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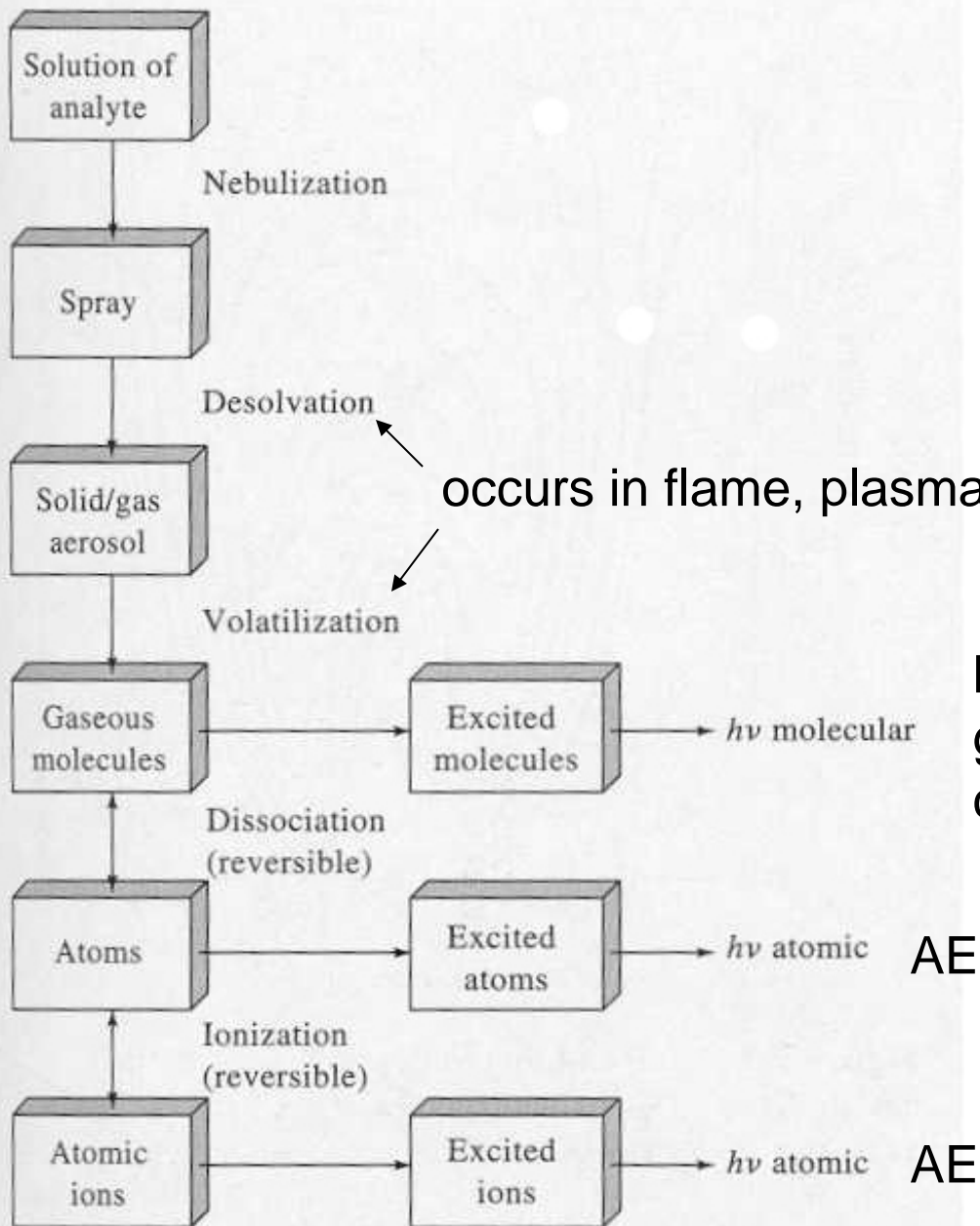
- Sample Atomization
- Atomic Absorption (AA)
- Atomic Fluorescence (AF)

- 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.

TABLE 9-1 Properties of Flames   They're HOT !

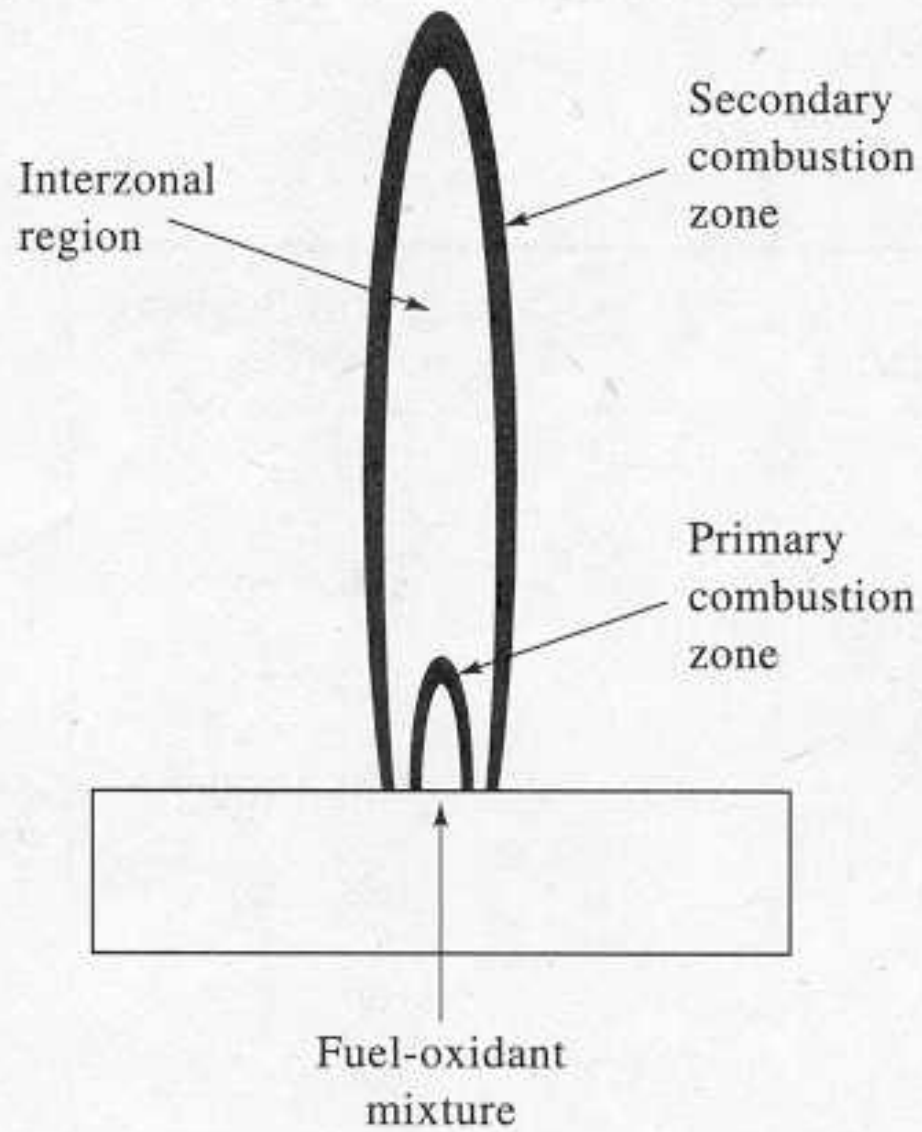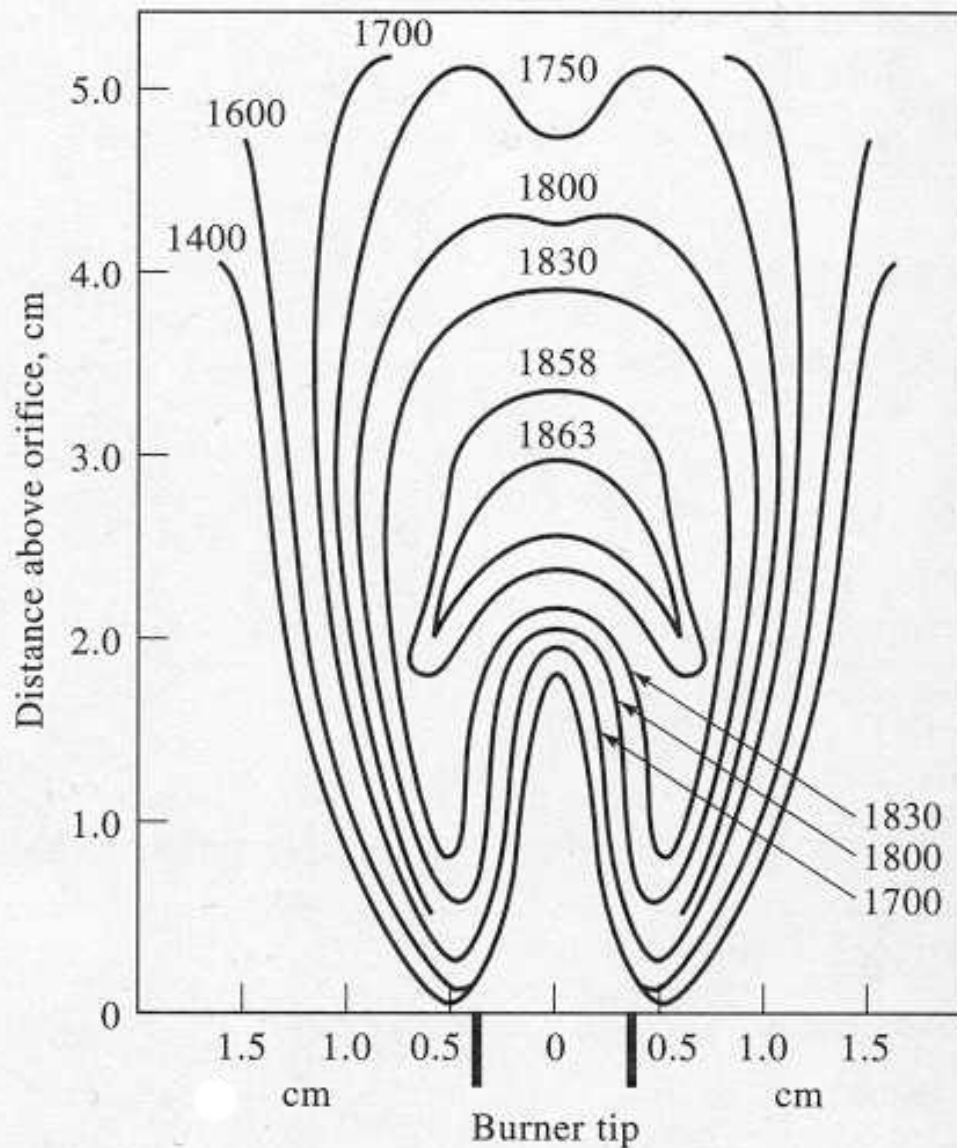| Fuel	Oxidant	Temperatures, °C	Maximum Burning Velocity (cm s^{-1})
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	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.)*
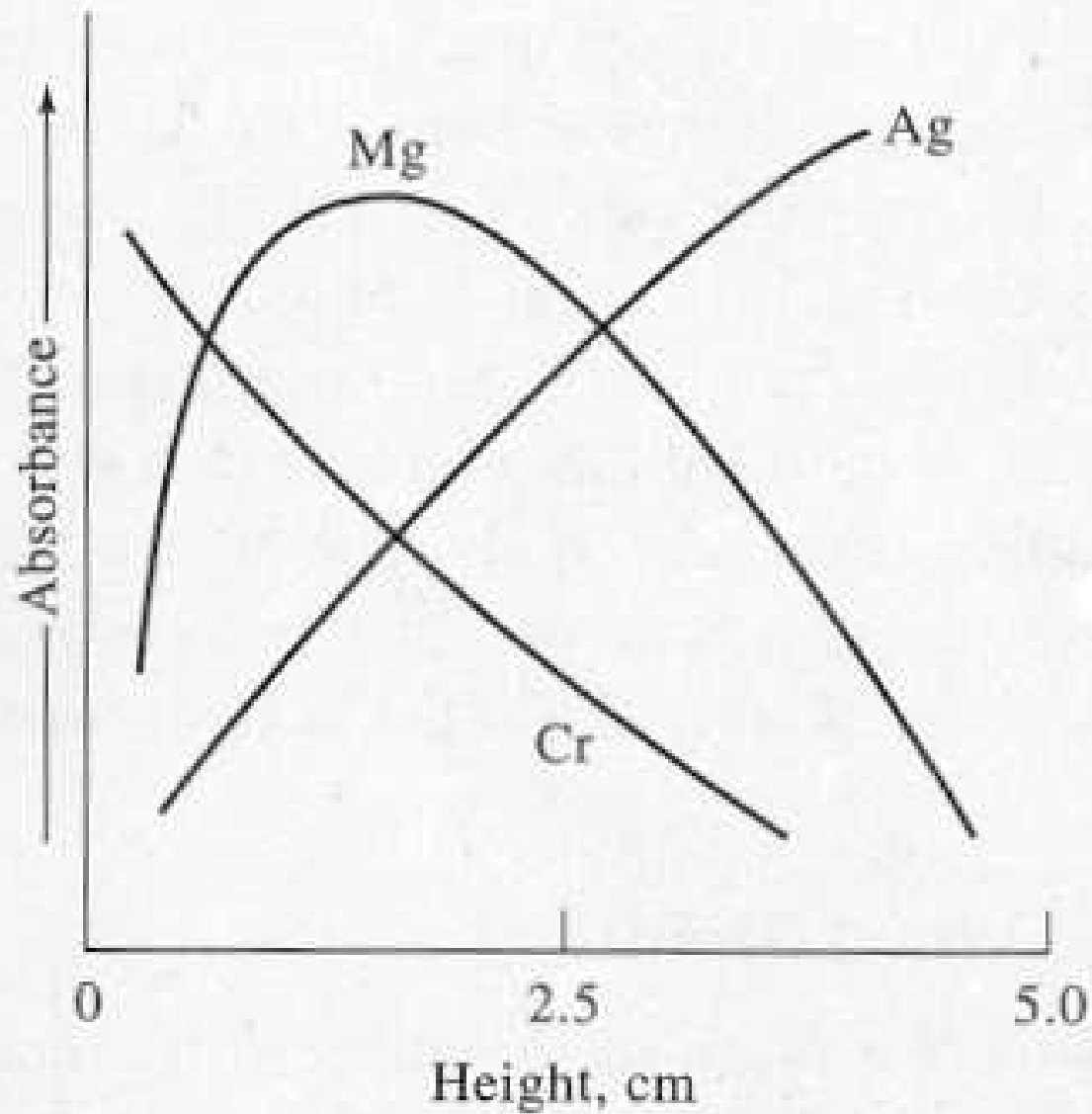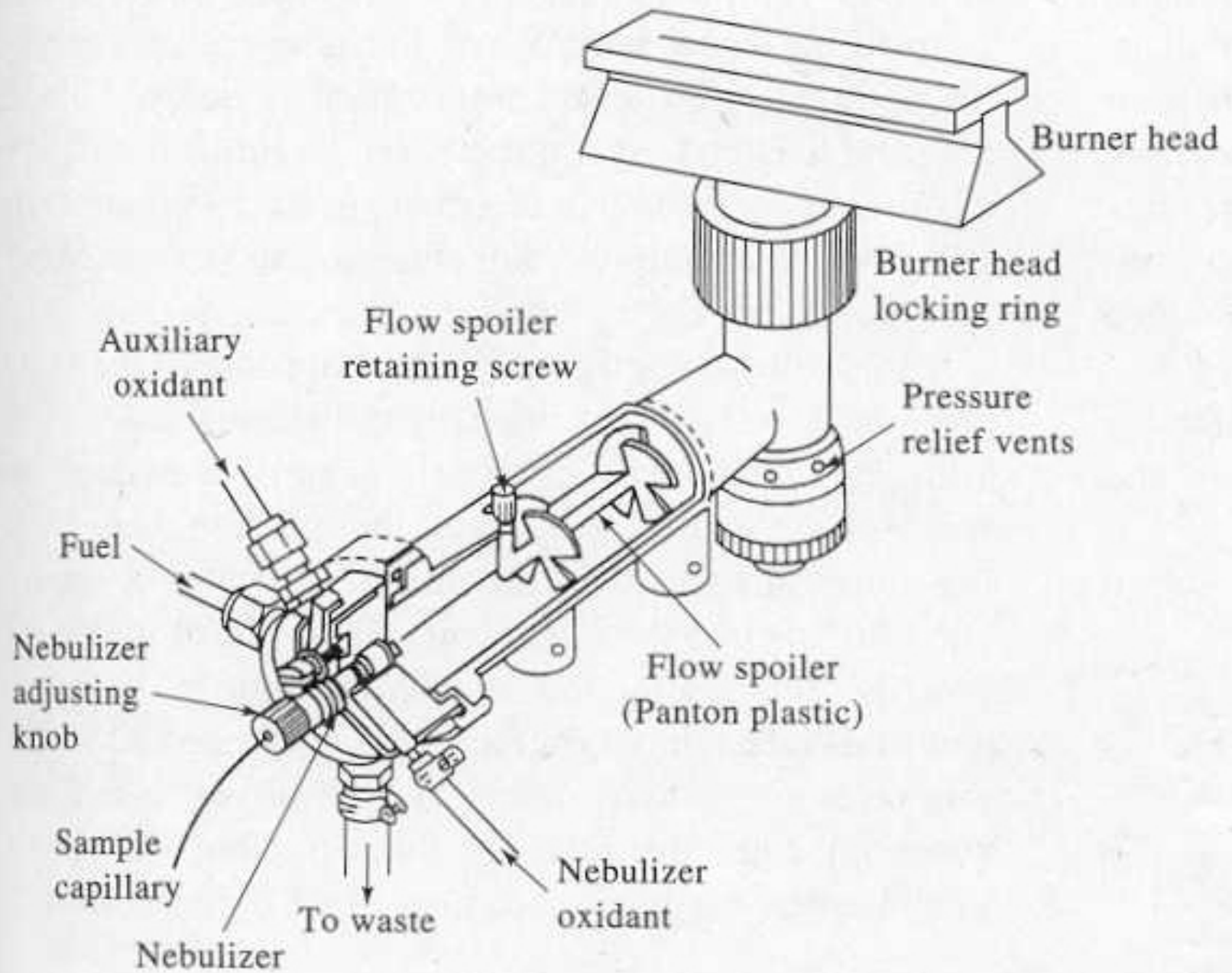
Figure 9-4 Flame absorbance profile for three elements.

Burner head

Burner head locking ring

Pressure relief vents

Flow spoiler retaining screw

Auxiliary oxidant

Flow spoiler (Panton plastic)

Fuel

Nebulizer adjusting knob

Sample capillary

Nebulizer

To waste

Nebulizer oxidant

AA Slot Burner and Flame

Internal gas flow

Graphite furnace

Window

Window

To spectro-photometer

Graphite tube

Light beam

O-ring

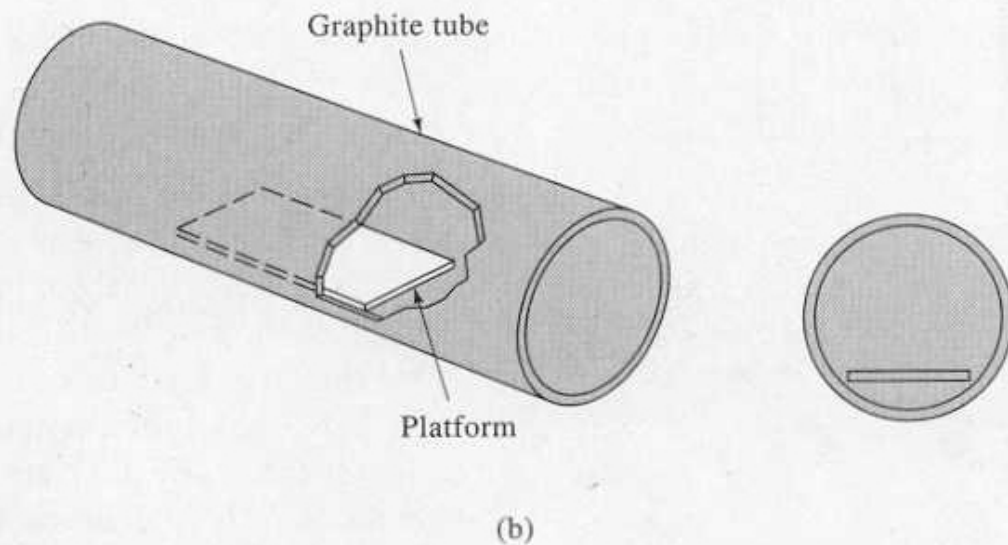O-ring

External gas flow

(a)
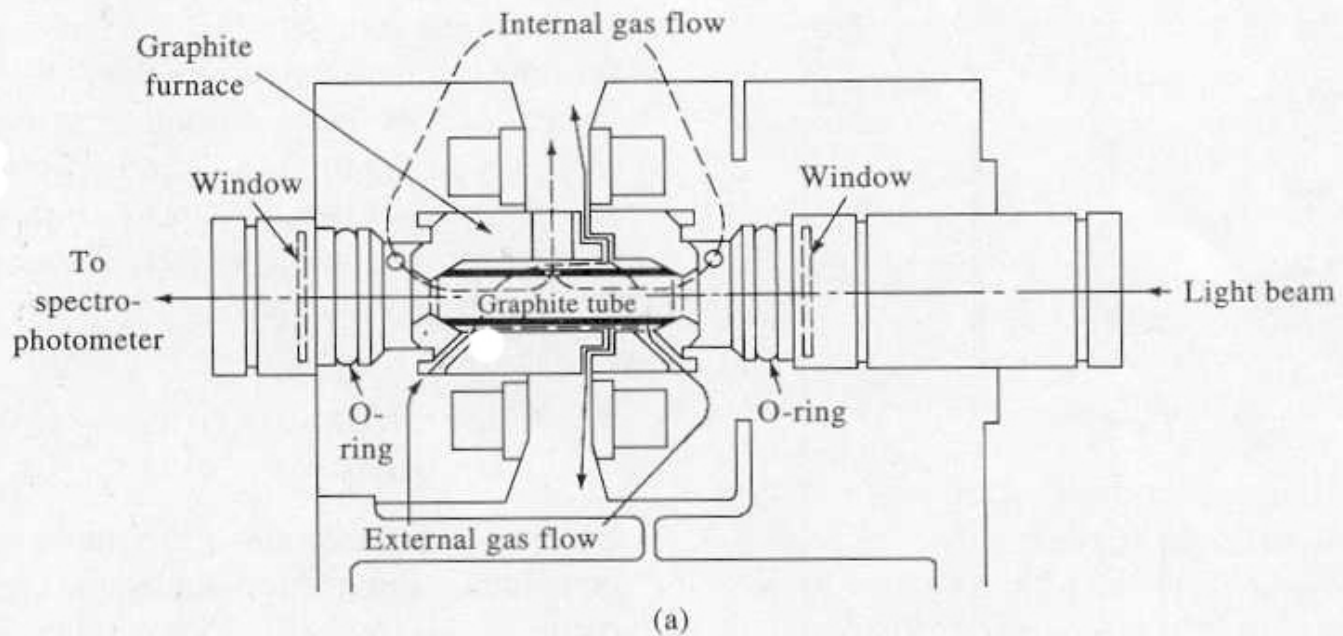
Graphite tube

Platform

(b)

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.

Sample introduction for solutions:

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

$$3\ BH_4^-\ +\ 3\ H^+\ +\ 4\ H_3AsO_3\ \rightarrow$$
$$3\ H_3BO_3\ +\ 4\ AsH_3\ +\ 3\ H_2O$$
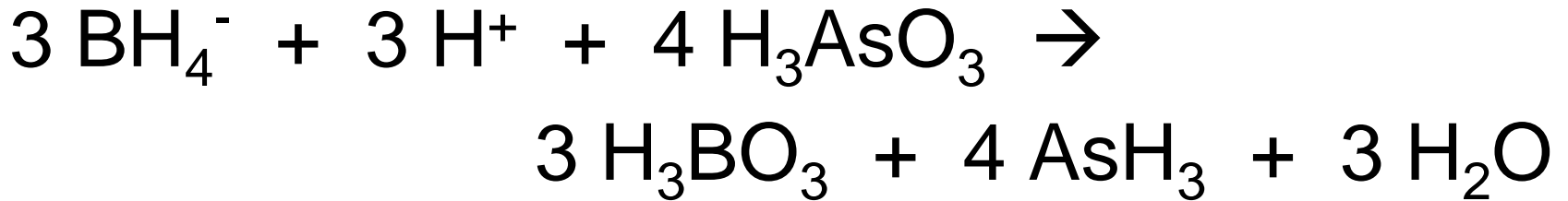
5) Cold vapor generation

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

Figure 9-9 A hydride generation and atomization system for atomic absorption spectrometry.
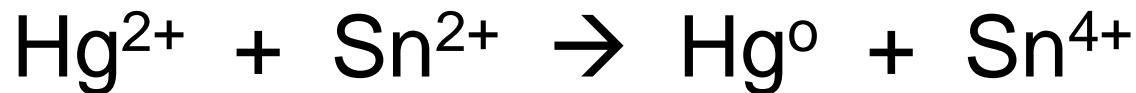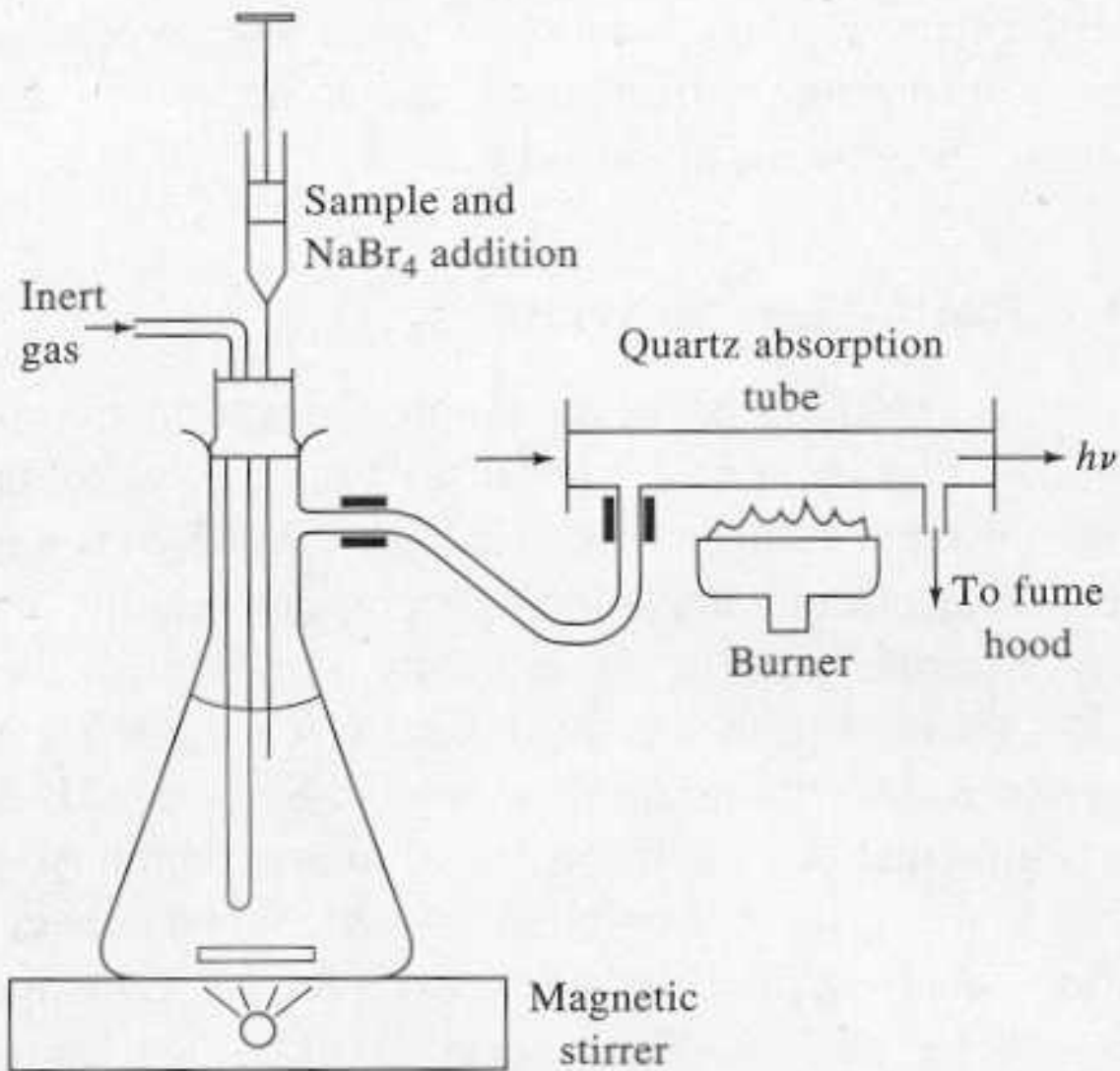
There are many possible variations for the hydride generation apparatus

Interferences in AA can be

- Spectral – atomic spectral lines overlap or are too close to resolve – these are rare & generally well known or characterized

- Matrix – scattering of radiation during atomization (smoke), enhancement by matrix elements, structured background – handled by background correction

- Chemical – reactions that take place to alter the analyte (like Ca atoms reacting with PO_4 to form a new species) – change conditions

Background Correction in AA

- Two-Line correction (not very common)
- Continuous source correction (very common)
- Zeeman background correction (common for graphite furnace instruments)
- Smith-Hieftje correction (relatively new '83)

Monochromator bandwidth

(a) Emission spectrum of source

P_0

Radiant power

0

1.0

(b) Sample absorption spectrum

$$A = \log \frac{P_0}{P}$$

Absorbance

0

(c) Emission spectrum after passage through sample and monochromator

Radiant power

P

0

λ_1 λ_2

Wavelength

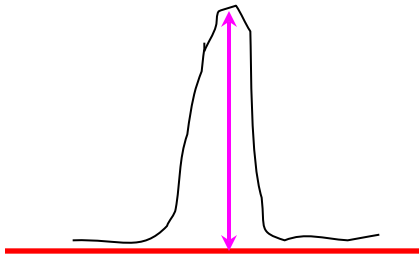**Figure 9-10** Absorption of a resonance line by atoms.
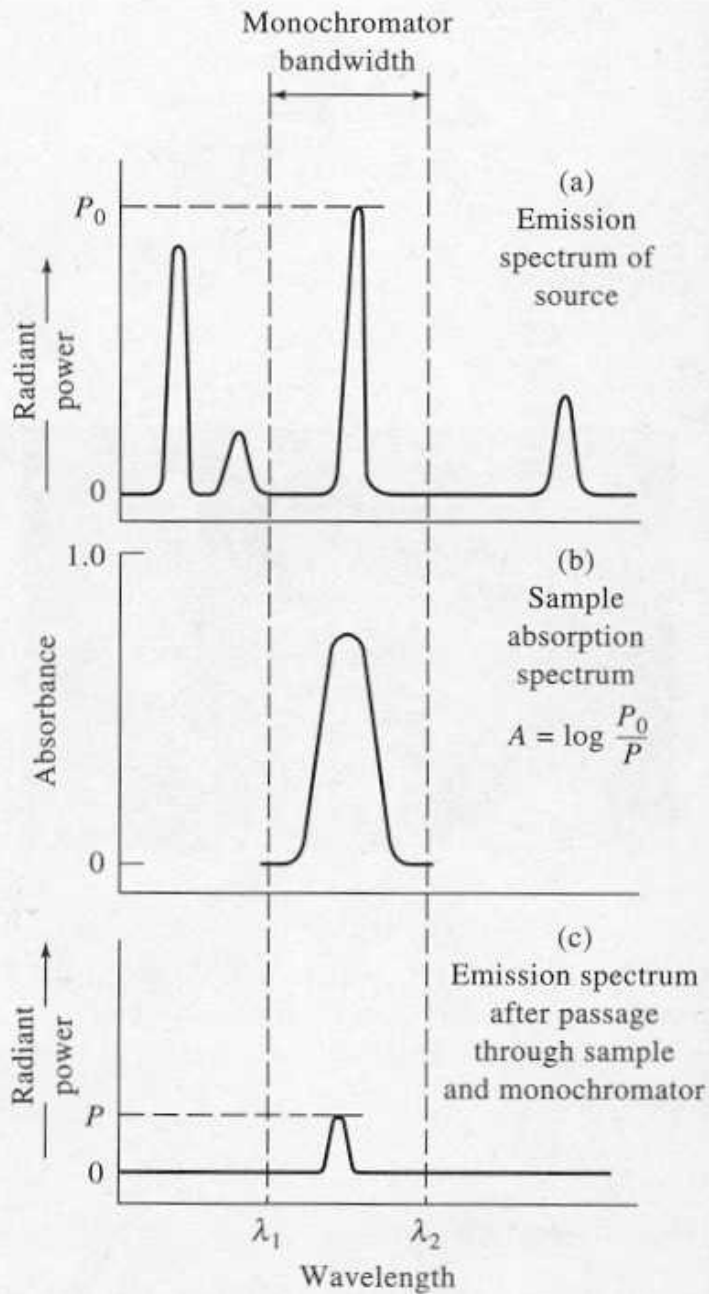
Normal or idealized situation for the absorption of source radiation in AA

Problems arise if the sample absorption is interfered with by a matrix component
- sloped baseline
- overlapping molecular band

Background correction is then needed

Normally assume baseline is flat not structured. In the absence of peak would have flat baseline Peak height easily measured
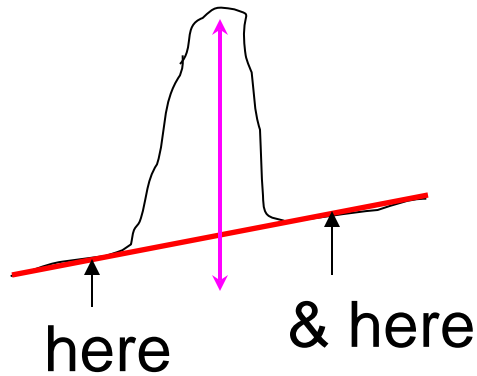
What if baseline is sloped?
How is peak height measured?

here   & here

Need measurement of baseline
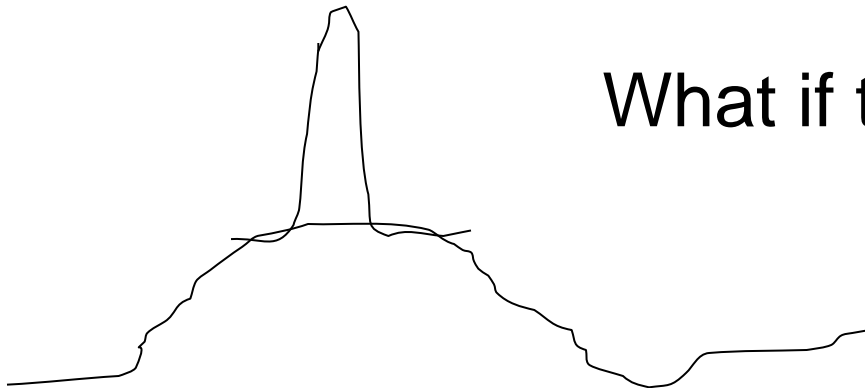
What if the baseline is really a mess?

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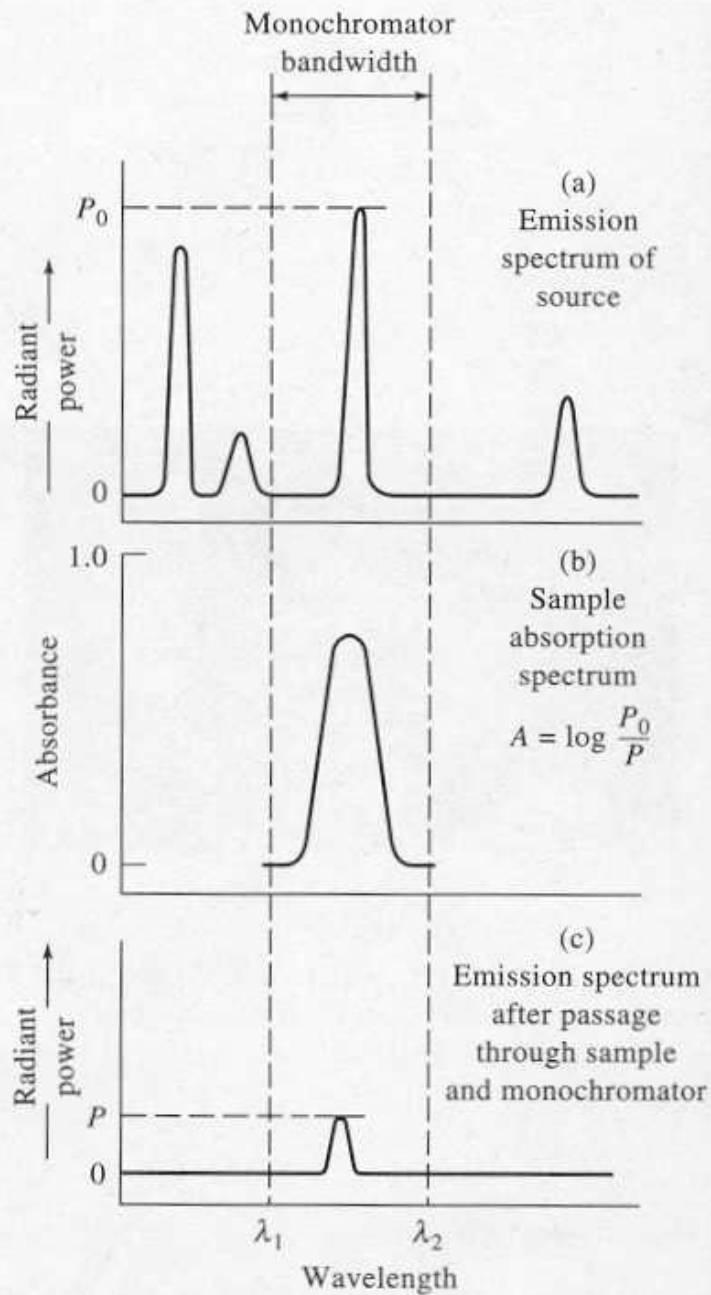
Figure 9-10 Absorption of a resonance line by atoms.

The AA source (HCL or EDL) tells us the absorbance at the λ of interest

Using another light source will allow us to determine the background absorbance

Typically we are interested in points on either side of the peak

line source
for AA

continuum
source for
background
correction

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

1 nm

P_0

"White" light source with monochromator bandpass ~ 1 nm

Typical broad absorption band width ~ 100 nm

Interaction of source with sample

P_A

$P = P_0 - P_A$

Signal to detector signal ∝ area

UV-vis Molecular Absorption

P_0

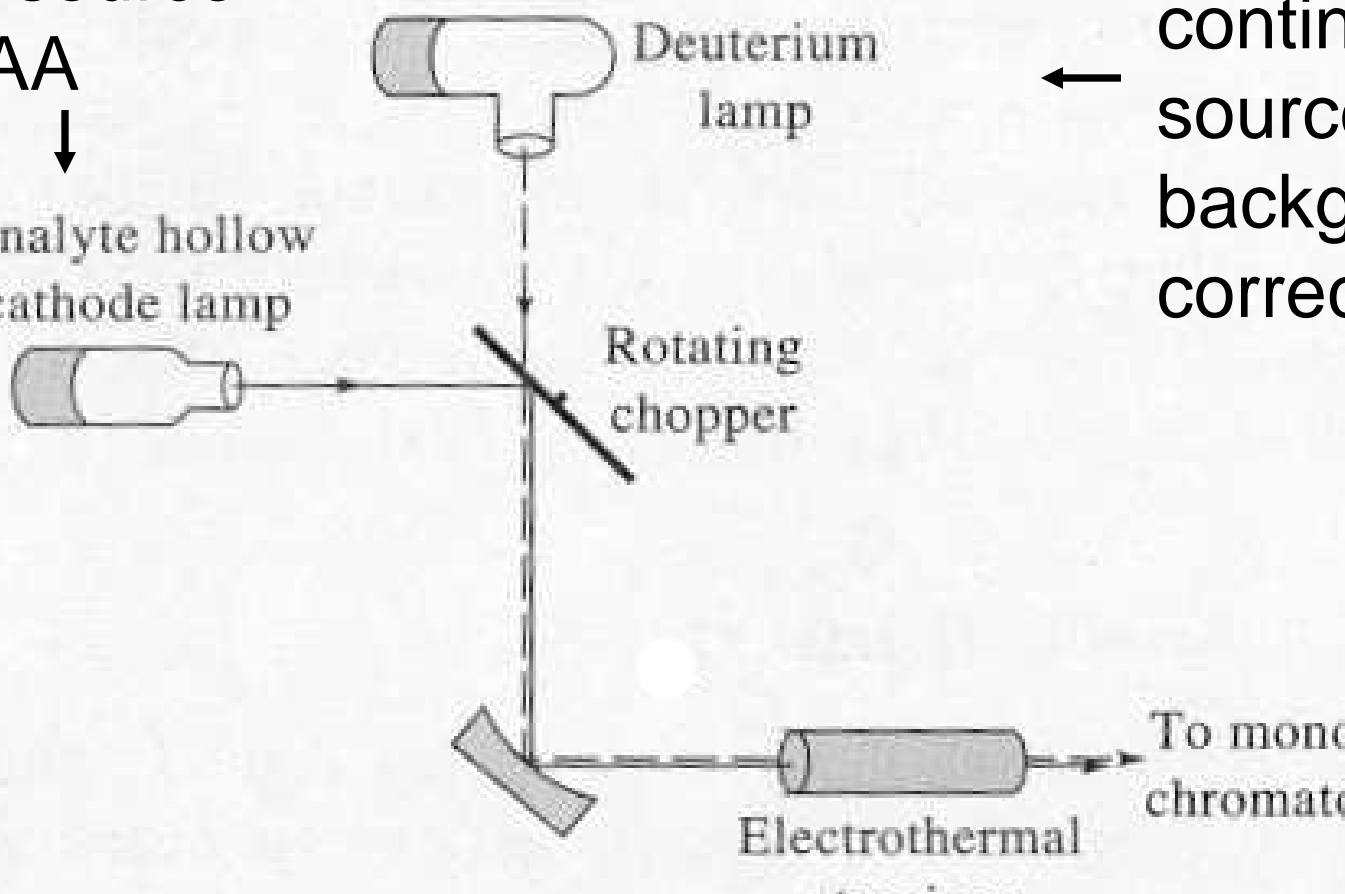"White" light source with monochromator bandpass ~ 1 nm

Sharp atomic absorption line width ~ 0.01 nm

Interaction of source with sample

P_A

$P = P_0 - P_A$

Signal to detector signal ∝ area, essentially none absorbed $P \cong P_0$
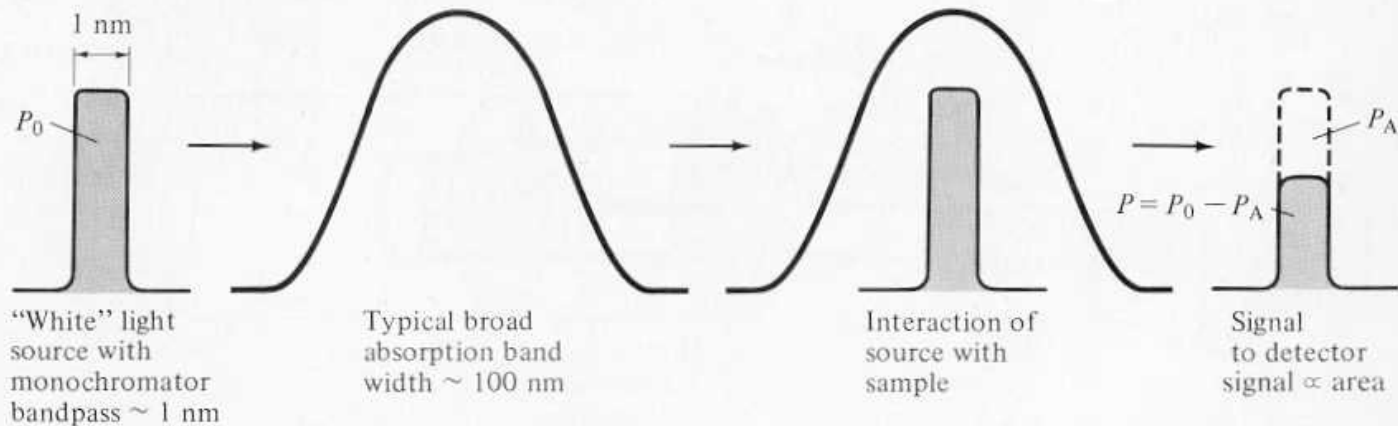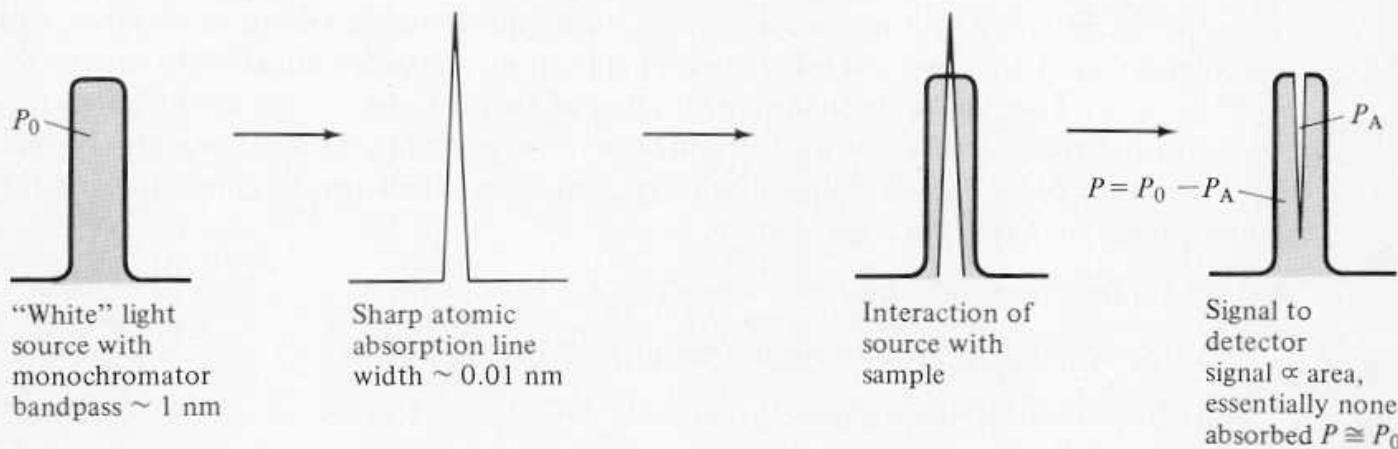
Attempt to use continuum source for Atomic Absorption

This shows (bottom) that a continuum source is not suitable for AA. However, it will work for background correction. The atomic line absorbs minimally, but the back-ground on either side of the line will be measured

The Zeeman effect splits the absorption peak in a magnetic field & shifts absorption to higher & lower wavelength. The new absorption peaks interact differently with polarized light allowing analyte & background absorbance to be measured
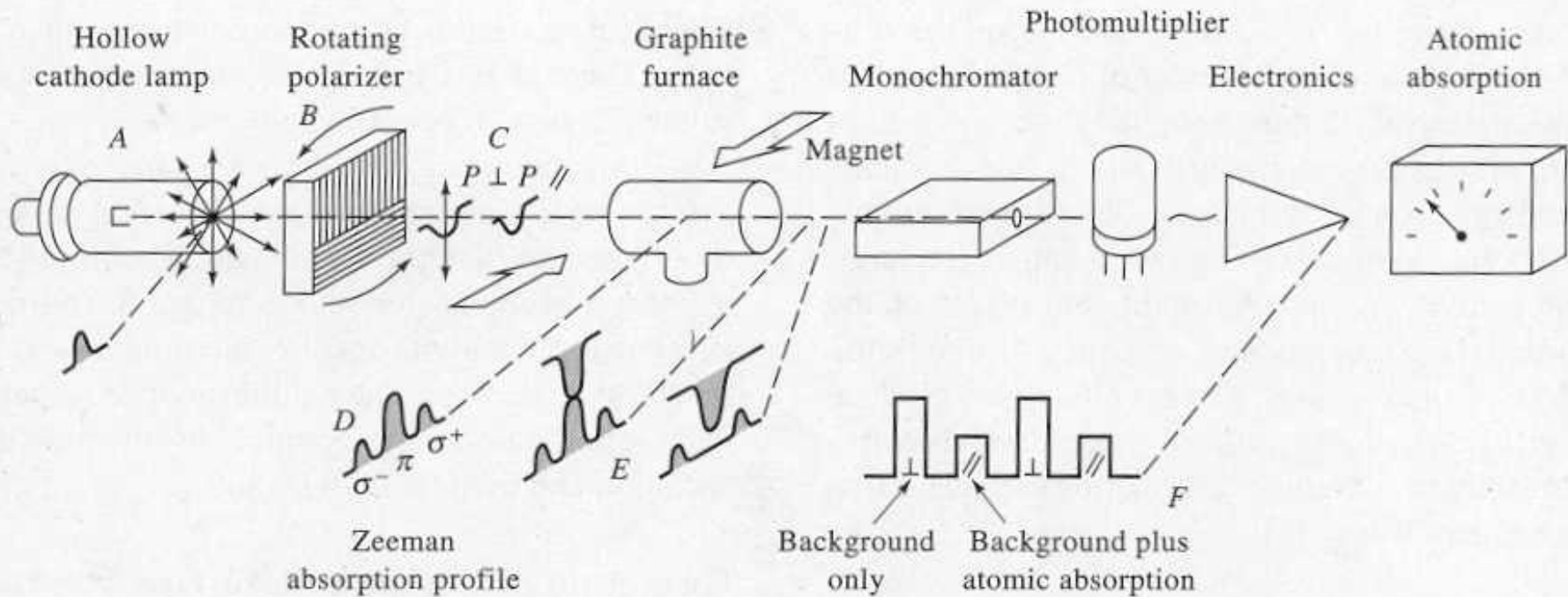
Figure 9-15   Schematic of an electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect.   *(Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)*
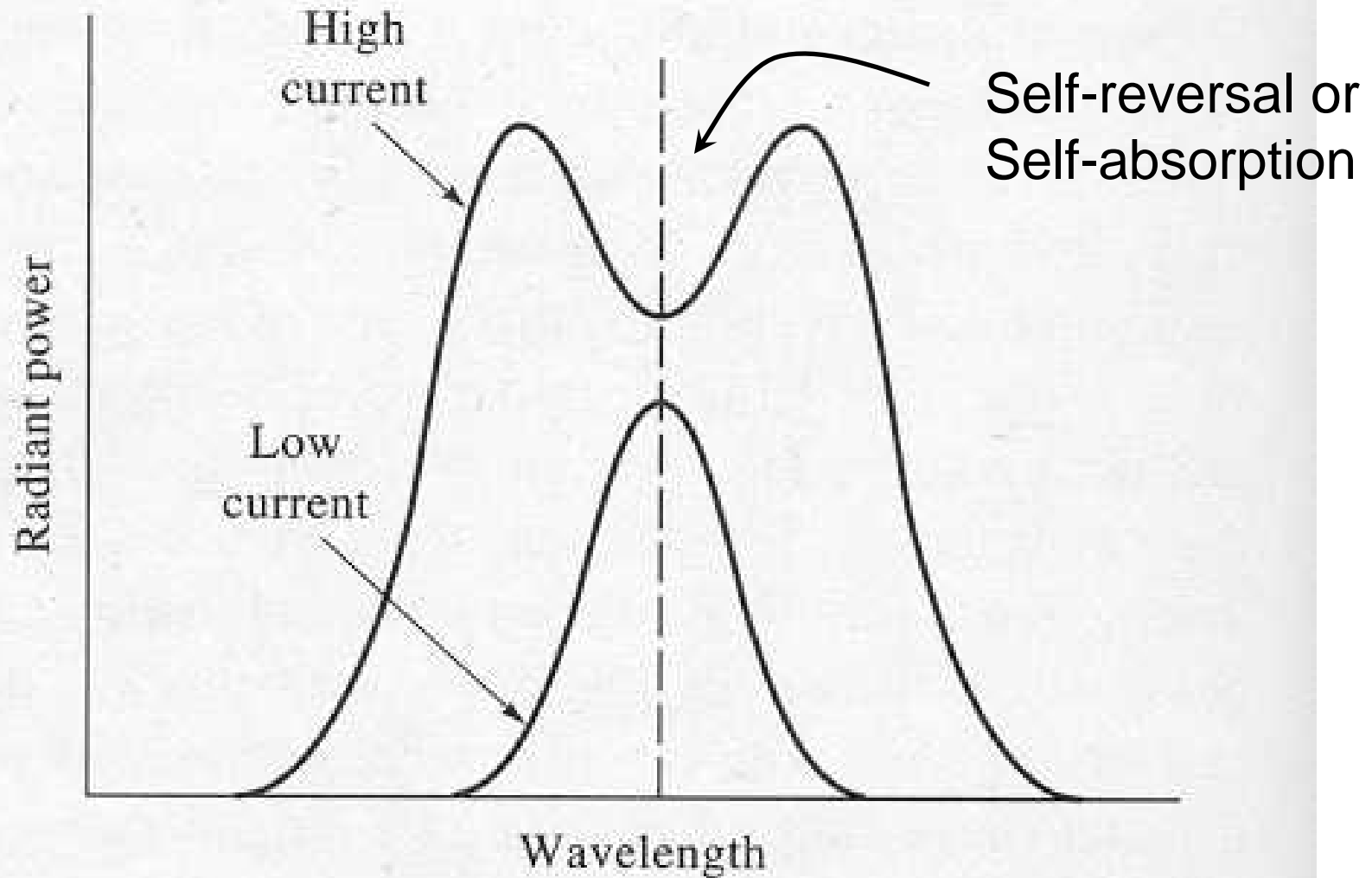
The Smith-Hieftje technique splits the HCL line

High current

Self-reversal or Self-absorption

Radiant power

Low current

Wavelength

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

Another type of matrix interference not alleviated by background correction involves variable amounts of analyte ionization in flames or plasmas

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

Element	Ionization Potential, eV	Fraction Ionized at the Indicated Pressure and Temperature			
		$p = 10^{-4}$ atm		$p = 10^{-6}$ atm	
		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.
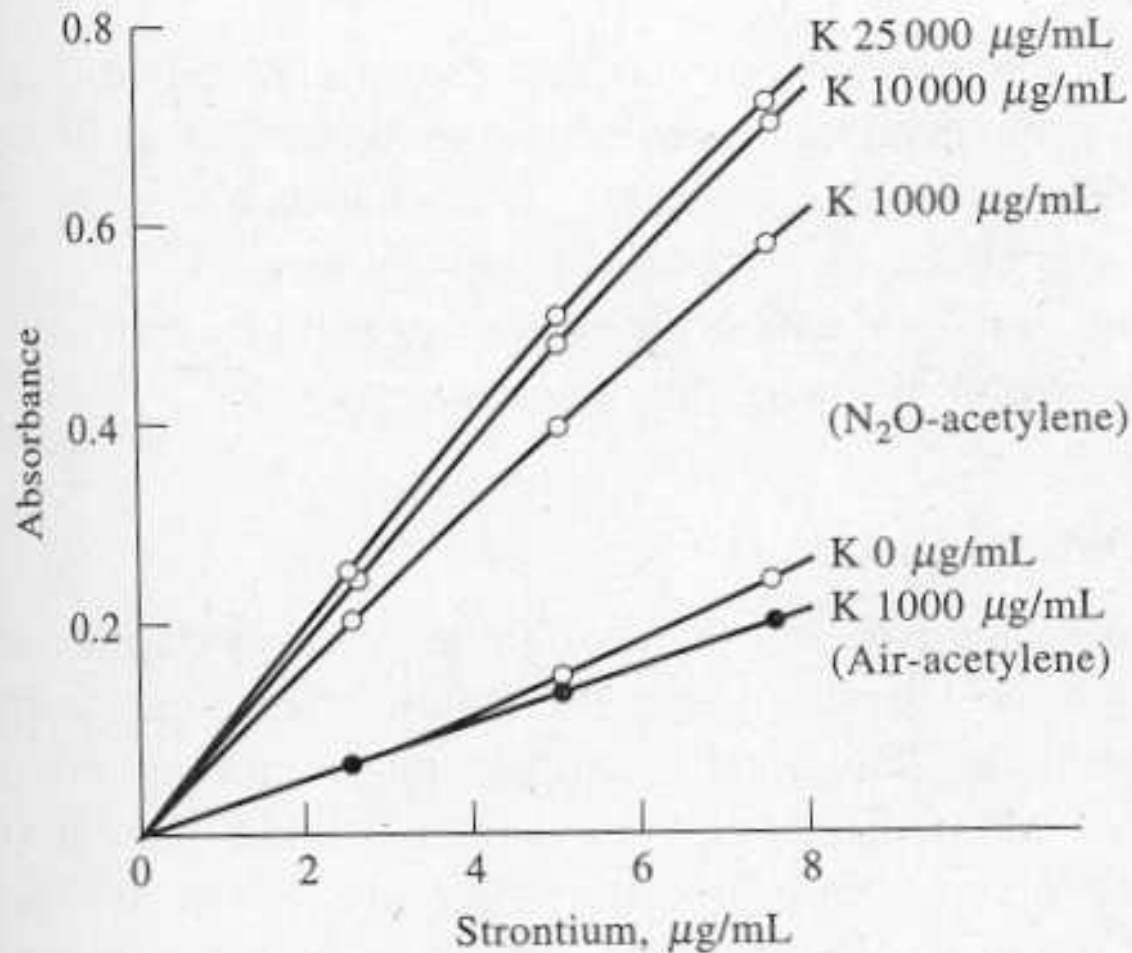
Figure 9-17 Effect of potassium concentration on the calibration curve for strontium. *(Reprinted with permission from J. A. Bowman and J. B. Willis, Anal. Chem., **1967**, 39, 1220. Copyright 1967 American Chemical Society.)*

One other factor (other than temp.) that influences degree of ionization is the presence of another easily ionized species. Here K enhances the Sr AA signal by suppressing Sr ionization

Atomic Fluorescence – use an intense light source to excite AF of elements in a flame or plasma.

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

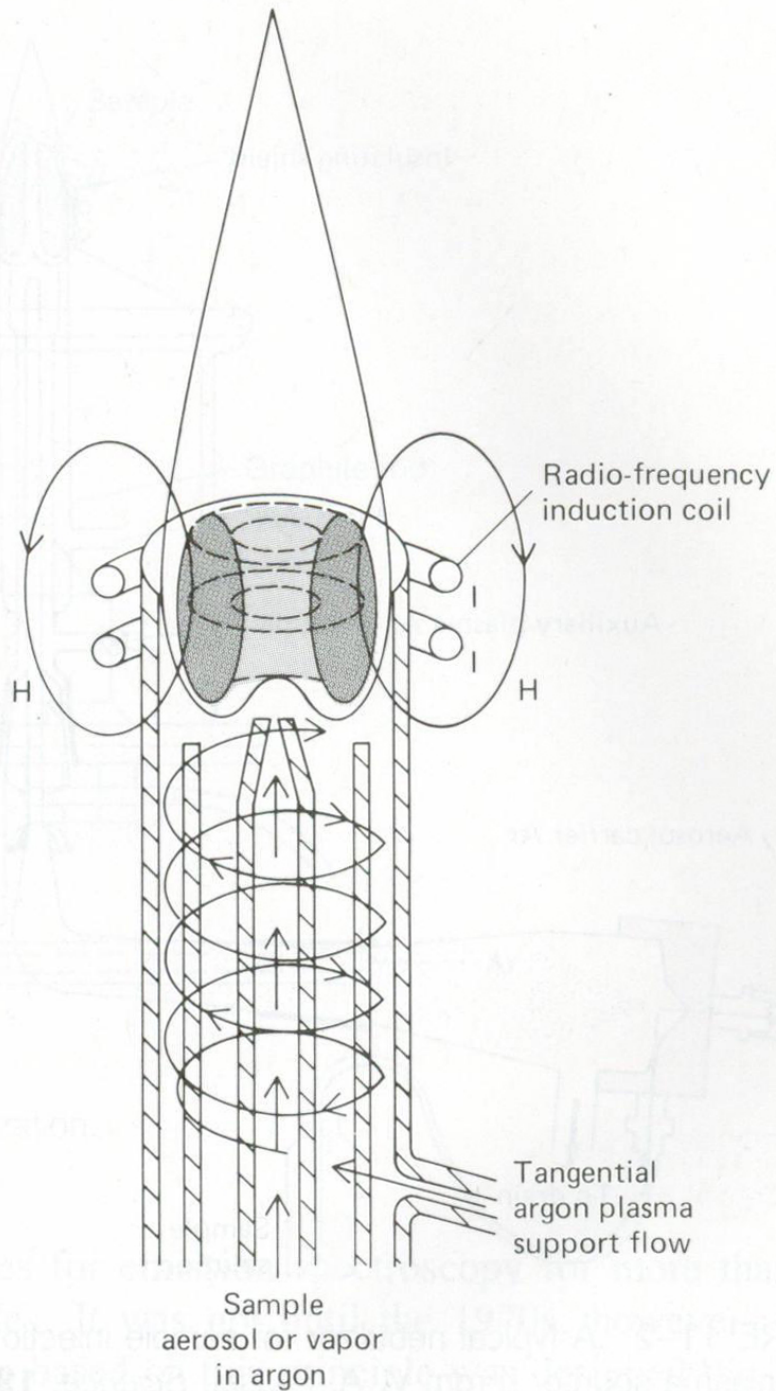*Nanogram/milliliter $= 10^{-3}$ μg/mL $= 10^{-3}$ ppm.

Emission Spectroscopy Using Plasmas, Arcs or Sparks

- Inductively Coupled Plasma (ICP)
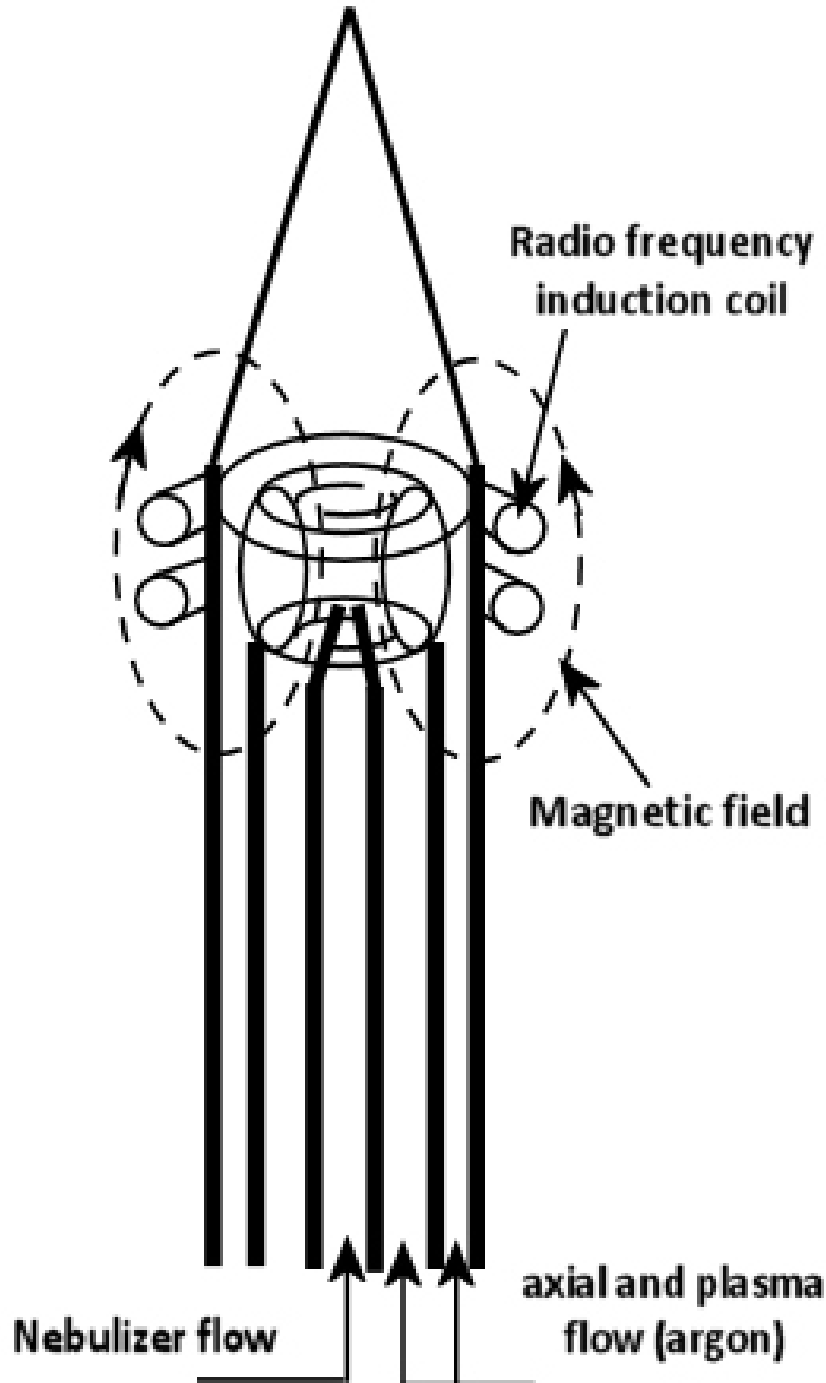- Direct Current Plasma (DCP)
- Arcs and Sparks

Plasma = hot ionized gas or region with such a significant number of charged species as to dramatically change its electrical & magnetic properties. Often called the 4th state of matter.

Radio-frequency induction coil

Tangential argon plasma support flow

Sample aerosol or vapor in argon

Inductively Coupled Plasma (ICP)

Radio frequency induction coil

Magnetic field

Nebulizer flow

axial and plasma flow (argon)

Insulating shield

Plasma Ar

Auxiliary plasma Ar (optional)

Aerosol carrier Ar

To drain

Sample solution
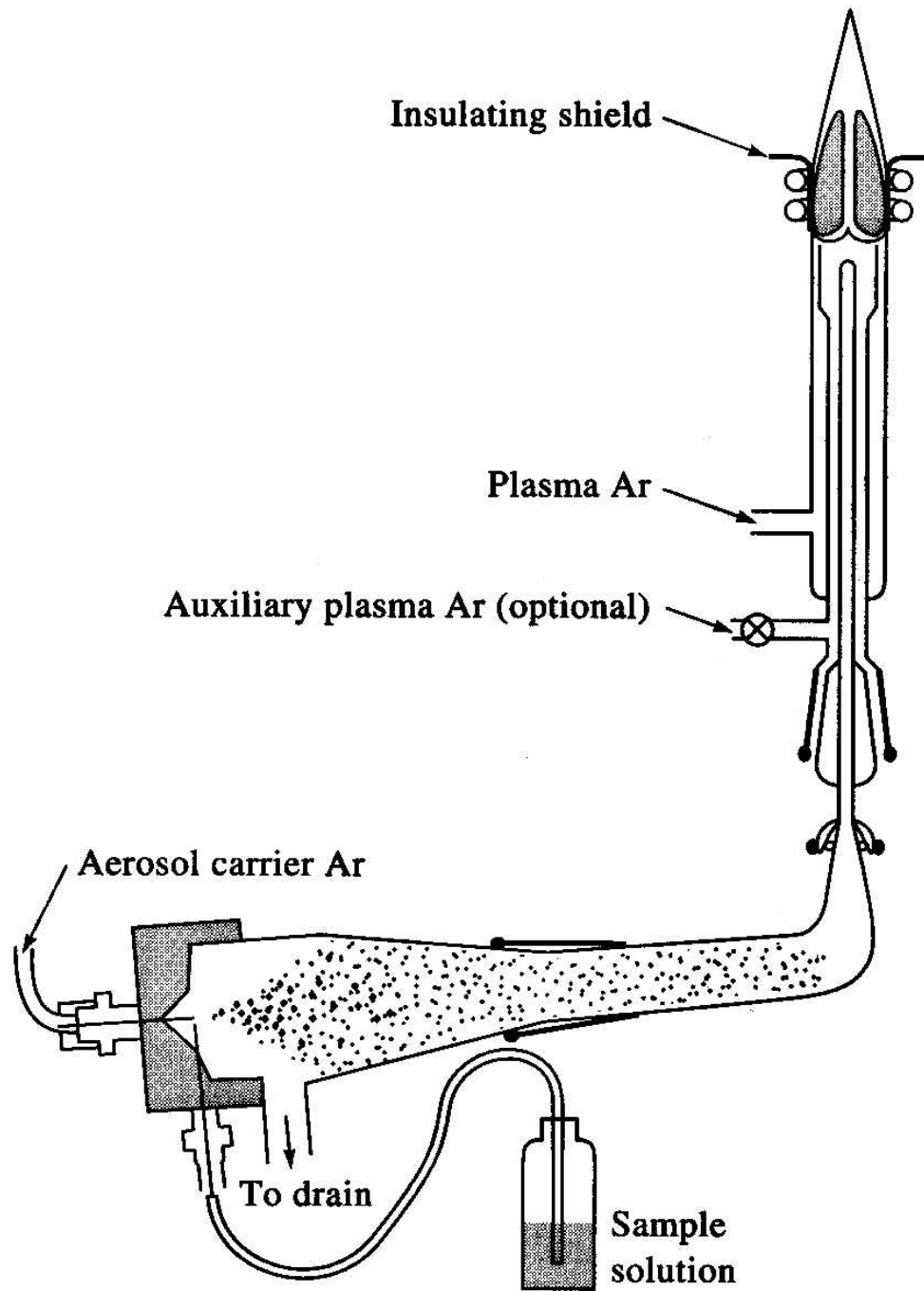
ICP Torch with sample introduction system (nebulizer and spray chamber)

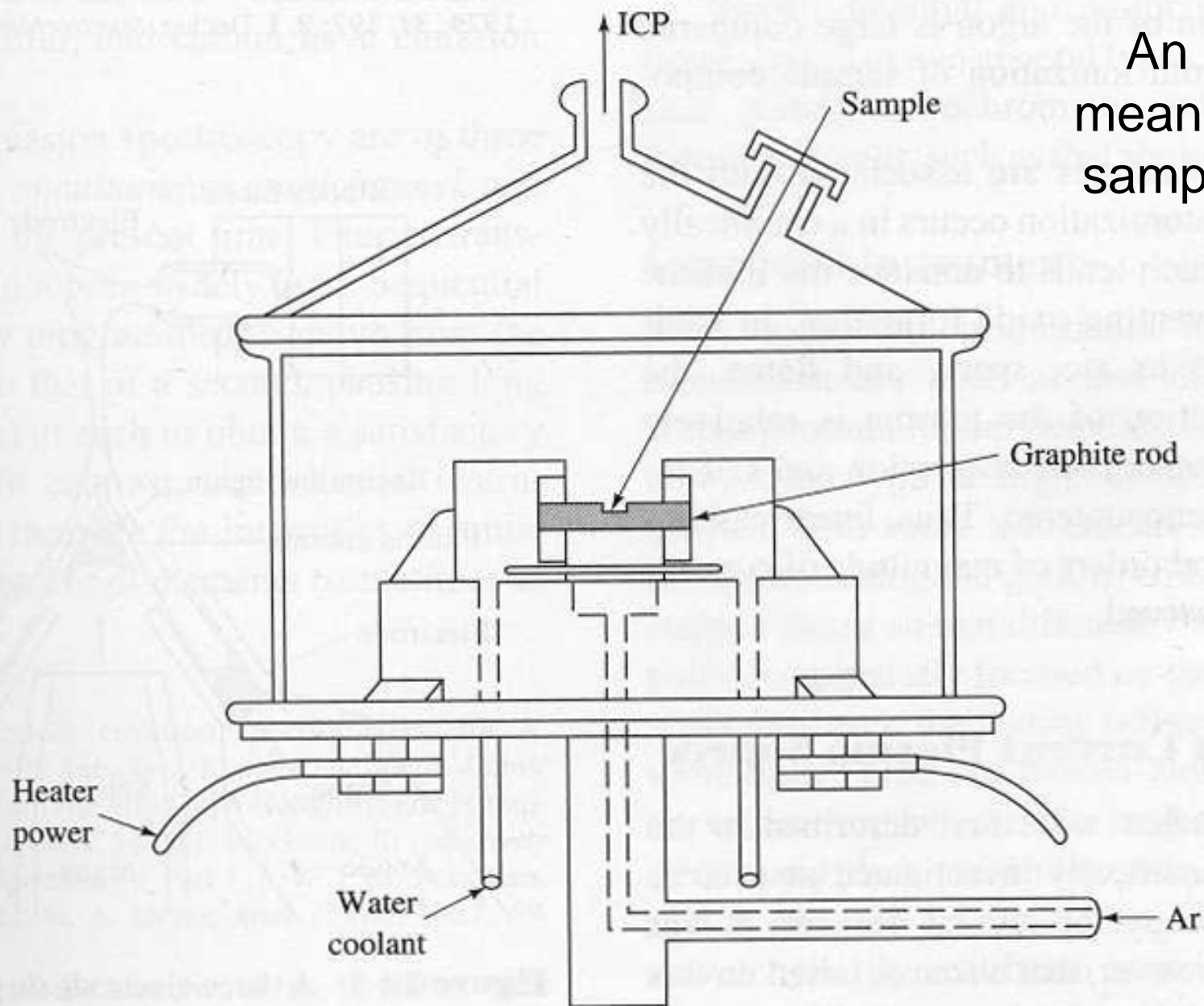An alternate means of getting sample into ICP

Figure 10-3 Device for electrothermal vaporization.

ICP Temps.

The viewing area for each element is typically reported as mm above the load coil

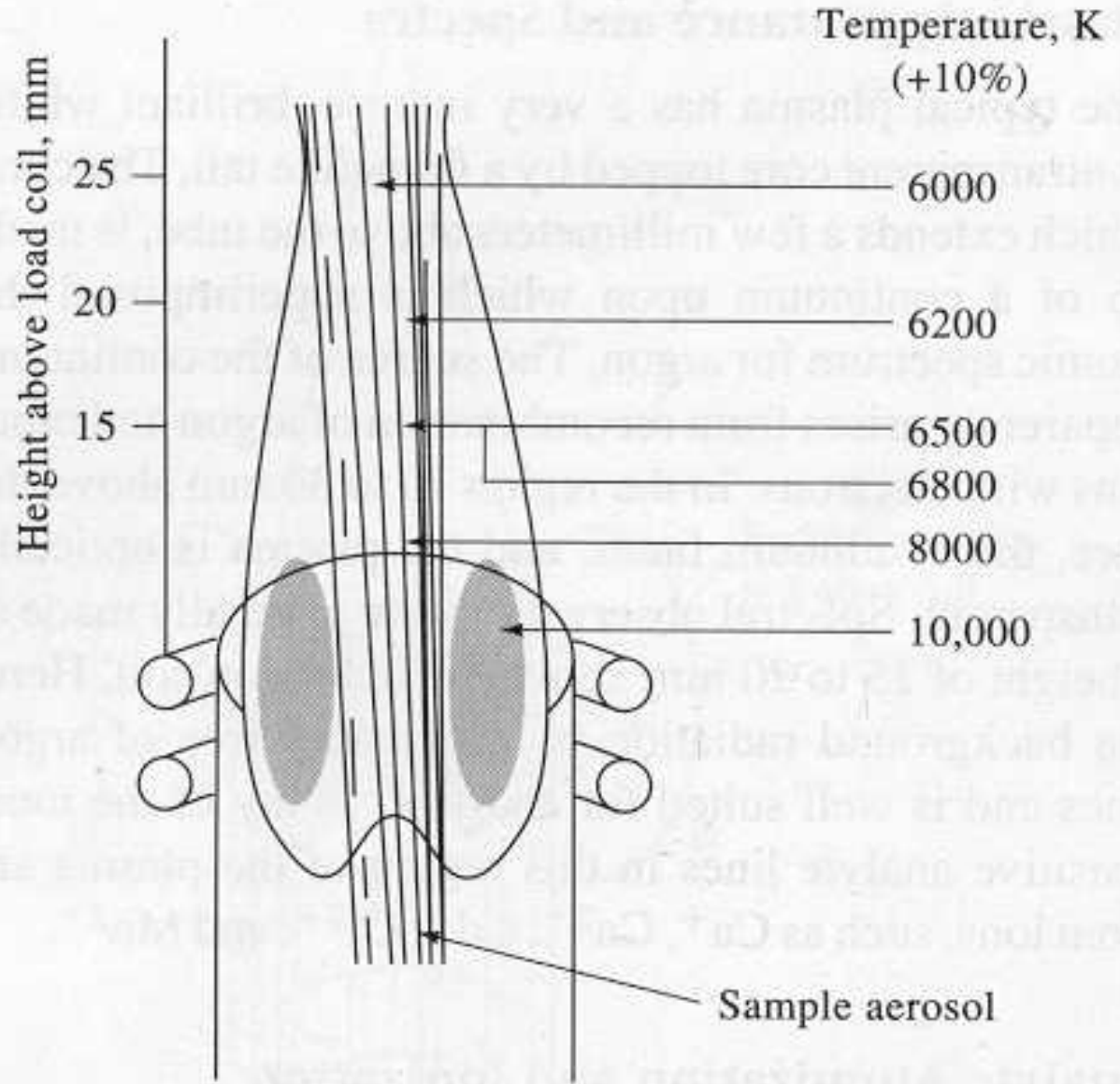**Figure 10-4** Temperatures in a typical inductively coupled plasma source. *(From V. A. Fassel, Science, 1978, 202, 186.*

Figure 10-5 A three-electrode dc plasma jet. *(Courtesy of Spectra Metrics, Inc. Haverhill, MA.)*

Direct Current Plasma (DCP) Torch

Lab will involve use of DCP for multielement analysis
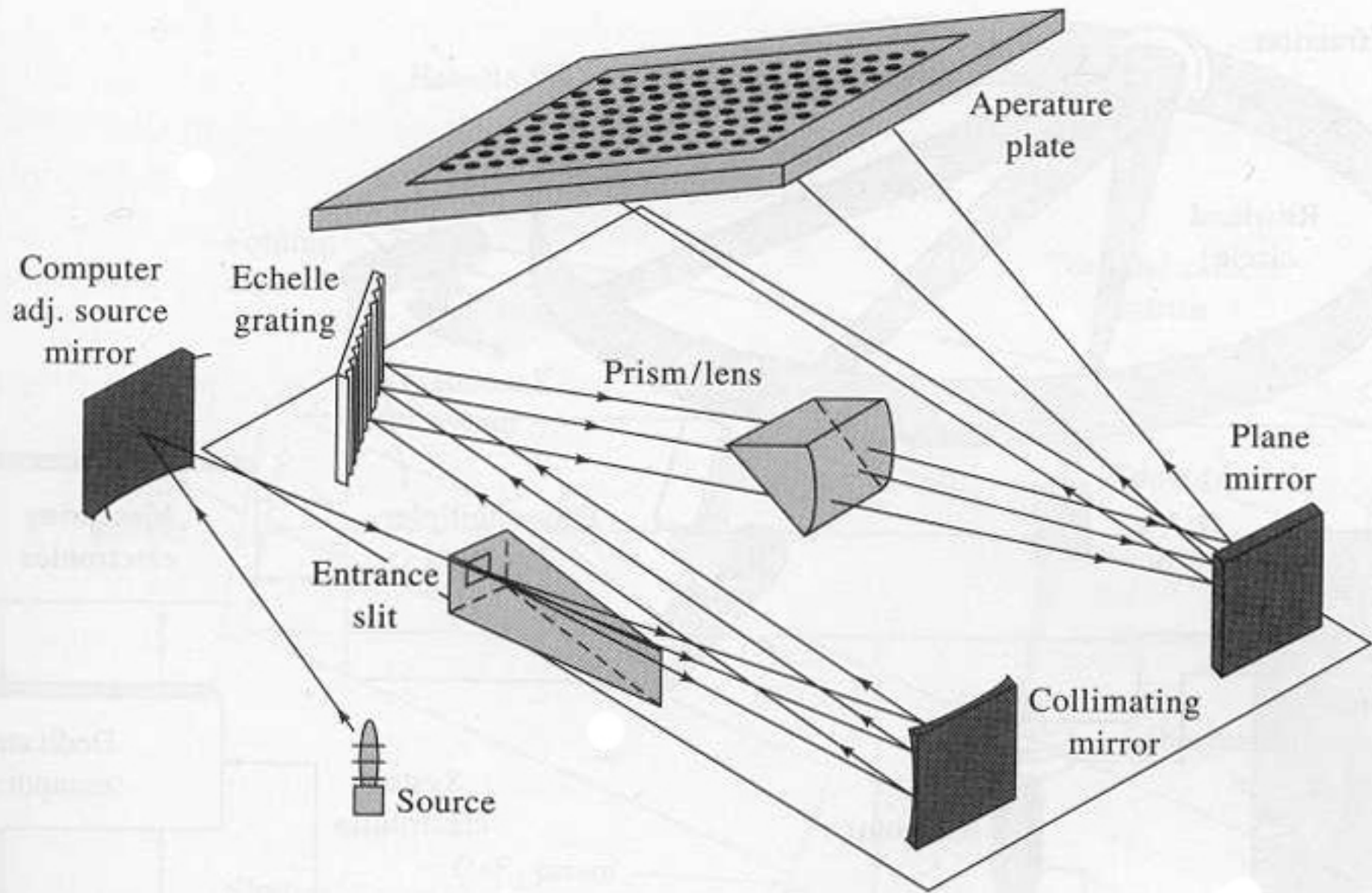
Figure 10-7 Schematic of an echelle polychromator system.

Echelle Spectrometer Optical Diagram

Charge injection transducer

Folding mirror

Toroidal camera mirror

LED

Custom echelle grating

Spherical collimating mirror

CaF$_2$ prism

Shutter

ICP source

Objective lens

Slit

Figure 10-9 Optical diagram of an echelle spectrometer with a charge-injection detector. *(From R. B. Bilhorn and M. B. Denton,* Appl. Spectrosc.*, 1990, 44, 1615. With permission.)*

Examination
window

Charge-injection
device

"Read" window

(a)

(b)
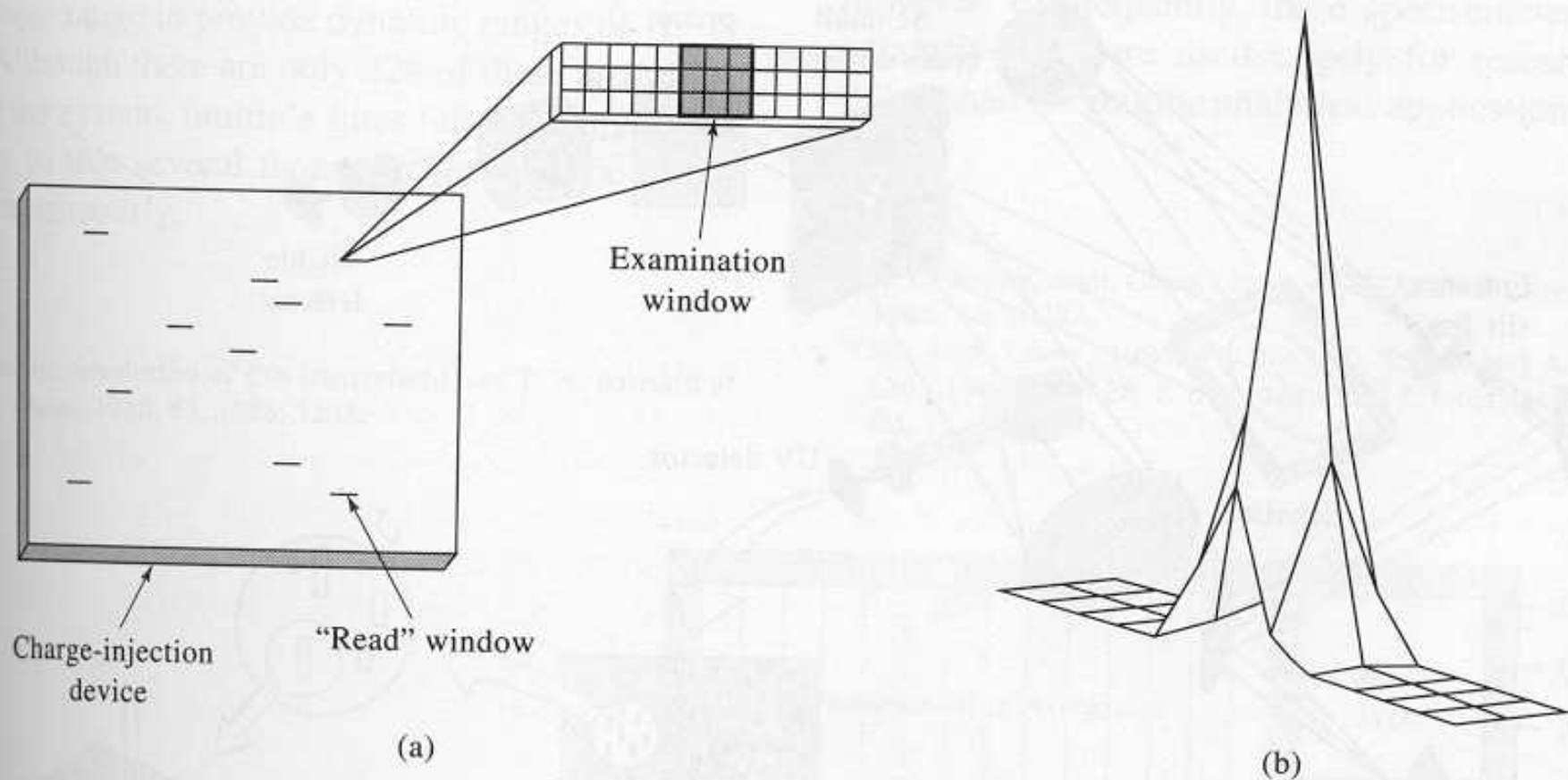
Figure 10-10 (a) Schematic representing the surface of a charge-injection device. The short horizontal lines represent the "read windows." A magnified image of one of the read windows is also shown. The nine central elements form t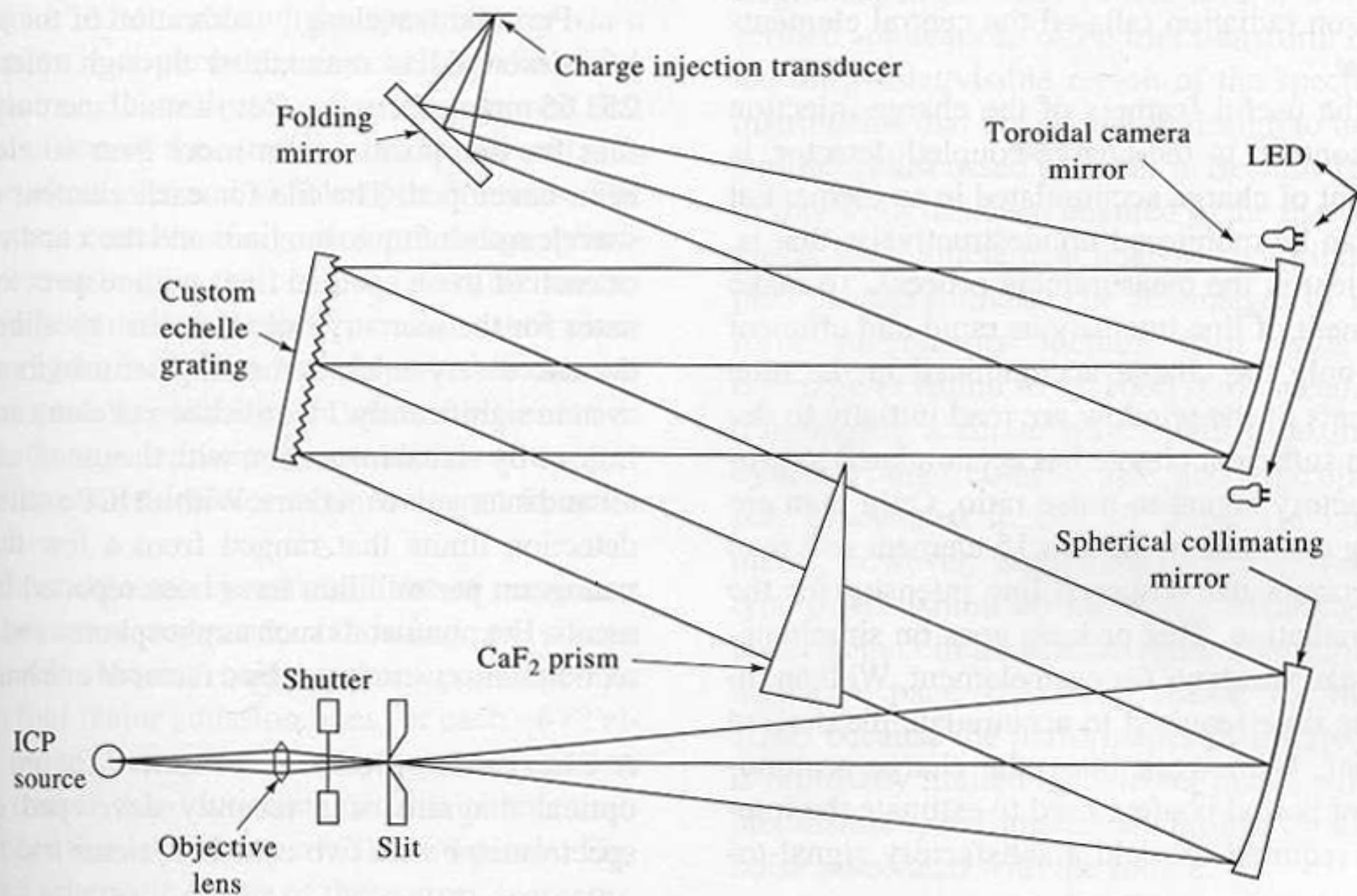he "examination window" where a line is positioned. (b) Intensity profile for an iron line. All of the radiation from the line falls on the 3×3 examination window. *(From R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., **1990**, 44, 1540. With permission.)*

Concave diffraction grating

Rowland circle

Movable primary slit

Secondary optics

Photomultipler detectors

Measuring electronics

Radio-frequency generator

ICP source

System electronics

Dedicated computer

Instrument control electronics

Gas flow regulation

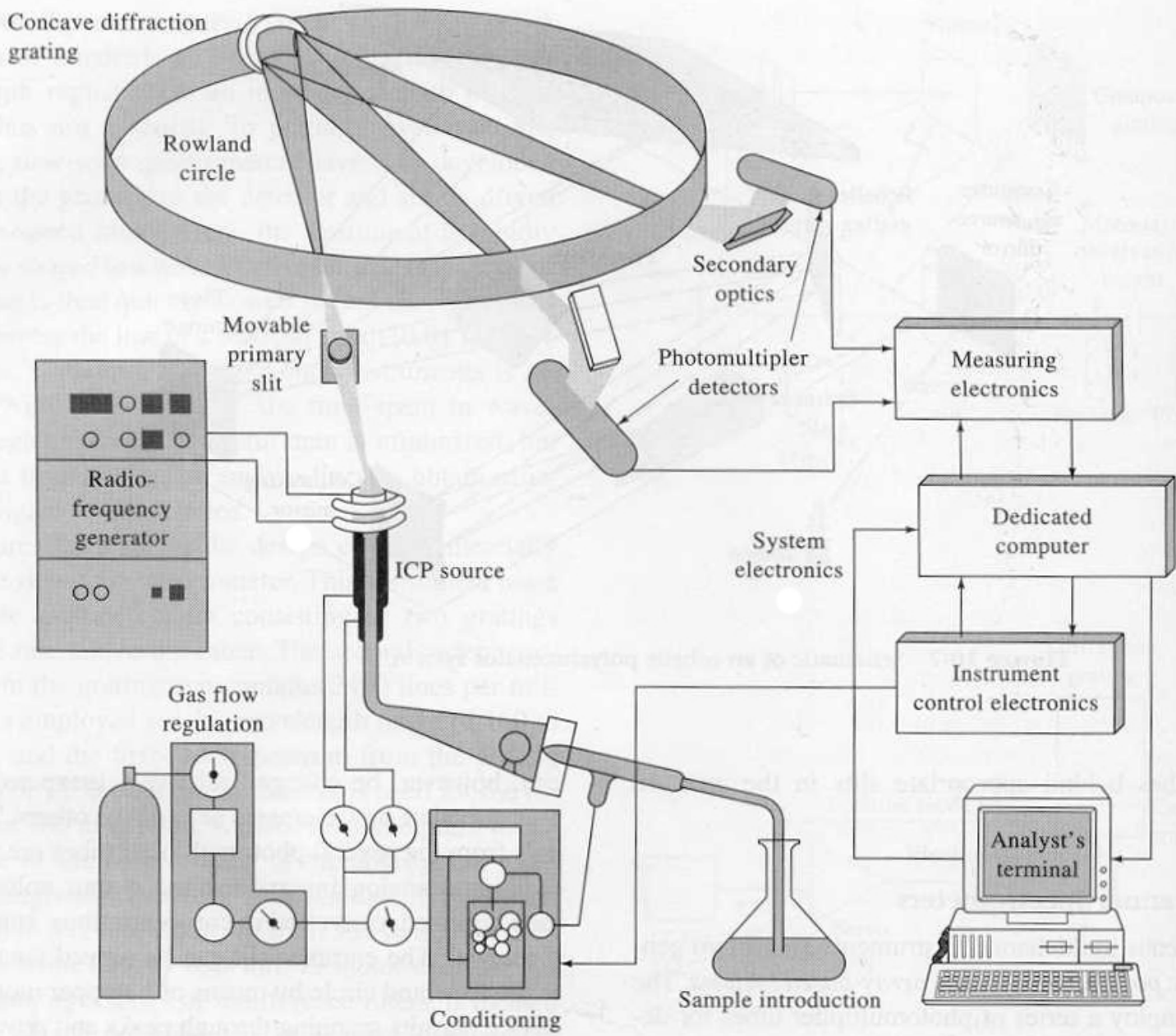Analyst's terminal

Conditioning

Sample introduction

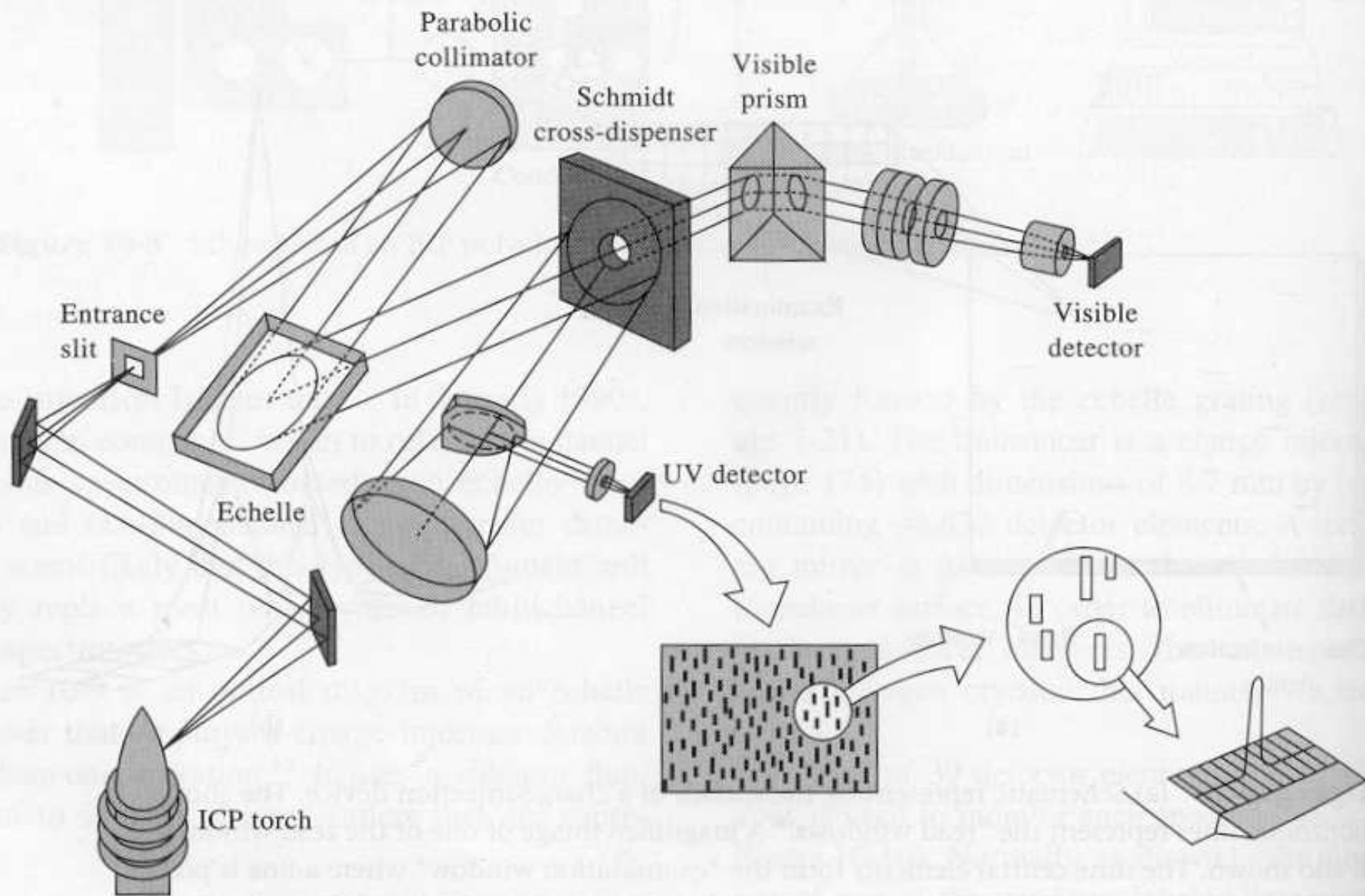**Figure 10-8** Schematic of an ICP polychromator. *(Courtesy of Thermo Jarrell Ash Corp.)*

Figure 10-11 An echelle spectrometer with segmented array of charge-coupled devices. *(From T. W. Barnard et al., Anal. Chem., 1993, 65, 1232. With permission.)*

Characterization of the Detection Power of ICP-AES

Detection limit (ng/mL)

Number of lines

■	< 10
■	10–30
□	30–100
▨	100–300

□	1–2
▦	3–6
▨	7–10
▨	11–16
▨	17–24

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**															

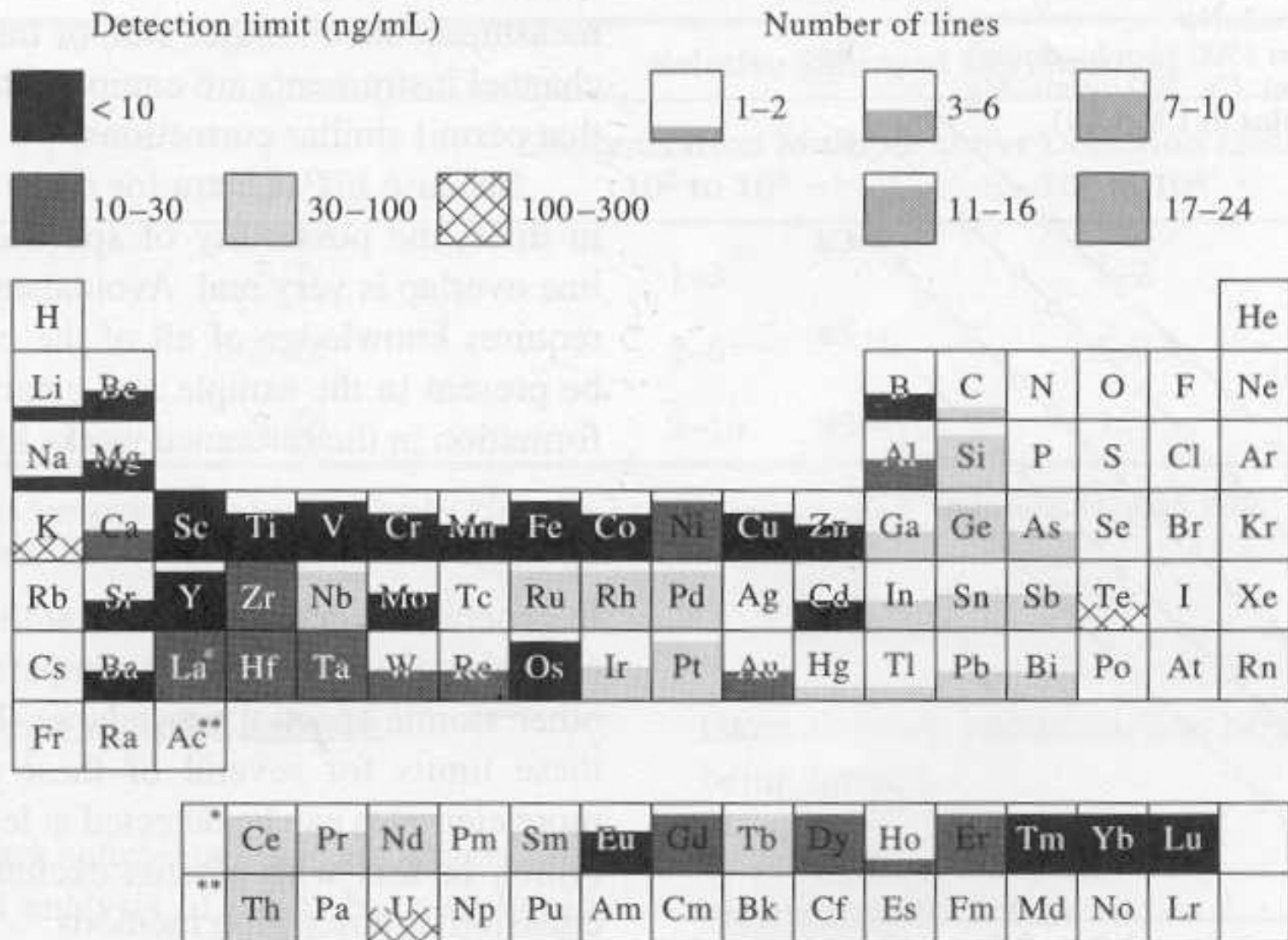| *	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 10-13 Periodic table characterizing the detection power and number of useful emission lines of ICP by employing a pneumatic nebulizer. The degree of shading indicates the range of detection limits for the useful lines. The area of shading indicates the number of useful lines.
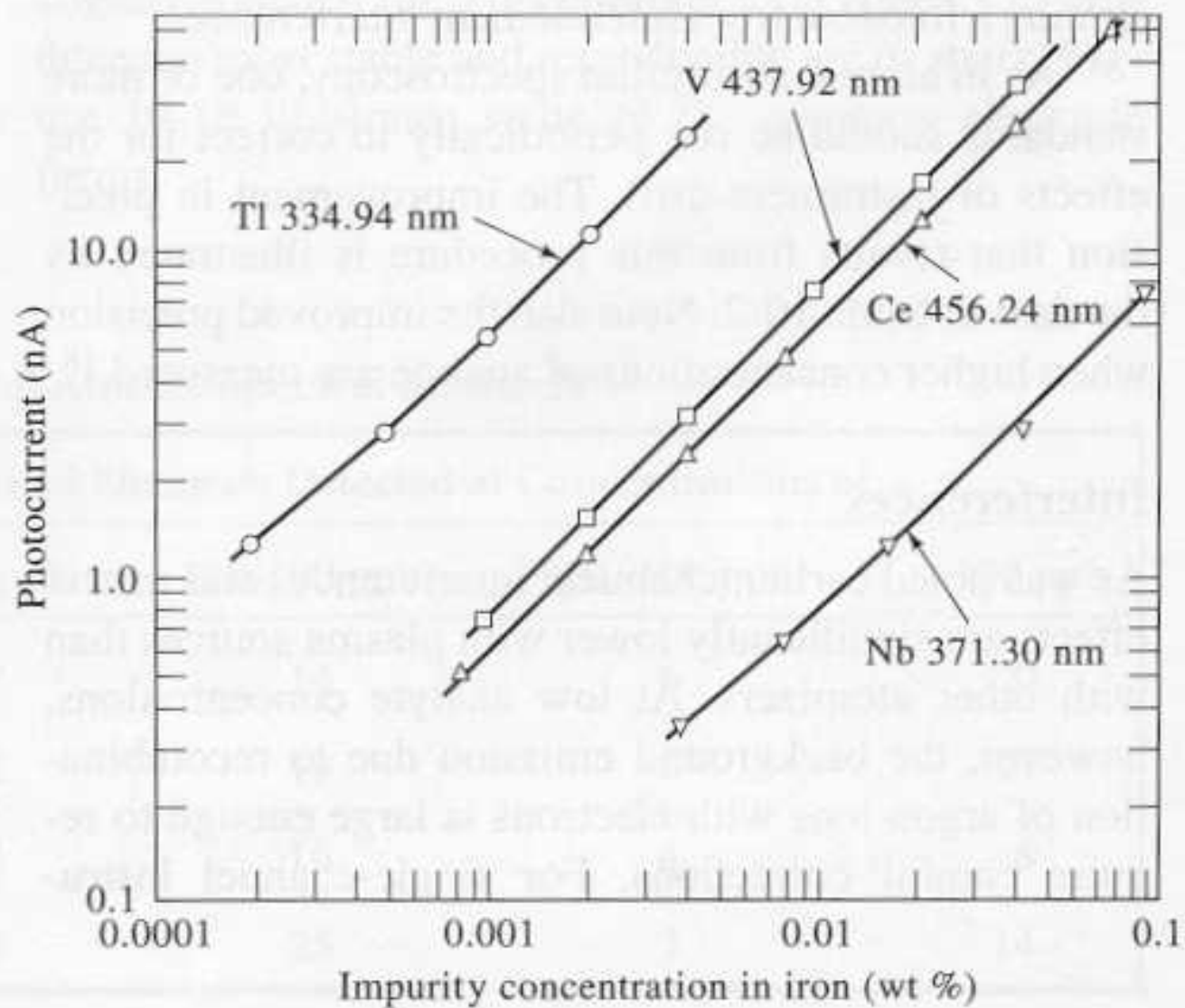
Figure 10-14 Typical calibration curves. *(From V. A. Fassel and R. N. Kniseley,* Anal. Chem., *1974, 46, 1117A. With permission.)*
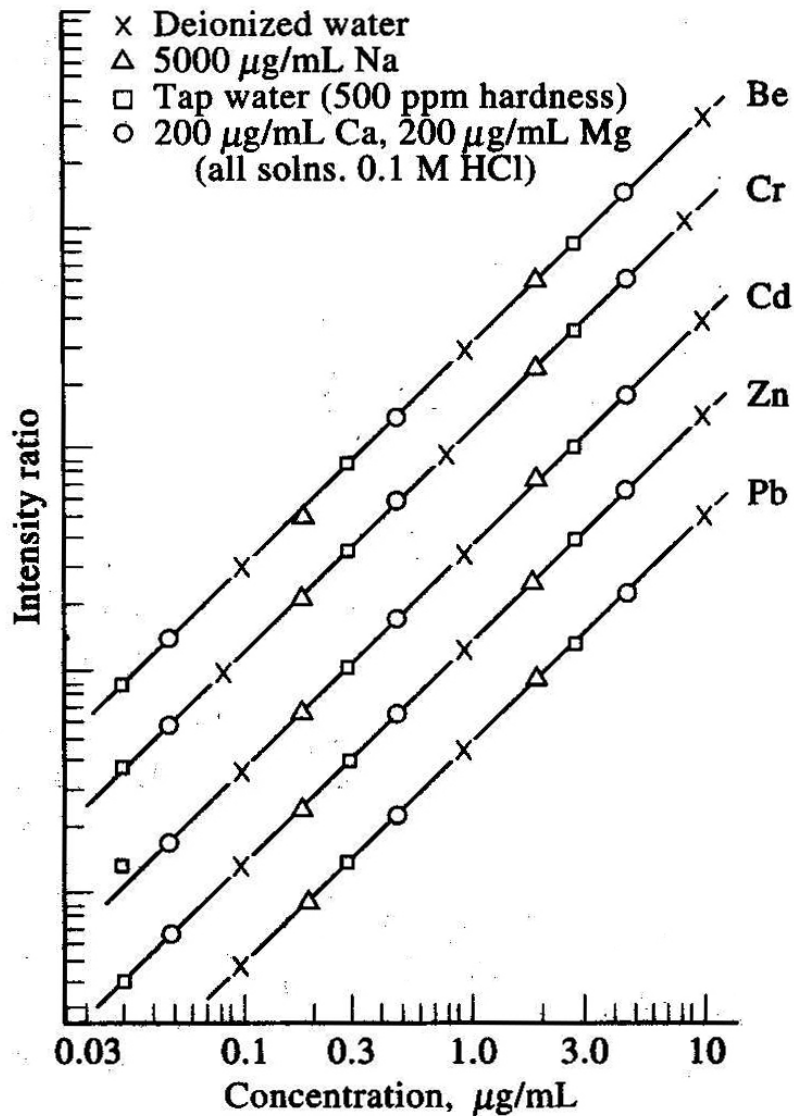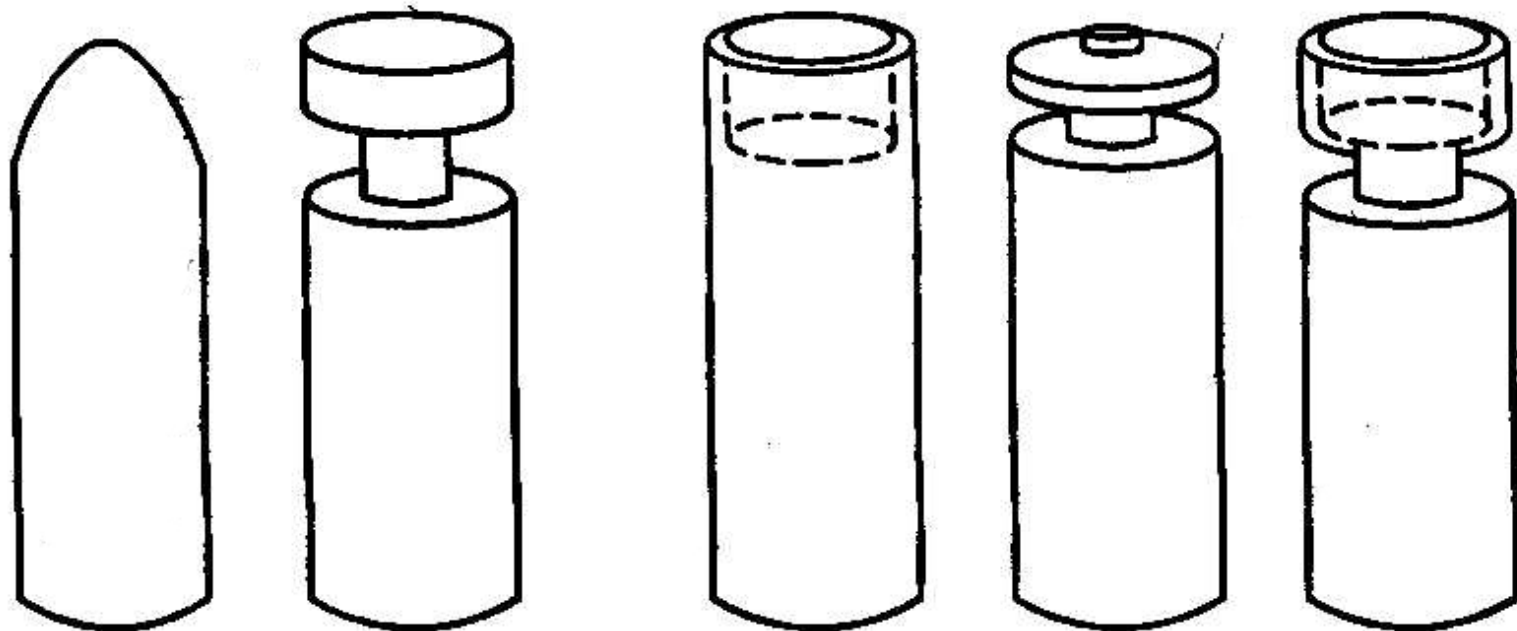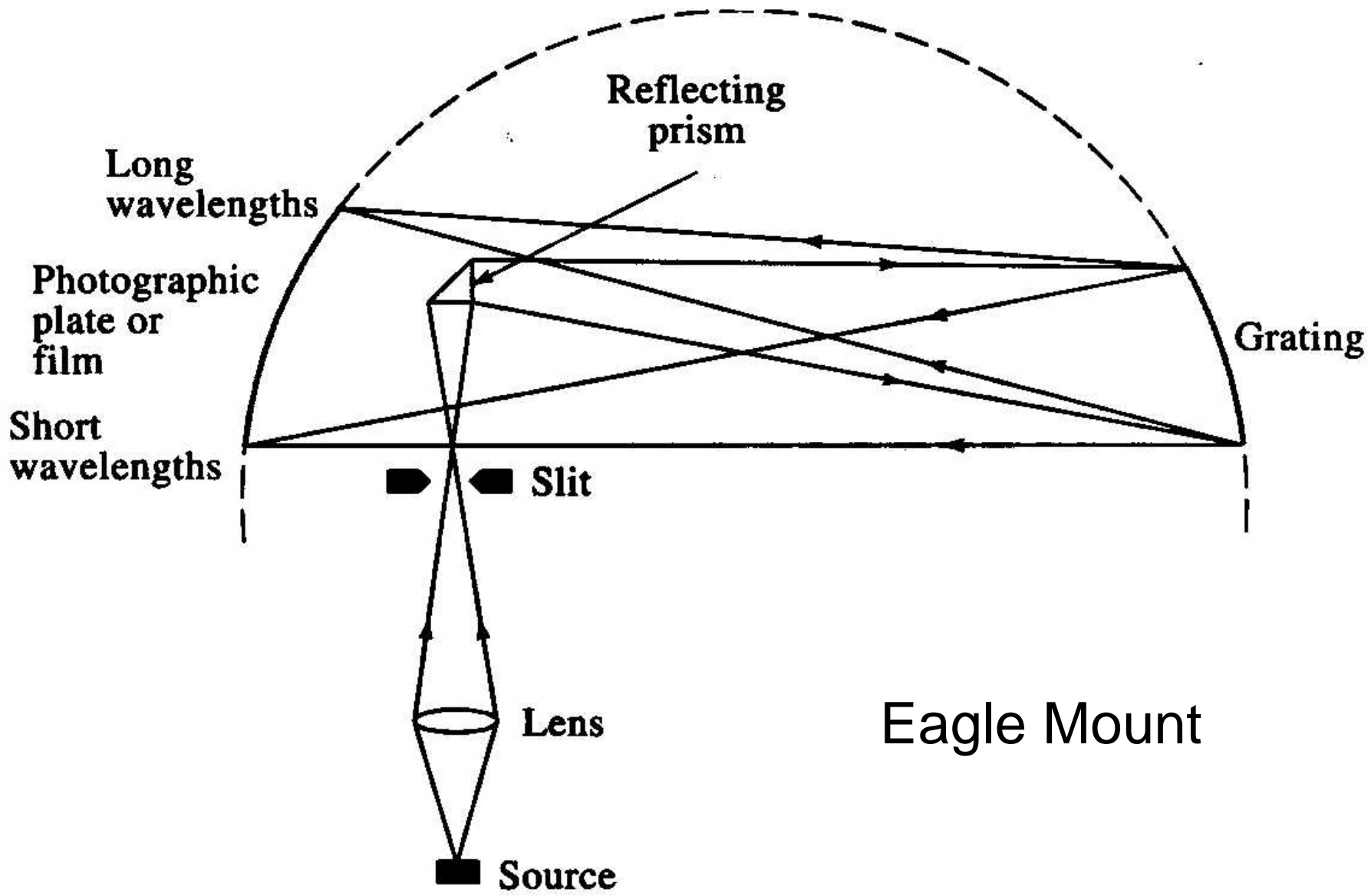
Figure 10-15 Calibration curves with an inductively coupled plasma source. Here, an yttrium line at 242.2 nm served as an internal standard. Notice the lack of interelement interference. *From V. A. Fassel*, Science, *1978, 202, 187.*

Counter
electrodes

Electrodes for
holding sample

Figure 10-16 Some typical graphite electrode shapes.
Narrow necks are to reduce thermal conductivity.

Reflecting prism

Long wavelengths

Photographic plate or film

Short wavelengths

Slit

Grating
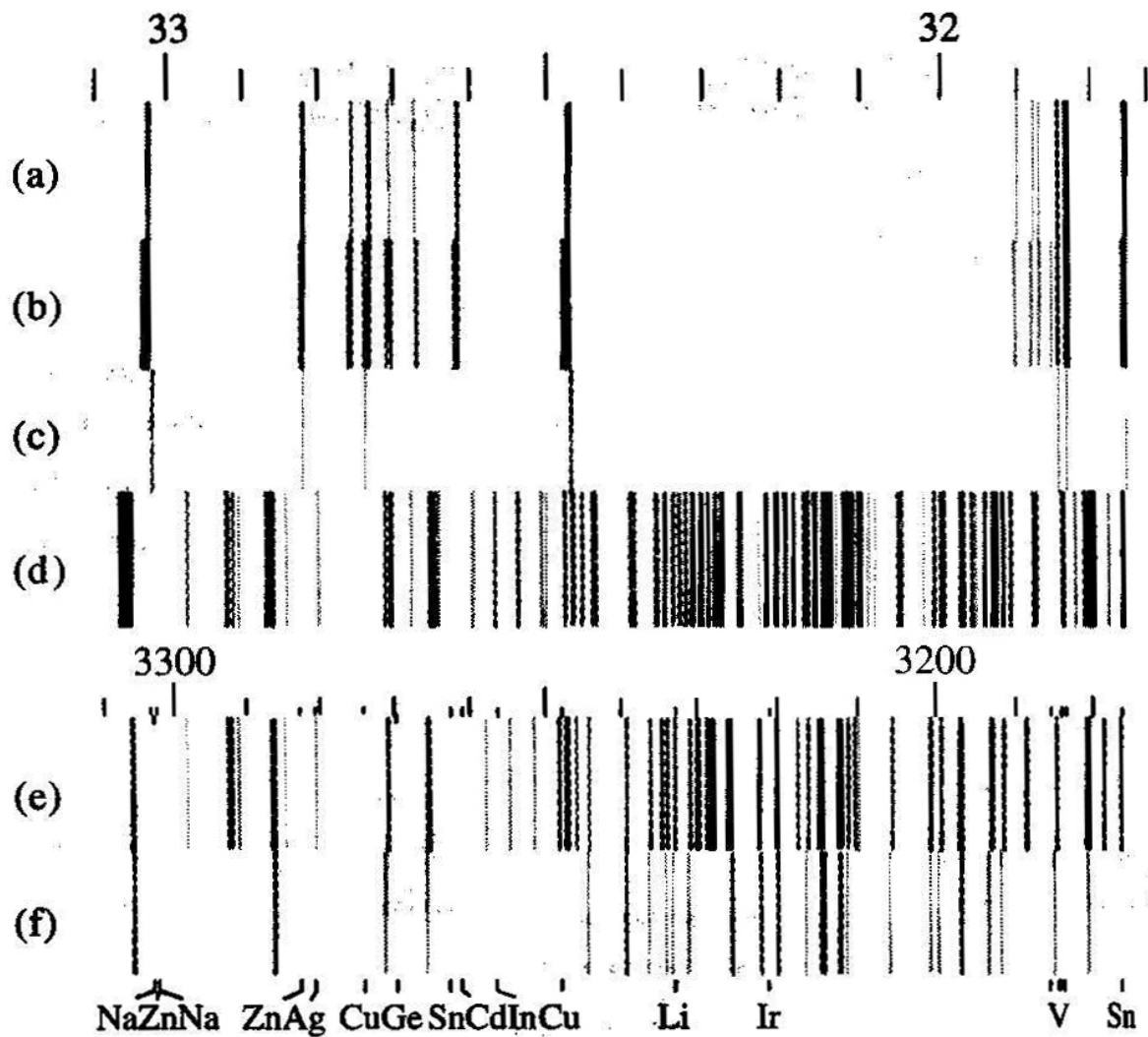
Lens

Source

Eagle Mount

Figure 10-18 Projected spectra by a comparator-densito-meter: (a), (b), and (c) spectra of sample at three different exposures; (d) iron spectrum on the sample plate; (e) and (f) iron spectra on the master plate.
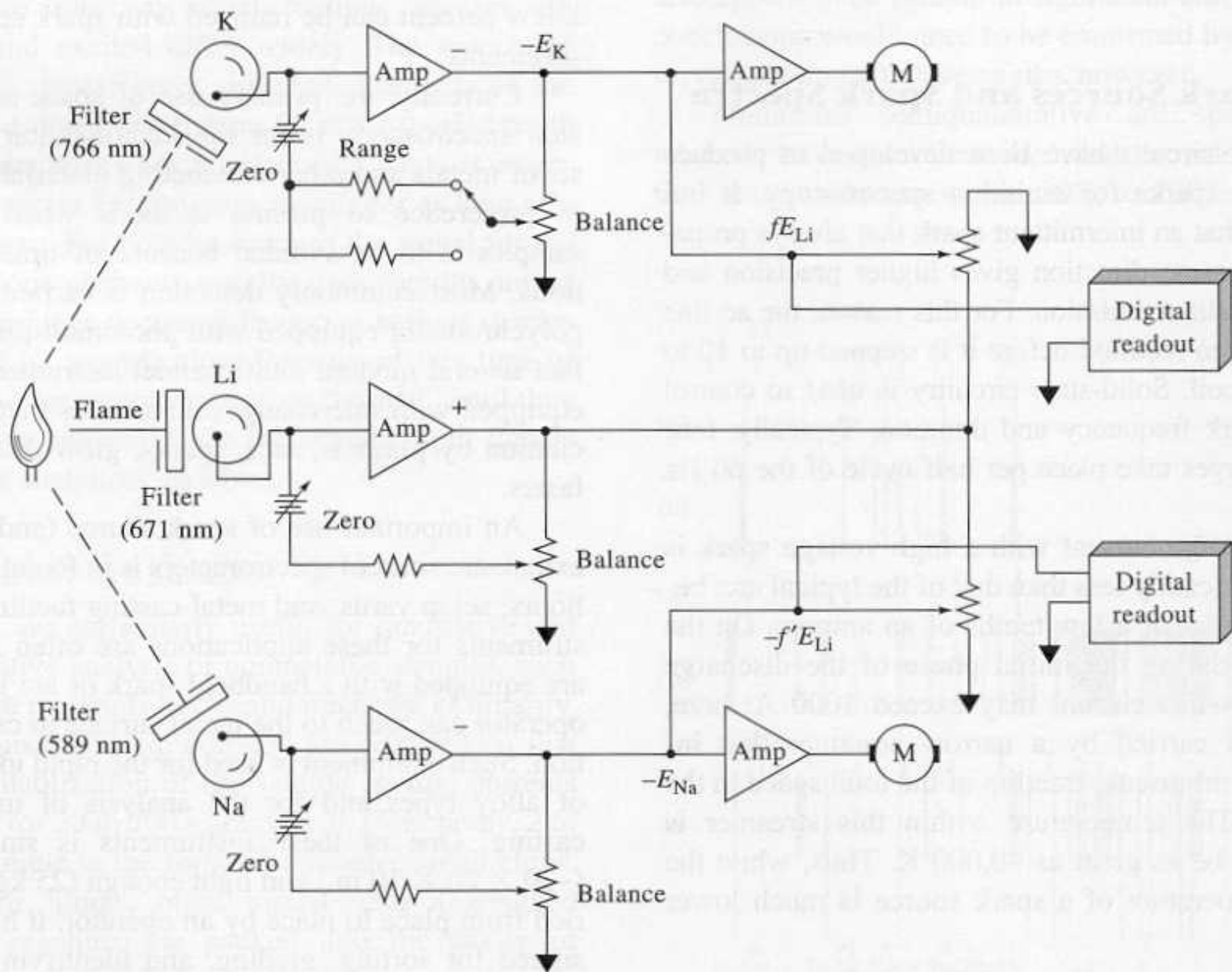
Figure 10-19 A three-channel photometer for monitoring emission by K, Li, and Na. *(From J. D. Ingle Jr. and S. R. Crouch, Spectrochemical Analysis, p. 254. Englewood Cliffs, NJ: Prentice-Hall, 1988. With permission.)*

TABLE 10-1   Desirable Properties of an Emission Spectrometer

1. High resolution (0.01 nm or $\lambda/\Delta\lambda > 100,000$)

2. Rapid signal acquisition and recovery

3. Low stray light

4. Wide dynamic range ($>10^6$)

5. Accurate and precise wavelength identification and selection

6. Precise intensity readings ($<1\%$ RSD at $500 \times$ the detection limit)

7. High stability with respect to environmental changes

8. Easy background corrections

9. Computerized operation: readout, storage data manipulation, etc.

TABLE 10-2   Effect of Standardization Frequency on Precision of ICP Data*

| Frequency of Recalibration, hr | Relative Standard Deviation, % | | | |
| | Concentration Multiple above Detection Limit | | | |
	10^1 to 10^2	10^2 to 10^3	10^3 to 10^4	10^4 to 10^5
0.5	3–7	1–3	1–2	1.5–2
2	5–10	2–6	1.5–2.5	2–3
8	8–15	3–10	3–7	4–8

*Data from: R. M. Barnes, in *Applications of Inductively Coupled Plasmas to Emission Spectroscopy*, R. M. Barnes, Ed., p. 16. Philadelphia: The Franklin Institute Press, 1978. With permission.

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods*

Method	Number of Elements Detected at Concentrations of				
	<1 ppb	1–10 ppb	11–100 ppb	101–500 ppb	>500 ppb
Inductively coupled plasma emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	19
Flame atomic fluorescence	4	14	16	4	6
Flame atomic absorption	1	14	25	3	14

*Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise. Data abstracted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, **1974**, *46*(13), 1111A. Copyright 1974 American Chemical Society.