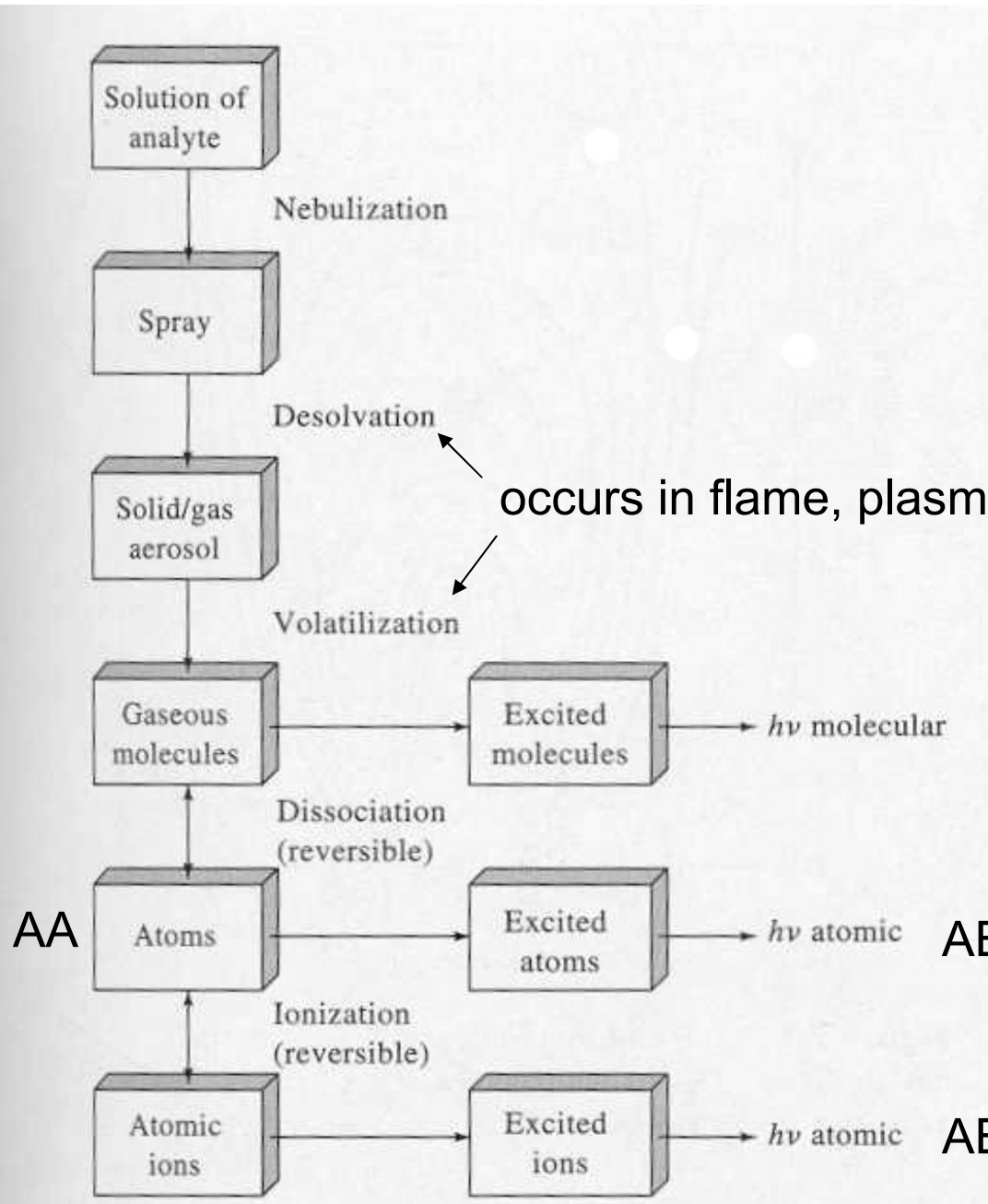


# Chapter 9: Atomic Absorption & Atomic Fluorescence Spectrometry

- 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



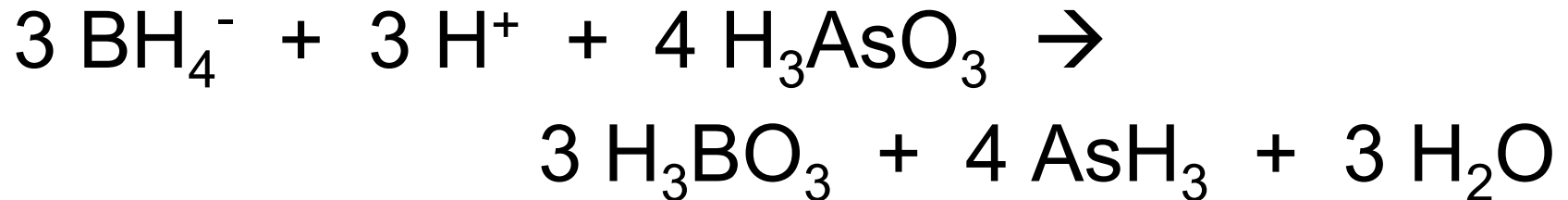
occurs in flame, plasma, etc.

Molecular emission is generally unwanted & can cause interference

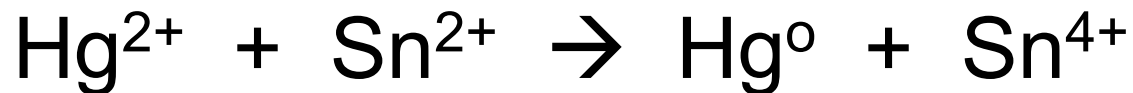
Figure 9-1 Processes occurring during atomization.

Sample introduction for solutions:

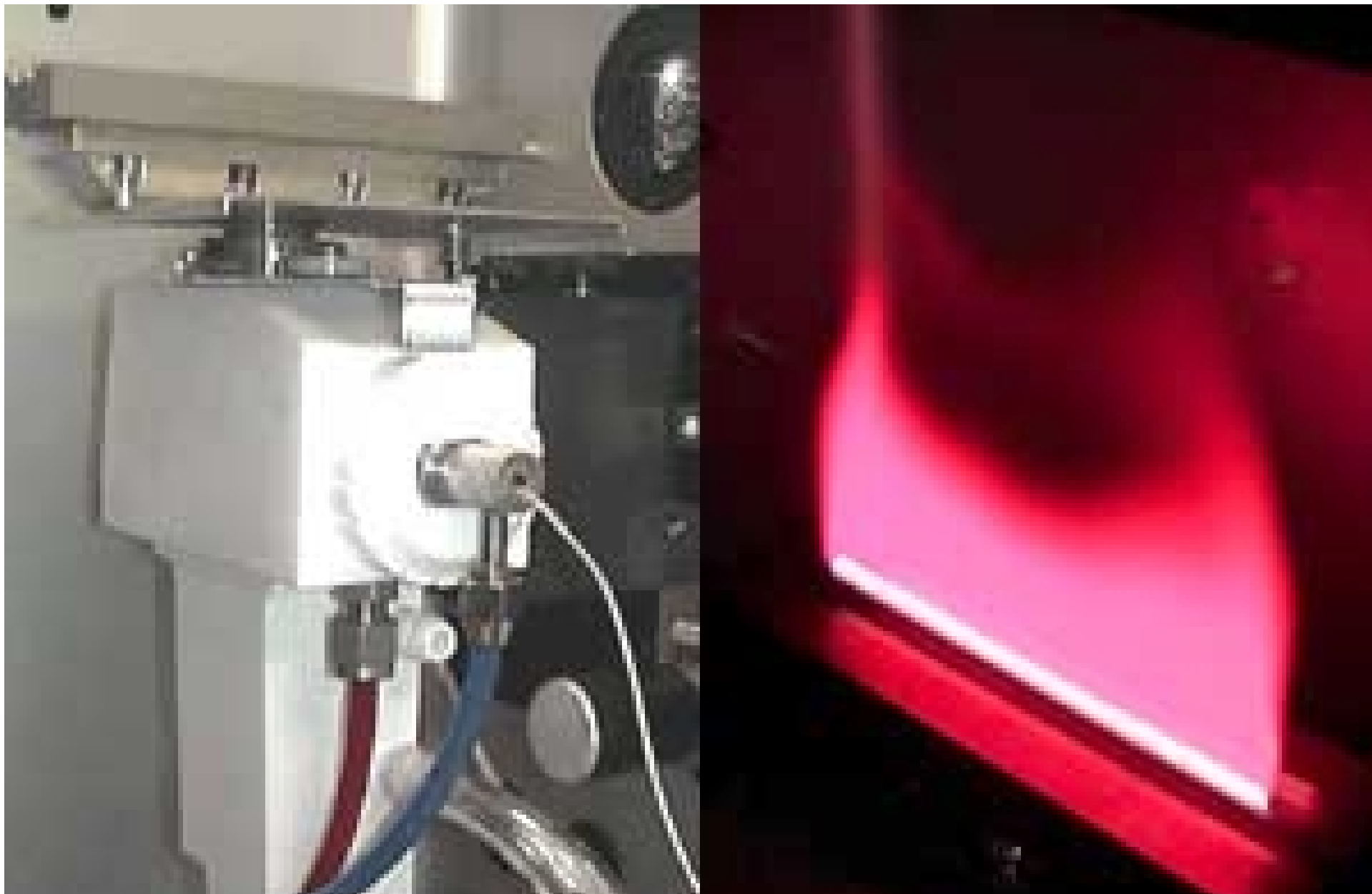
- 1) Pneumatic nebulizers
- 2) Ultrasonic nebulizers
- 3) Electrothermal vaporizers
- 4) Hydride generation

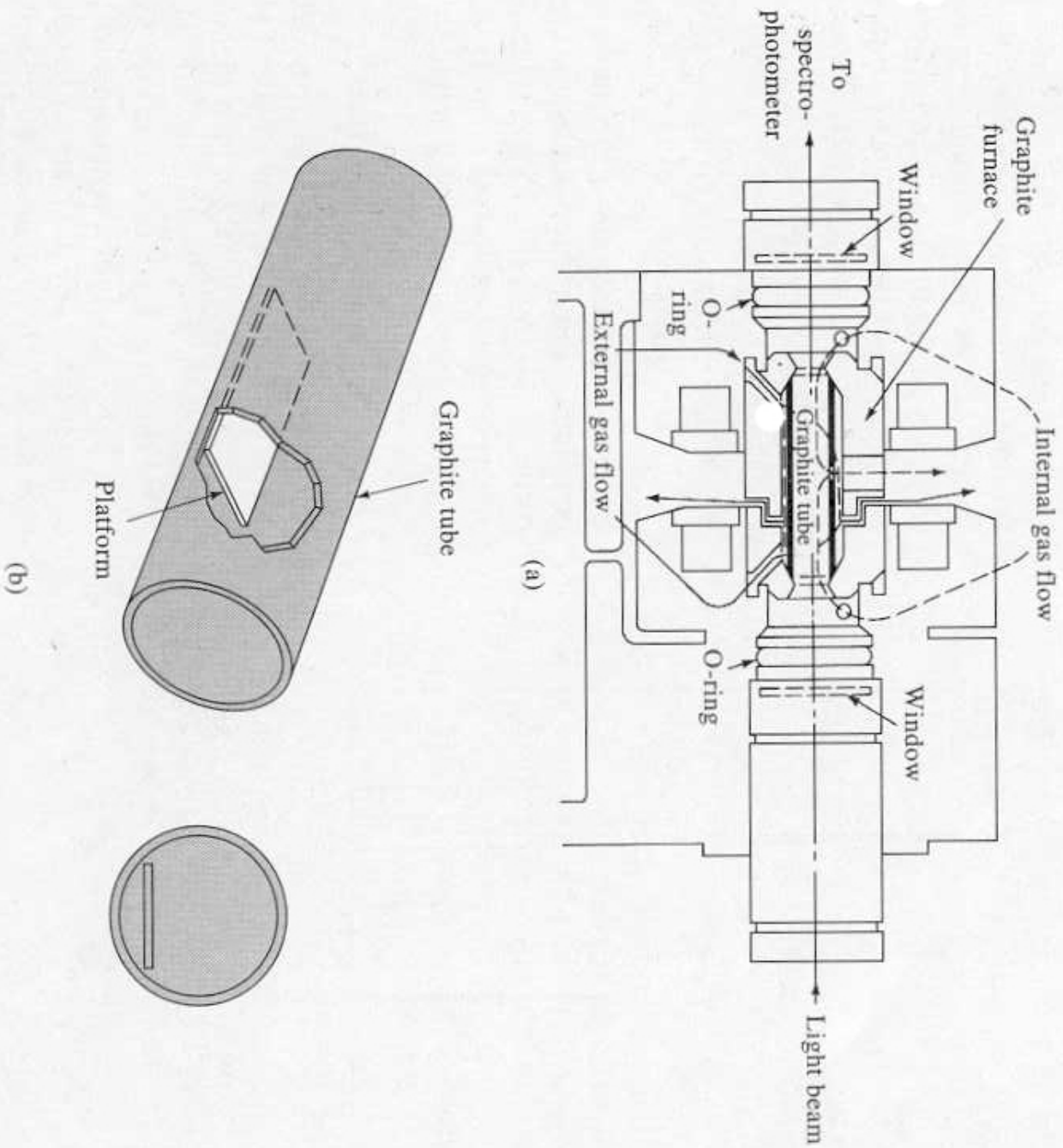


- 5) Cold vapor generation



# AA Slot Burner and Flame

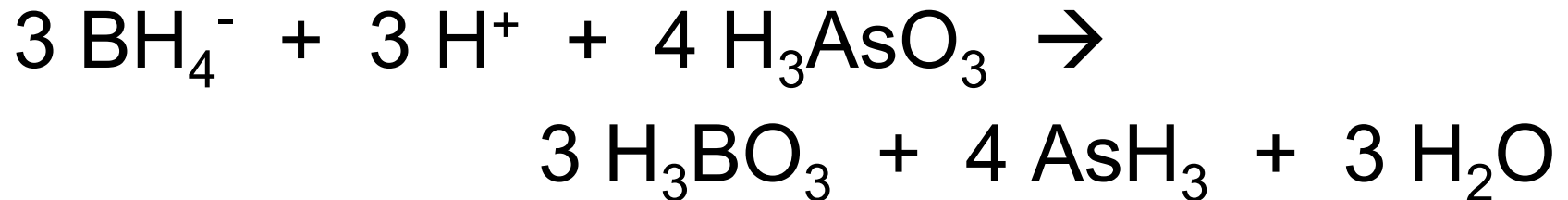




**Figure 9-6** (a) Cross-sectional view of a graphite furnace. (Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.) (b) The L'vov platform and its position in the graphite furnace.

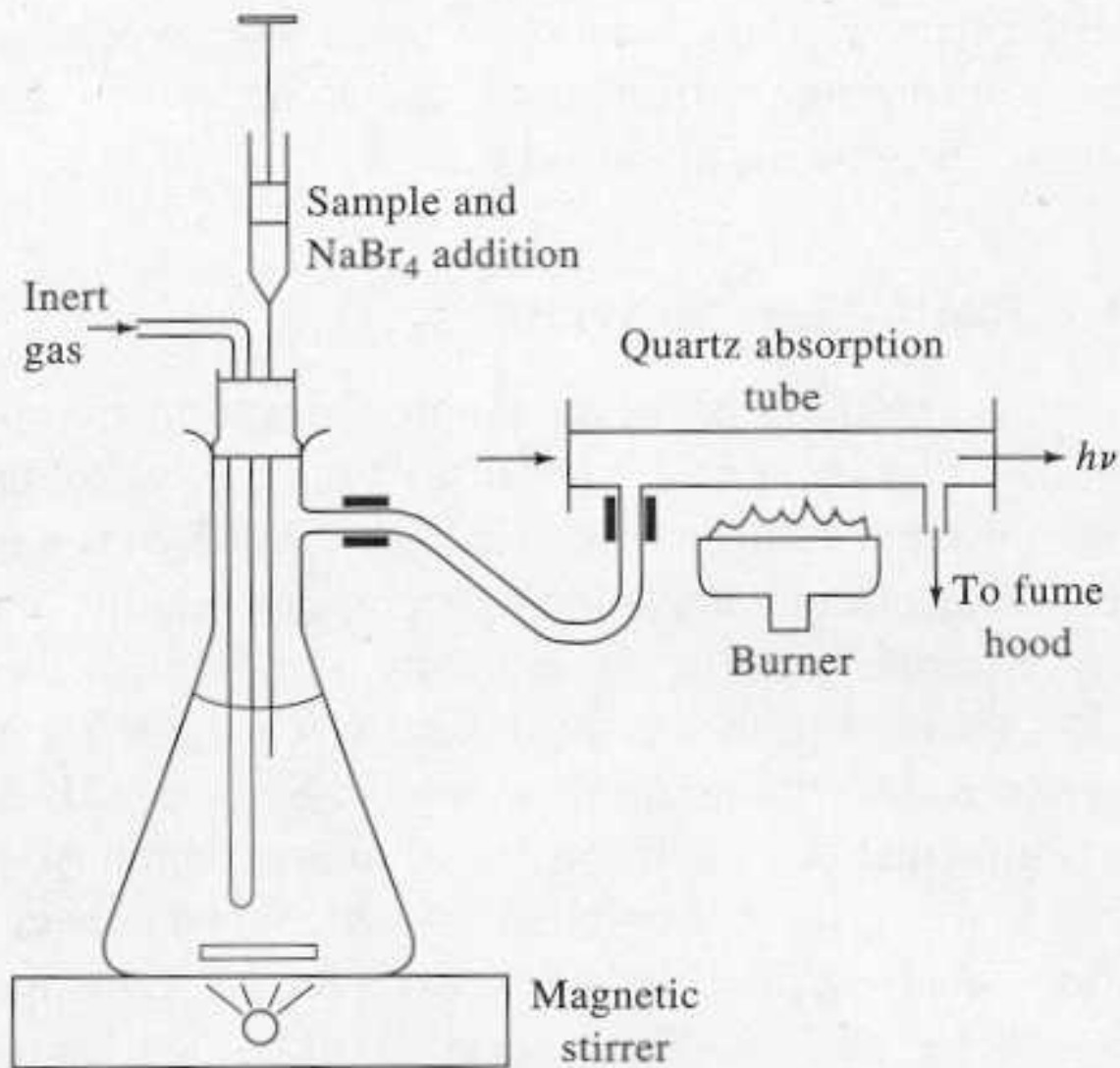
Sample introduction for solutions:

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



- 5) Cold vapor generation





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

There are many possible variations for the hydride generation apparatus

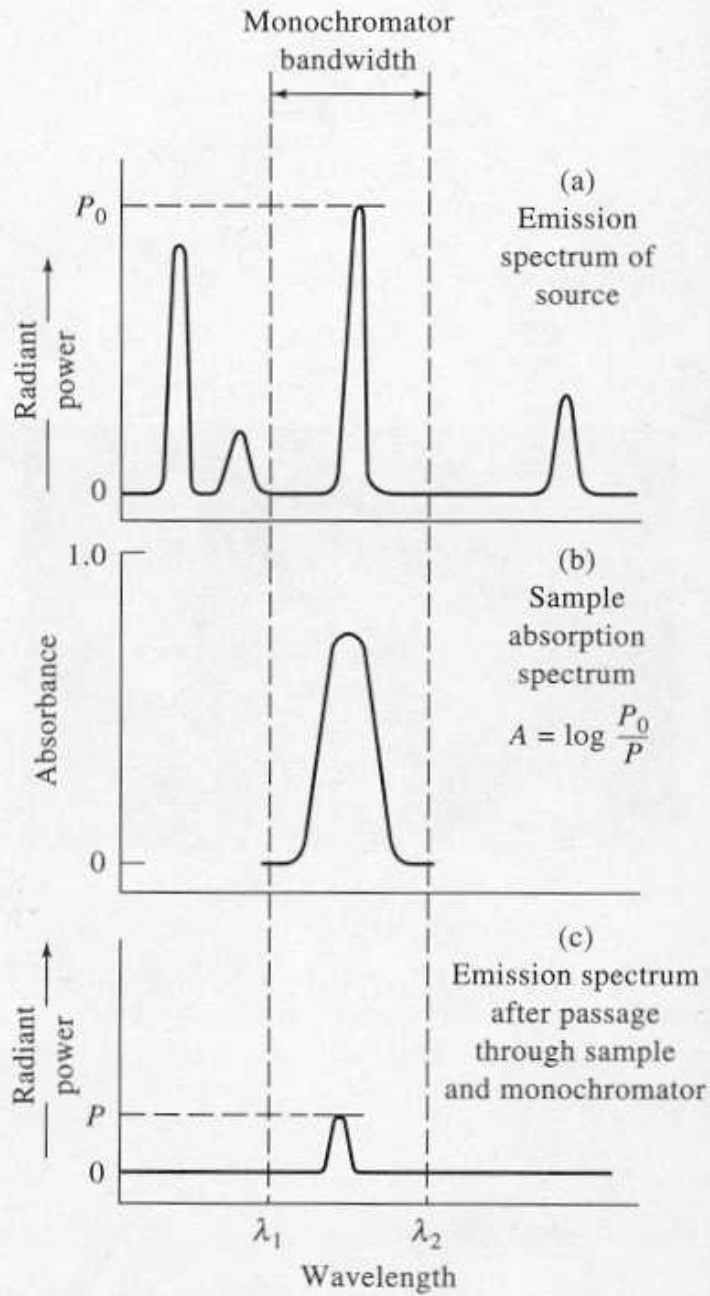
## Interferences in AA can be

- 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  $\text{PO}_4$  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)

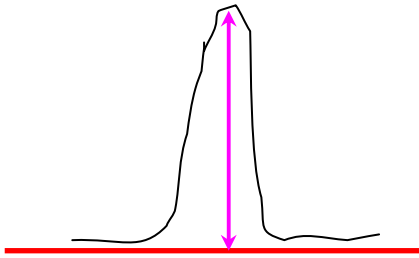


**Figure 9-10** Absorption of a resonance line by atoms.

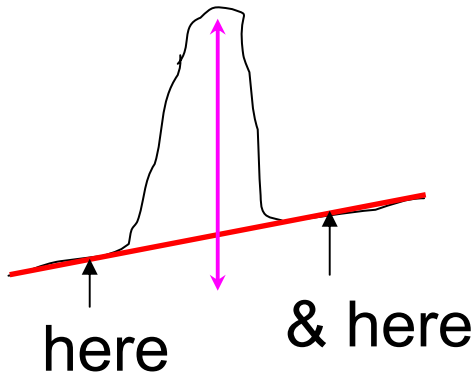
Normal or idealized situation for the absorption of source radiation in AA

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

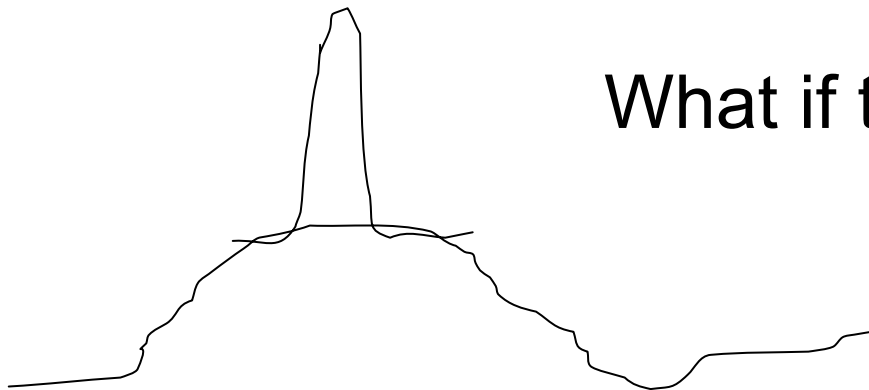
Background correction is then needed



Normally assume baseline is flat  
not structured. In the absence  
of peak would have flat baseline  
Peak height easily measured

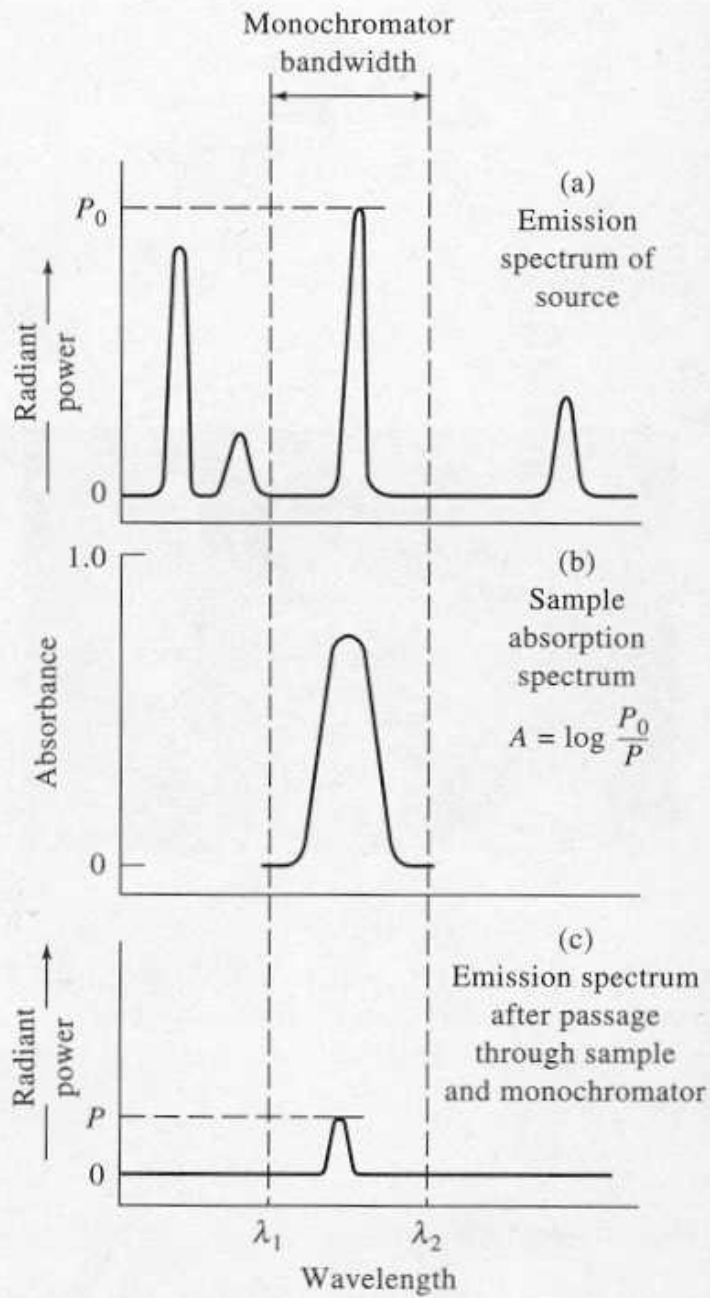


What if baseline is sloped?  
How is peak height measured?  
Need measurement of baseline



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  $\lambda$  of interest

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

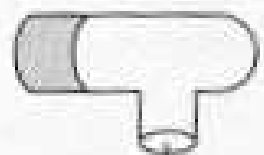
Typically we are interested in points on either side of the peak

line source  
for AA

Analyte hollow  
cathode lamp

Deuterium  
lamp

continuum  
source for  
background  
correction



Rotating  
chopper



Electrothermal  
atomizer

To mono-  
chromator

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

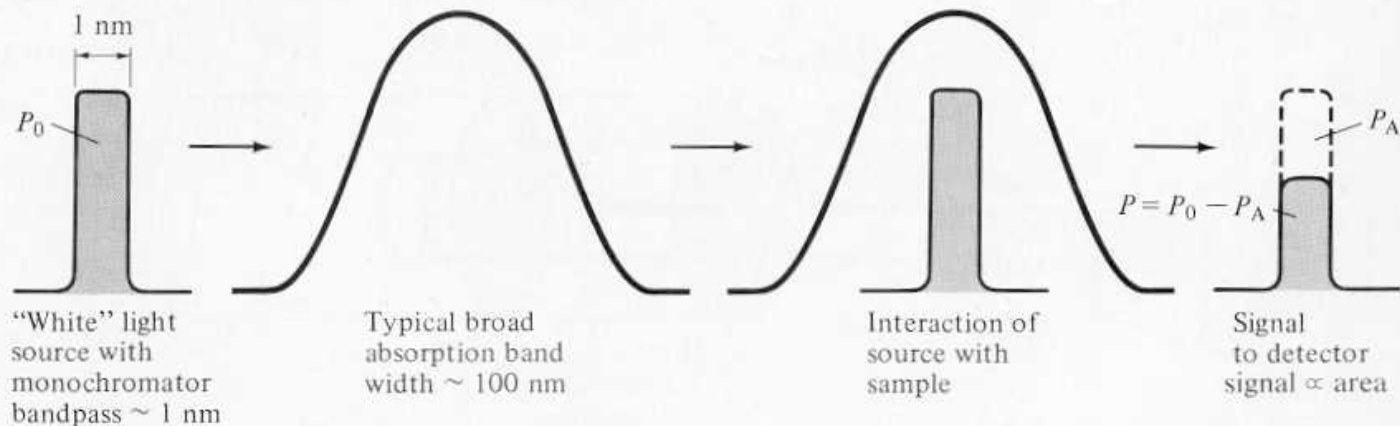


FIGURE 13-7 Conventional UV-VIS spectrophotometry.

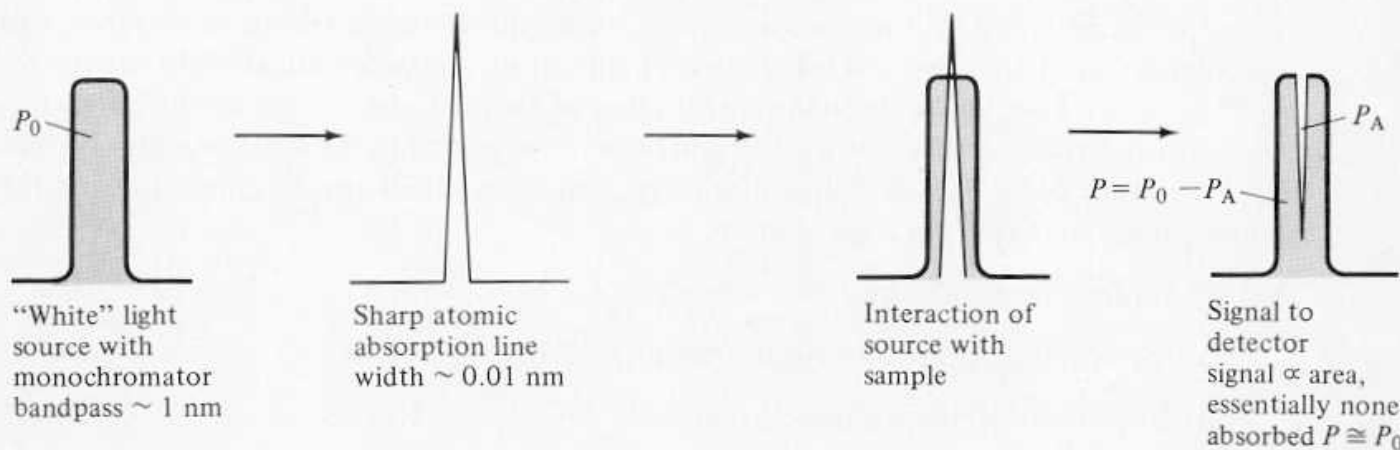


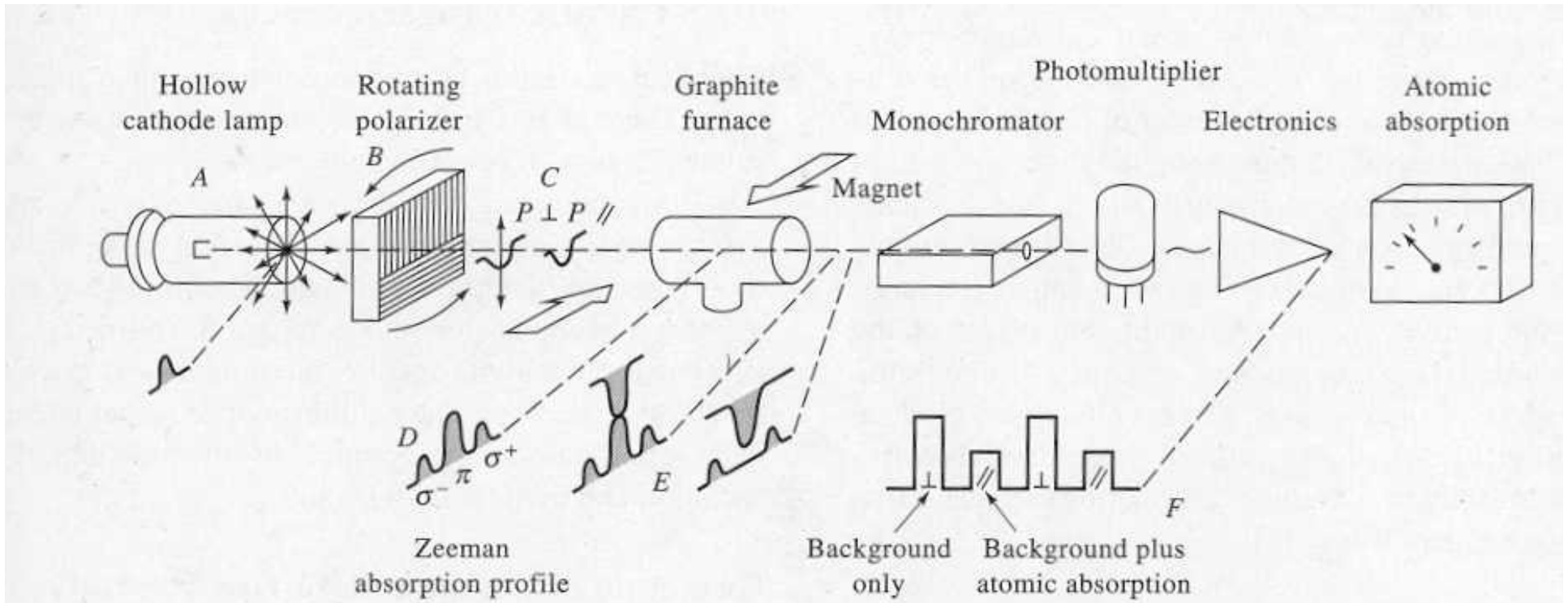
FIGURE 13-8 Attempt to use conventional UV-VIS source for atomic absorption.

This shows (bottom) that a continuum source is not suitable for AA.

However, it will work for background correction.

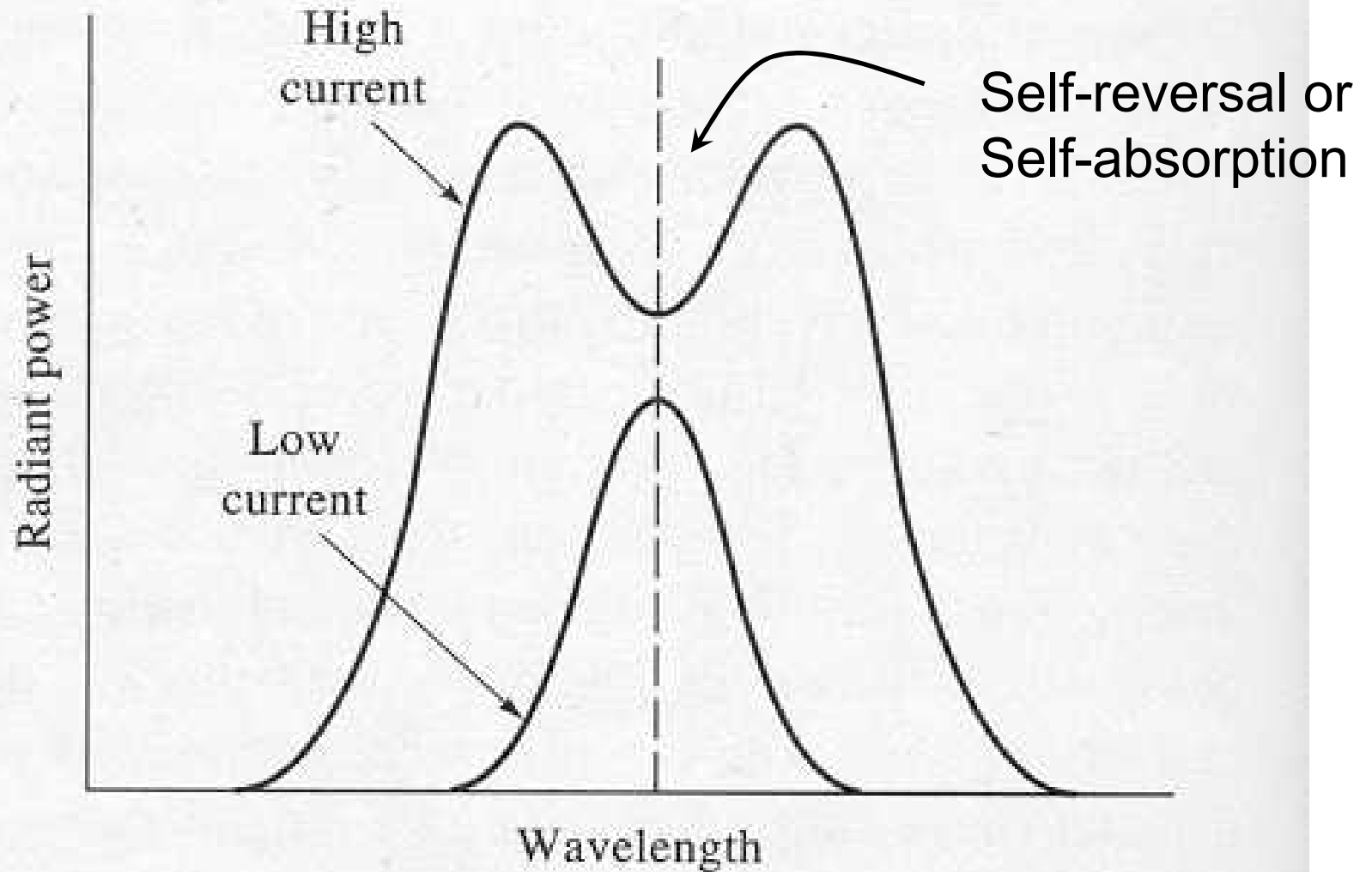
The atomic line absorbs minimally, but the background on either side of the line will be measured

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



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

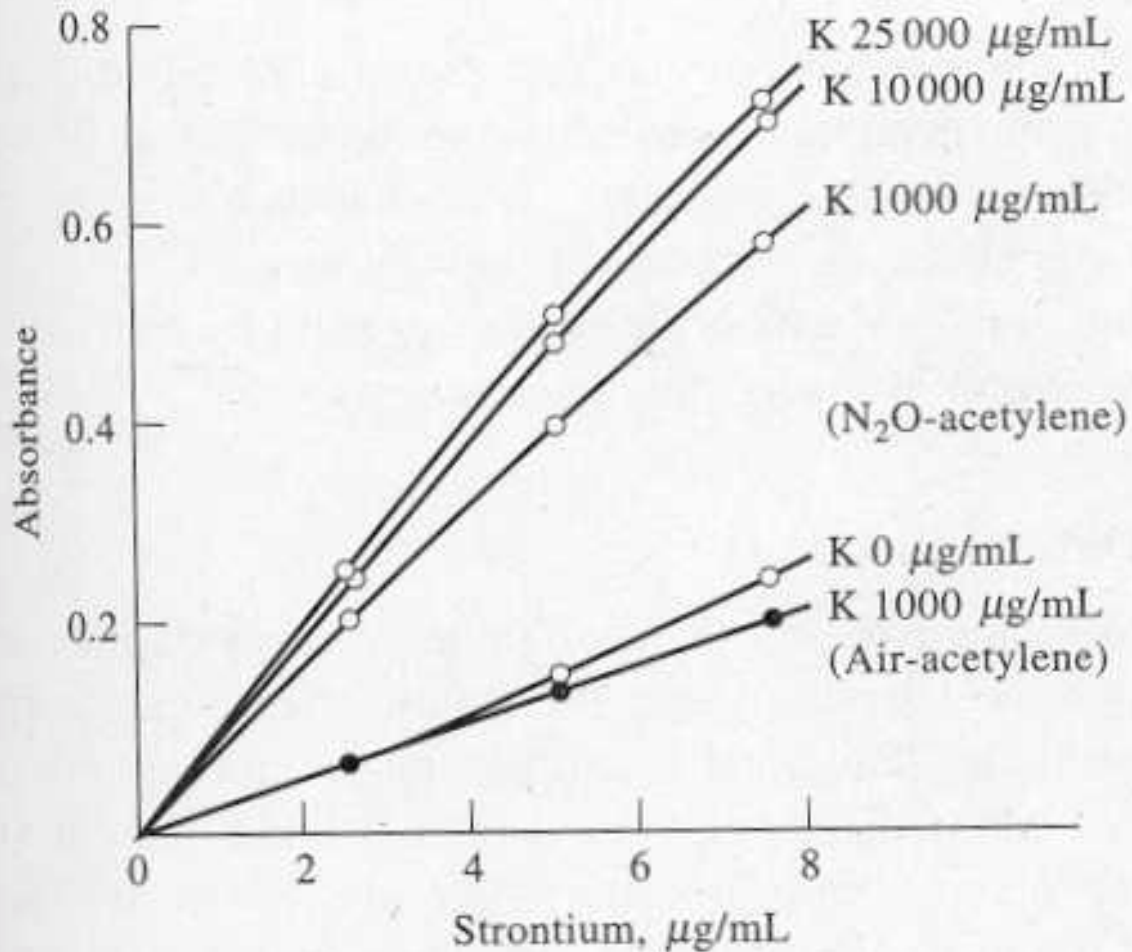


Another type of matrix interference not alleviated by background correction involves variable amounts of analyte ionization in flames or plasmas

**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	$3 \times 10^{-5}$	0.11	0.0003	0.67
Mg	7.644	$4 \times 10^{-7}$	0.01	$4 \times 10^{-6}$	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†

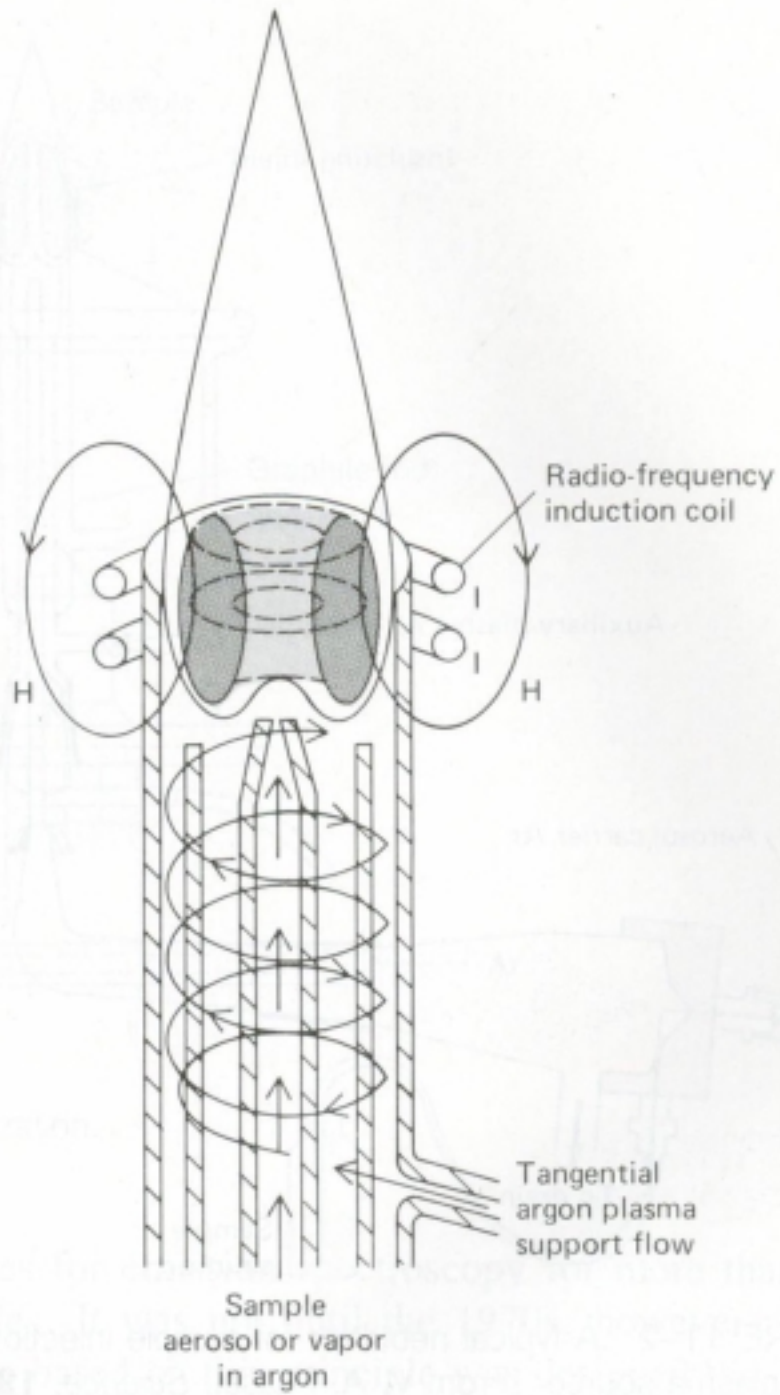
Element	AAS‡ Flame	AAS Electrothermal	AES‡ Flame	AES‡ ICP	AES‡ Flame
Al	30	0.005	5	2	5
As	100	0.02	0.0005	40	100
Ca	1	0.02	0.1	0.02	0.001
Cd	1	0.0001	800	2	0.01
Cr	3	0.01	4	0.3	4
Cu	2	0.002	10	0.1	1
Fe	5	0.005	30	0.3	8
Hg	500	0.1	0.0004	1	20
Mg	0.1	0.00002	5	0.05	1
Mn	2	0.0002	5	0.06	2
Mo	30	0.005	100	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 =  $10^{-3}$   $\mu\text{g/mL}$  =  $10^{-3}$  ppm.

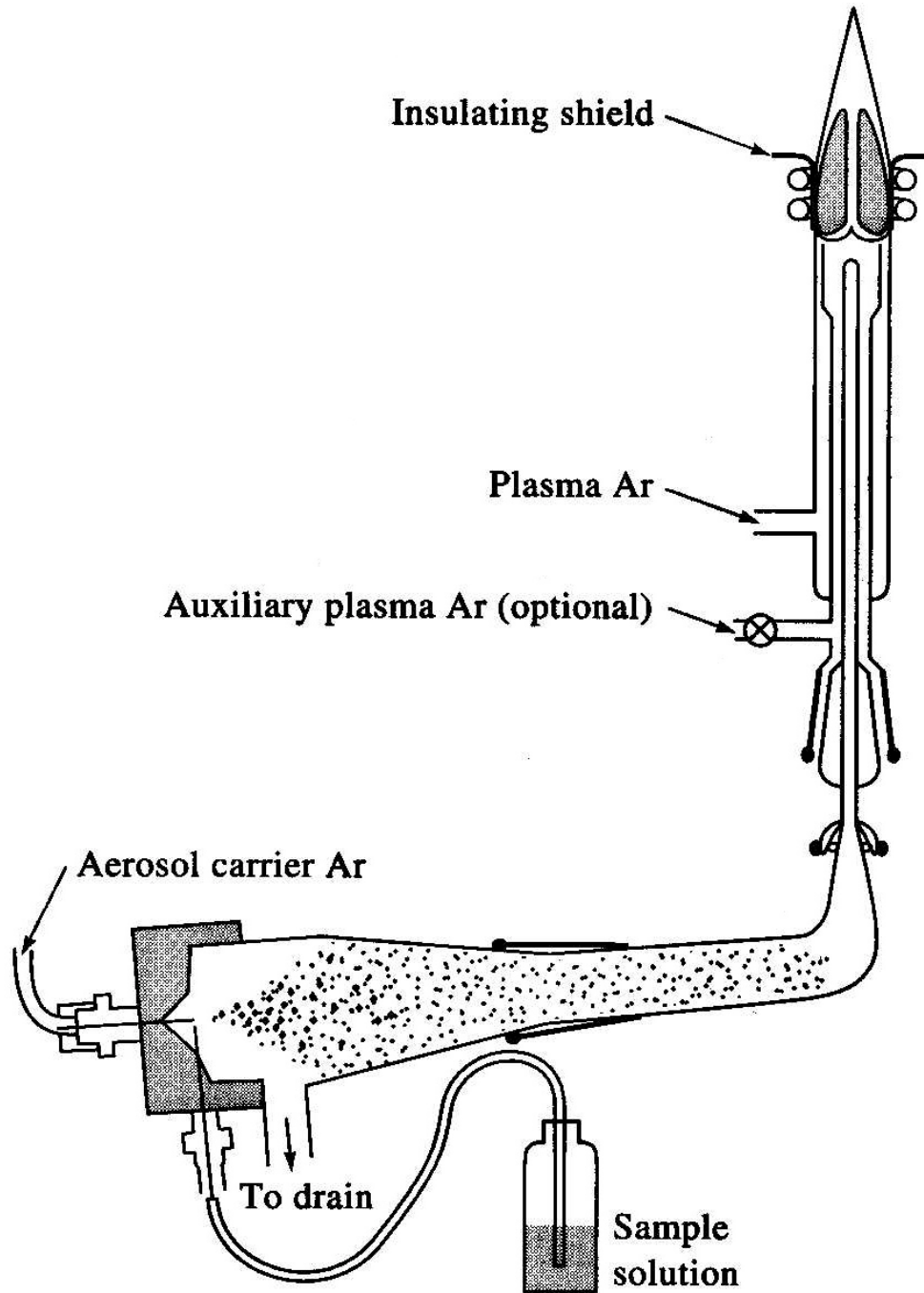
# Chapter 10: Emission Spectroscopy Using Plasmas, Arcs or Sparks

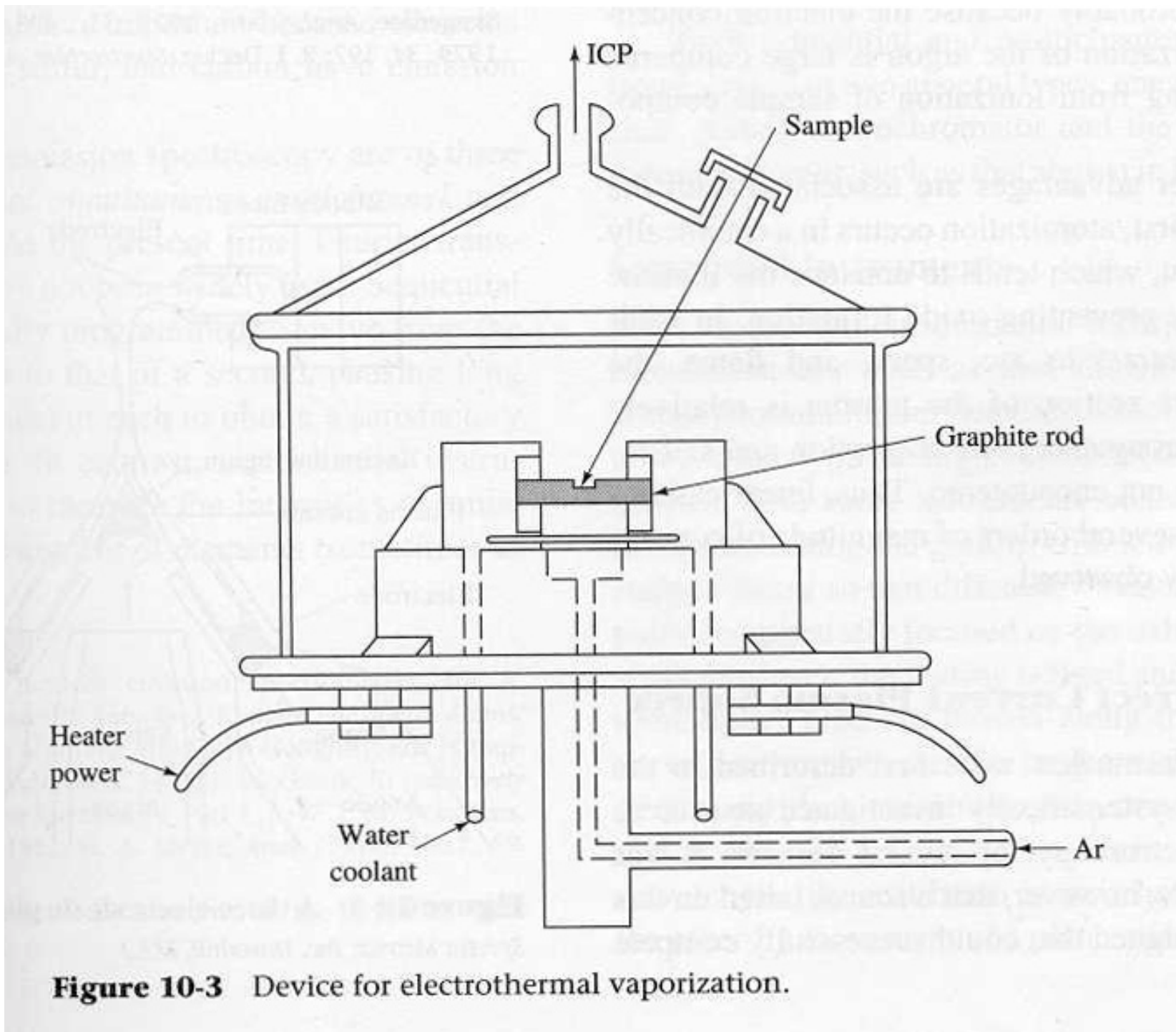
- Inductively Coupled Plasma (ICP)
- Direct Current Plasma (DCP)
- Arcs and Sparks

# Inductively Coupled Plasma (ICP)



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





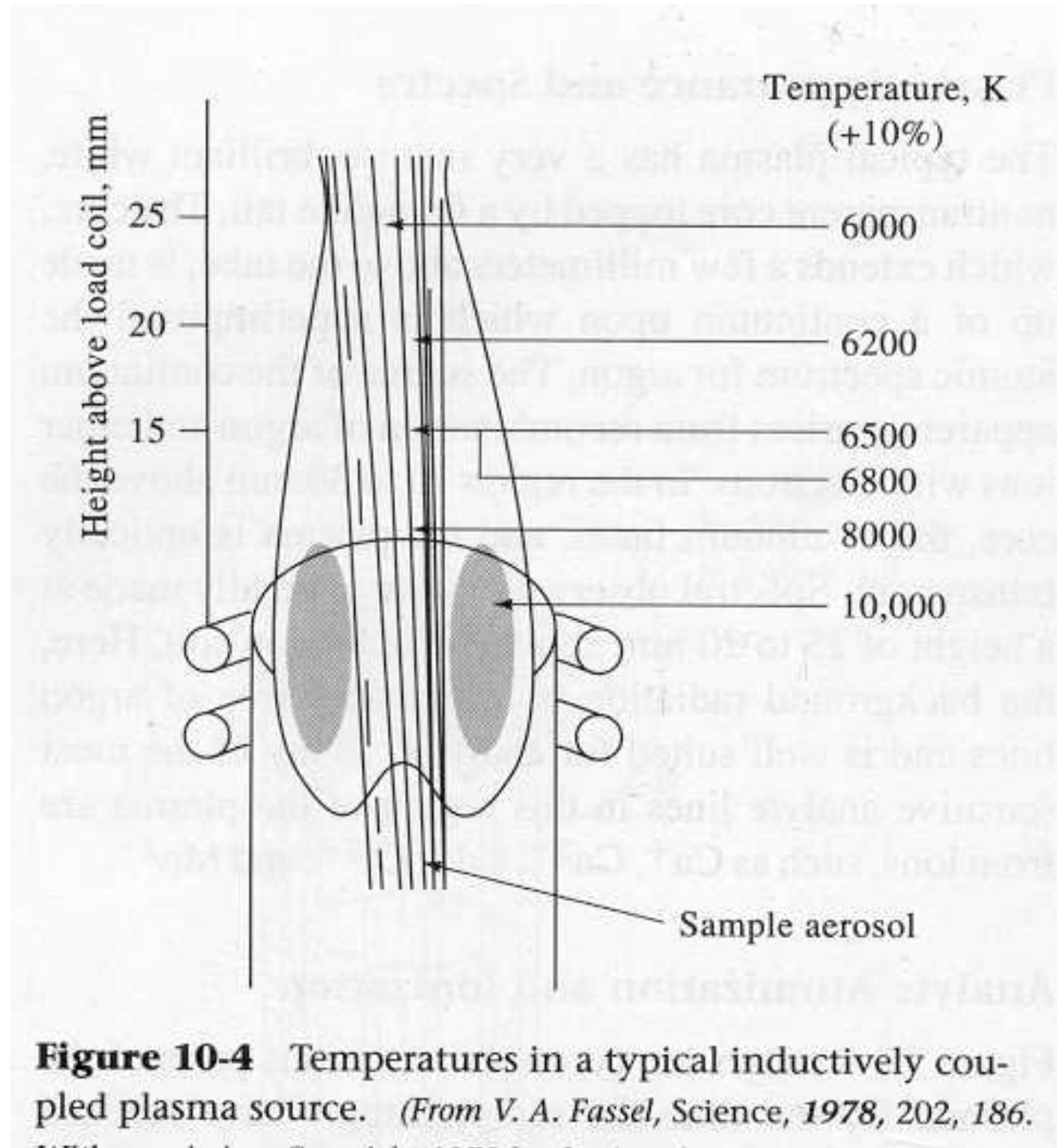
mate  
getting  
to ICP

**Figure 10-3** Device for electrothermal vaporization.



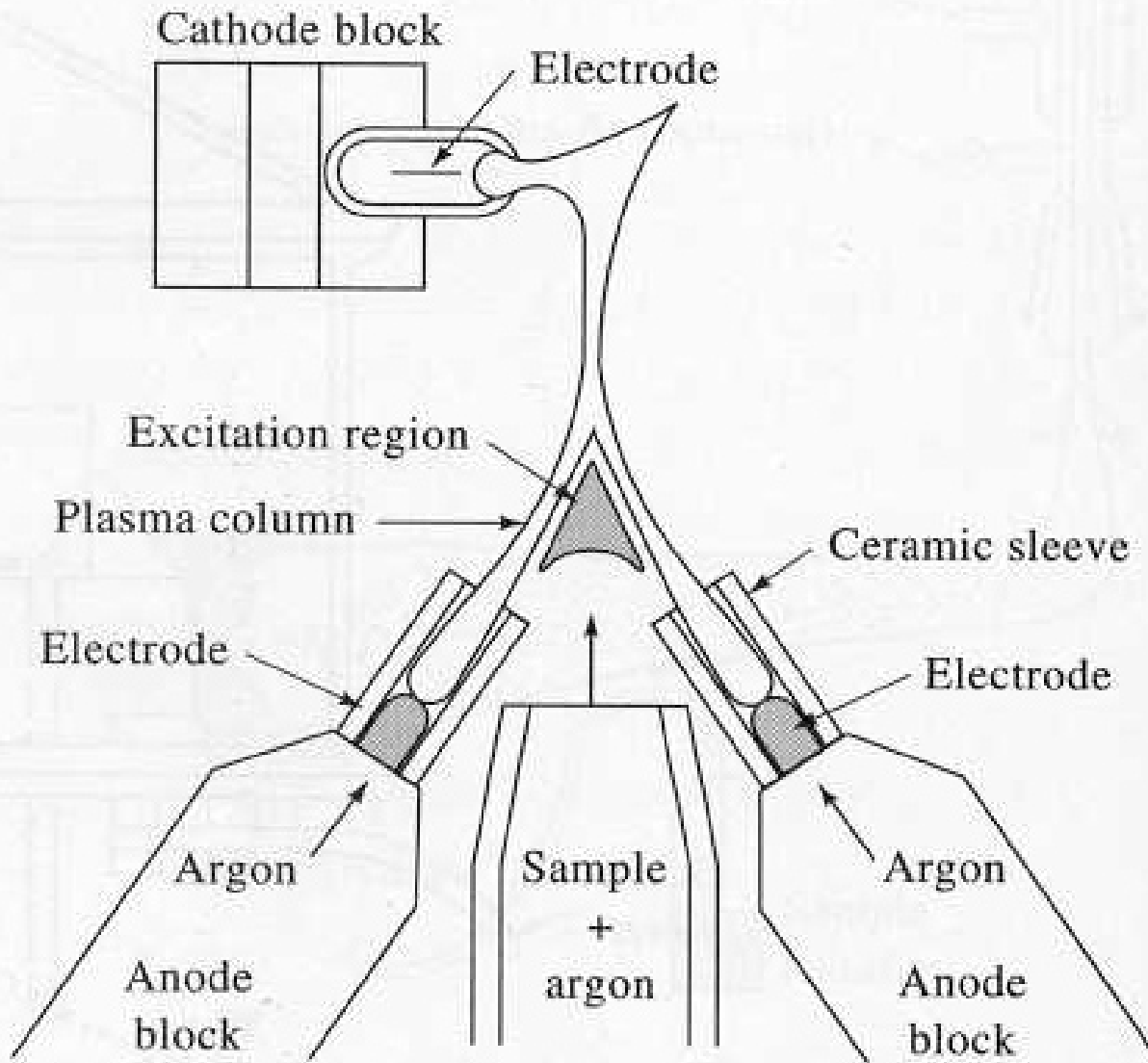
## ICP Temps.

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

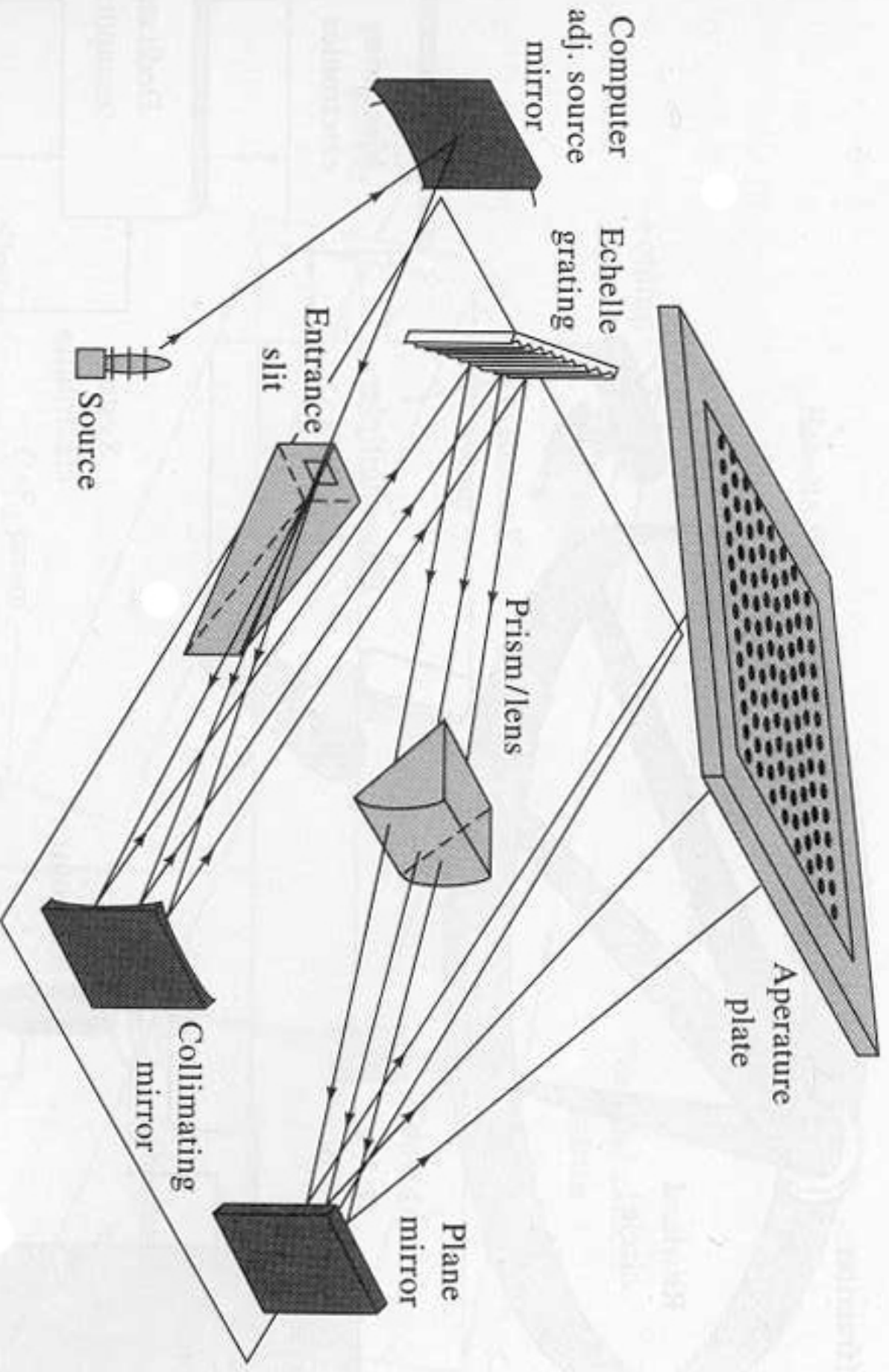


# Direct Current Plasma (DCP) Torch

Lab will involve use of DCP for multielement analysis

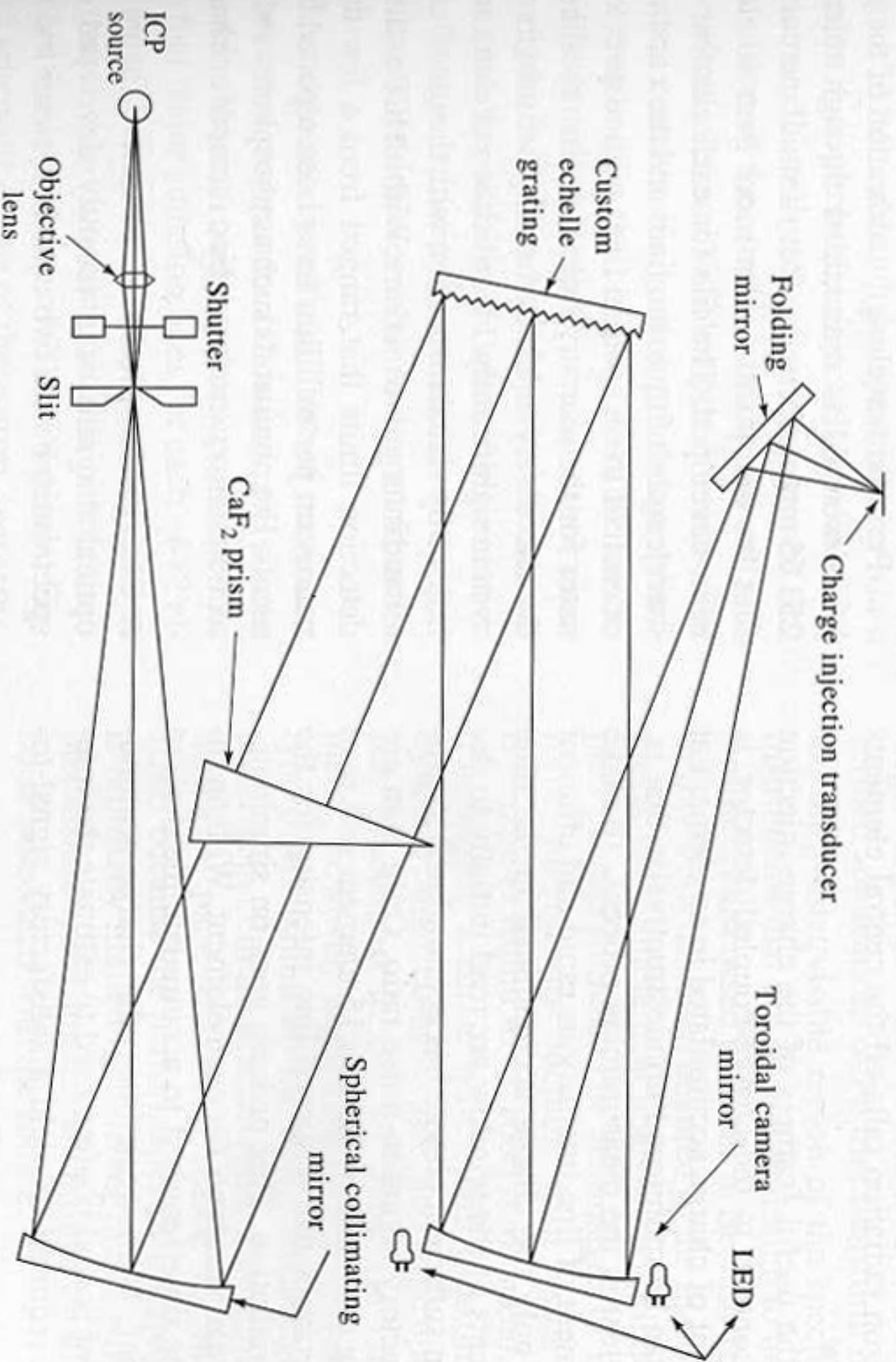


**Figure 10-5** A three-electrode dc plasma jet. (Courtesy of Spectra Metrics, Inc. Haverhill, MA.)



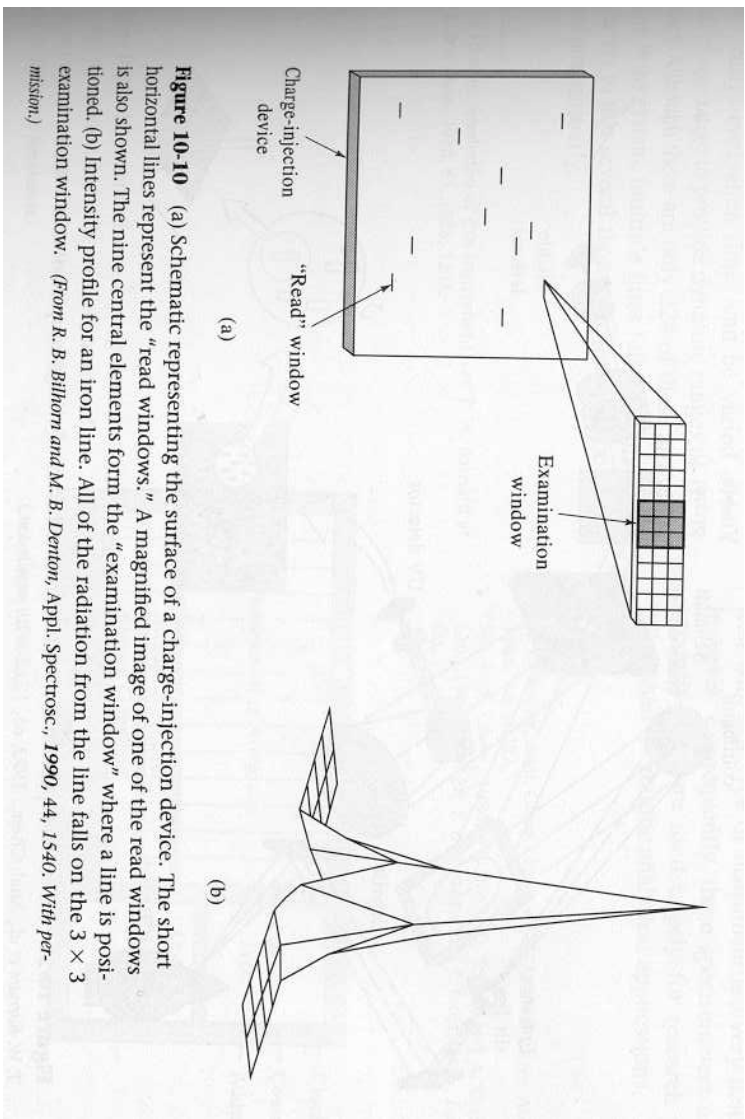
**Figure 10-7** Schematic of an echelle polychromator system.

### Echelle Spectrometer Optical Diagram

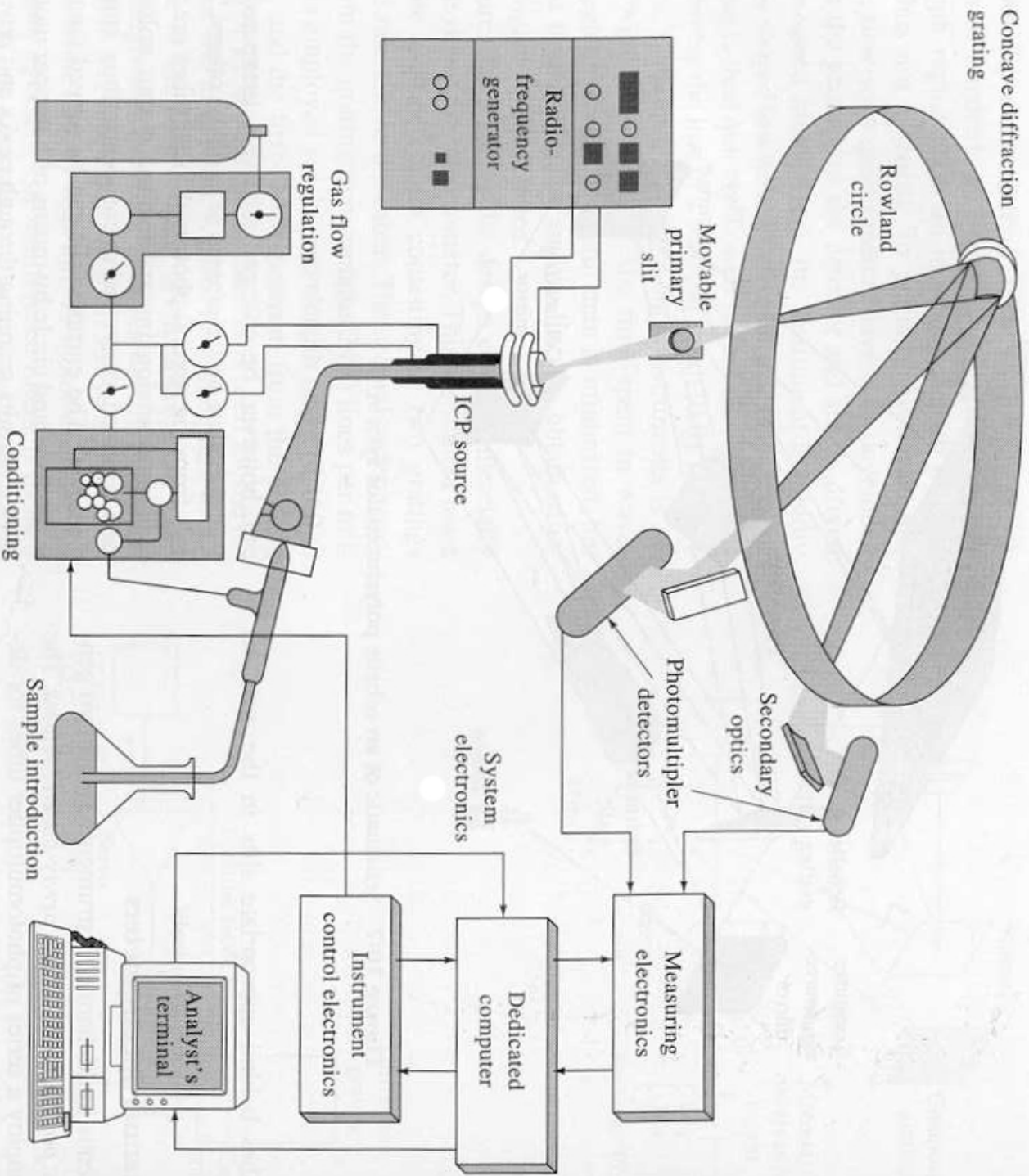


**Figure 10-9** Optical diagram of an echelle spectrometer with a charge-injection detector.

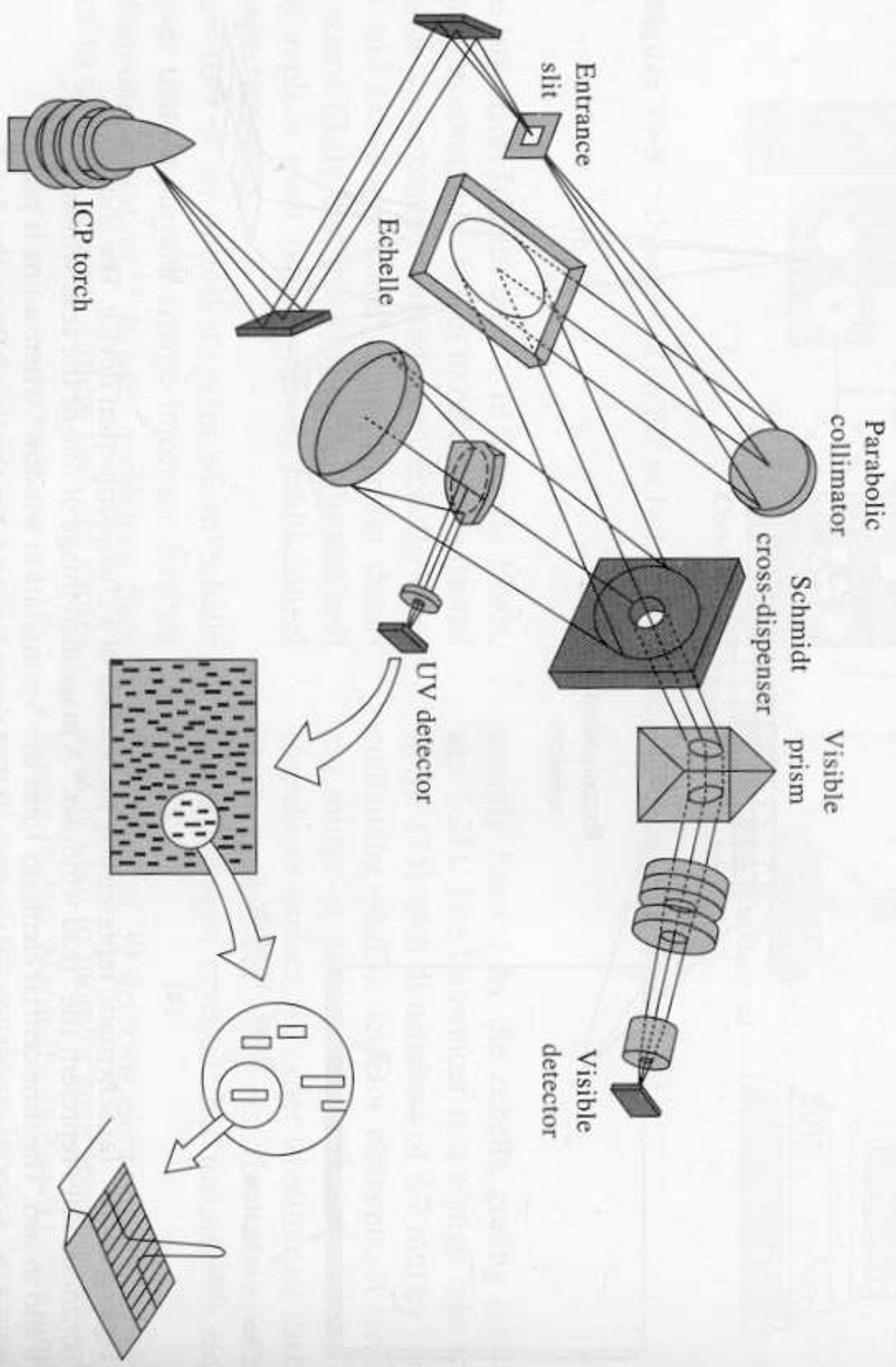
(From R. B. Bilhorn and M. B. Denton, *Appl. Spectrosc.*, 1990, 44, 1615. With permission.)



**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 the "examination window" where a line is positioned. (b) Intensity profile for an iron line. All of the radiation from the line falls on the  $3 \times 3$  examination window. (From R. B. Bilhorn and M. B. Denton, *Appl. Spectrosc.*, 1990, 44, 1540. With permission.)



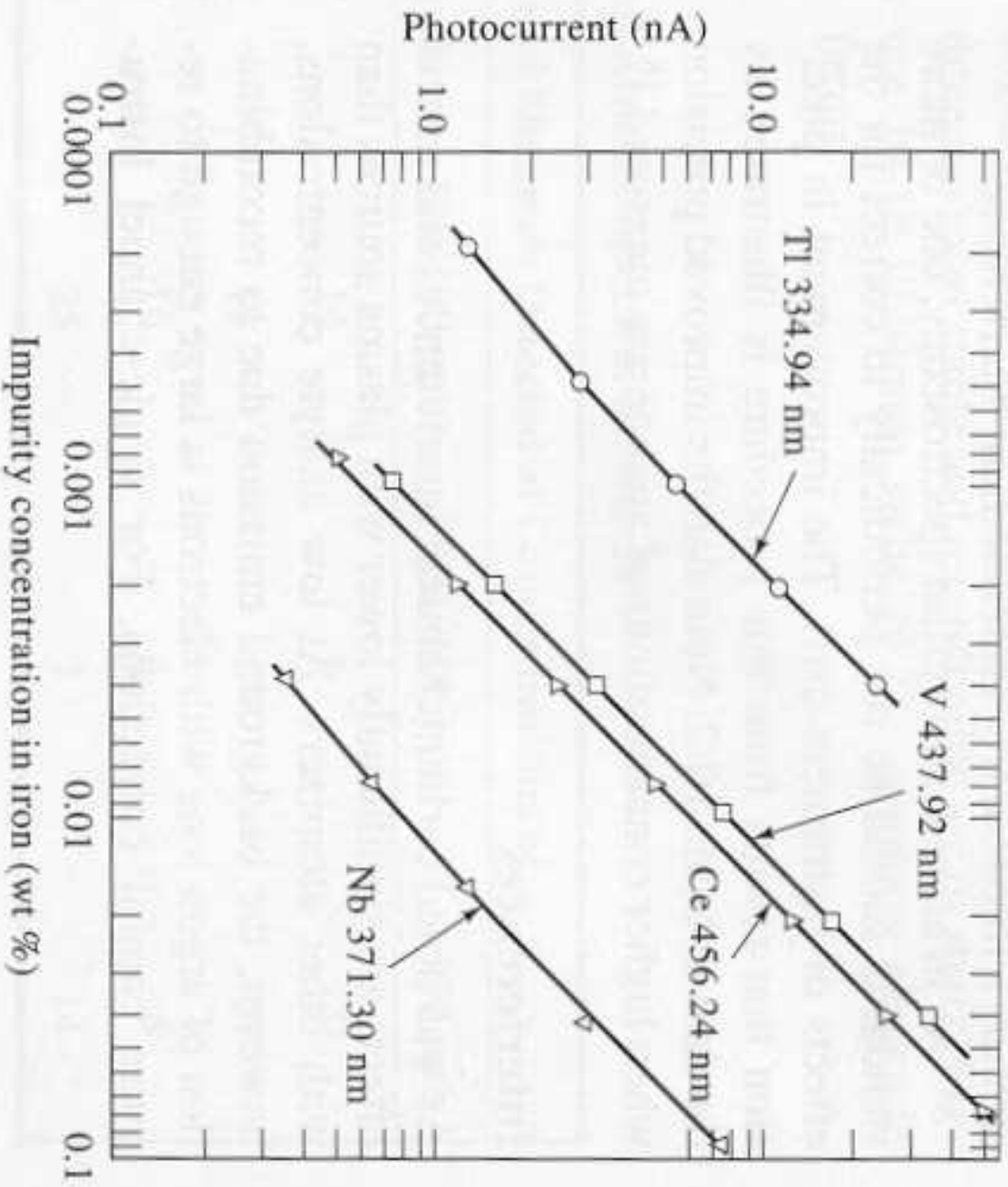
**Figure 10-8** Schematic of an ICP polychromator. (Courtesy of Thermo Jarrell Ash Corp.)



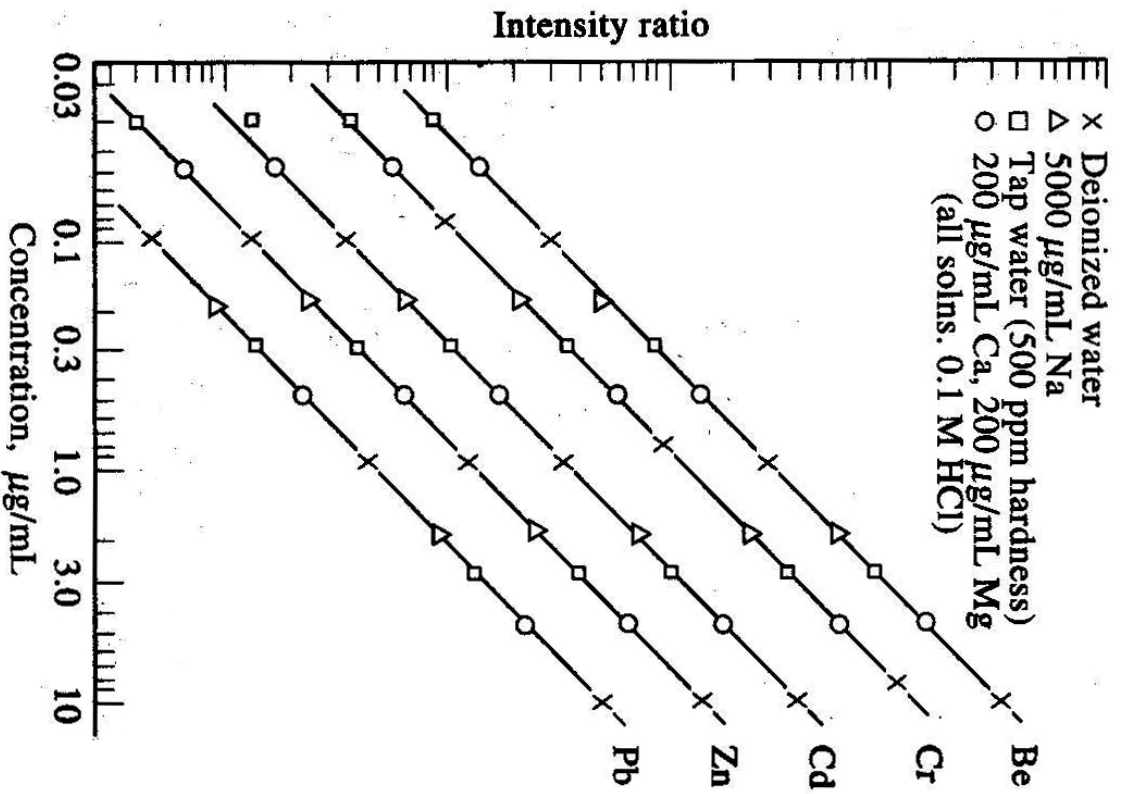
**Figure 10-11** An echelle spectrometer with segmented array of charge-coupled devices. (From T. W. Barriard et al., *Anal. Chem.*, 1993, 65, 1232. With permission.)



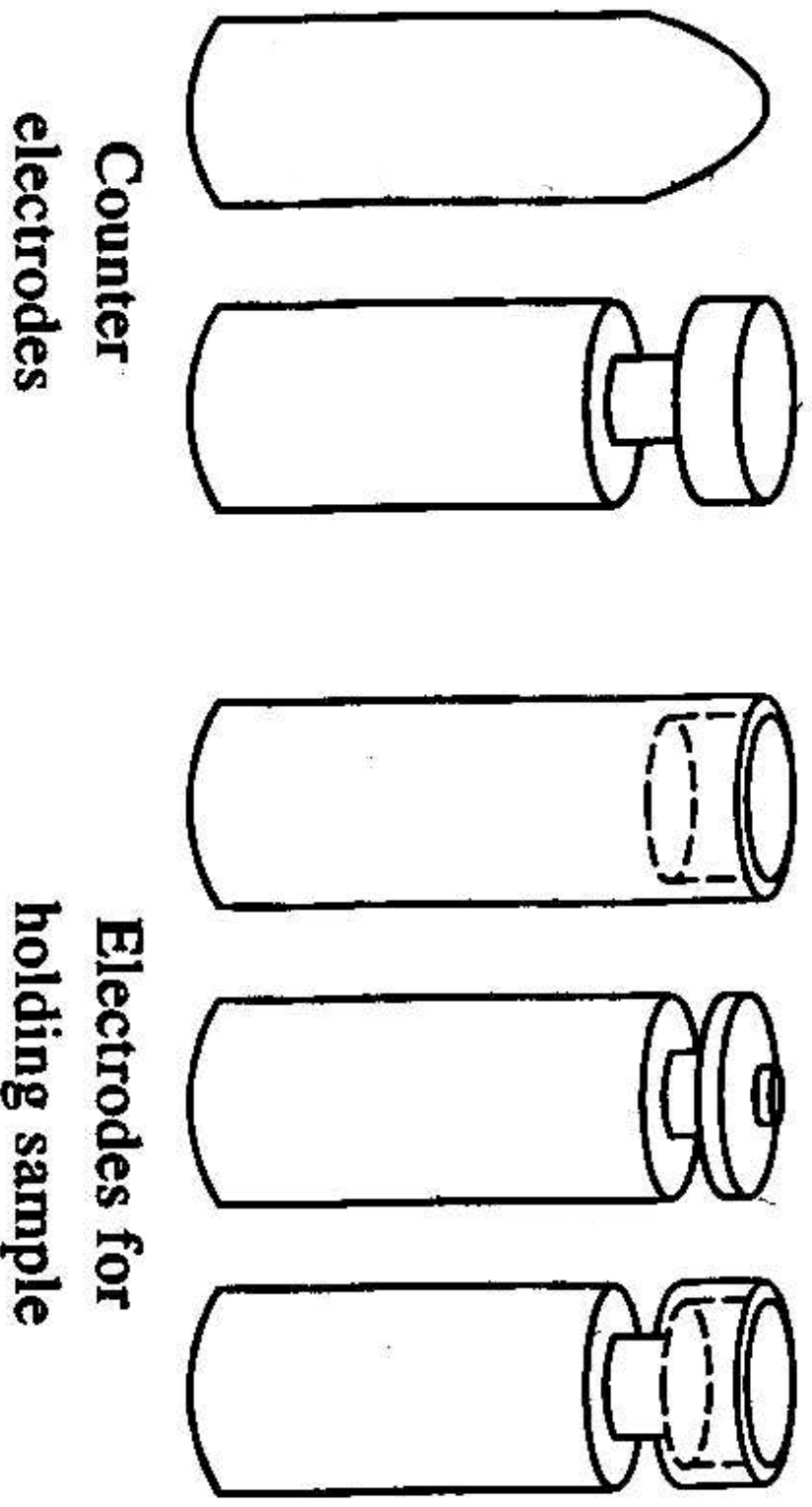




**Figure 10-14** Typical calibration curves. (From V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, 1974, 46, 1117A. With permission.)



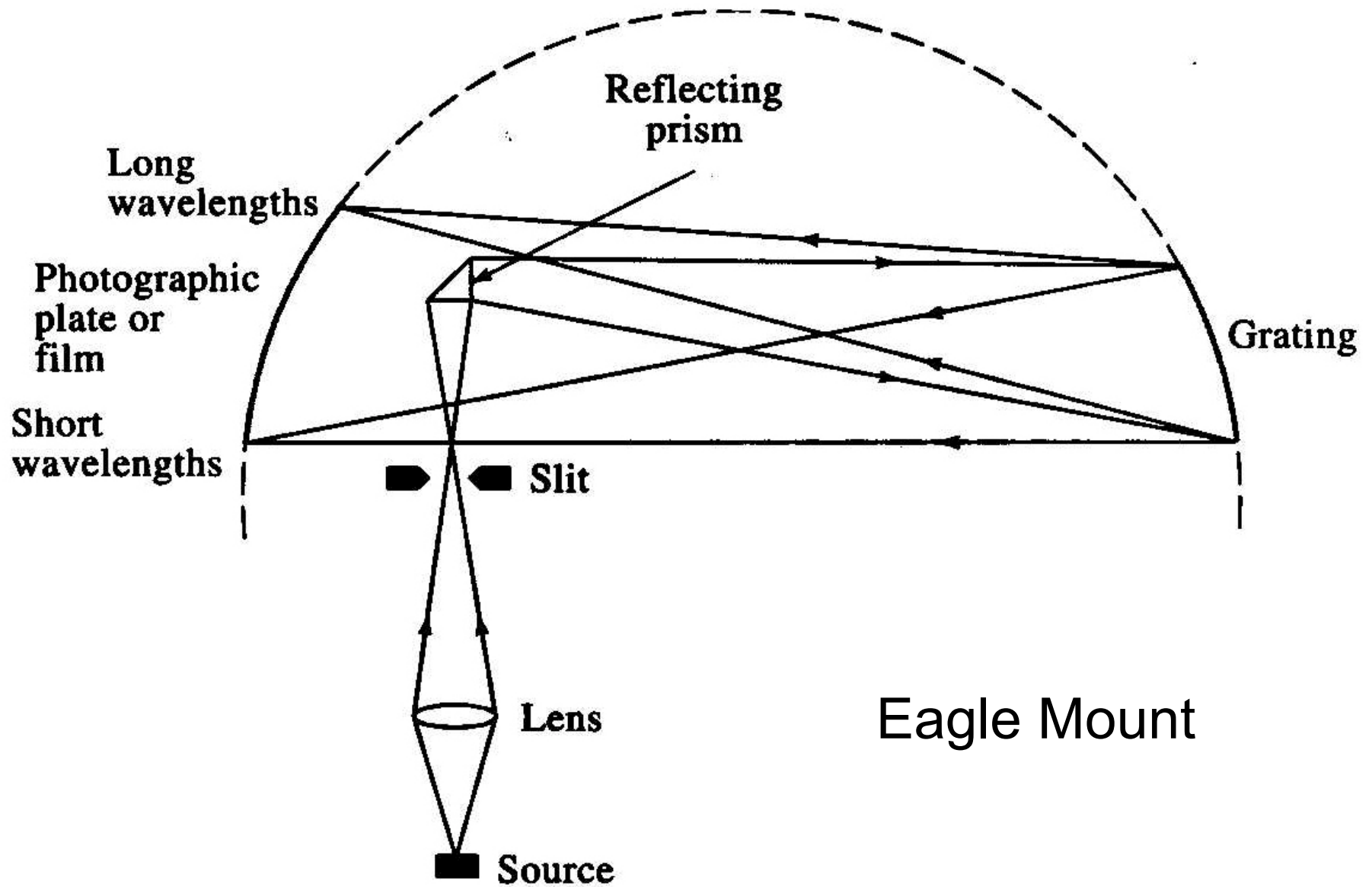
**Figure 10-15** Calibration curves with an inductively coupled plasma source. Here, an yttrium line at 242.2 nm served as an internal standard. Notice the lack of interelement interference. From V. A. Fassel, *Science*, 1978, 202, 187.

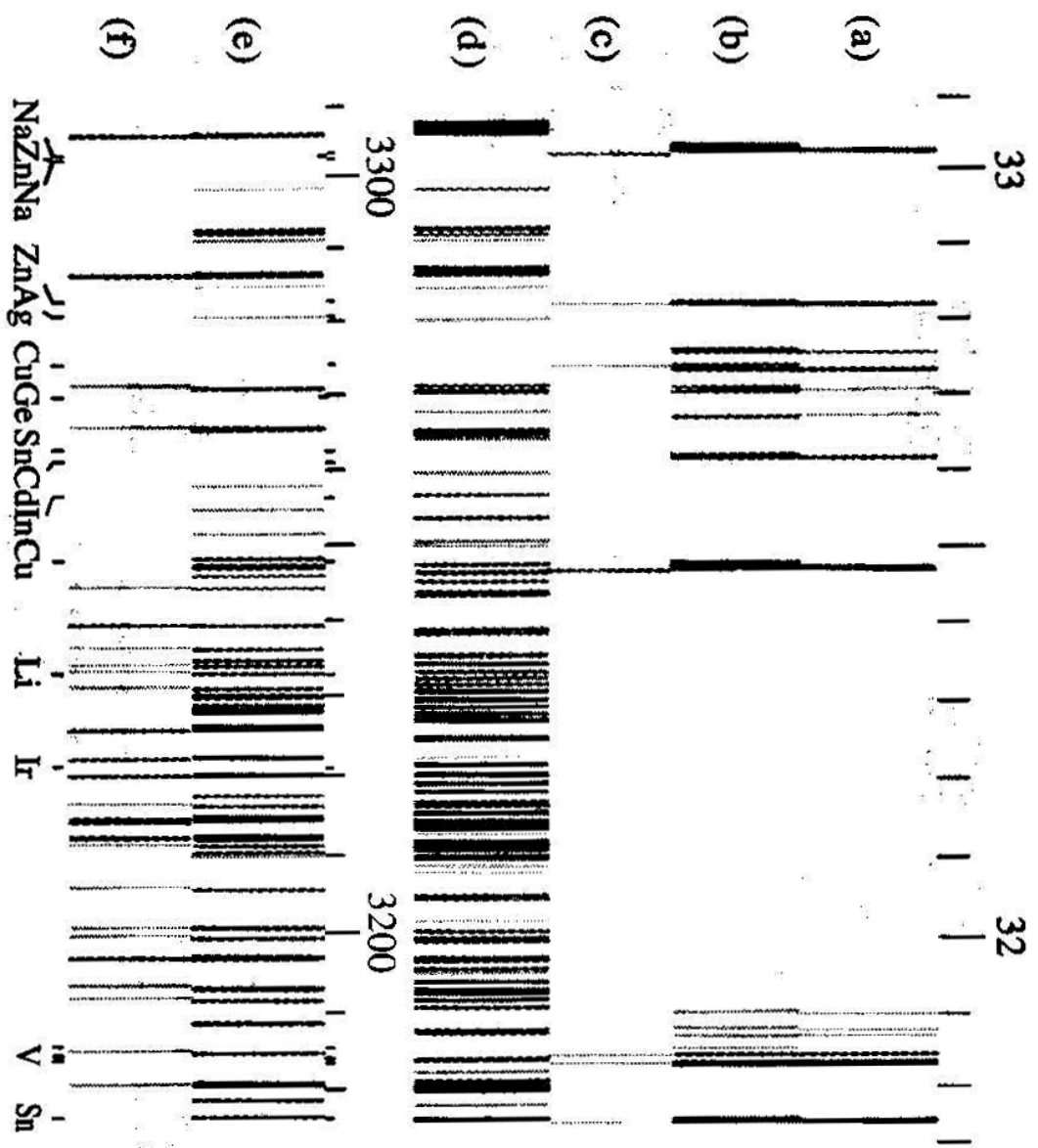


Counter  
electrodes

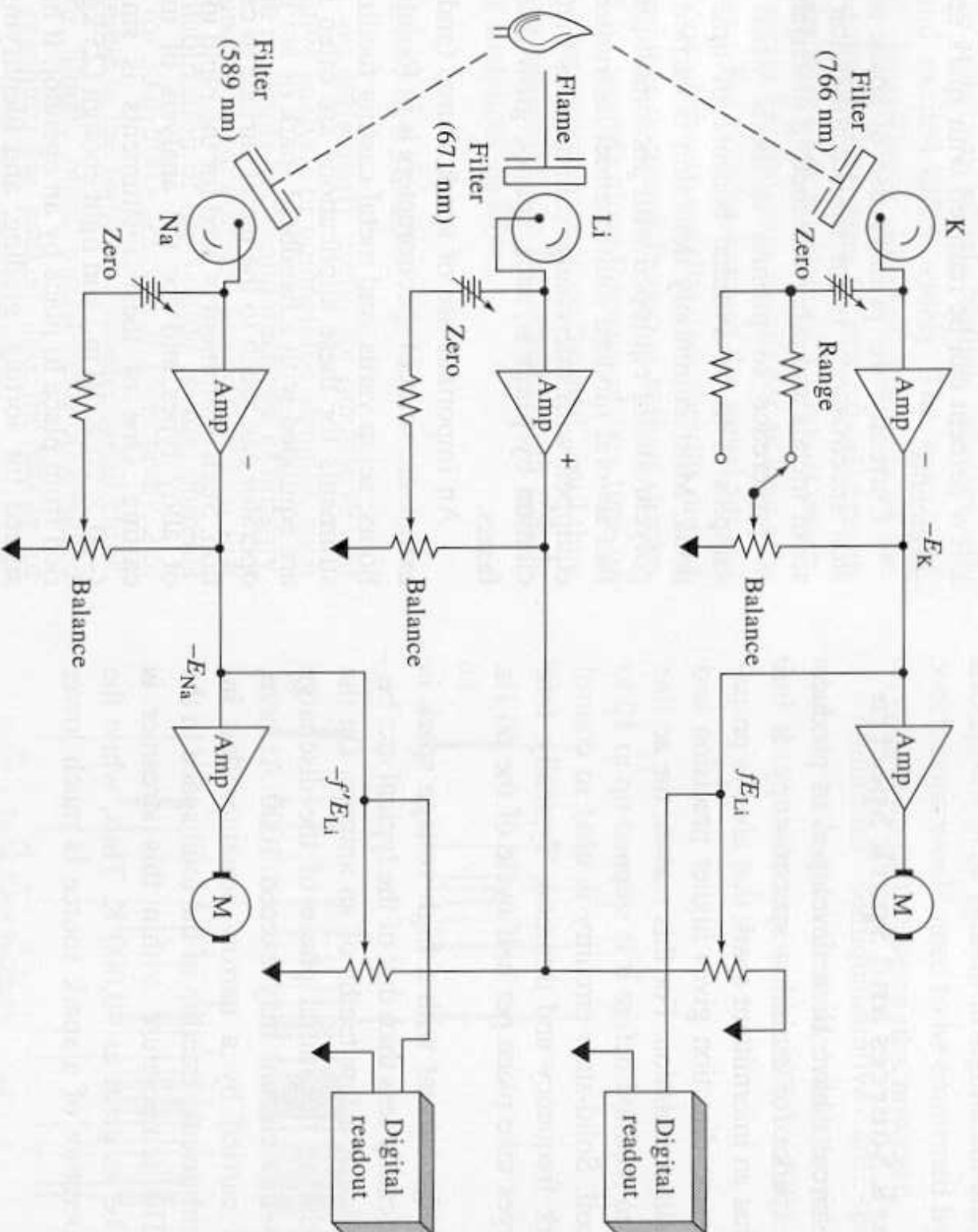
Electrodes for  
holding sample

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





**Figure 10-18** Projected spectra by a comparator-densitometer: (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 ( $0.01 \text{ nm}$  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, %			
	10 <sup>1</sup> to 10 <sup>2</sup>	Concentration Multiple above 10 <sup>2</sup> to 10 <sup>3</sup>	Detection Limit 10 <sup>3</sup> to 10 <sup>4</sup>	10 <sup>4</sup> to 10 <sup>5</sup>
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.



