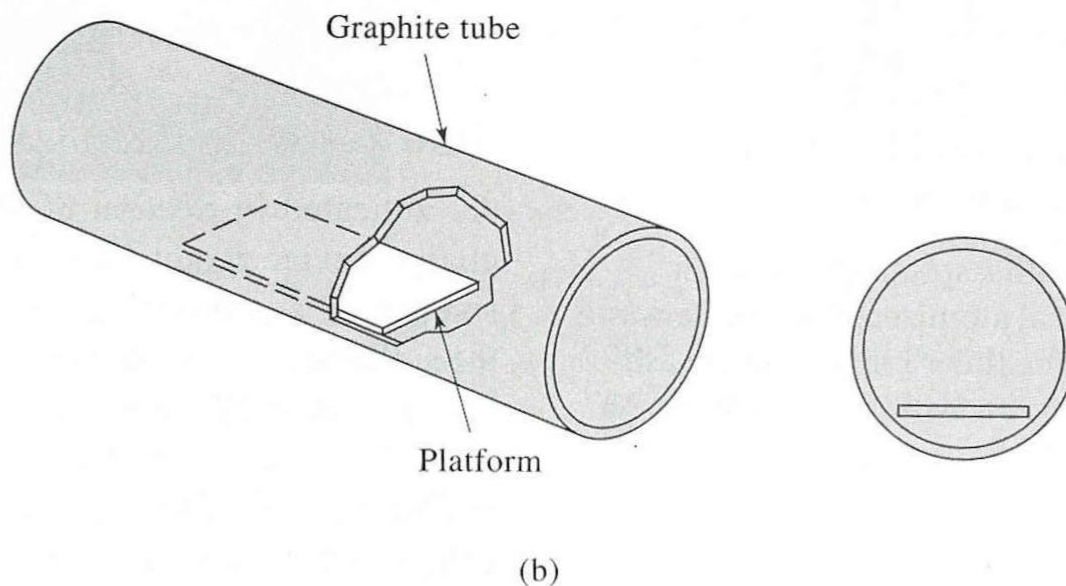


Figure 9-6 (a) Cross-sectional view of a graphite furnace. (Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.) (b) The L'vov platform and its position in the graphite furnace. (Reprinted with permission from W. Slavin, *Anal. Chem.*, 1982, 54, 689A. Copyright 1982 American Chemical Society.)

Optical Atomic Spectrometry

Electrothermal Atomization

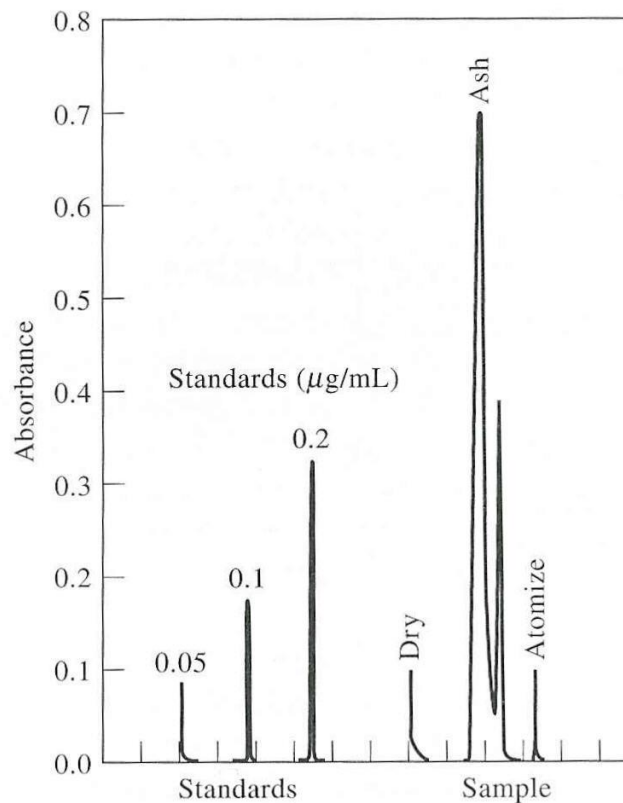


Figure 9-7 Typical output from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 µL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively. (Courtesy of Varian Instrument Division, Palo Alto, CA.)

Optical Atomic Spectrometry

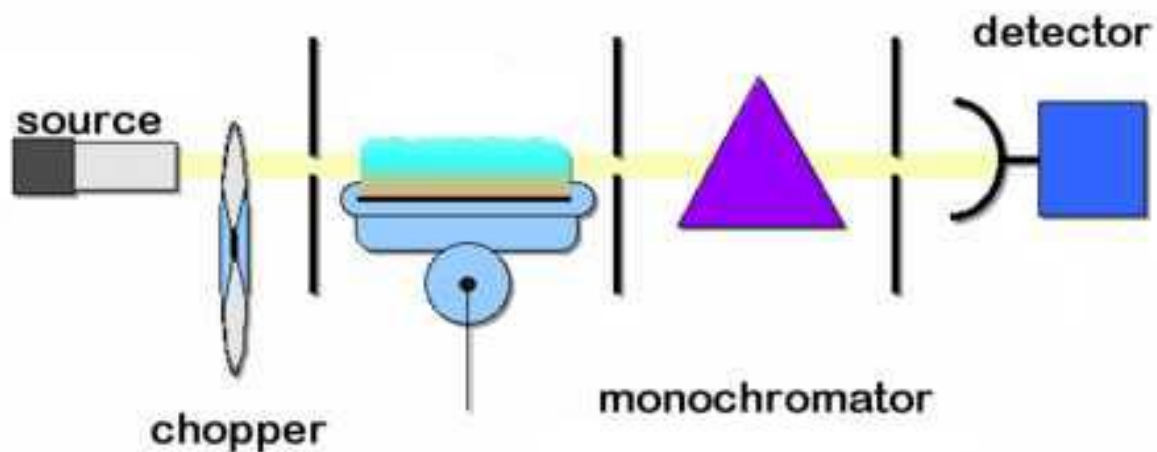
Spectrophotometers

- **Single-beam**
- **Double beam**

Optical Atomic Spectrometry

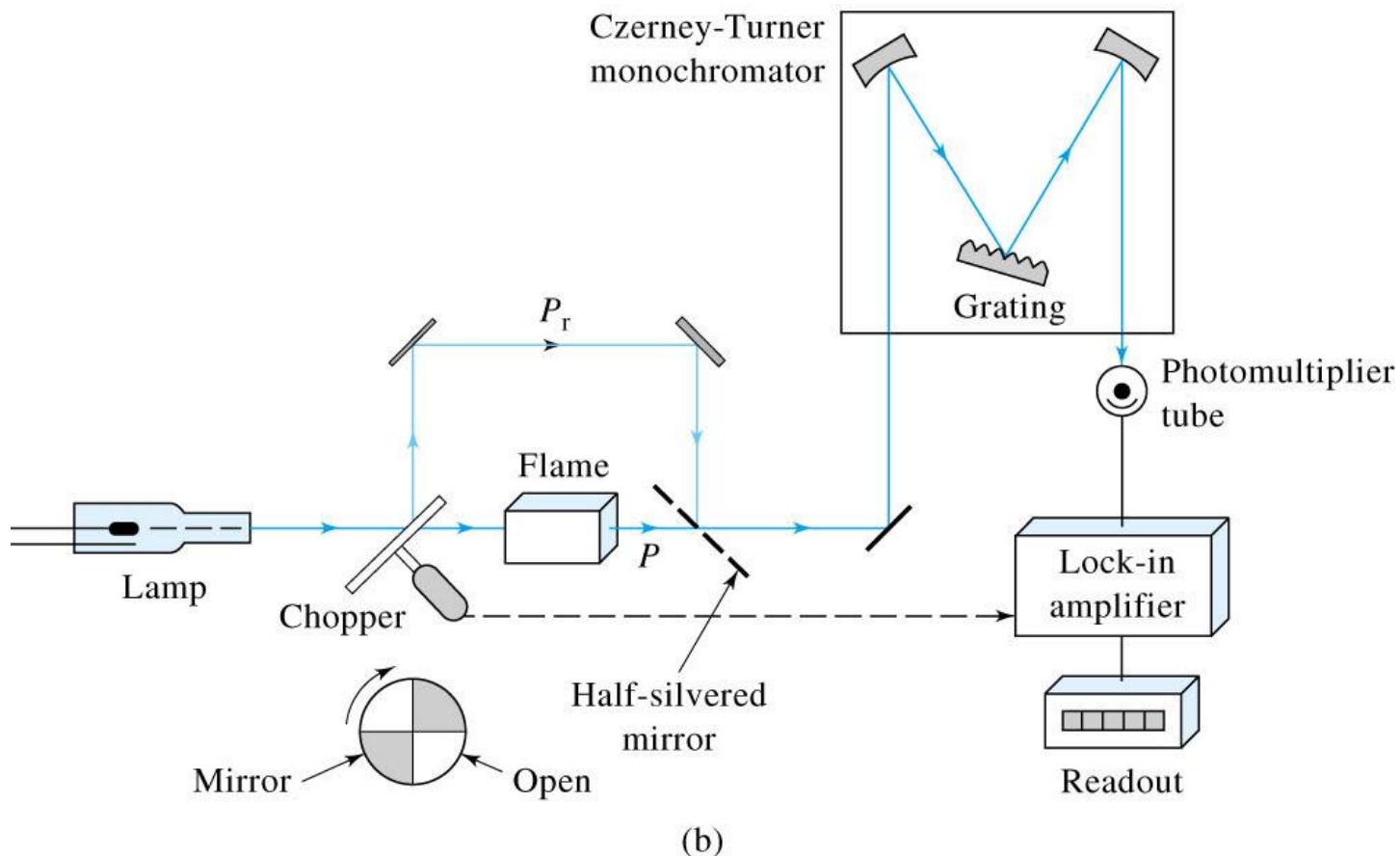
Atomic absorption equipment

In its simplest form, an AA resembles a single beam spectrophotometer.



Optical Atomic Spectrometry

Double-beam



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Optical Atomic Spectrometry

Single Beam

- Simple
- Must run blank

Double-beam

- Simple
- No blank, but must run other background correction

Optical Atomic Spectrometry

Interferences in AAS

- Spectral interferences
- Chemical interferences

Optical Atomic Spectrometry

Spectral Interferences

Occur when the absorption or emission of an interfering species overlaps or is very close to the analyte absorption or emission.

Also interferences occur as products such as oxides are produced in the flame with diameters greater than the wavelength of light and scatter the incident beam.

Optical Atomic Spectrometry

Correction for Spectral Interferences

Two line method

Uses a line from the source as a reference.

The line needs to be close to the analyte line but not absorbed by the analyte.

So any decrease in power of the reference line after calibration is assumed to arise from absorption or scattering of matrix products in the sample.

Optical Atomic Spectrometry

Correction for Spectral Interferences

Continuum source method

A D_2 lamp provides a source of continuous radiation through the UV region.

A chopper is used to alternate the continuum source and hollow cathode lamp through a graphite tube atomizer.

Absorbance of D_2 radiation is then subtracted from the analyte beam giving a background correction.

Optical Atomic Spectrometry

Continuum source method

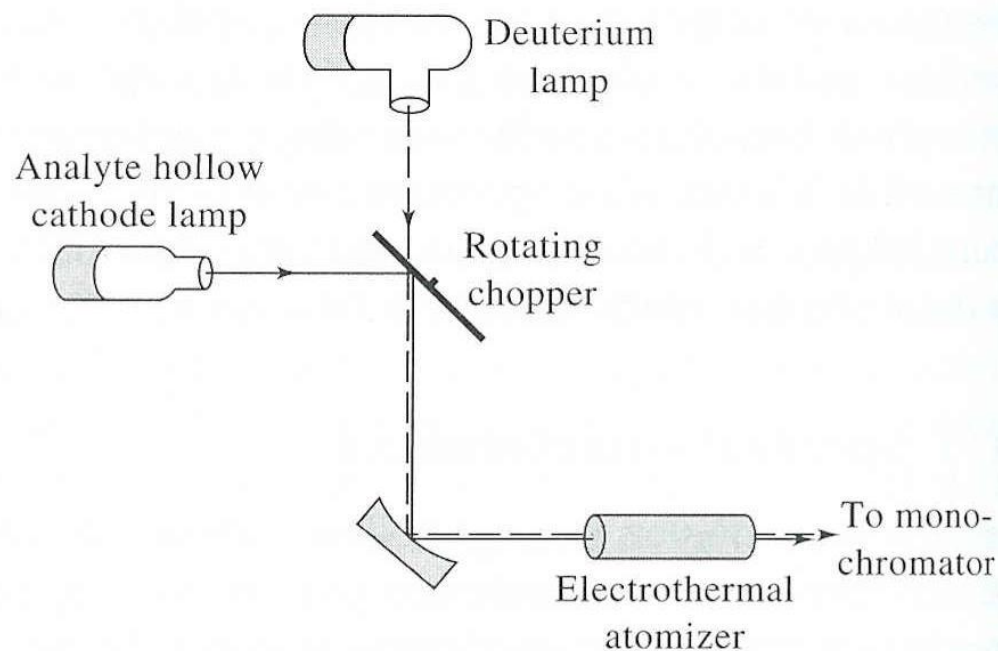


Figure 9-14 Schematic of a continuum-source background correction system. Note that the chopper can be dispensed with by alternately pulsing each lamp.

Optical Atomic Spectrometry

Correction for Spectral Interferences

Source Self-reversal Correction (Smith-Hieftje)

When high currents are used for a hollow cathode lamp, a large concentration of nonexcited atoms are produced.

These absorb the radiation from the excited species, giving a minimum at the center of a band.

Optical Atomic Spectrometry

Source Self-reversal Correction (Smith-Hieftje)

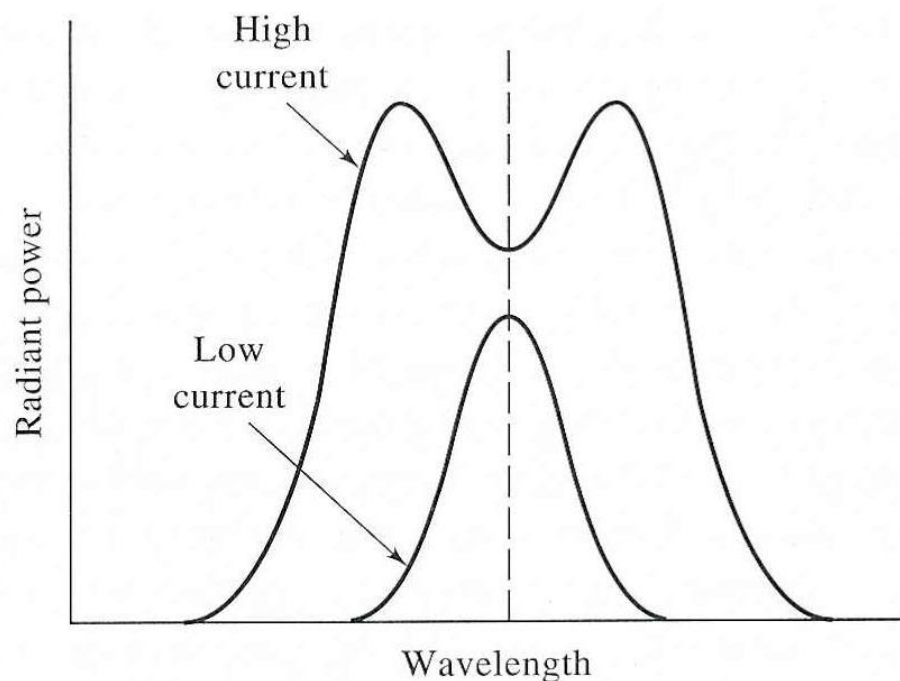


Figure 9-16 Emission line profiles for a hollow-cathode lamp operated at high and low currents.

Optical Atomic Spectrometry

Chemical Interferences

Arise from various chemical processes occurring during atomization and alter the absorption characteristic of the analyte.

More common than spectral interferences.

Optical Atomic Spectrometry

Chemical Interferences

Formation of compounds of low volatility

Most common type of chemical interference.

Anions form compounds of low volatility with the analyte and reduce the rate of atomization of the analyte.

This gives low absorbance results.

Ex. Ca absorbance decrease with increasing concentration of sulfate or phosphate.

Optical Atomic Spectrometry

Chemical Interferences

Formation of compounds of low volatility

This interference can be minimized by :

- Using higher temperatures
- Using releasing agents

Example: Add strontium or La ions to Ca sample to react with phosphate and eliminate interference.

- Using protective agents

Form stable but volatile species with the analyte.

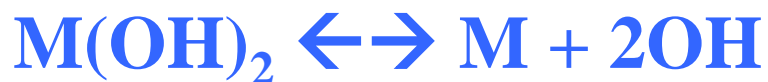
A common reagent is EDTA.

Optical Atomic Spectrometry

Chemical Interferences

Dissociation Equilibrium

In the flame or furnace, analyte undergoes dissociation and association reactions.



The molecular bands of metal oxides or hydroxides are more intense than the lines for the atoms or ions.

Optical Atomic Spectrometry

Chemical Interferences

Ionization Equilibrium

In high temperature flames, ionization increases and produce high concentrations of free electrons in the flame.



The degree of ionization of M^+ can decrease if several species ionize and produce more electrons, this shifts the equilibrium back to M .

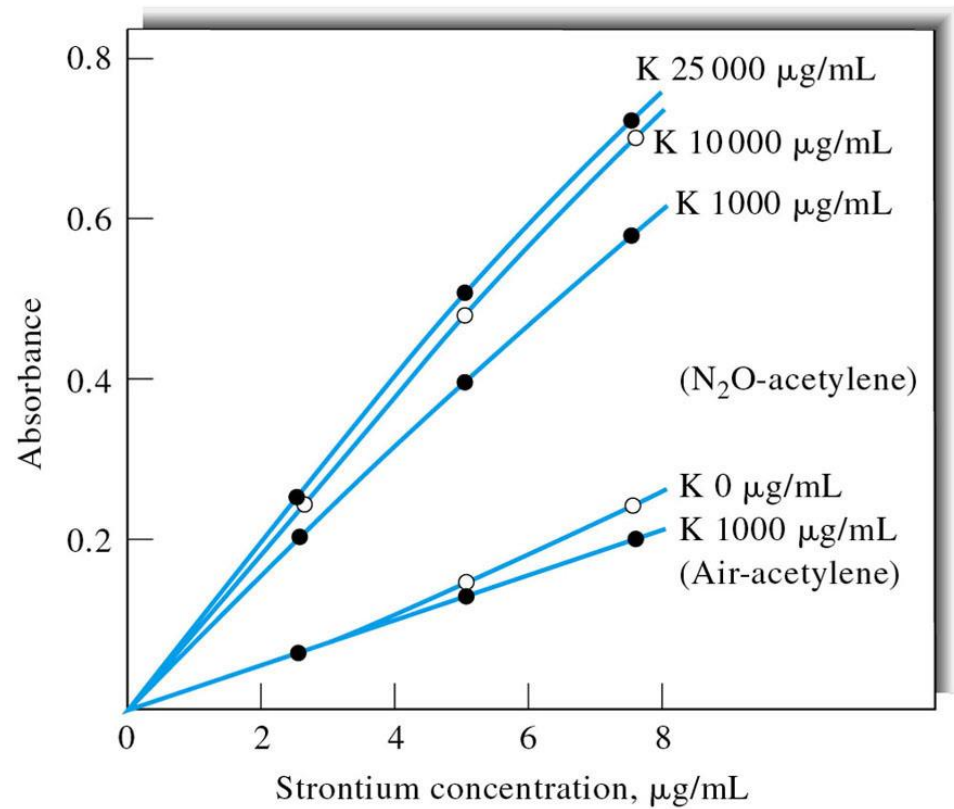
Optical Atomic Spectrometry

Chemical Interferences

Ionization Equilibrium

The degree of ionization of M^+ can decrease if several species ionize and produce more electrons, this shifts the equilibrium back to M .

This occurs with the addition of an ionization suppressor (like **K** in this example).



Assignment

Test 2- Lectures 8 to 11 and 14 (not 12 & 13) – Friday March 1st

- Read Chapter 8
- Read Chapter 9
- HW8 Chapter 8: 1, 4-9
- HW9 Chapter 9: 1-5, 7-9, 19
- HW8 – Due 3/04/24
- HW9 – Due 3/06/24