Chapter 8: An Introduction to Optical Atomic Spectrometry

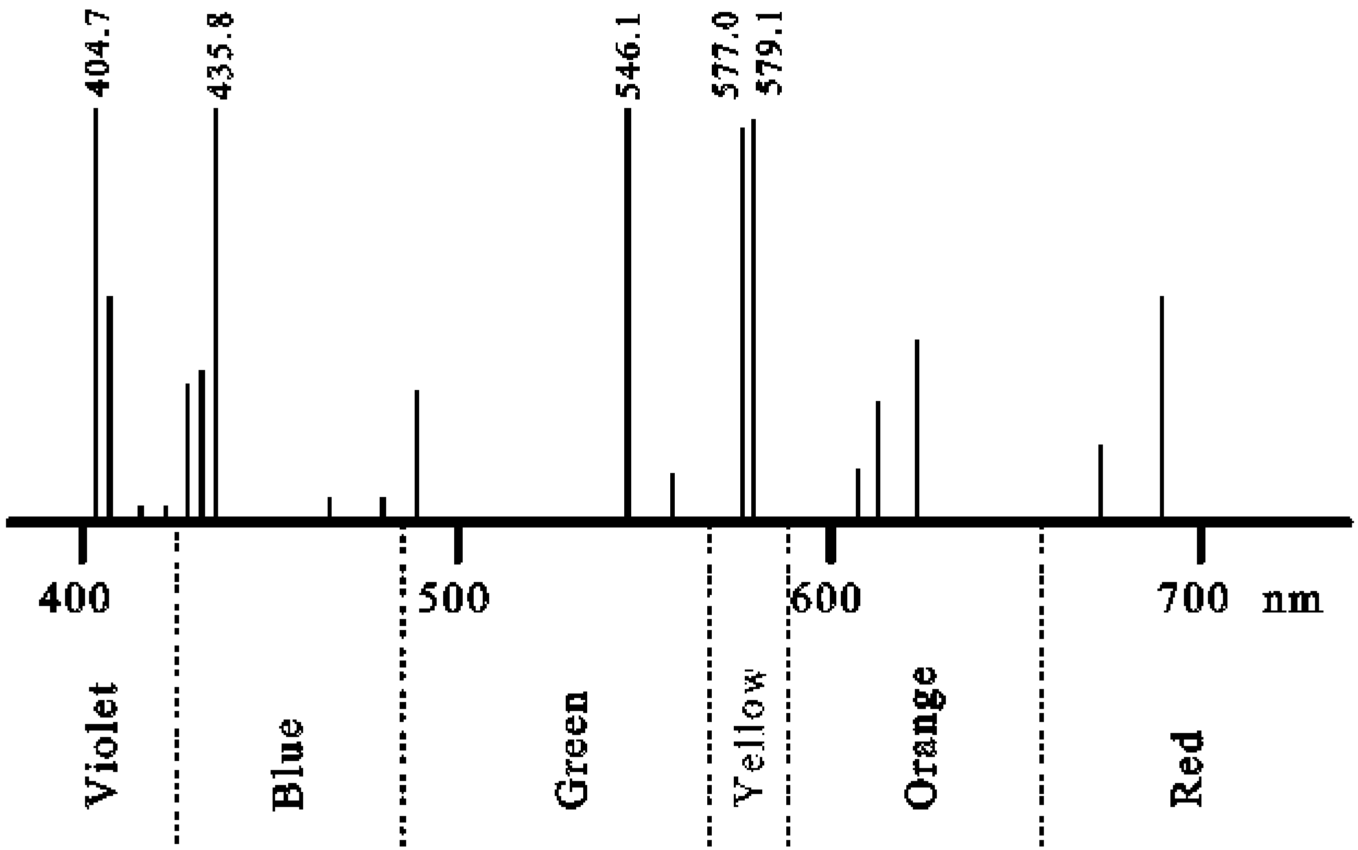
- Optical Atomic Spectra
- Atomization Methods
- Sample Introduction Methods

- Optical Spectrometry as opposed to MS
- Optics are similar to Molecular Absorption and Fluorescence Spectrometry

Basics

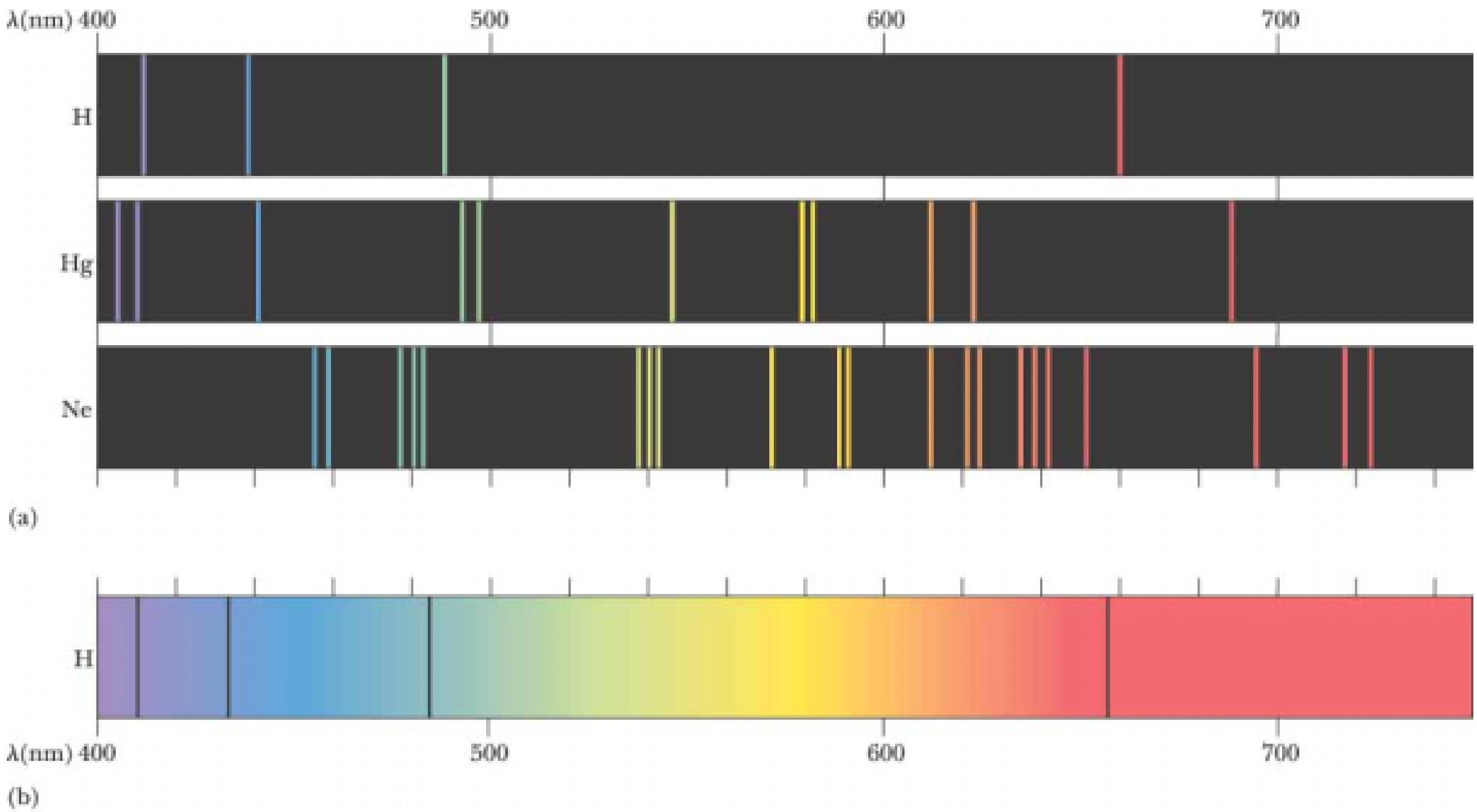
- Generally solution samples (sometimes solids)
- Aspirate sample into flame or plasma
- Or heat sample to atomize
- Observe emission from excited state (AE)
- Or use light source to measure atomic absorption (AA)
- Or use light source to generate atomic fluorescence (AF)

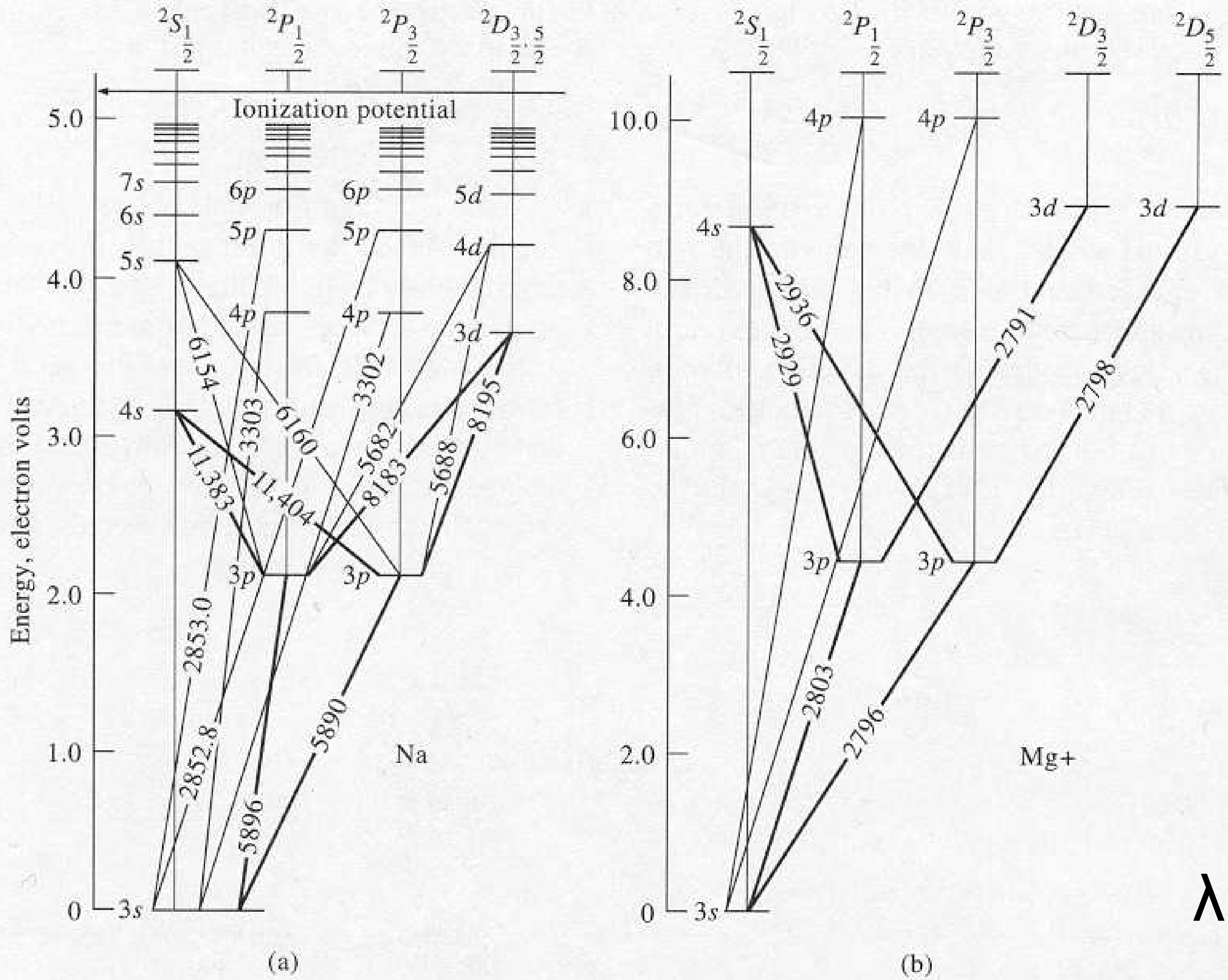
Atomic spectra are line spectra



Some prominent lines in the atomic spectrum of mercury (Hg)

Other atomic spectra – many lines per spectra, lines are very narrow





λ in Å

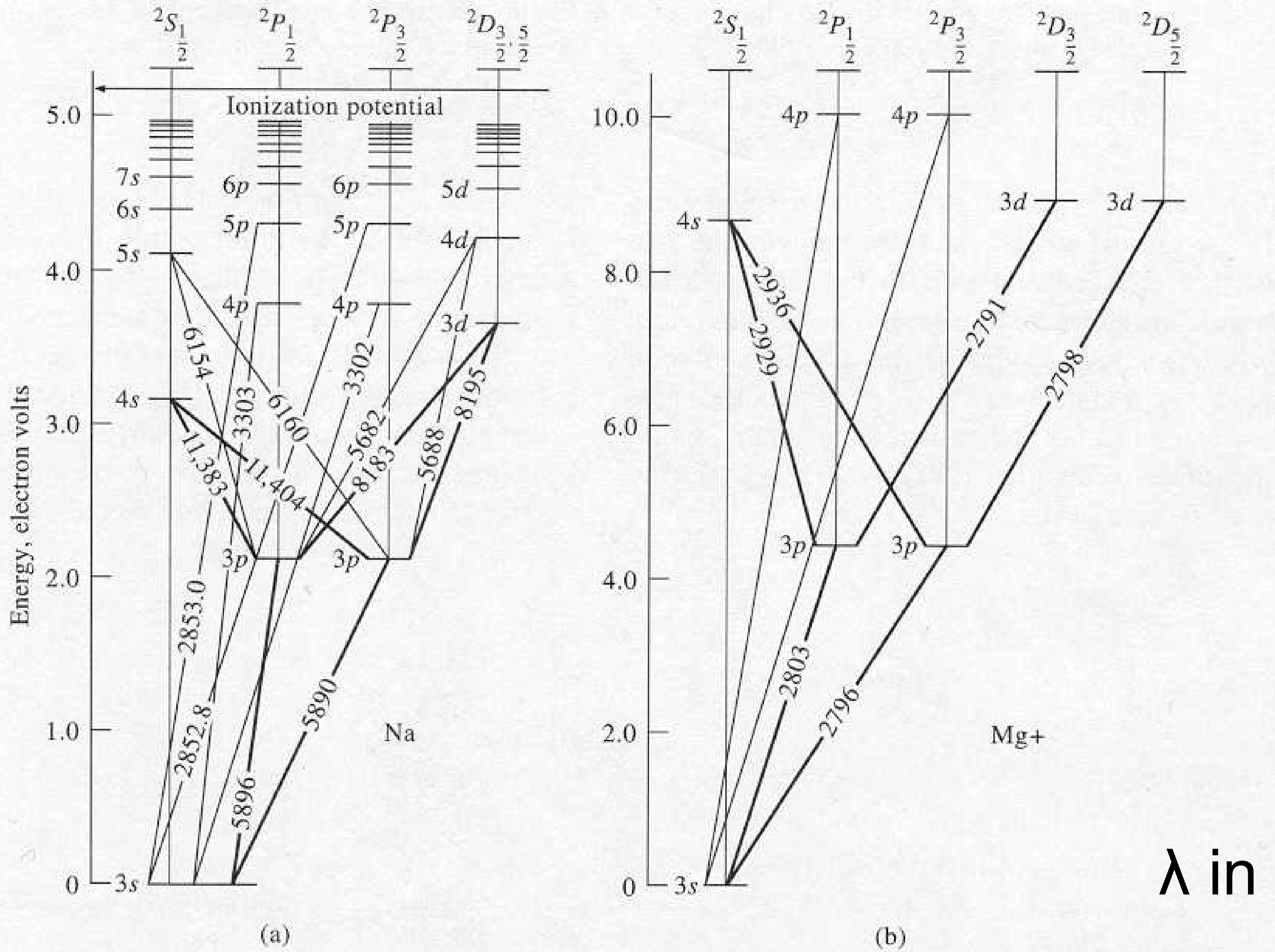
Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

Absorption & emission lines come from discrete transitions

Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



λ in Å

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.

Absorption & emission lines come from discrete transitions

Resonance fluorescence lines involve the ground state

Others involve a two step process

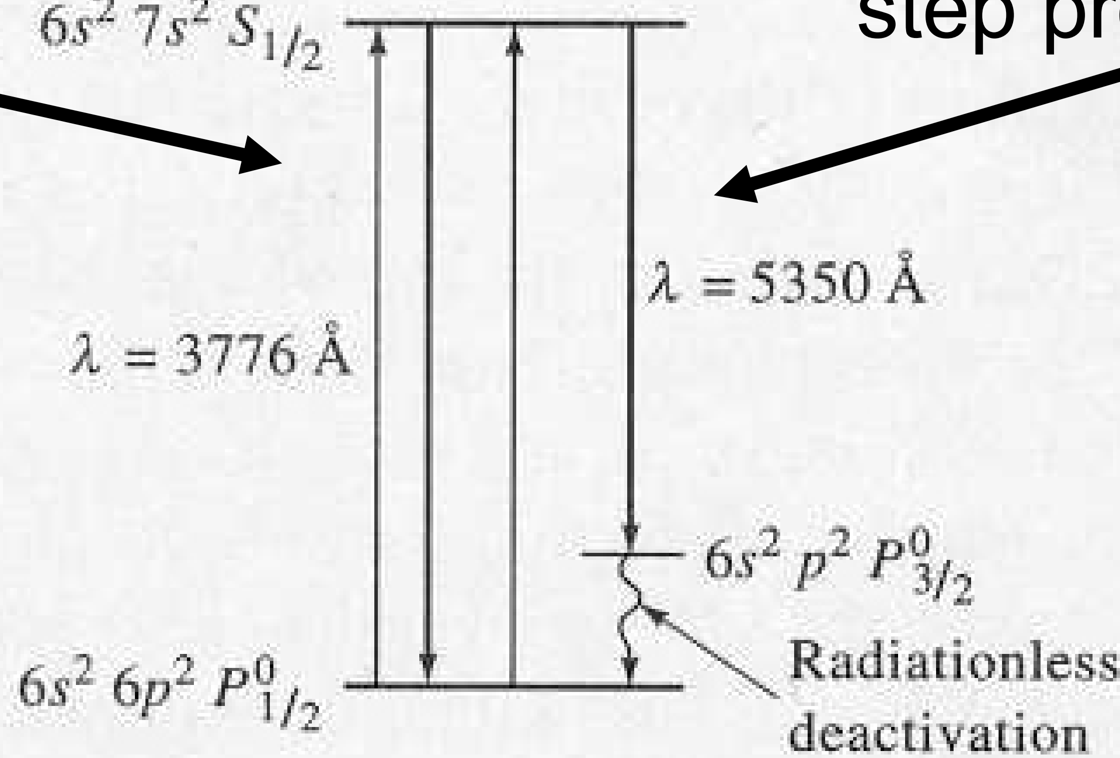


Figure 8-5 Energy level diagram for thallium showing the source of two fluorescence lines.

Atomic line widths are important when considering spectral resolution, absorption experiments, etc.

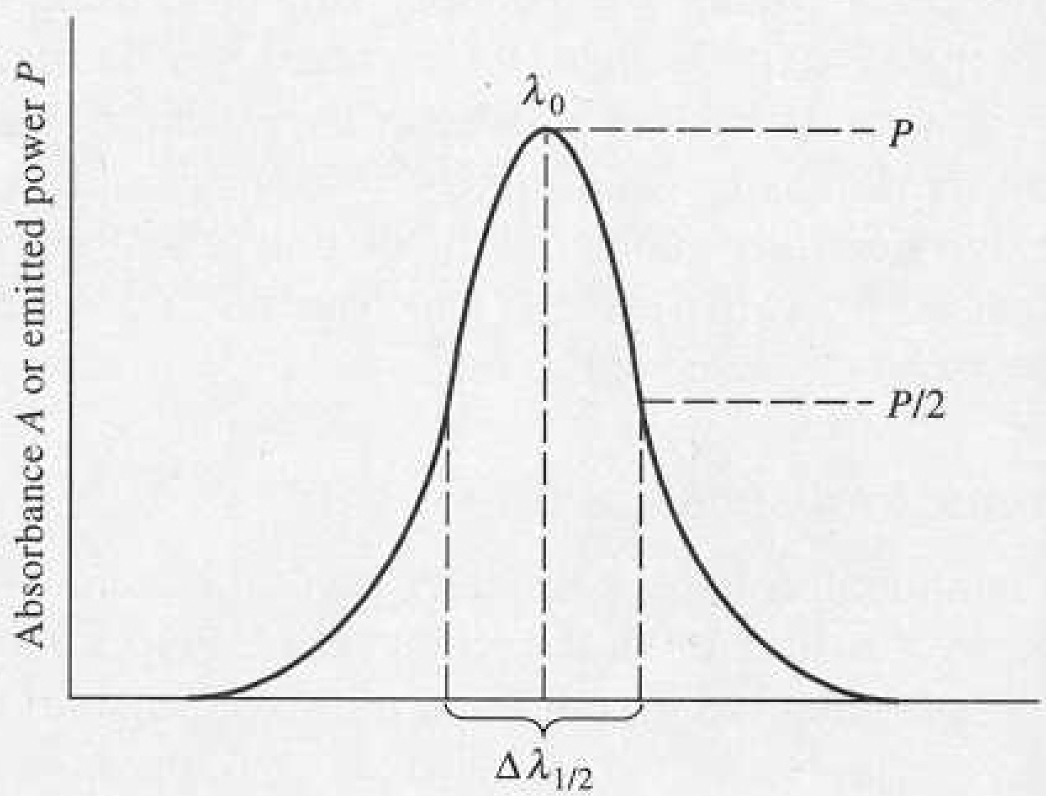
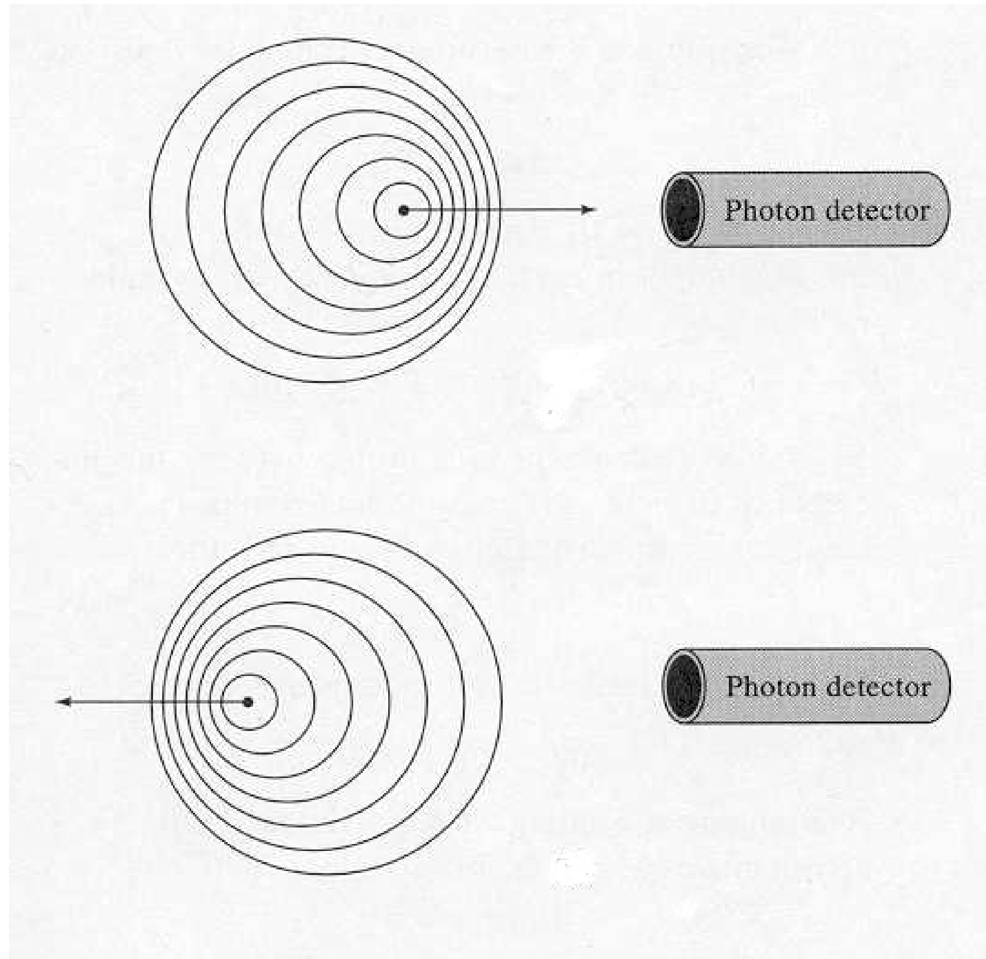


Figure 8-6 Profile of an atomic line showing definition of the effective line width $\Delta\lambda_{1/2}$.

Doppler broadening occurs due to the observed compression and expansion of light waves as an atom moves toward or away from the radiation source



Other broadening effects include

- pressure or collisional broadening (10^{-4} Å)
- broadening from uncertainty effects
- electric & magnetic field effects

Temperature effects from Boltzmann equation

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp\left(-\frac{E_j}{kT}\right)$$

N = population of state P = statistical factor

E_j = energy difference k = Boltzmann constant

T = temp o & j signify ground & excited states

Molecular emission in flames & plasmas is generally unwanted
may obscure part of the spectrum & cause interference

Note similarity of spectra

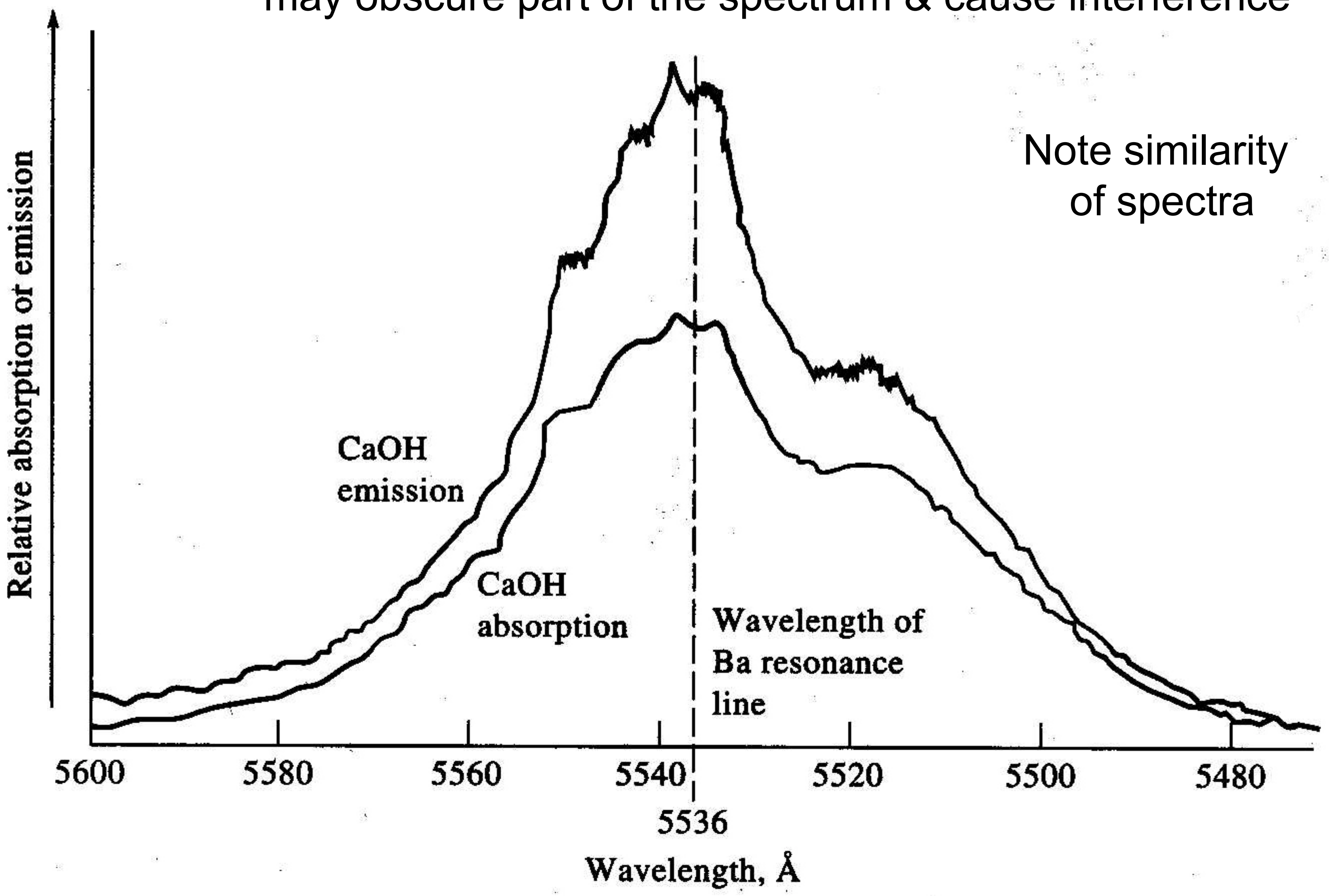


Figure 8-8 Molecular flame and flame absorption spectra for CaOH and Ba.

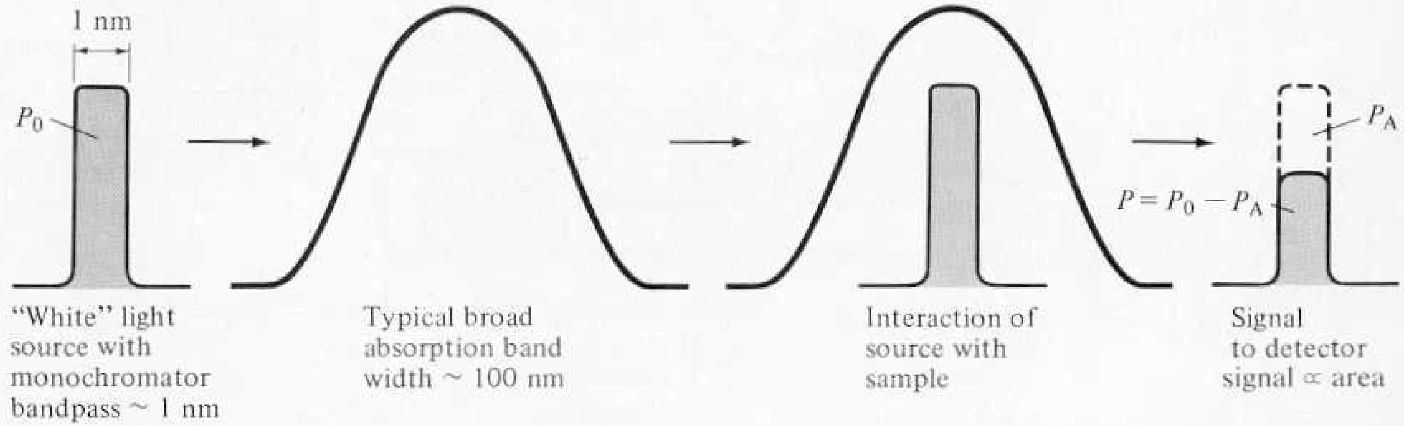


FIGURE 13-7 Conventional UV–VIS spectrophotometry.

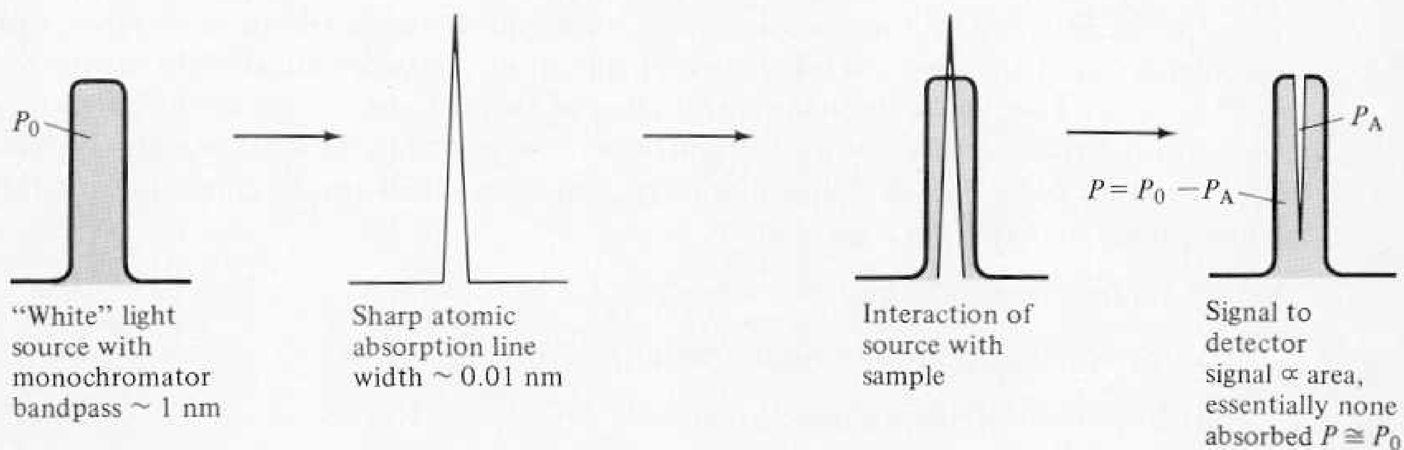
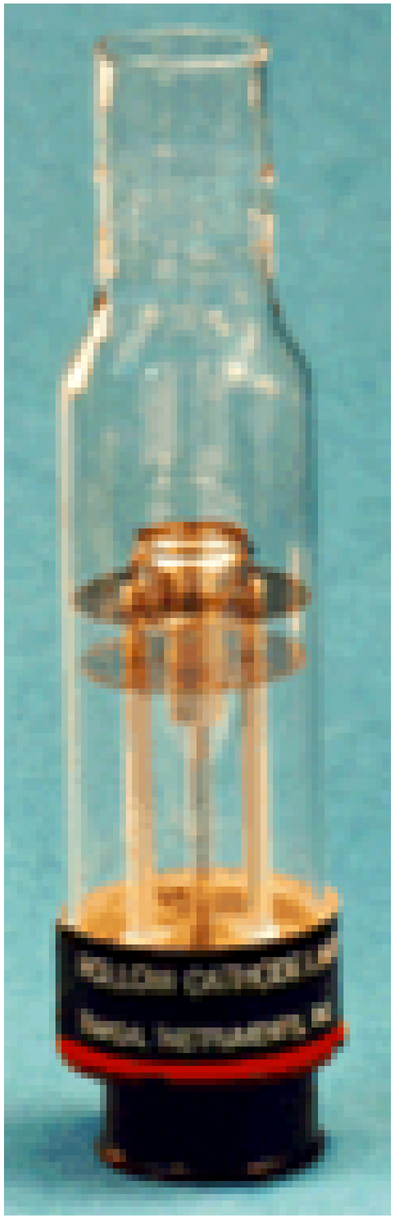
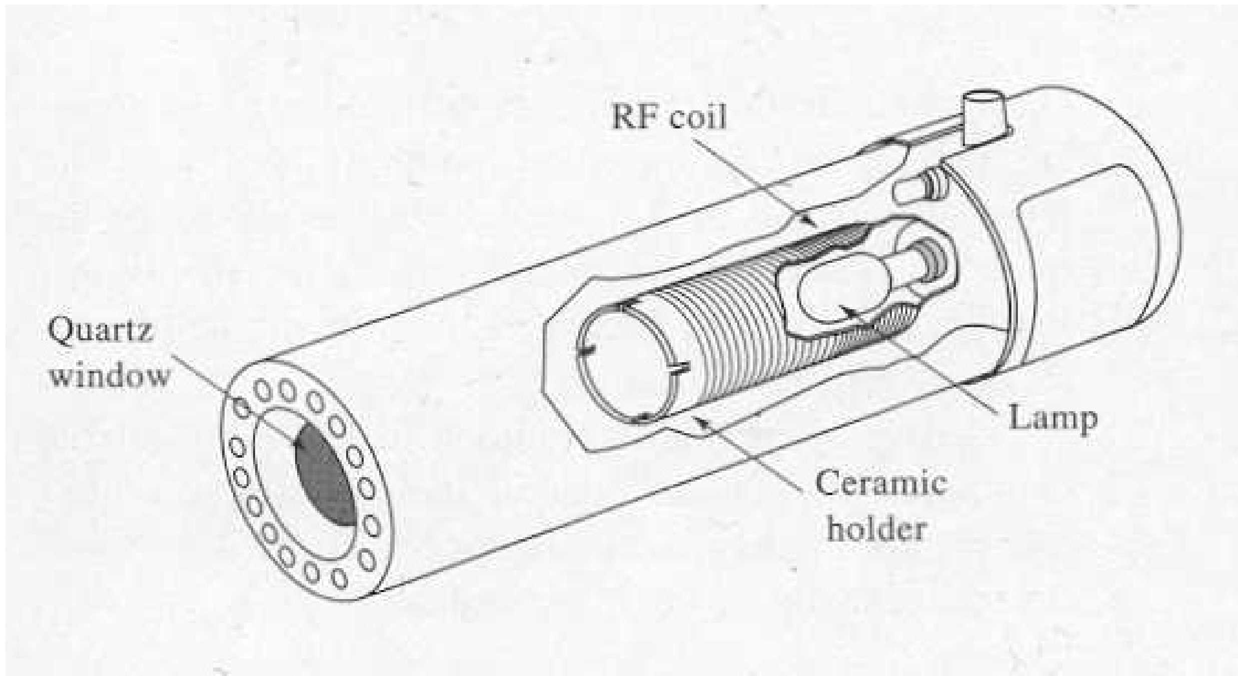


FIGURE 13-8 Attempt to use conventional UV–VIS source for atomic absorption.

Hollow Cathode Lamp (HCL) and Electrodeless Discharge Lamp (EDL)





These lamps produce only the spectral output from the element of interest and therefore are ideally suited to atomic absorption experiments

The sample must be converted to its atomic state which can be done at high temp. in a flame, furnace, plasma, arc or spark

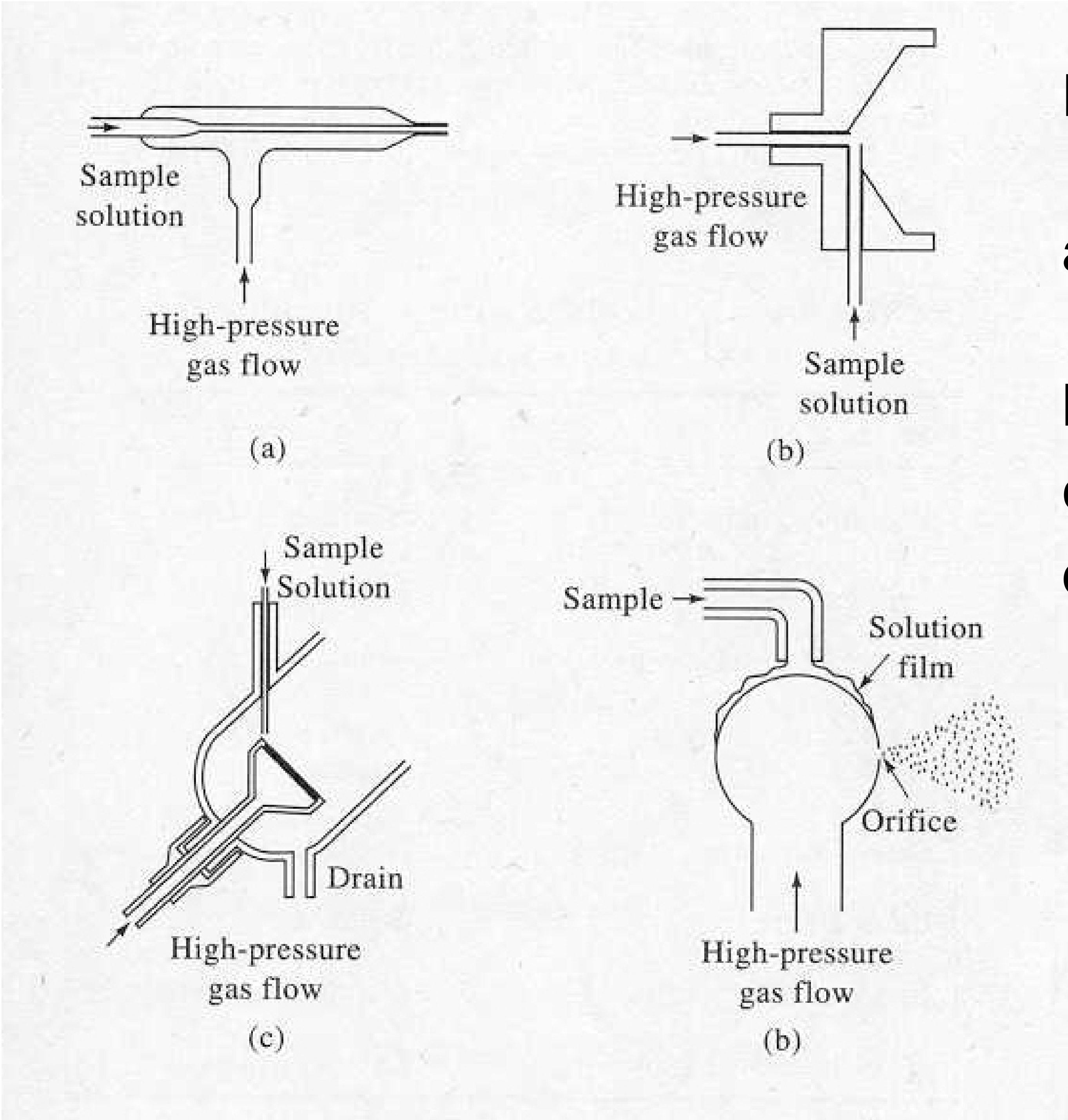
TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy

Type of Atomizer	Typical Atomization Temperature, °C
Flame	1700–3150
Electrothermal vaporization (ETV)	1200–3000
Inductively coupled argon plasma (ICP)	4000–6000
Direct current argon plasma (DCP)	4000–6000
Microwave-induced argon plasma (MIP)	2000–3000
Glow discharge plasma (GD)	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)

Introducing the sample to the high temperature source can be tricky

TABLE 8-2 Methods of Sample Introduction in Atomic Spectroscopy

Method	Type of Sample
Pneumatic nebulization	Solution or slurry
Ultrasonic nebulization	Solution
Electrothermal vaporization	Solid, liquid, solution
Hydride generation	Solution of certain elements
Direct insertion	Solid, powder
Laser ablation	Solid, metal
Spark or arc ablation	Conducting solid
Glow discharge sputtering	Conducting solid



Pneumatic nebulizers

a) concentric tube
b) cross-flow
c) fritted disk
d) Babington

Sample introduction for solutions:

1) Pneumatic nebulizers
2) Ultrasonic nebulizers
3) Electrothermal vaporizers
4) Hydride generation

$$3\ BH_4^- + 3\ H^+ + 4\ H_3AsO_3 \rightarrow 3\ H_3BO_3 + 4\ AsH_3 + 3\ H_2O$$

5) Cold vapor generation

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^o + Sn^{4+}$$

Solid sample introduction:

1) Laser ablation – zap sample with laser and sweep atoms into flame/plasma
2) Direct sample insertion – place sample directly in atomizer (e.g. furnace)
3) Electrothermal atomizers – electrically heat graphite or tantalum boat
4) Arc/Spark ablation – coat sample on electrode or place in electrode well or cup
5) Glow discharge technique – see p 204

Chapter 9: Atomic Absorption & Atomic Fluorescence Spectrometry

- Sample Atomization
- Atomic Absorption (AA)
- Atomic Fluorescence (AF)

- Both AA and AF require a light source
- Like Molecular Absorption & Fluorescence, in AA high intensity is NOT required, in AF high intensity results in greater sensitivity

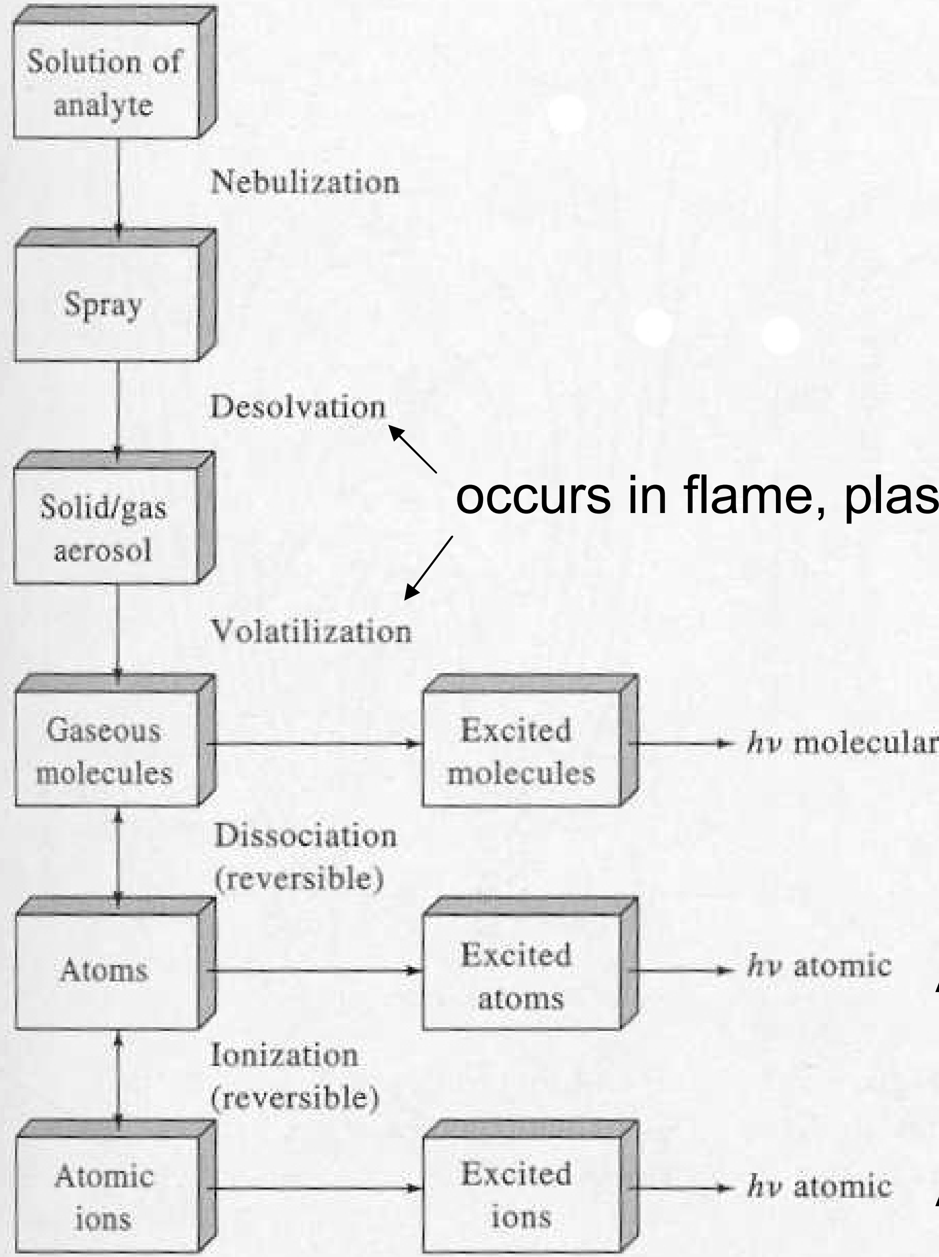


Figure 9-1 Processes occurring during atomization.

occurs in flame, plasma, etc.

Molecular emission is generally unwanted & can cause interference

AA

AE

AE

TABLE 9-1 Properties of Flames

They're HOT !

Fuel	Oxidant	Temperatures, °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

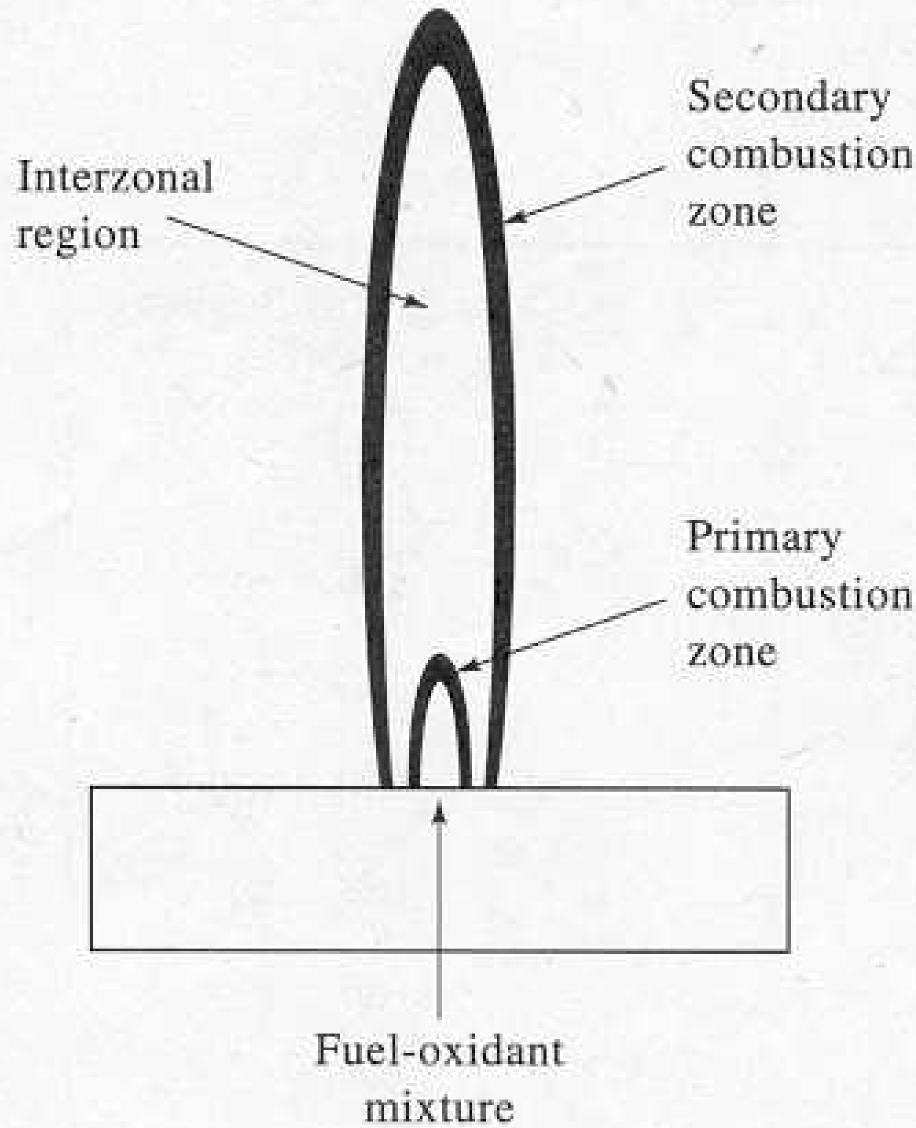


Figure 9-2 Regions in a flame.

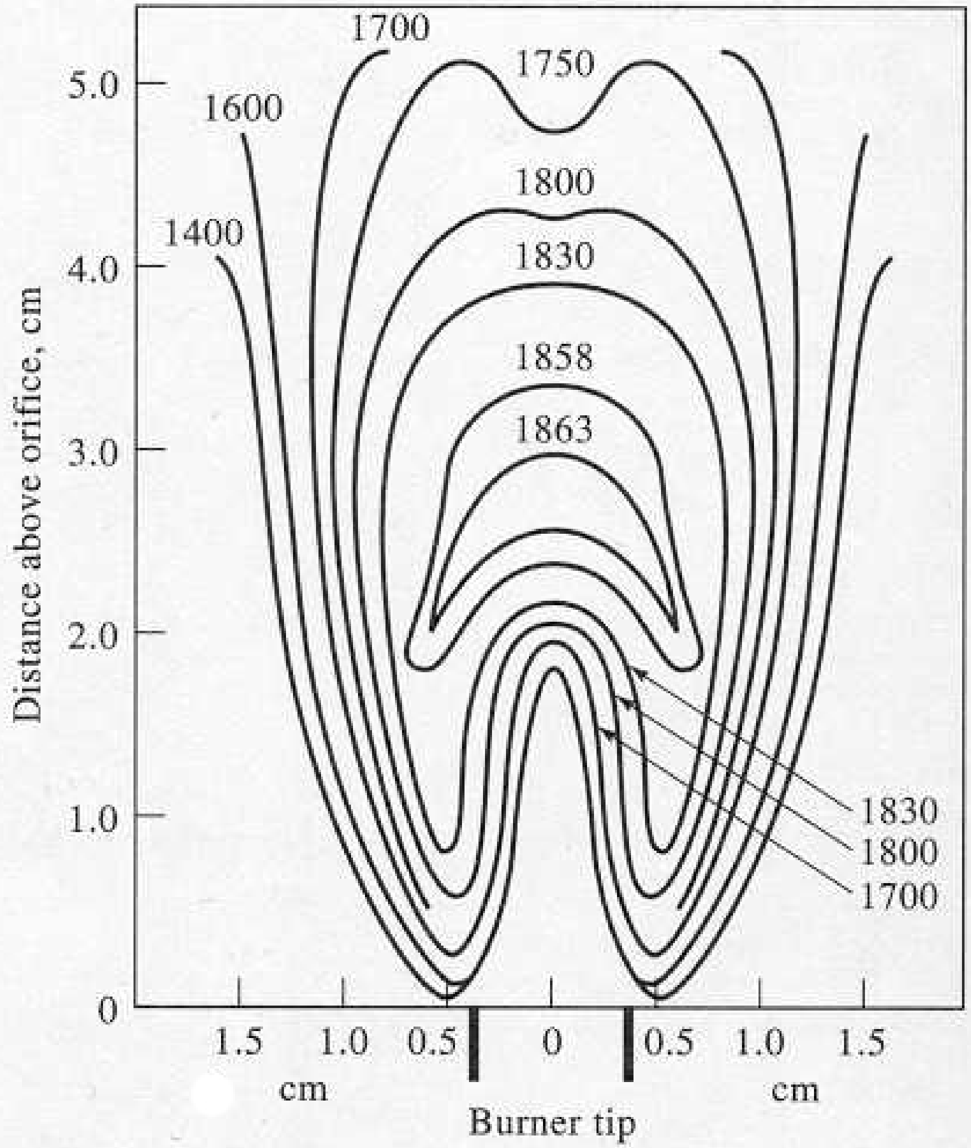


Figure 9-3 Temperature profiles in °C for a natural gas/air flame. *(From B. Lewis and G. vanElbe,* J. Chem. Phys., ***1943****,* 11, *94. With permission.)*

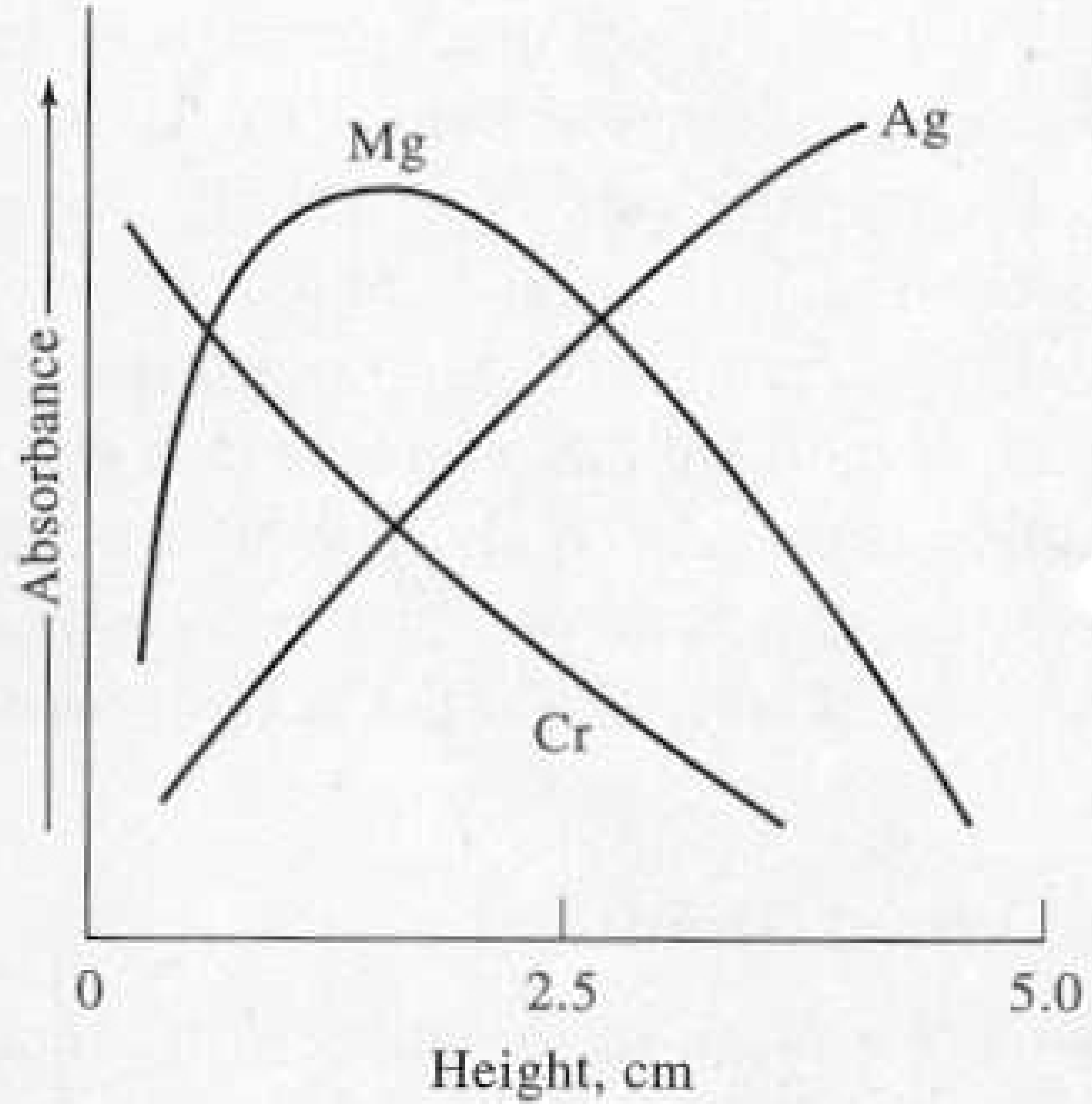
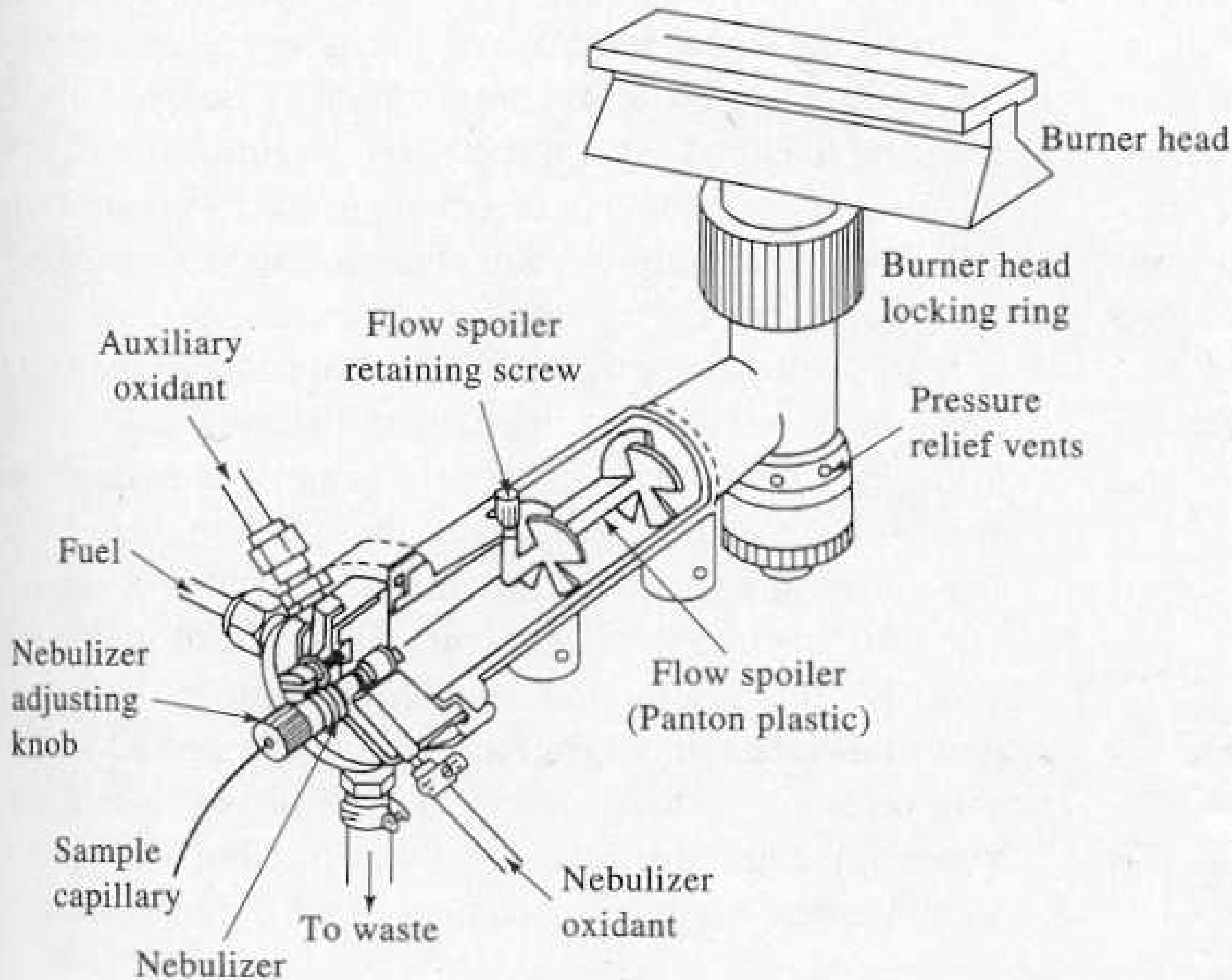


Figure 9-4 Flame absorbance profile for three elements.


Burner head
Burner head locking ring
Pressure relief vents
Flow spoiler retaining screw
Auxiliary oxidant
Fuel
Nebulizer adjusting knob
Sample capillary
Nebulizer
To waste
Nebulizer oxidant
Flow spoiler (Panton plastic)

AA Slot Burner and Flame

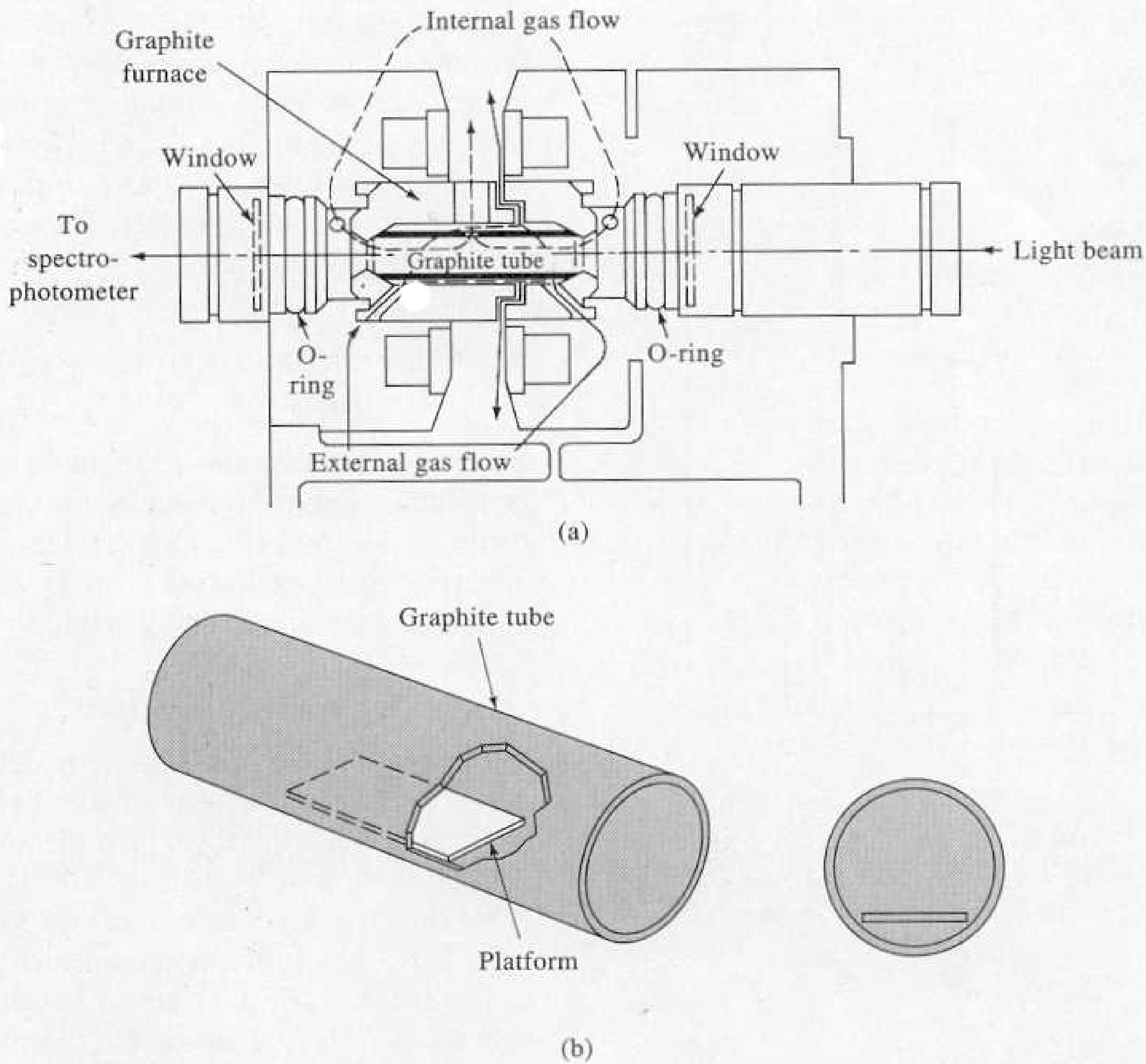



Figure 9-6 (a) Cross-sectional view of a graphite furnace. *(Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.)* (b) The L'vov platform and its position in the graphite furnace.

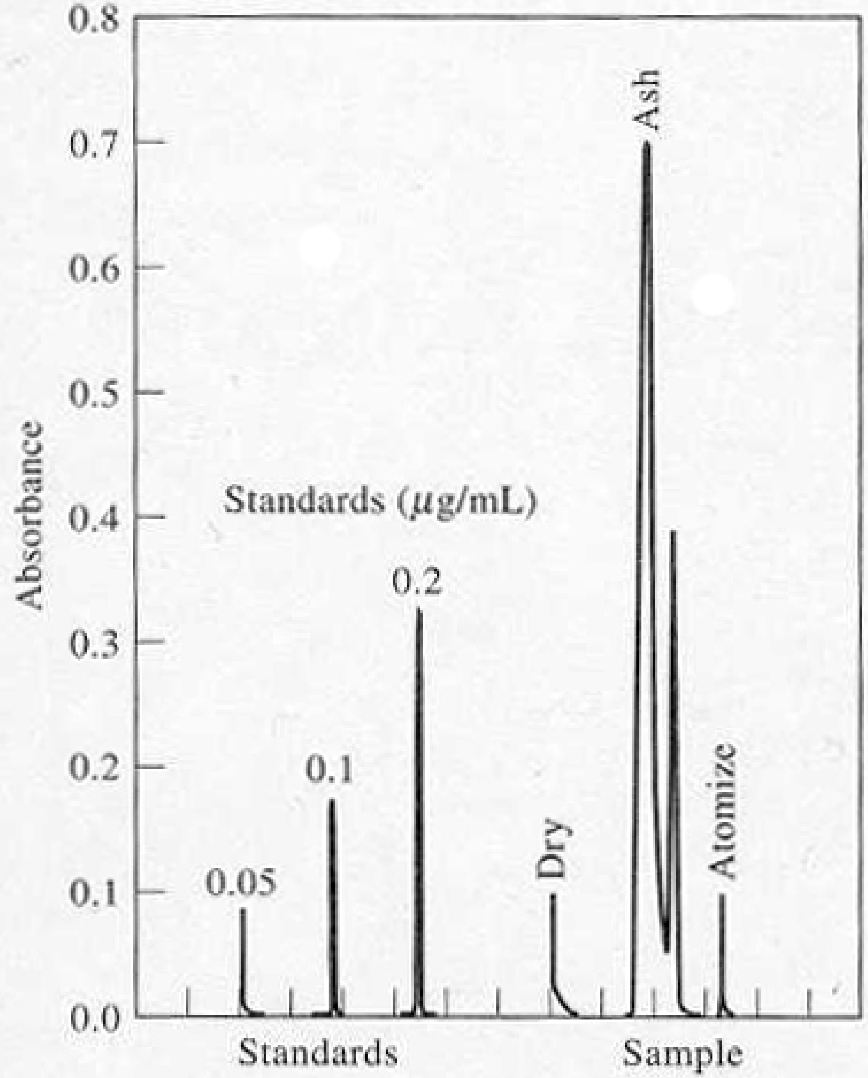


Figure 9-7 Typical output from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 μL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively. *(Courtesy of Varian Instrument Division, Palo Alto, CA.)*

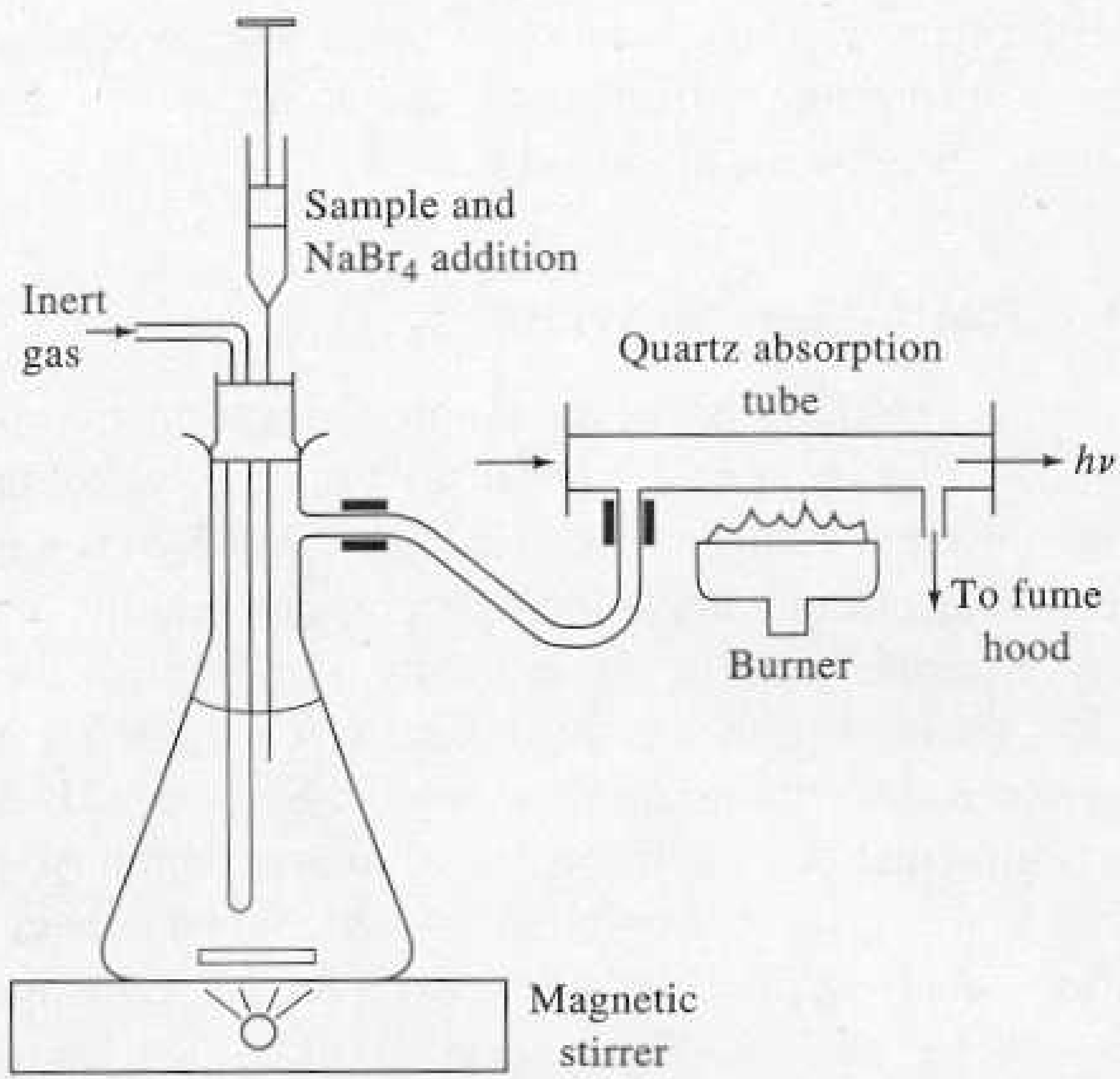


Figure 9-9 A hydride generation and atomization system for atomic absorption spectrometry.

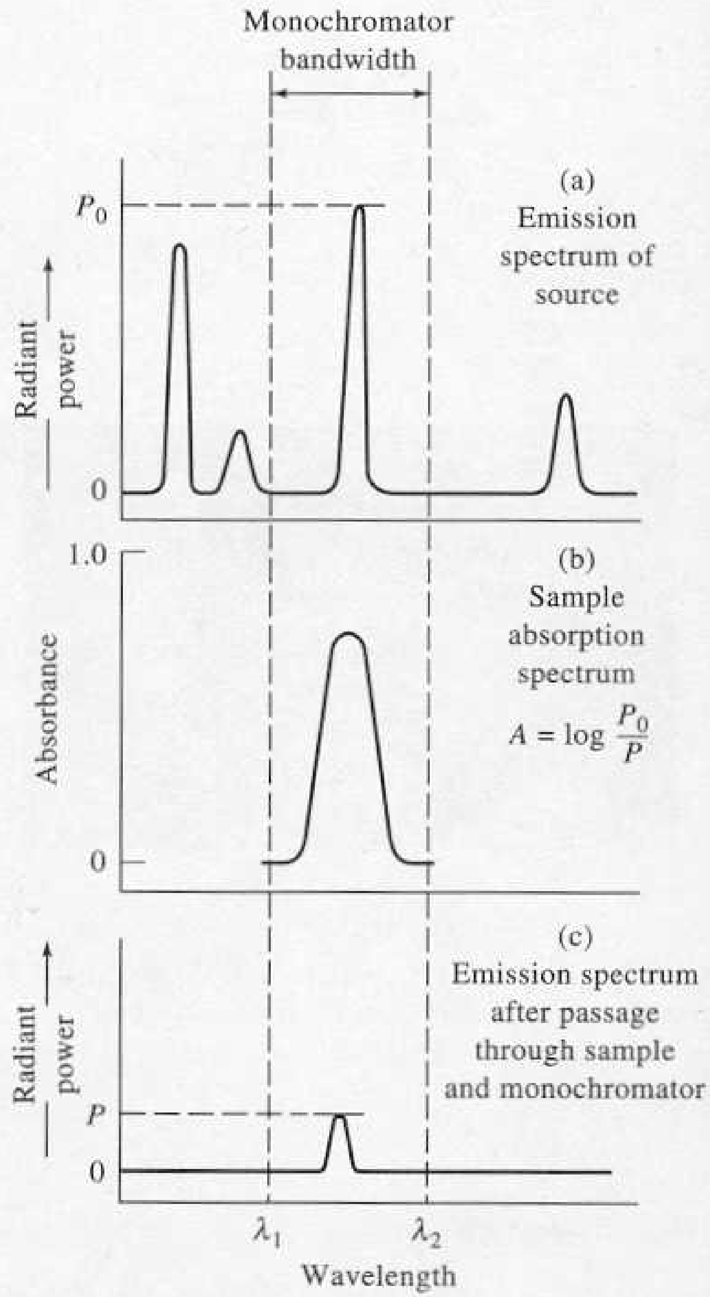


Figure 9-10 Absorption of a resonance line by atoms.

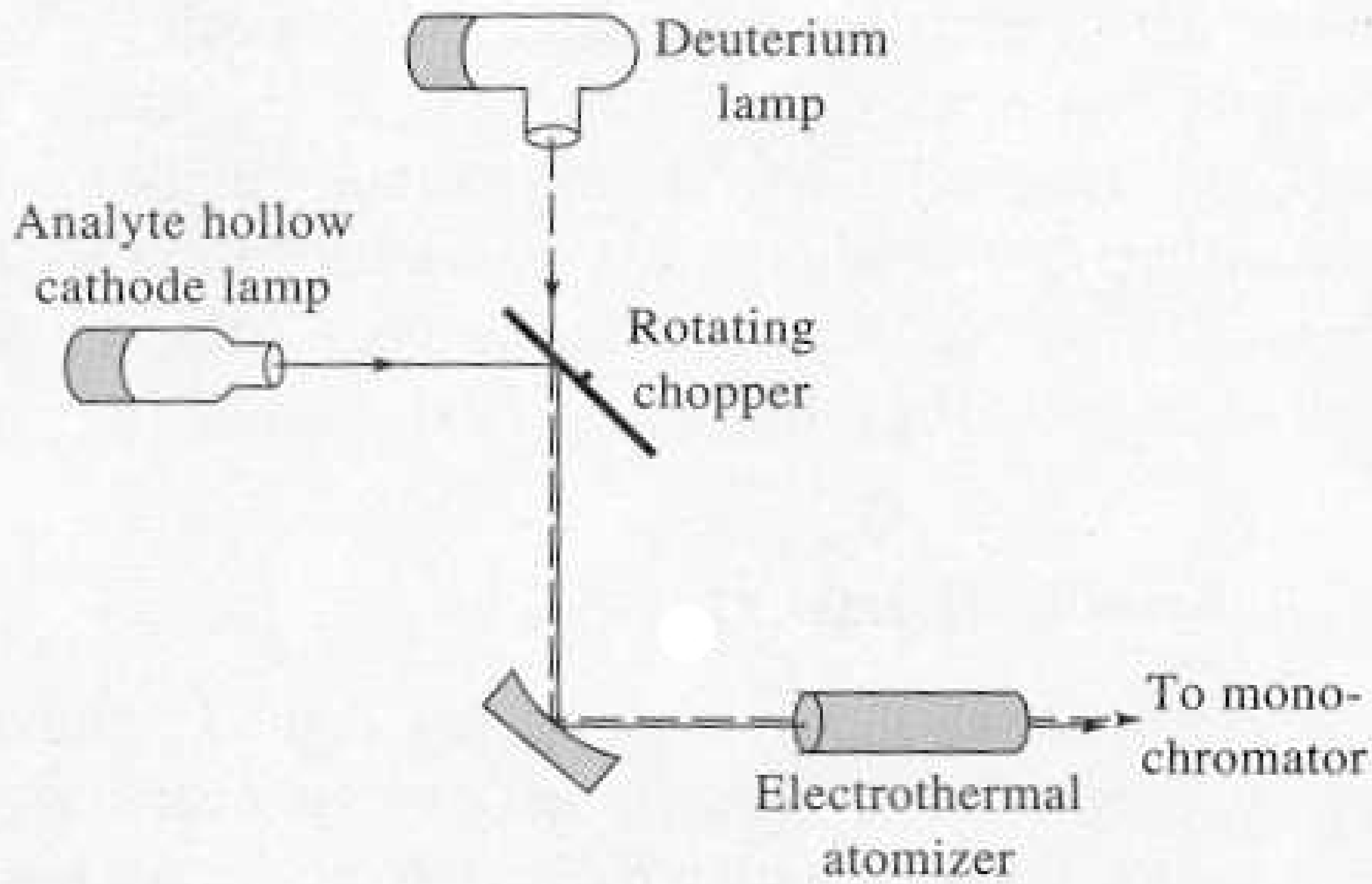


Figure 9-14 Schematic of a continuum-source background correction system. Note that the chopper can be dispensed with by alternately pulsing each lamp.

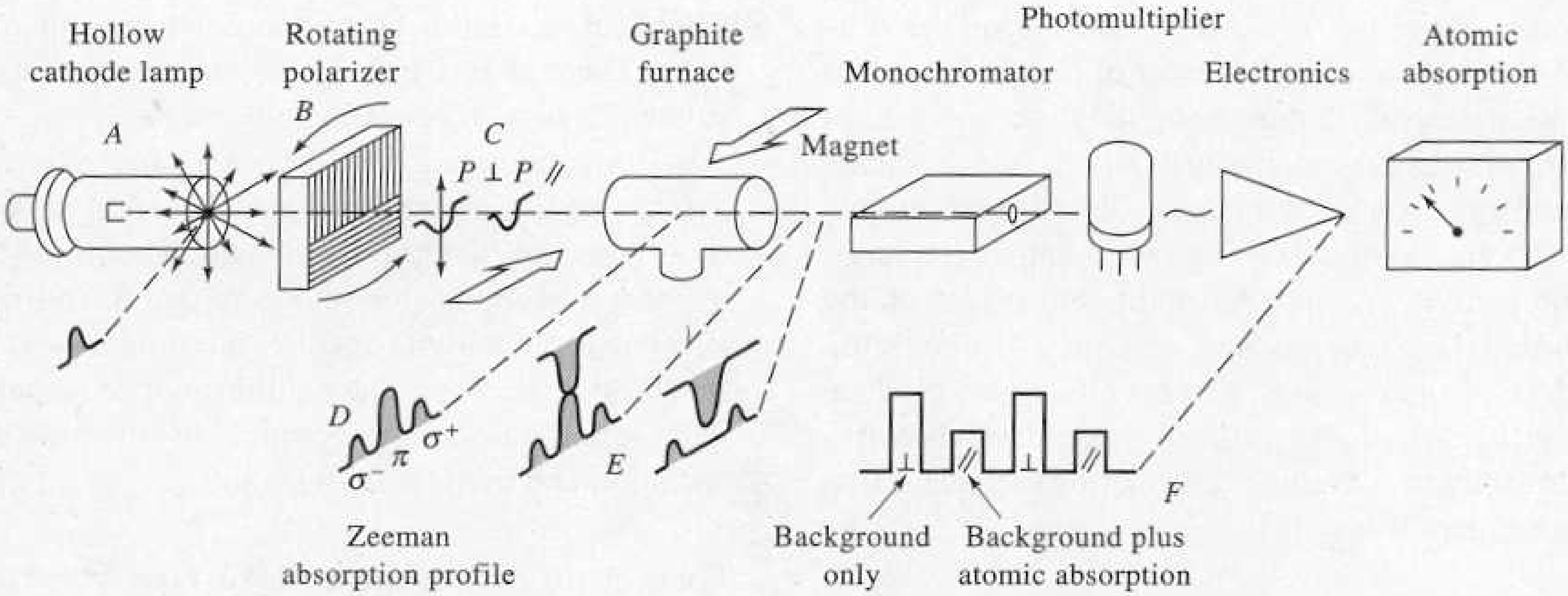


Figure 9-15 Schematic of an electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect. *(Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)*

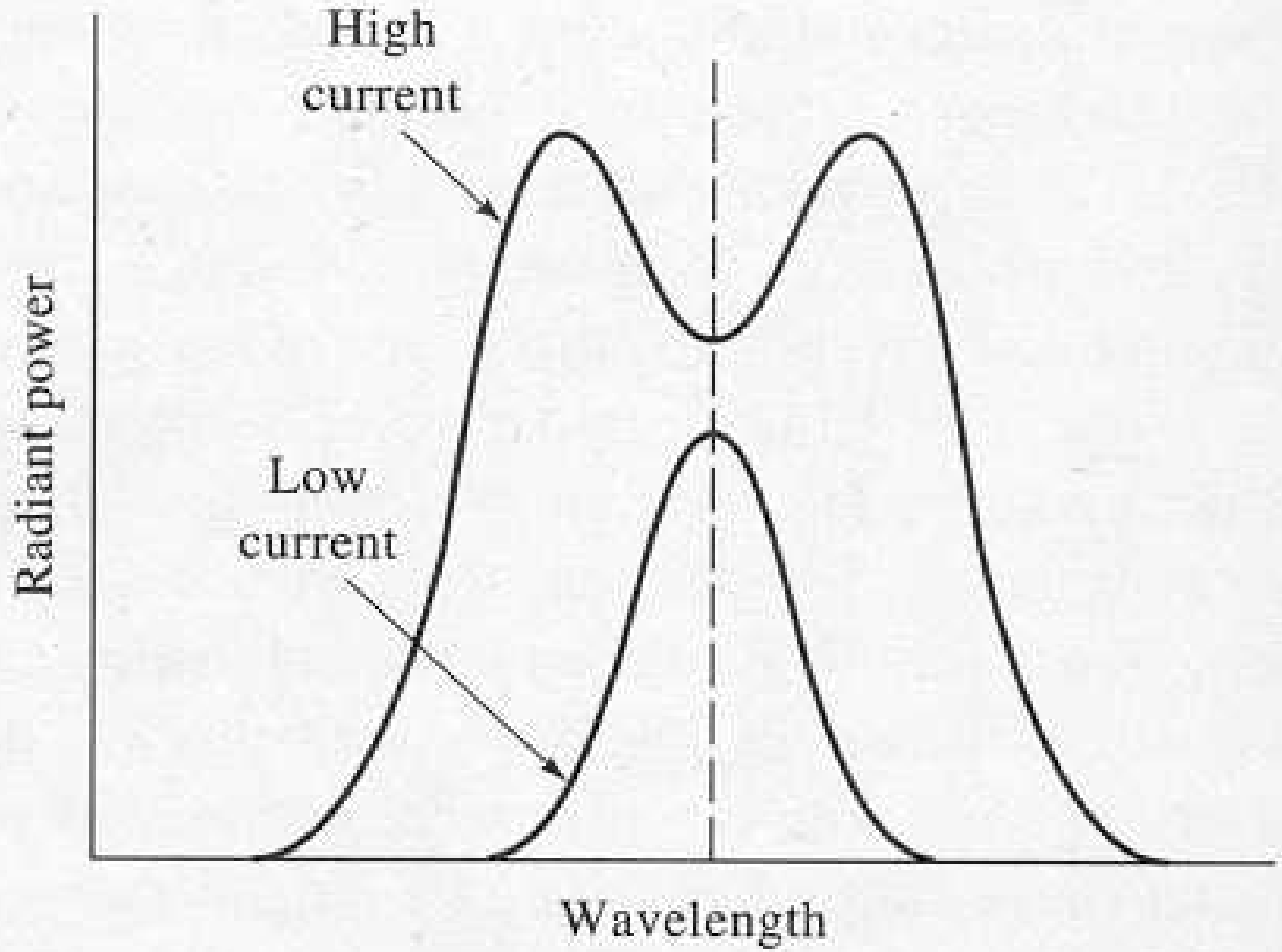


Figure 9-16 Emission line profiles for a hollow-cathode lamp operated at high and low currents.

TABLE 9-2 Degree of Ionization of Metals at Flame Temperatures*

		Fraction Ionized at the Indicated Pressure and Temperature			
	Ionization Potential, eV	$p = 10^{-4}$ atm		$p = 10^{-6}$ atm	
Element		2000 K	3500 K	2000 K	3500 K
Cs	3.893	0.01	0.86	0.11	>0.99
Rb	4.176	0.004	0.74	0.04	>0.99
K	4.339	0.003	0.66	0.03	0.99
Na	5.138	0.0003	0.26	0.003	0.90
Li	5.390	0.0001	0.18	0.001	0.82
Ba	5.210	0.0006	0.41	0.006	0.95
Sr	5.692	0.0001	0.21	0.001	0.87
Ca	6.111	3×10^{-5}	0.11	0.0003	0.67
Mg	7.644	4×10^{-7}	0.01	4×10^{-6}	0.09

*Data from B. L. Vallee and R. E. Thiers, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 6, p. 3500. New York: Interscience, 1965. Reprinted with permission of John Wiley & Sons, Inc.

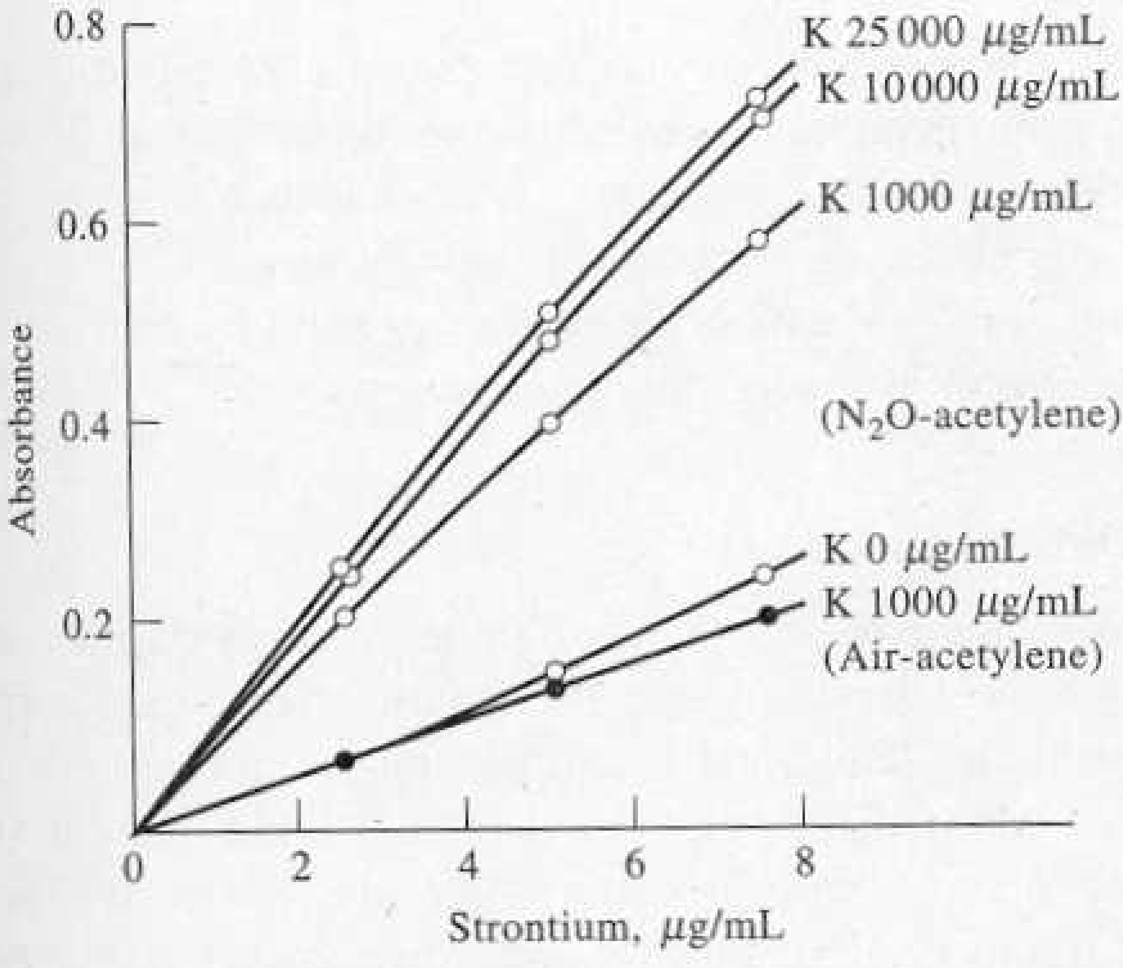


Figure 9-17 Effect of potassium concentration on the calibration curve for strontium. *(Reprinted with permission from J. A. Bowman and J. B. Willis,* Anal. Chem., *1967, 39, 1220. Copyright 1967 American Chemical Society.)*

TABLE 9-3 Detection Limits (ng/mL)* for Selected Elements†

Element	AAS‡ Flame	AAS§ Electrothermal	AES‡ Flame	AES‡ ICP	AFS‡ Flame
Al	30	0.005	5	2	5
As	100	0.02	0.0005	40	100
Ca	1	0.02	0.1	0.02	0.001
Cd	1	0.0001	800	2	0.01
Cr	3	0.01	4	0.3	4
Cu	2	0.002	10	0.1	1
Fe	5	0.005	30	0.3	8
Hg	500	0.1	0.0004	1	20
Mg	0.1	0.00002	5	0.05	1
Mn	2	0.0002	5	0.06	2
Mo	30	0.005	100	0.2	60
Na	2	0.0002	0.1	0.2	—
Ni	5	0.02	20	0.4	3
Pb	10	0.002	100	2	10
Sn	20	0.1	300	30	50
V	20	0.1	10	0.2	70
Zn	2	0.00005	0.0005	2	0.02

*Nanogram/milliliter = 10^{-3} μg/mL = 10^{-3} ppm.