Chapter 10: Atomic Emission Spectrometry

Read: pp. 254 – 266 **Problems: 10-2,5,6**

- Excited-state atoms emit UV-visible line spectra that are useful for qualitative and quantitative analysis.
- Flame and plasma sources are commonly used for AES.
- Plasma sources offer several advantages:
  - Lower interelement interference due to high temperature
  - Good emission spectra are obtained for a single set of excitation conditions
  - Simultaneous detection of multiple elements
  - Improved detection figures of merit compared to flame AAS and AES

Inductively Coupled Plasma Source

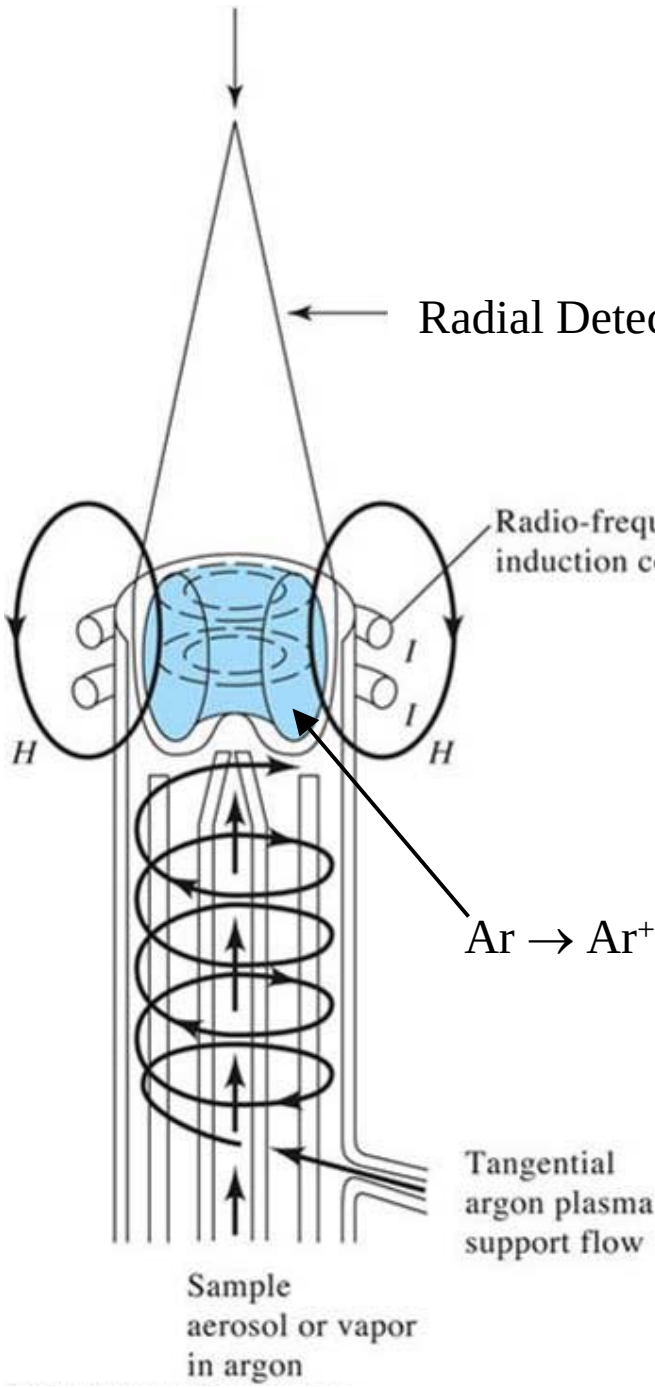

Figure 10-1

Inductively Coupled Plasma Source

- High temperature
- Uniform temperature
- Inert environment (Ar)

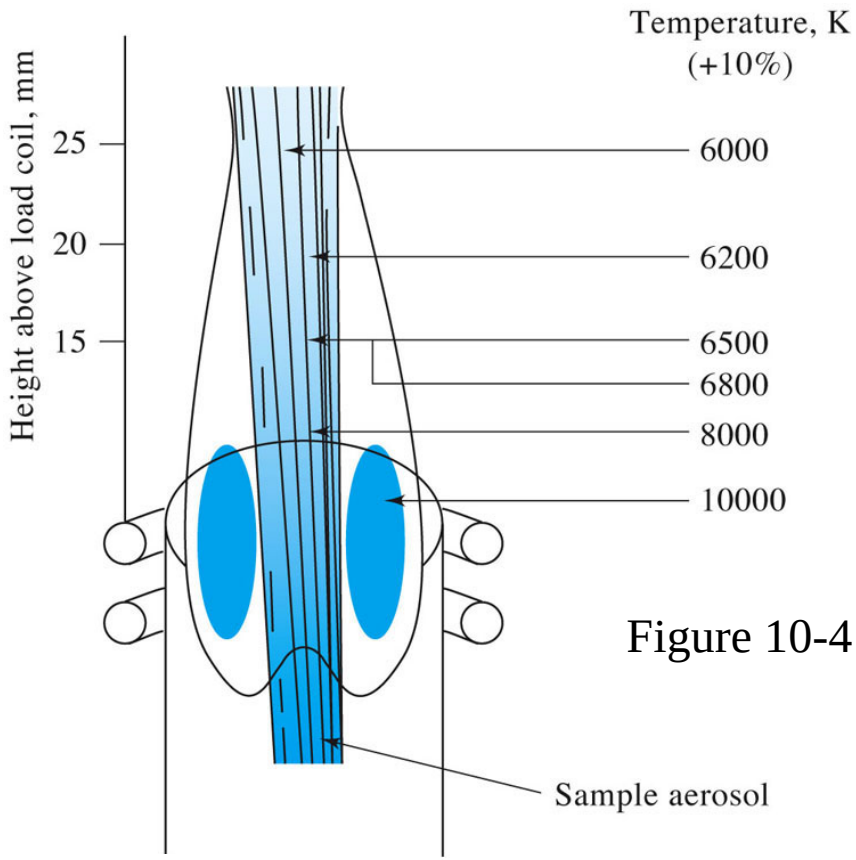

Figure 10-4

Leads to more complete atomization and fewer chemical interferences. Lower detection limits and broader linear range than flame sources.

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% relative standard deviation at 500 × the detection limit)
7. High stability with respect to environmental changes
8. Easy background corrections
9. Computerized operation: readout, storage data manipulation, etc.

Plasma Emission Spectrometers

1. Sequential Spectrometers: one wavelength at a time
   a. Slew-scanning (one PMT with two-speed linear scan)
   b. Scanning Echelle (one PMT, two-dimensional scan)

   Typically used for 10 – 15 elements/sample (max)

2. Simultaneous Multichannel Spectrometers: multiwavelength
   a. Polychromators (series of PMTs)
   b. Spectrographs (two-dimensional CID or CCD)

   Typically used for 50 – 60 elements/sample (max)

3. Fourier-Transform Spectrometers: multiwavelength

   Expensive, not widely used.

A Typical Multichannel Spectrograph

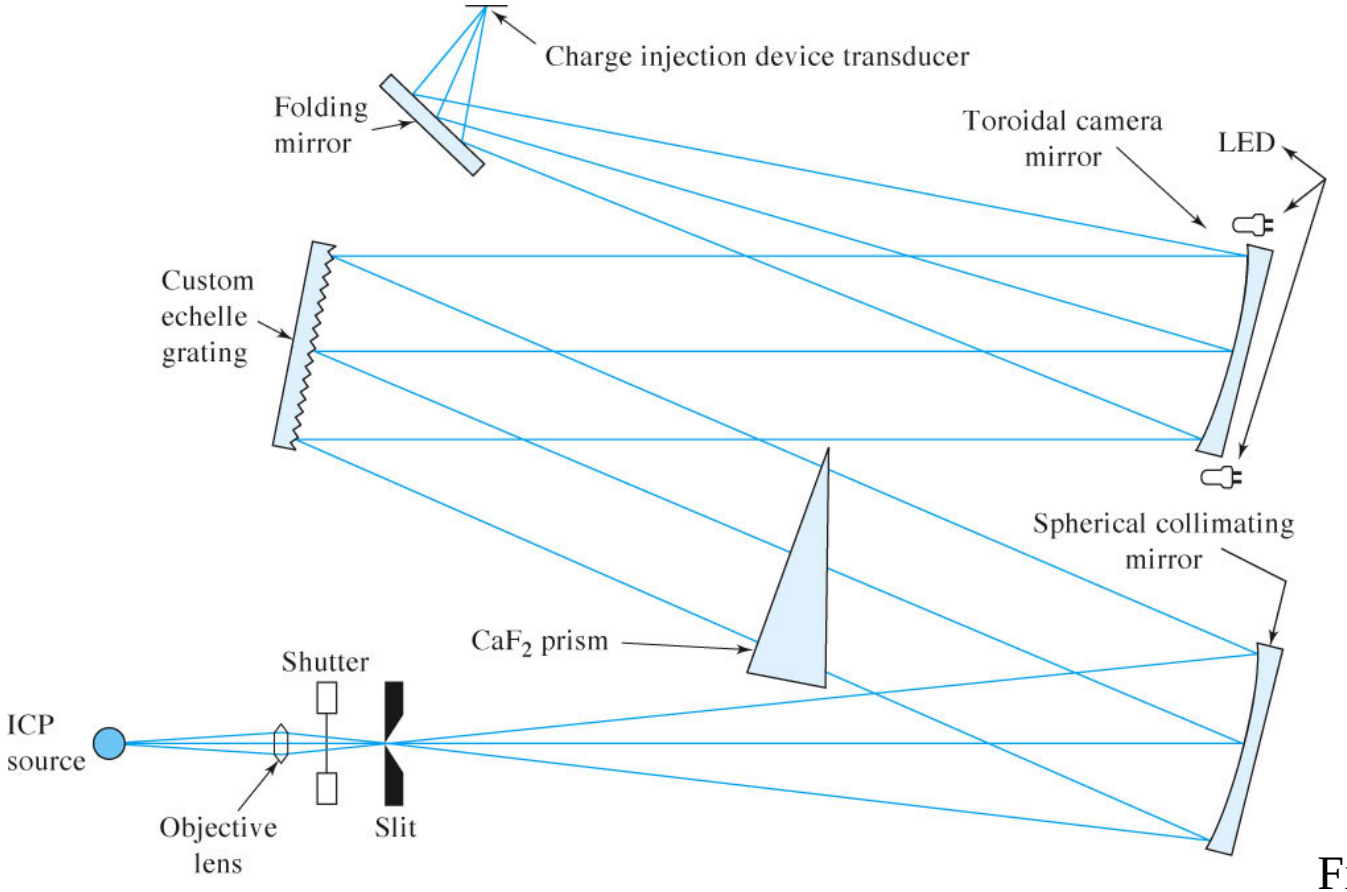

Figure 10-9

Echelle Grating Monochromator

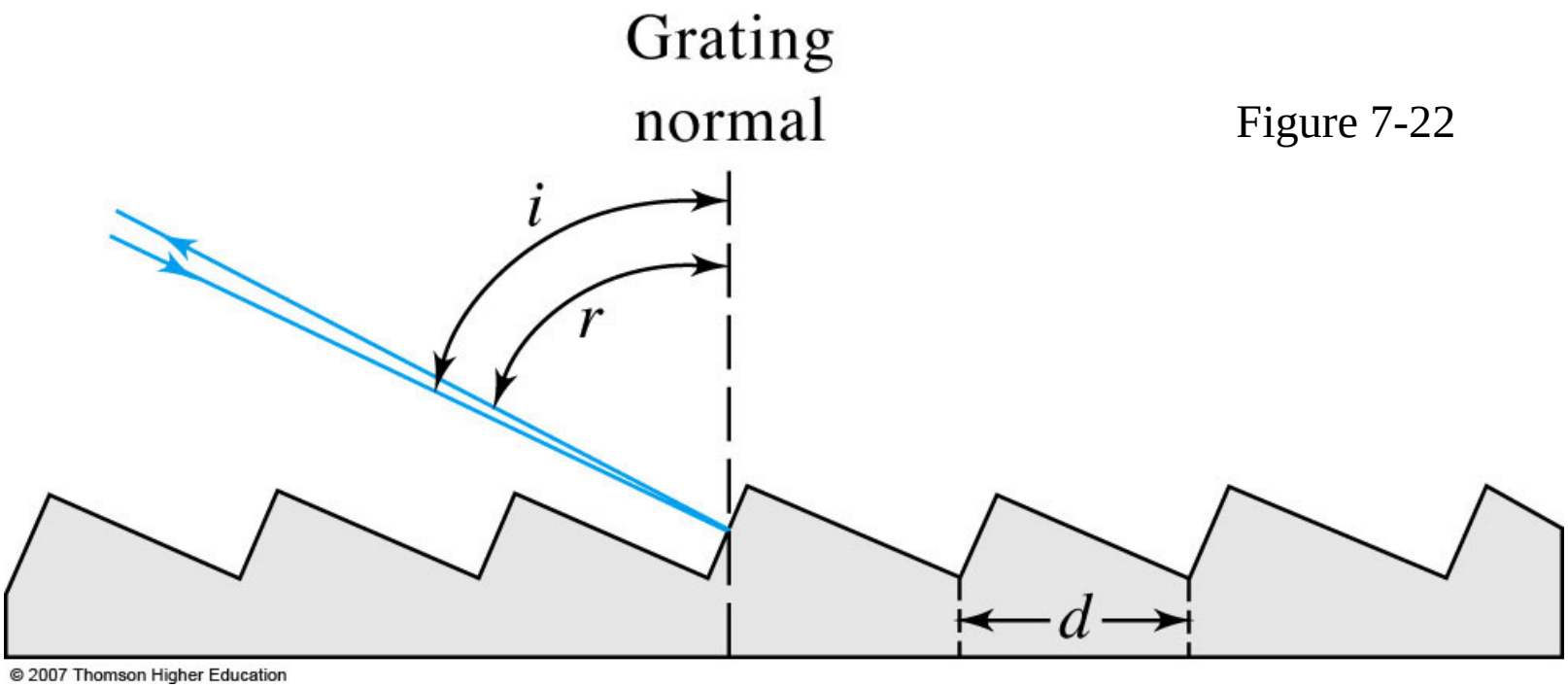

Figure 7-22

Grating spacing is coarse (d < 300 grooves/mm). Blaze angle is much larger than conventional grating and short side is used for reflection.

Echelle Grating Monochromator

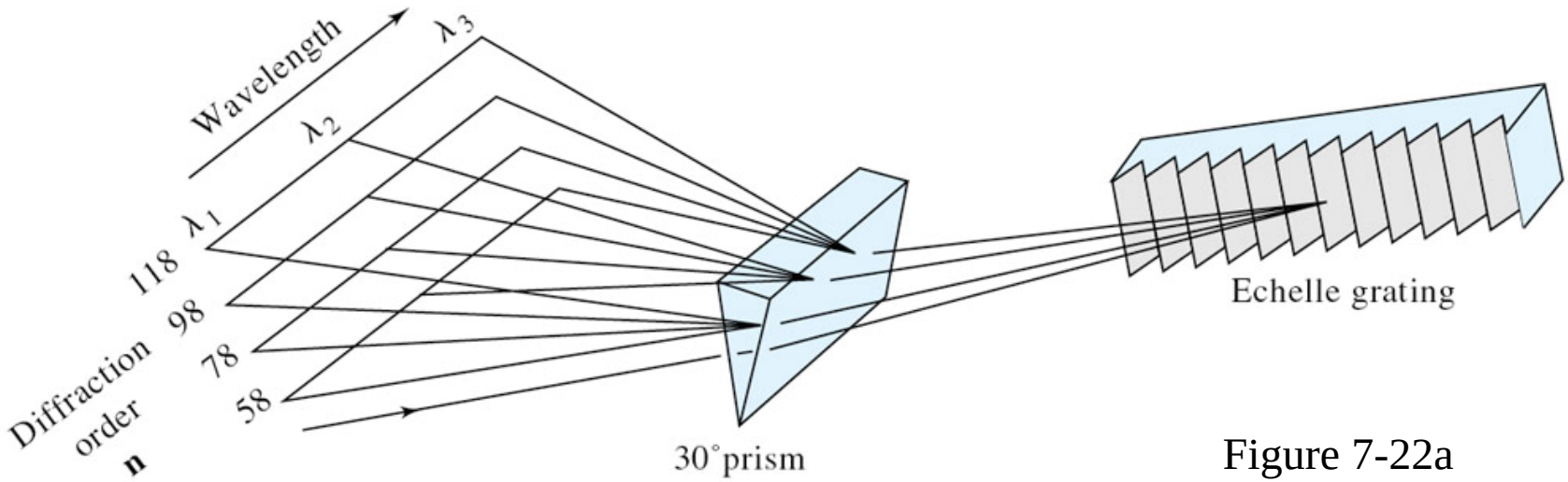

Figure 7-22a

Combination of echelle grating and prism disperses wavelengths in two dimensions. So multichannel detectors are common.

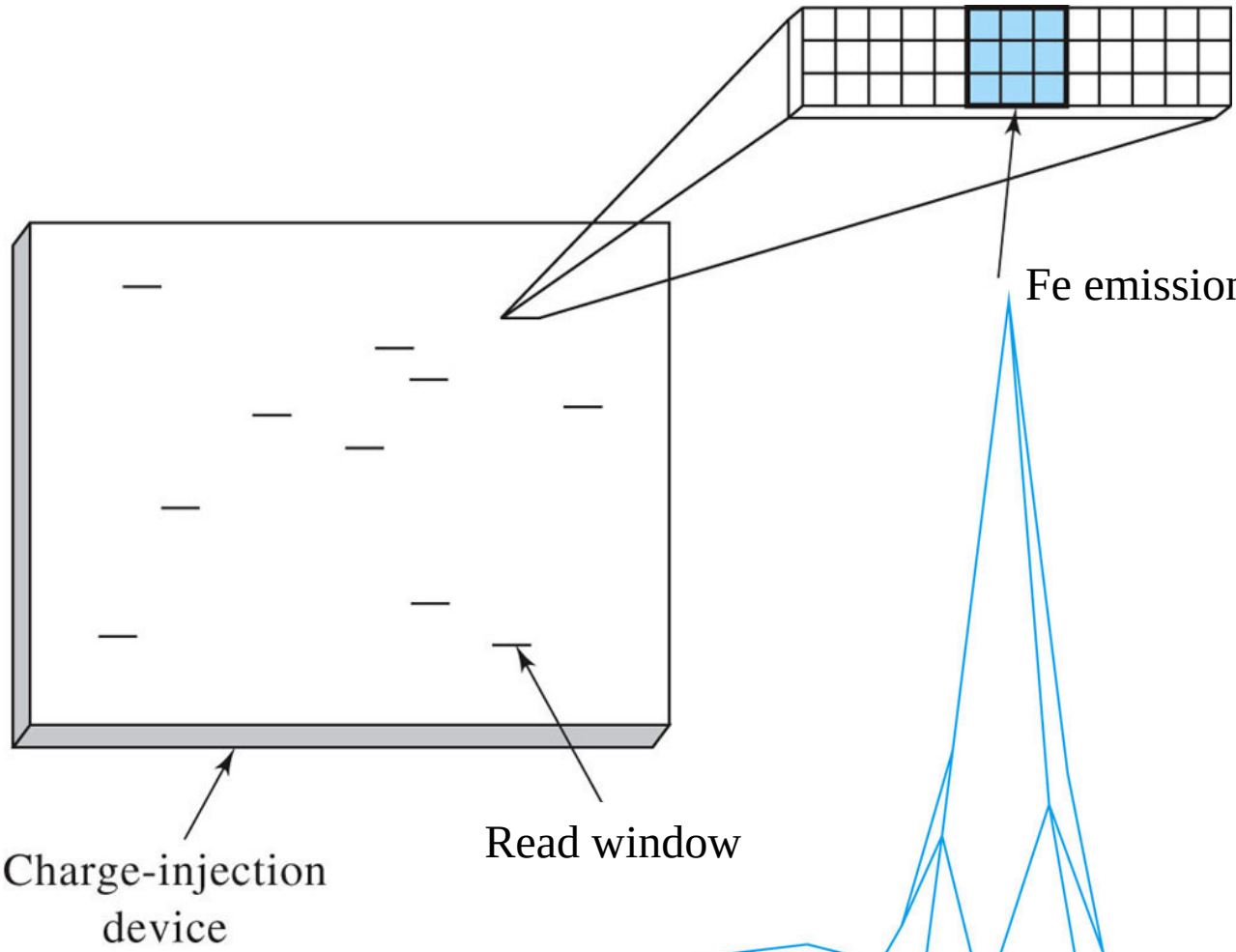

Figure 10-10

Mask is used to isolate emission lines for element of interest on CID or CCD detector.

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

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
ICP 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

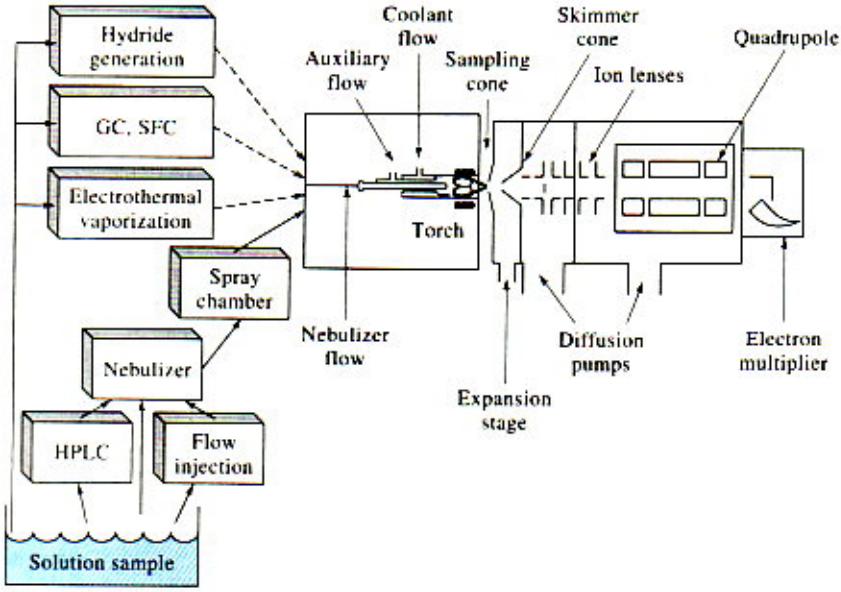

FIGURE 11-12 Schematic of an ICPMS system. Dotted lines show introduction of gaseous samples; solid lines show introduction of liquid samples. HPLC = high-performance liquid chromatography, SFC = supercritical fluid chromatography. (From N. P. Vela, L. K. Olson, and J. A. Caruso, *Anal. Chem.*, **1993**, *65*, 585A. Figure 1, p. 587A. Copyright 1993 American Chemical Society.)

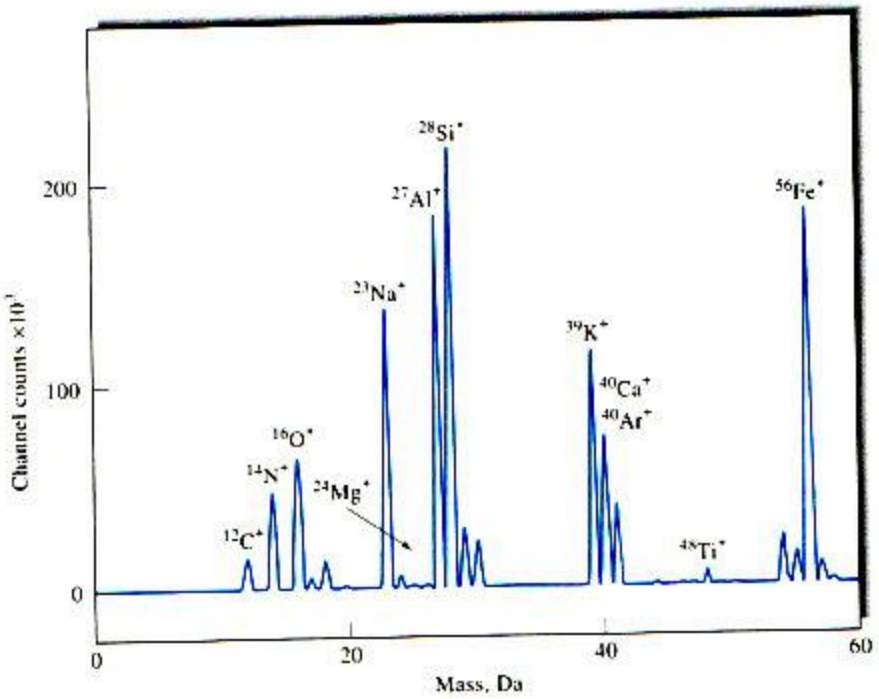

FIGURE 11-14 Spectrum of a standard rock sample obtained by laser ablation–ICPMS. Major components (%): Na, 5.2; Mg, 0.21; Al, 6.1; Si, 26.3; K, 5.3; Cu, 1.4; Ti, 0.18; Fe, 4.6. (From *Inorganic Mass Spectrometry*, F. Adams, R. Gijbek, and R. Van Grieken, eds., p. 297, New York: Wiley, 1988. With permission.)

Mass spectra are simpler and easier to interpret than emission spectra (100's-1000's lines). 90% of elements in table can be detected, measurement times of 10s per element, LODs are 0.1 to 10 ppb for many elements, and RSDs are 2-4%.