Chapter 9: Atomic Absorption Spectrometry

Read: pp. 230 – 249 **Problems: 9-1,3,5,6,8**

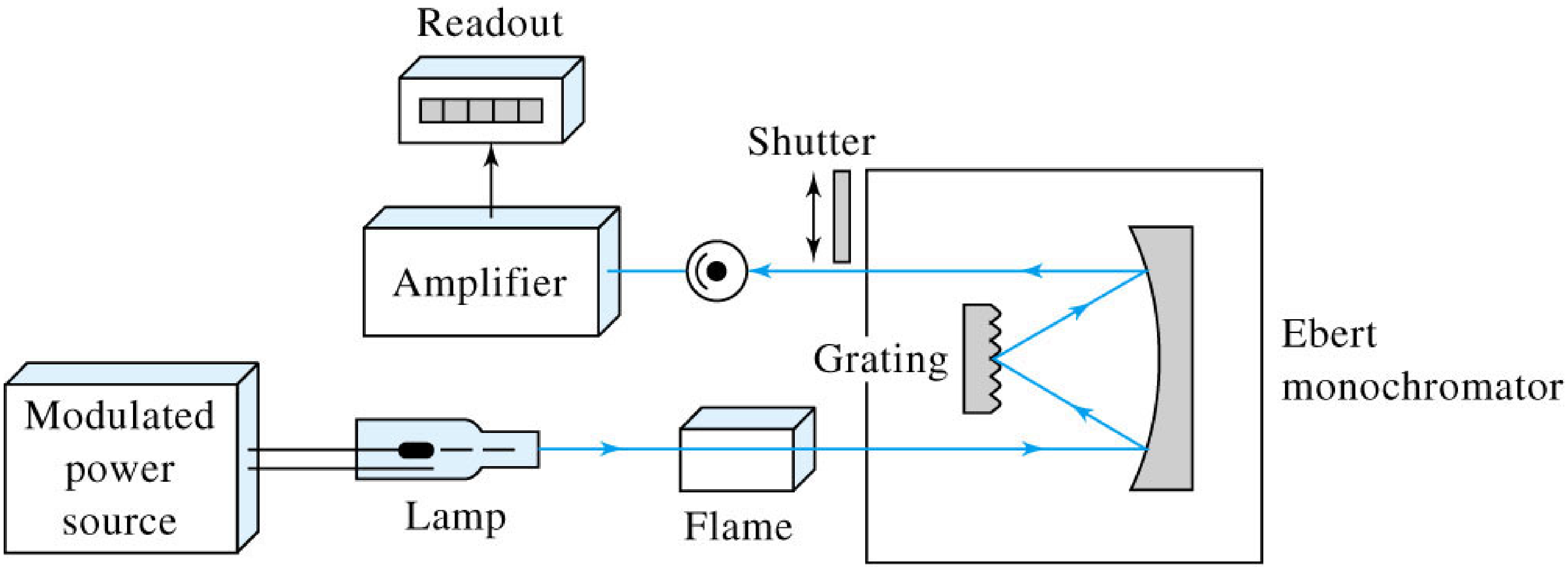


Figure 9-13a

$$\boxed{A(\lambda) = \varepsilon(\lambda)bC = \log P_o/P}$$

Flame-Burner

In AAS, the flame functions as (i) sample holder, (ii) desolvation source, and (iii) volatilization source.

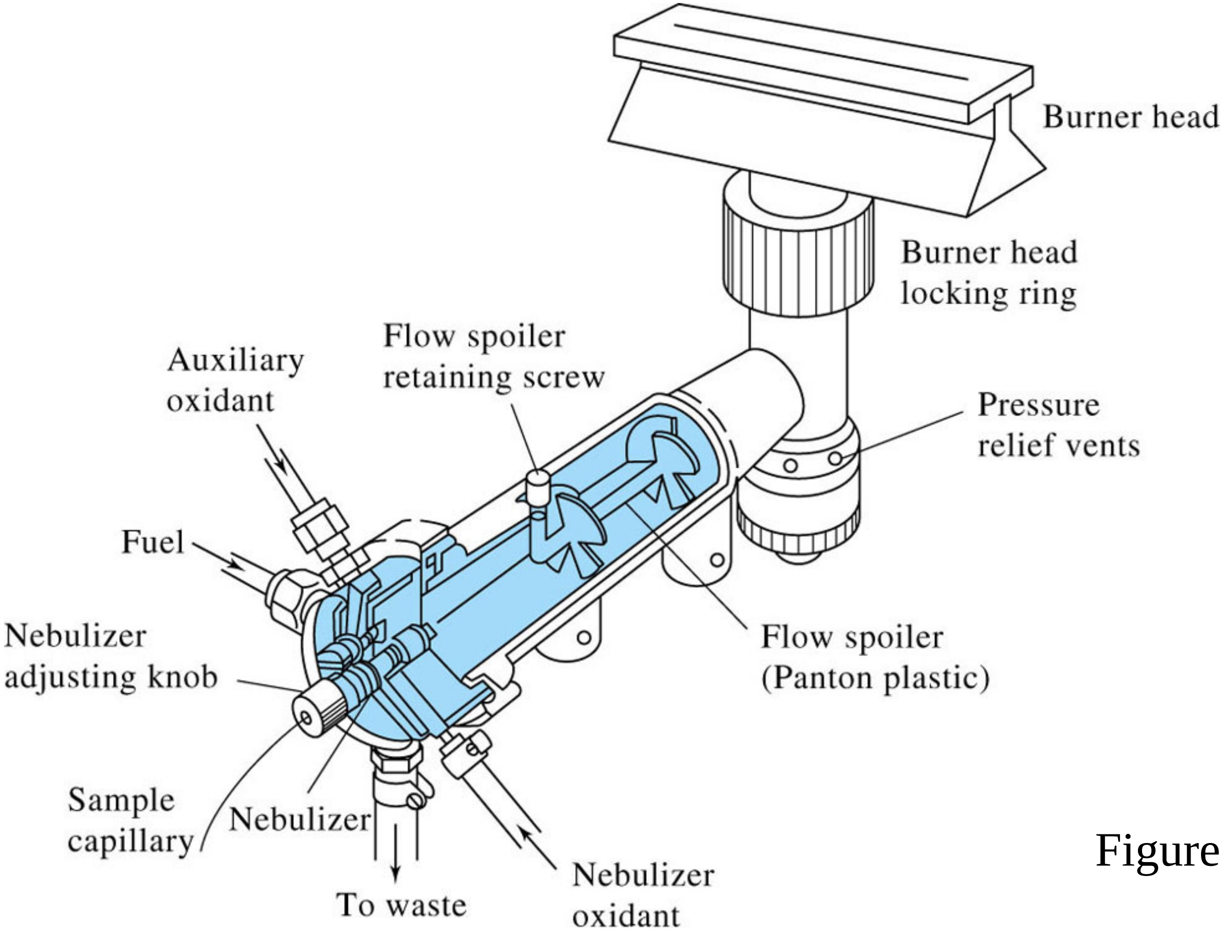


Figure 9-5

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

Flame Structure

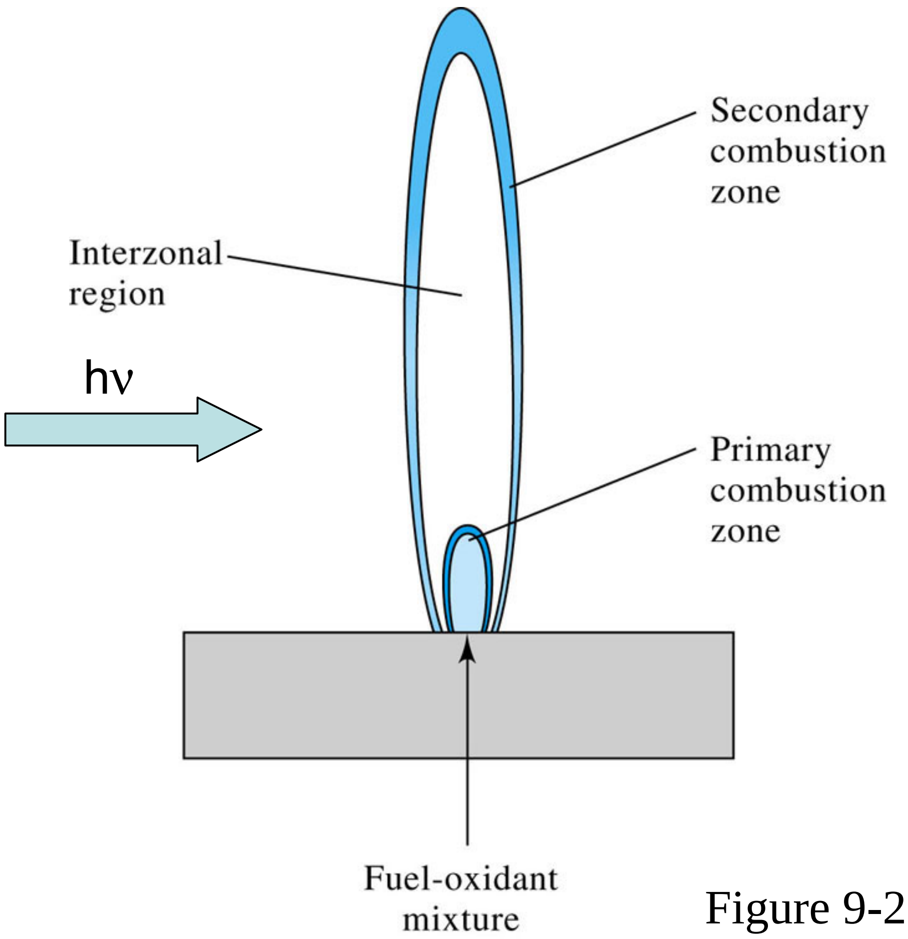


Figure 9-2

Primary zone:
C_2, CH, and other radical emission

Secondary zone:
oxygen present so stable molecular oxides are formed for some metals

Interzonal regions:
hot region, most widely used for analysis

Optimum analysis position in the flame depends on the particular element and its chemistry:

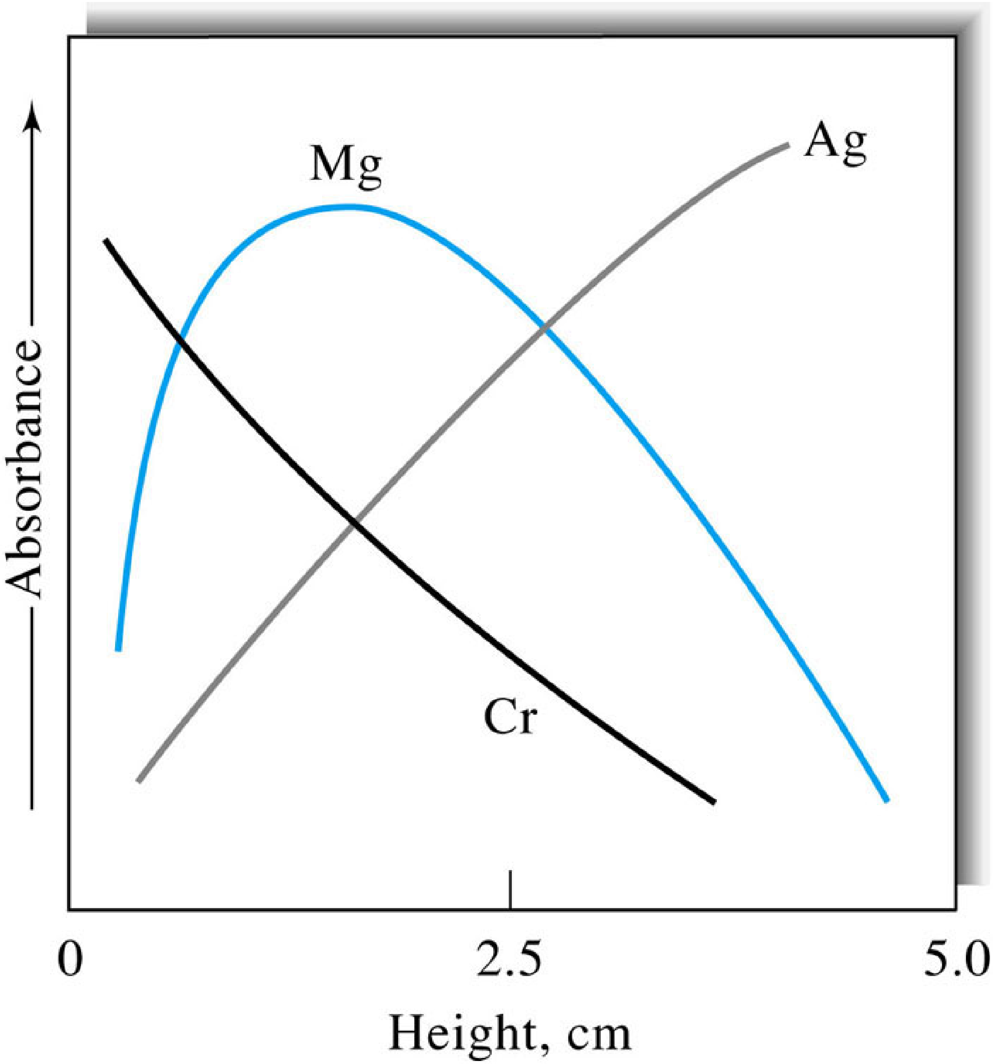


Figure 9-4

Line Source – Hollow Cathode Lamp

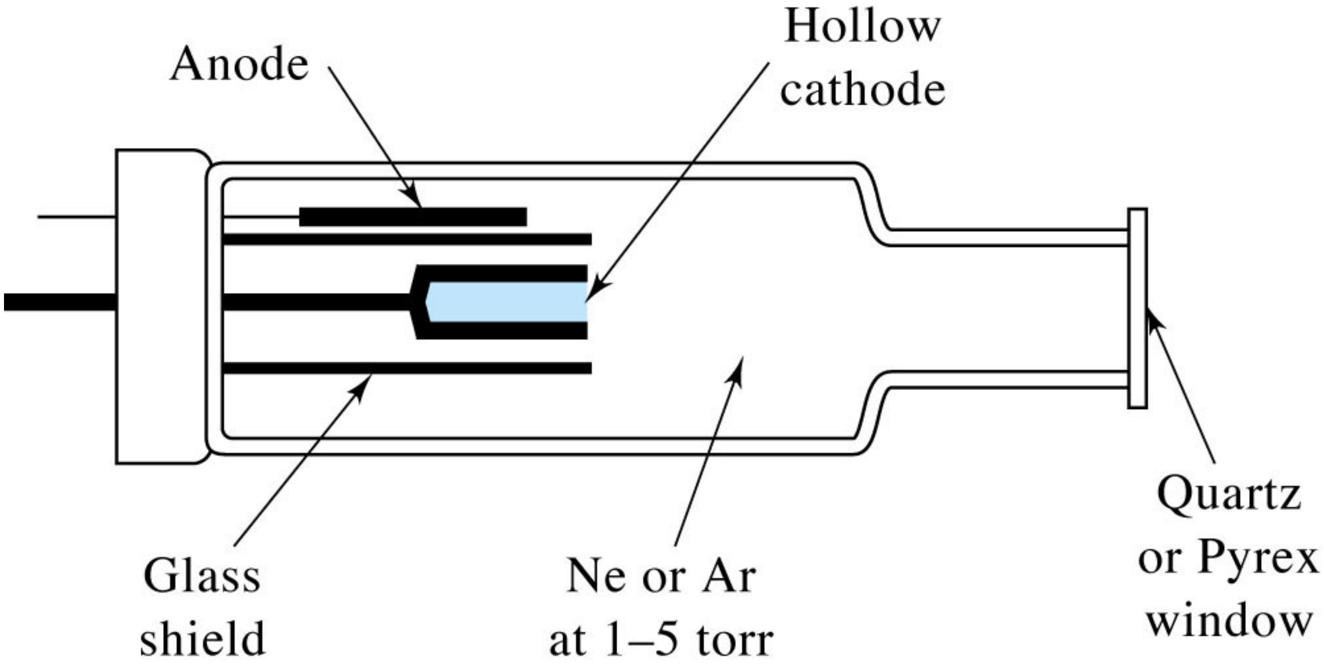


Figure 9-11

Cathode material made of the element of interest, e.g. Na HCL for the analysis of Na. An individual lamp is needed for each element. So AAS is a one-element-at-a-time measurement!

Desired line of source is selected with monochromator:

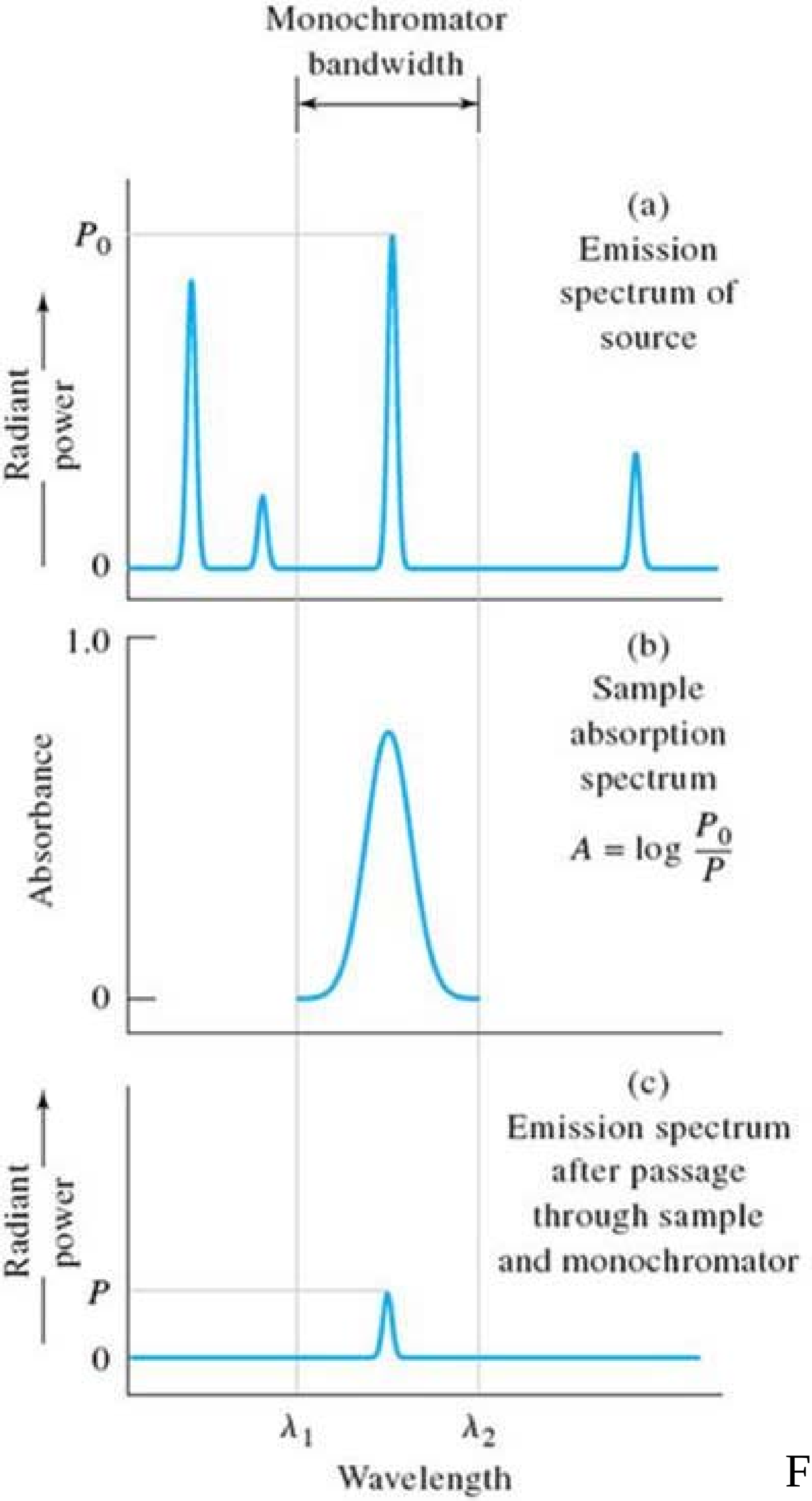


Figure 9-10

Monochromator – Wavelength Separator

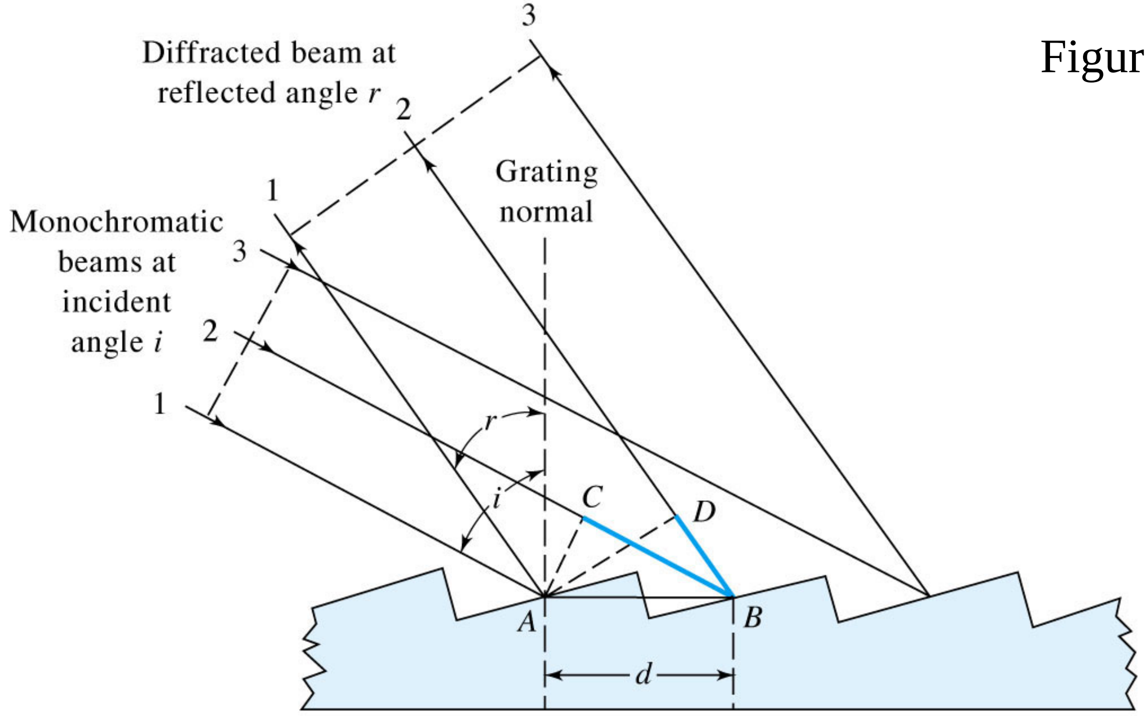


Figure 7-21

$n\lambda = d(\sin i + \sin r)$

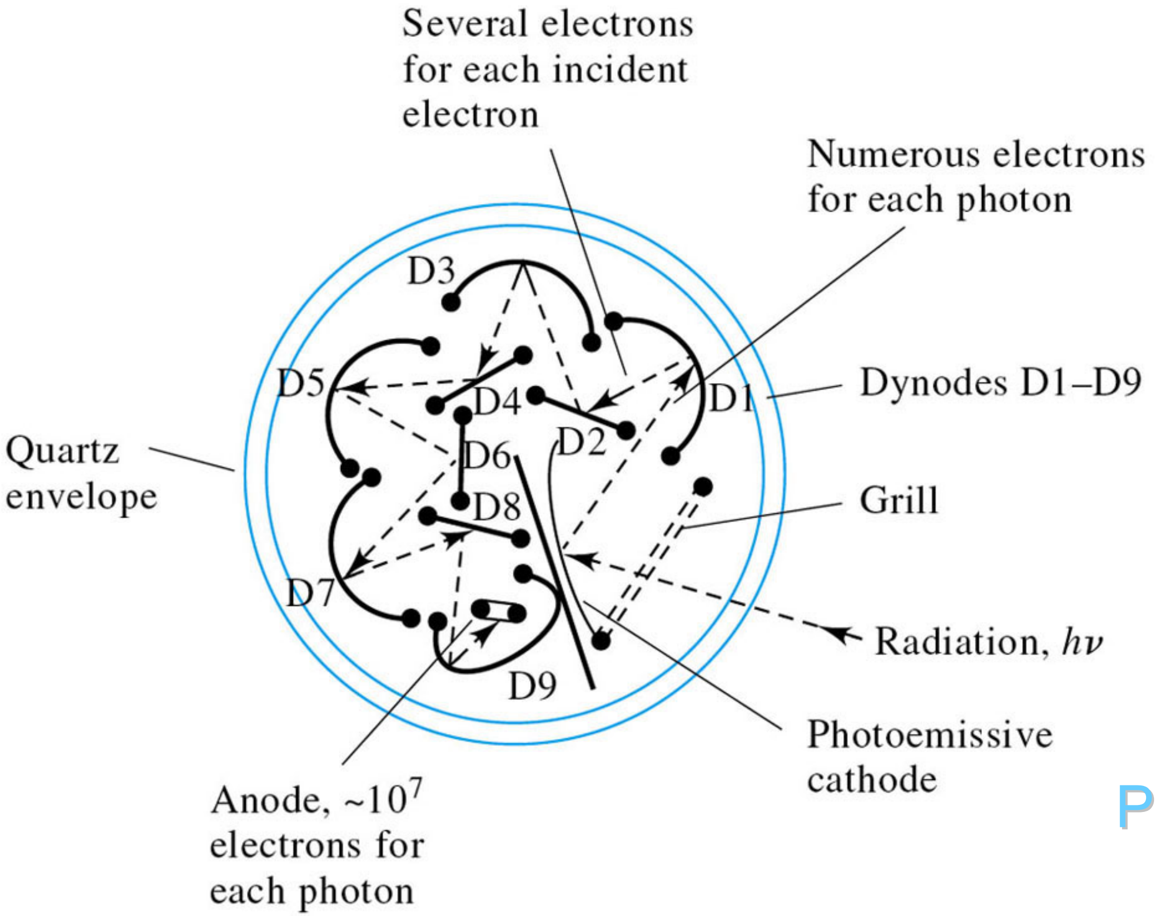
$R = \lambda/\Delta\lambda = nN$

N = grooves/mm

Properties: light gathering power, stray light rejection, resolution, and linear dispersion

Optical Detectors

Single vs. multichannel detectors!



$$\boxed{S = kP + k_d}$$

Photomultiplier tube

Figure 7-31b

Single-Beam Spectrometer:

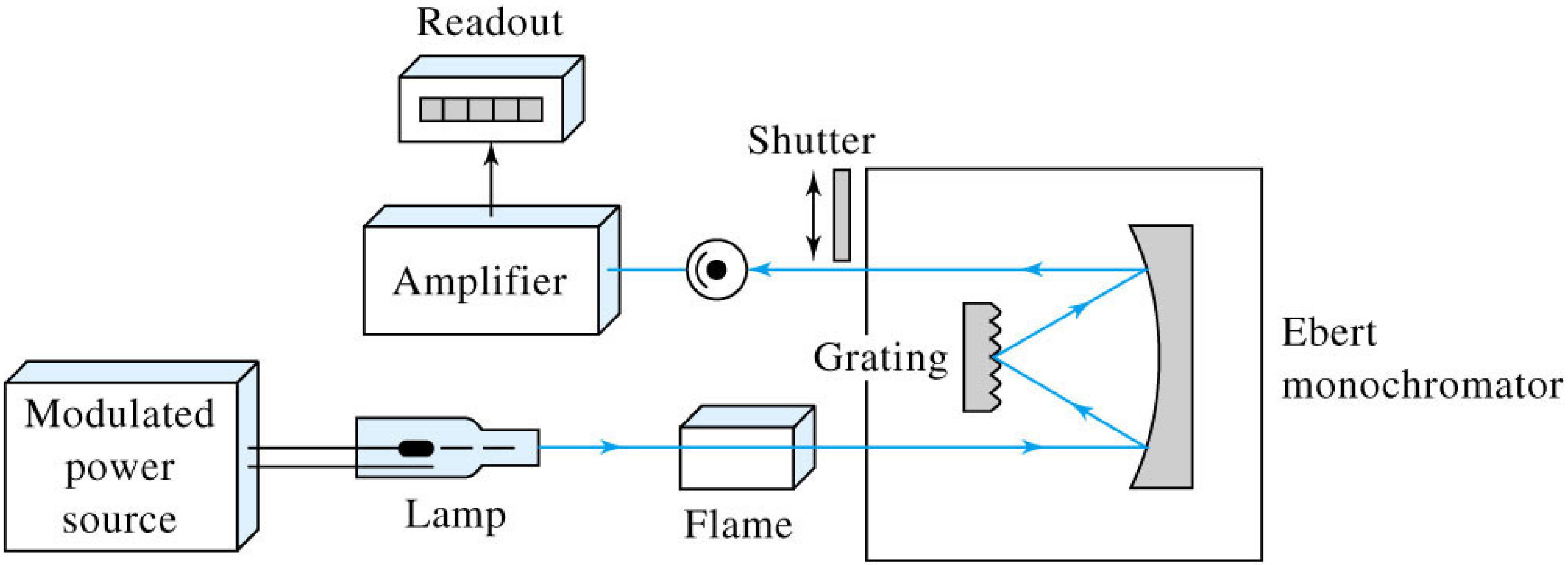


Figure 9-13a

Double-Beam Spectrometer:

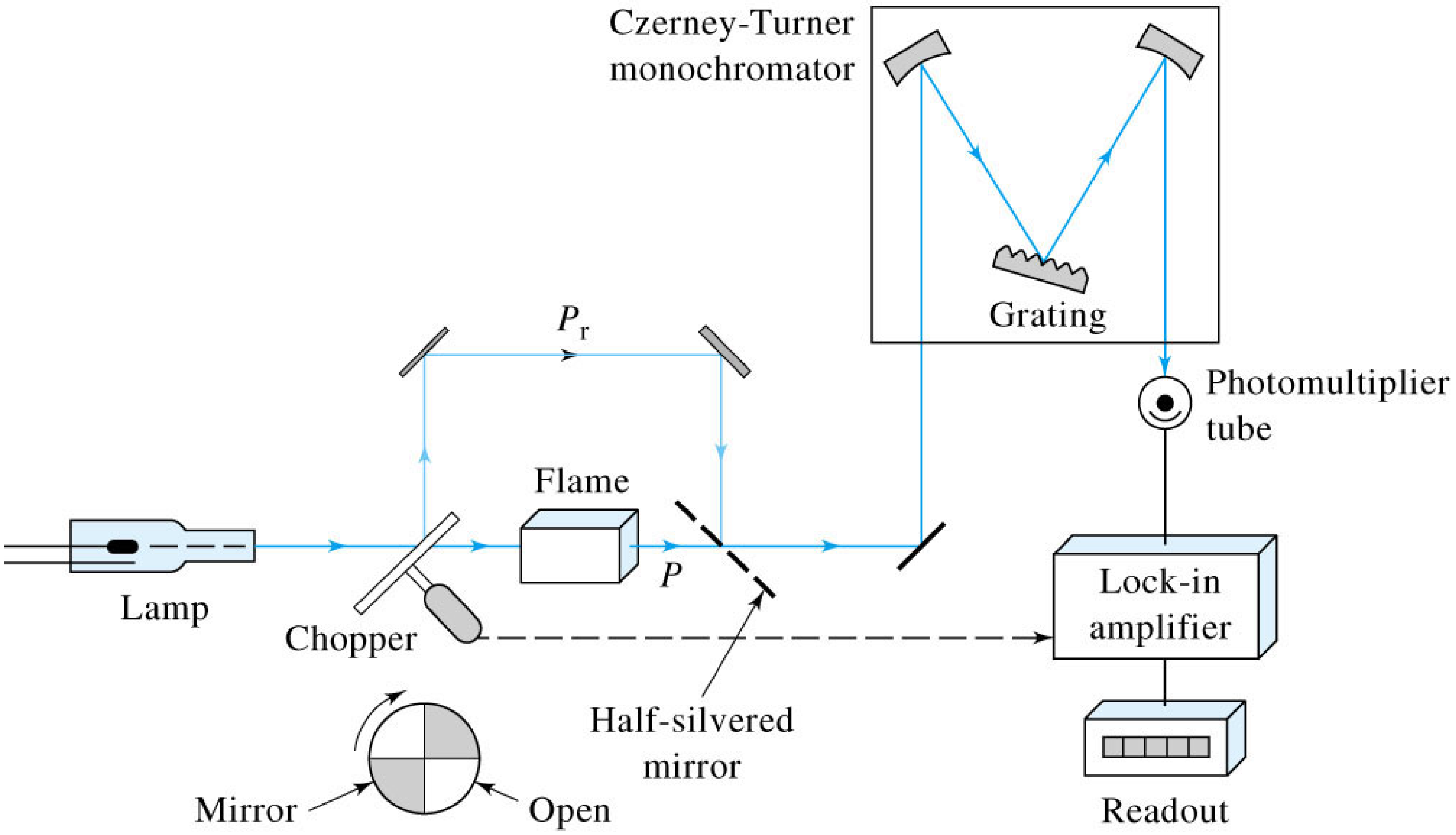


Figure 9-13b

TABLE 9-3 Detection Limits (ng/mL)[a] for Selected Elements

Element	AAS Flame	AAS Electrothermal	AES Flame	AES ICP	AFS Flame
Al	30	0.1	5	0.2	5
As	200	0.5	—	2	15
Ca	1	0.25	0.1	0.0001	0.4
Cd	1	0.01	2000	0.07	0.1
Cr	4	0.03	5	0.08	0.6
Cu	2	0.05	10	0.04	0.2
Fe	6	0.25	50	0.09	0.3
Hg	500	5	—	—	5
Mg	0.2	0.002	5	0.003	0.3
Mn	2	0.01	—	0.01	1
Mo	5	0.5	100	0.2	8
Na	0.2	0.02	0.1	0.1	0.3
Ni	3	0.5	600	0.2	0.4
Pb	8	0.1	200	1	5
Sn	15	5	300	—	200
V	25	1	200	0.06	25
Zn	1	0.005	50000	0.1	0.1

Typical Figures of Merit for AAS

- Detection limits: ng/mL (ppb) for flame
  pg/mL (ppt) for electrothermal
- Linear range: $10^3 – 10^4$ for flame
  10^2 for electrothermal
- Precision: 1 – 2% RSD for flame
  5 – 10% RSD for electrothermal
- Accuracy: 1 – 2% for flame
  % for flame

Remember: mg/L = ppm ug/L = ppb ng/L = ppt

Chemical Problem

Typical data for the determination of lead (Pb^{2+}) by graphite furnace AAS in standards was 0.05 μg/mL (0.09 AU), 0.1 μg/mL (0.16 AU), 0.2 μg/mL (0.31 AU) and in a sample of canned orange juice was 0.10 AU. Assume that these absorbance data were obtained for 2 μL aliquots of standards and sample. Calculate the concentration of lead in the orange juice sample.

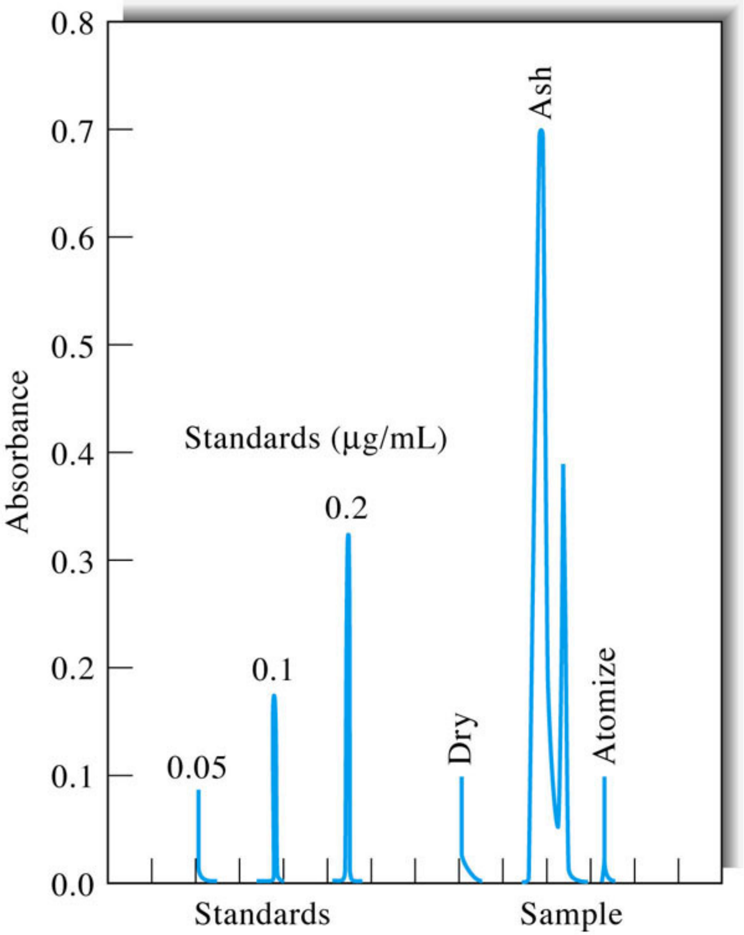
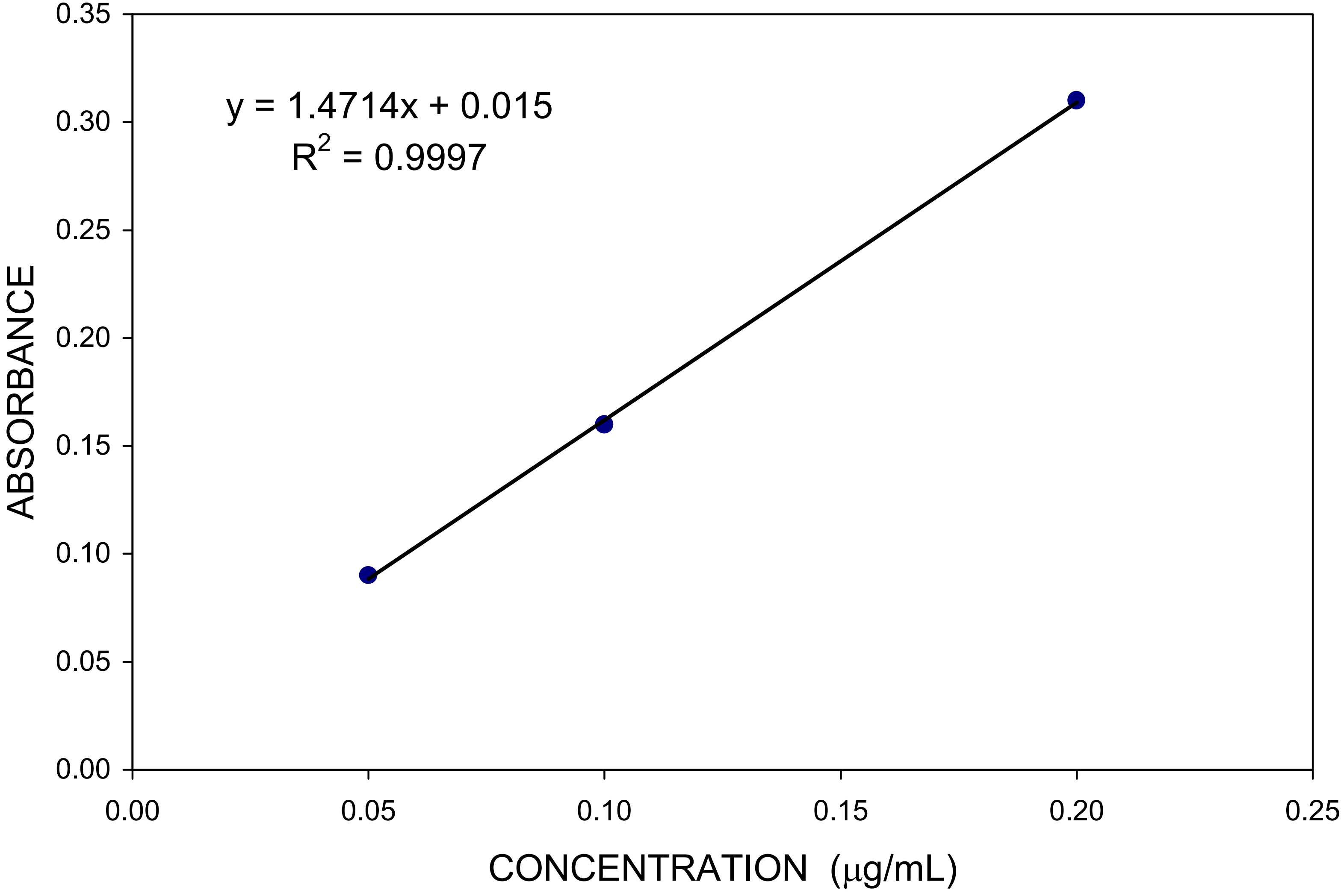


Figure 9-7

Calibration Curve for Pb^{2+}



Calibration equation: $A = 1.4714\,C + 0.015$

Orange juice sample: $A = 0.10$

$$C = \frac{A - 0.015}{1.4714} = \frac{0.10 - 0.015}{1.4714} = 0.058\ \mu\text{g/mL Pb}^{2+}$$

Spectral and Chemical Interferences

Remember: Goal is neutral atoms in the gas phase!

- Absorption or emission of an interfering species overlaps or lies so close to the analyte absorption or emission that resolution is not possible. *Rare with HCLs.*
- Presence of combustion products that exhibit broadband absorption or particulates that scatter radiation. Both diminish power of transmitted beam and lead to positive errors.

If caused by fuel/oxidant mixture, then correction is possible by running a blank and performing background subtraction.

More troublesome problem when absorption or scattering results from the sample matrix.

- Interference by anions that form low volatility complexes with the analyte, and thus reduce the atoms formed. Lead to negative errors. Can be corrected by
  - Releasing agents (cations added to preferentially react)
  - Protecting agents (e.g., EDTA added to protect analyte cation)
- Dissociation equilibria

  $MO \leftrightarrow M + O$

  $M(OH)_2 \leftrightarrow M + 2\ OH$
- Ionization equilibria

  $M \leftrightarrow M^+ + e^-$

In both cases, analyte atoms are not all in the proper form to absorb or emit at desired wavelength. Lead to negative errors.

Terms to Know!!!

ablation
aerosol
atomic absorption
atomic emission
atomic fluorescence
atomization
background correction
Boltzman distribution
chemical interference
detection limit
Doppler effect
graphite furnace
hollow cathode lamp
ionization interference
matrix
nebulization
releasing agent
self-absorption
spectral interference
ionization suppressor