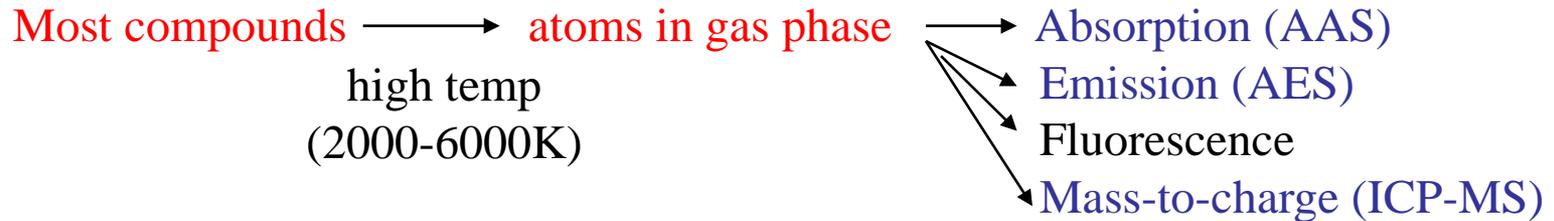


Atomic Spectrometry



Advantages of Atomic Spectroscopy:

- High sensitivity (LOD; usually ppm, sometimes ppt level)
- Multi-element analysis: AES, ICP-MS
- Good reproducibility (RSD = 1~2%)

Overview of Atomic Spectrometry

Bandwidth of radiation that is absorbed or emitted:

Molecular spectroscopy: ~100 nm

Atomic spectroscopy: ~0.01 nm

(very sharp line spectra → little overlap between the spectra of different elements
→ can measure multi-elements simultaneously; ~60 elements)

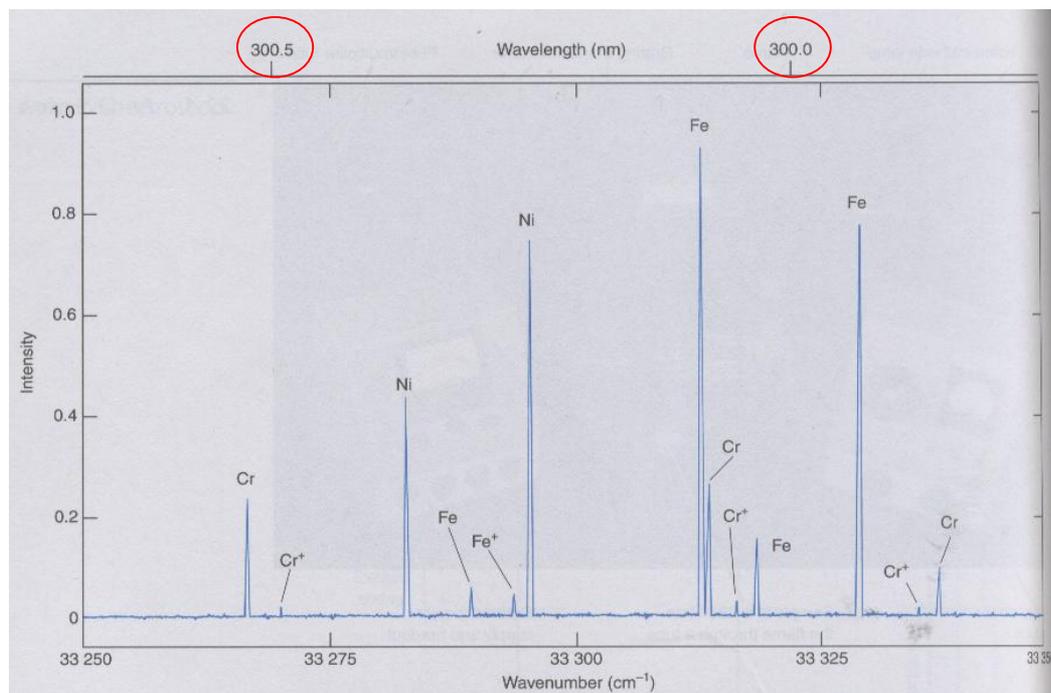


Figure 22-3 A tiny portion of the emission spectrum of a steel hollow-cathode lamp, showing sharp lines from gaseous Fe, Ni, and Cr atoms and weak lines from Cr⁺ and Fe⁺ ions. The resolution is 0.001 nm, which is comparable to the true linewidths. [From A. P. Thorne, *Anal. Chem.* **1991**, 63, 57A.]

Atomic Energy Level Diagram

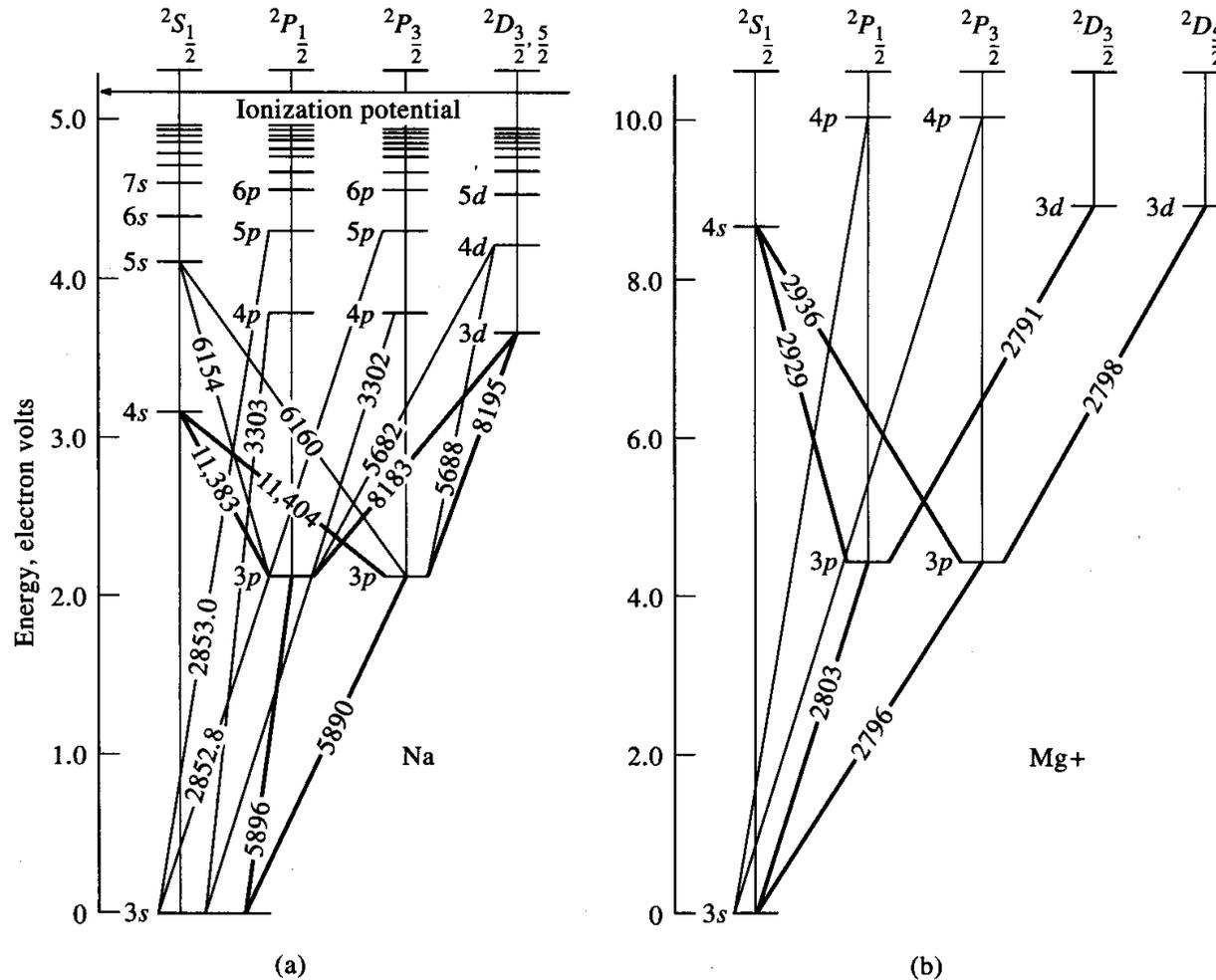


Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

Line Broadening in Atomic Spectra

In atomic spec, absorption and emission lines are very sharp

Three sources of line broadening:

- (1) Uncertainty effect: $\sim 10^{-4}$ nm
- (2) Doppler effect: $\sim 10^{-2}$ nm – 10^{-3} nm
- (3) Pressure effect (collision broadening): $\sim 10^{-2}$ – 10^{-3} nm

Uncertainty broadening (natural line width)

Heisenberg uncertainty principle:

the shorter the lifetime of the excited state,

→ the more uncertain in its energy relative to the ground state

$$\delta E \cdot \delta t \geq h/2\pi$$

δE ; the uncertainty in the energy difference between the ground and excited states

δt ; life time of the excited state before it decays to the ground state

h ; Planck's constant

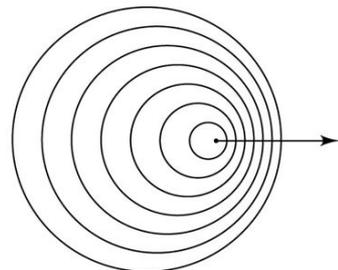
Line Broadening in Atomic Spectra

Doppler broadening

Atoms in hot flame: atomic motions in every direction → causes Doppler broadening

Doppler linewidth ; $\delta\lambda = \lambda (7 \times 10^{-7}) (T/M)^{1/2}$

T; temperature, M; atomic mass

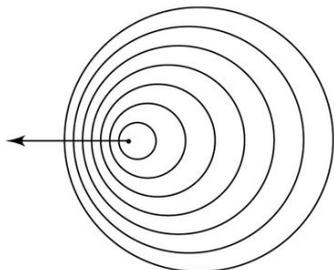


(a)



A rapidly moving atom in flames

If the motion is toward a photon detector,
→ the wavelength of radiation emitted or absorbed:
decreases (high frequency)



(b)



If the atom is receding from the photon detector,
→ the wavelength of radiation emitted or absorbed:
increase (low frequency)

Line Broadening in Atomic Spectra

Doppler broadening

For an emission near $\lambda = 300$ nm from Fe ($M = 56$) at 2500K

Doppler linewidth ; $\delta\lambda = \lambda (7 \times 10^{-7}) (T/M)^{1/2} = (300 \text{ nm}) (7 \times 10^{-7}) (2500\text{K}/56)^{1/2} = \underline{0.0014 \text{ nm}}$

An order of magnitude greater than the natural linewidth

Pressure broadening (Collisional broadening)

Collisions of the absorbing or emitting atoms with other atoms or ions in heating medium

- shorten the lifetime of the excited state
- or
- causes the change in the energy level of the ground and excited states.

- line broadening

High pressure → higher collisional frequency → greater line broadening

Effect of Temperature on Atomic Spectra

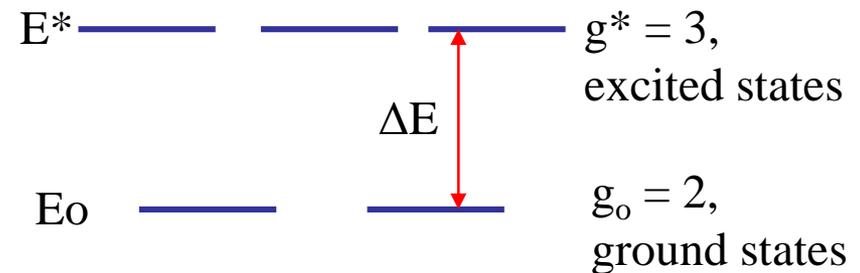
Temp is a critical factor in determining

- the degree to which a given sample breaks down to atoms (atomization efficiency)
- the extent to which a given atom is found in its ground state, excited state or ionized states

Boltzman Distribution

- describes the **relative populations of different states at thermal equilibrium**
- the relative population of any two states is

$$N^*/N_o = (g^*/g_o) \exp(-\Delta E/kT)$$



N^* : the number of atoms in an excited state

N_o : the number of atoms in the ground state

g : degeneracy (the number of states available at each energy level)

T ; temperature,

k ; Boltzman constant($1.31 \times 10^{-23} \text{J/K}$)

Effect of Temperature on Atomic Spectra

Sodium atom at 2600K (in acetylene-air flame)

$$N^*/N_o = (g^*/g_o) \exp(-\Delta E/kT)$$

$$\Delta E = 3.371 \times 10^{-19} \text{J/atom}$$

$$g_o = 1, g^* = 2$$

$$\text{Thus, } N^*/N_o = (2/1) \exp[(-3.371 \times 10^{-19}) / (1.381 \times 10^{-23} \text{J/K})(2600\text{K})] = 1.67 \times 10^{-4}$$

0.0167% of the atoms are in the excited state (99.9833% in ground state)

If the temperature is 2610K (from 2600K)

$$N^*/N_o = (2/1) \exp[(-3.371 \times 10^{-19}) / (1.381 \times 10^{-23} \text{J/K})(2610\text{K})] = 1.74 \times 10^{-4}$$

0.0174% of the atoms are in the excited state (99.9826% in ground state)

$[(1.74 - 1.67) \times 100\%] / 1.67 = 4\%$ increase in the population of the excited state

$[(99.9833 - 99.9826) \times 100\%] / 99.9833 = 0.07\%$ decrease in the population of the ground state

Effect of Temperature on Atomic Absorption and Emission

Sodium atom at 2600K

0.0167% of the atoms are in the excited state (99.9833% in ground state)

If the temperature is 2610K (from 2600K)

0.0174% of the atoms are in the excited state (99.9826% in ground state)

10-K rise in temperature:

Almost no change (0.07% decrease) in the ground-state population:

→ No noticeable change in an atomic absorption

4% increase in the excited-state population:

→ Emission intensity rise by 4%

In atomic emission spectroscopy, the flame temperature should be kept very stable

(ICP: high temp → high sensitivity, stable plasma temp → reproducible data)

Atomization Methods

Atomizer :converts a sample to an atomic vapor

Atomization: Flames (AAS, AES; liquid sample)

Furnaces (AAS, AES; solid sample)

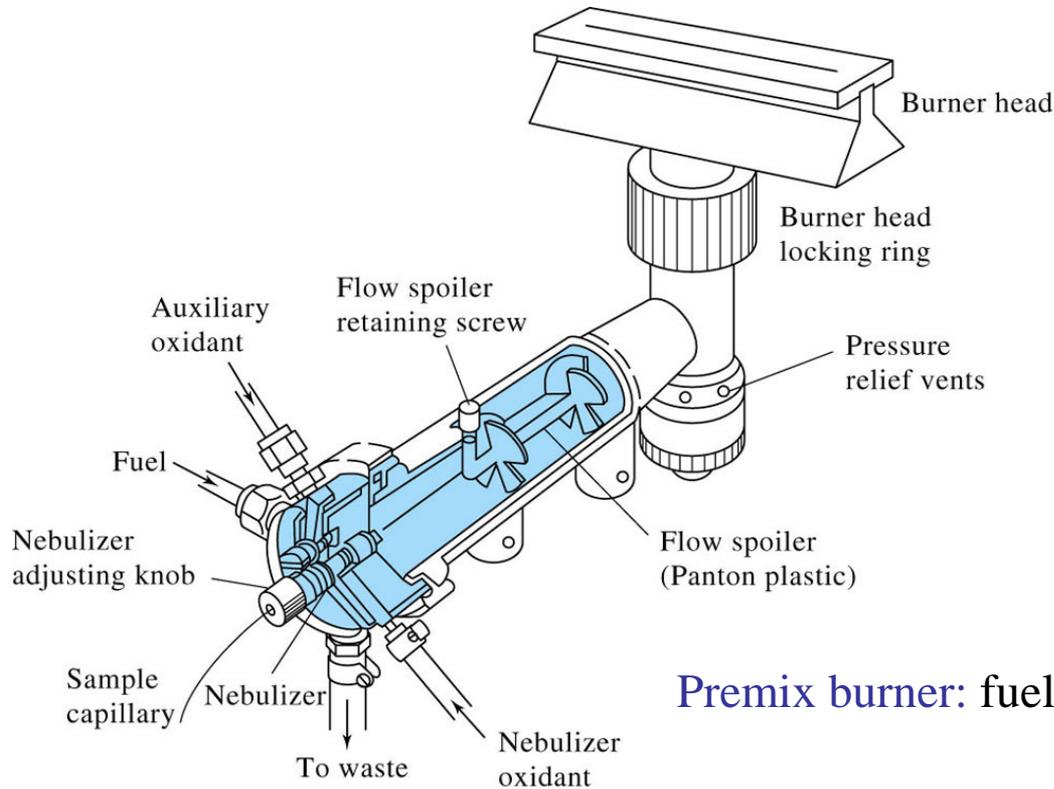
Plasma (AES, ICP-MS; liquid sample)

The precision and accuracy of AS: are critically dependent upon:
atomization step & sample introduction method

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 (?)

Atomization Methods



Premix burner: fuel, oxidant, and sample are premixed.

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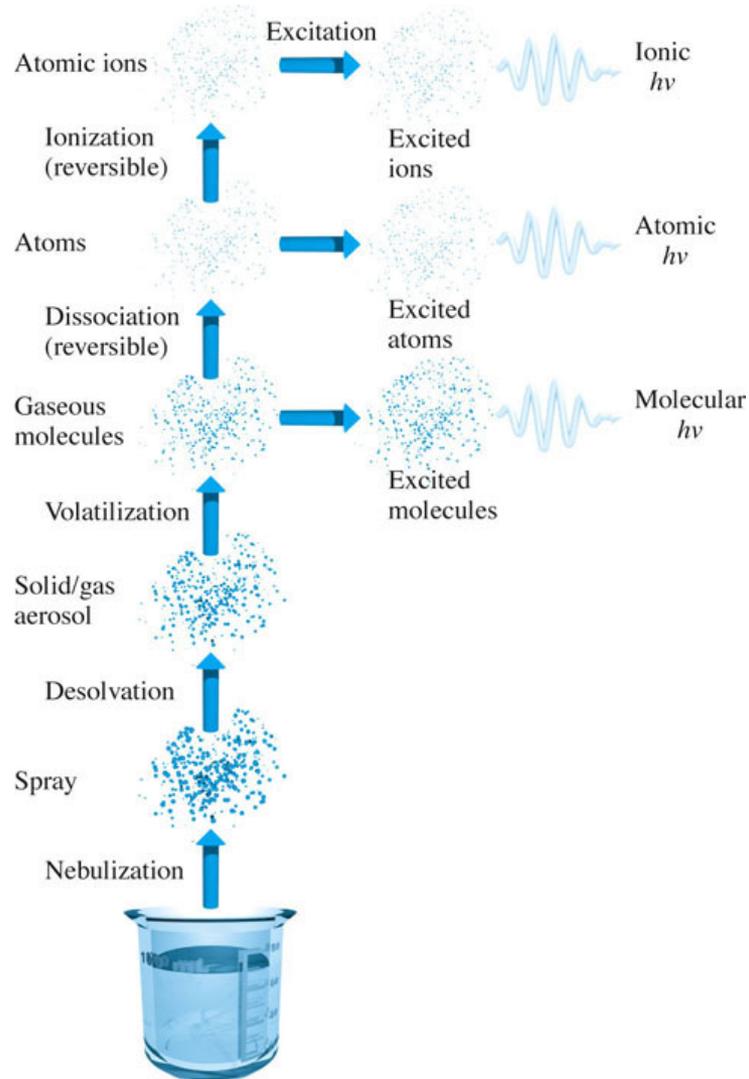
Nebulization: formation of a small droplets

Aerosol: a fine suspension of liquid (solid) particles in a gas

Nebulizer: create an aerosol from the liquid sample

“aerosol reaching the flame contains only about 5% of initial sample”

Atomization Methods



Analyte solution

Electrothermal Vaporizer (for liquid & solid)

Graphite Furnace

- An electrically heated **graphite furnace**
- offers greater sensitivity than that provided by flames
 - requires less sample (1-100 μL for furnace, 1-2 mL for flames)

- Sample introduction and atomization occur simultaneously

- Relative precision is worse:
5-10% RSD
(flame: 1%)

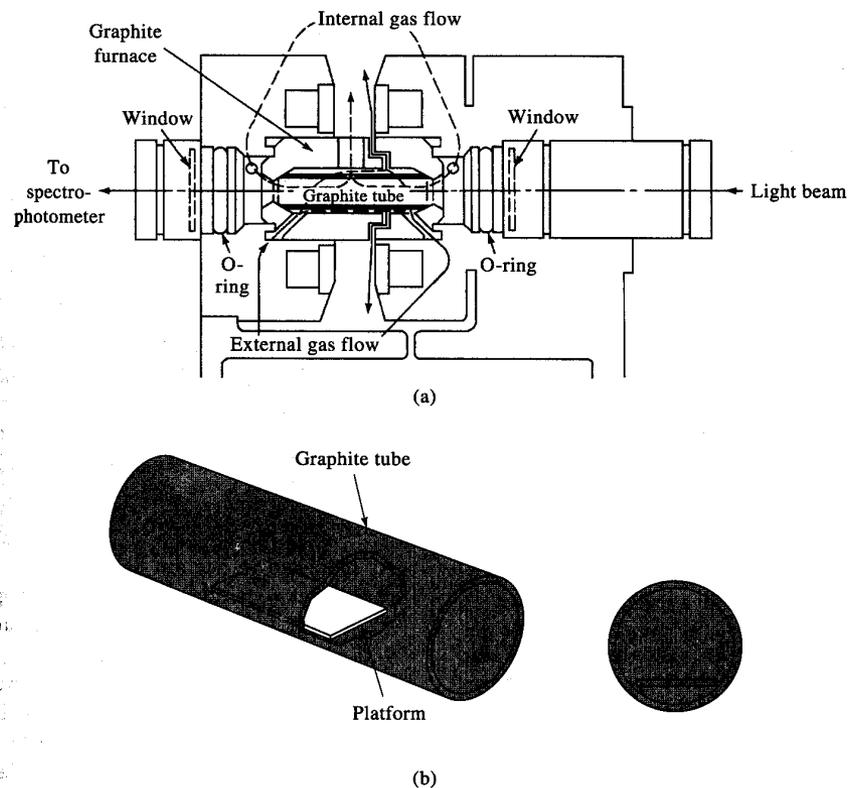


Figure 9-6 (a) Cross-sectional view of a graphite furnace. (Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.) (b) The L'vov platform and its position in the graphite furnace. (Reprinted with permission from W. Slavin, Anal. Chem., 1982, 54, 689A. Copyright 1982 American Chemical Society.)

Atomic Absorption Spectrometry

Two most common sample atomization method: flame and electrothermal ato
Light source: hollow cathode lamp

Flame Atomization

TABLE 9-1 Properties of Flames

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

- **Air oxidant: 1700 – 2400 °C, only for easily decomposed samples**
- **O₂, nitrous oxide: 2500 – 3100 °C, only for more refractory samples**
- **The sample, fuel, and oxidant flow rates and height should be optimized for ea**

Hollow Cathode Lamp in AAS

Monochromators cannot isolate lines narrower than $10^{-3} - 10^{-2}$ nm.

→ To get narrow lines of the correct frequency,

→ Use of **hollow cathode lamp** containing **the same element that being analyzed**

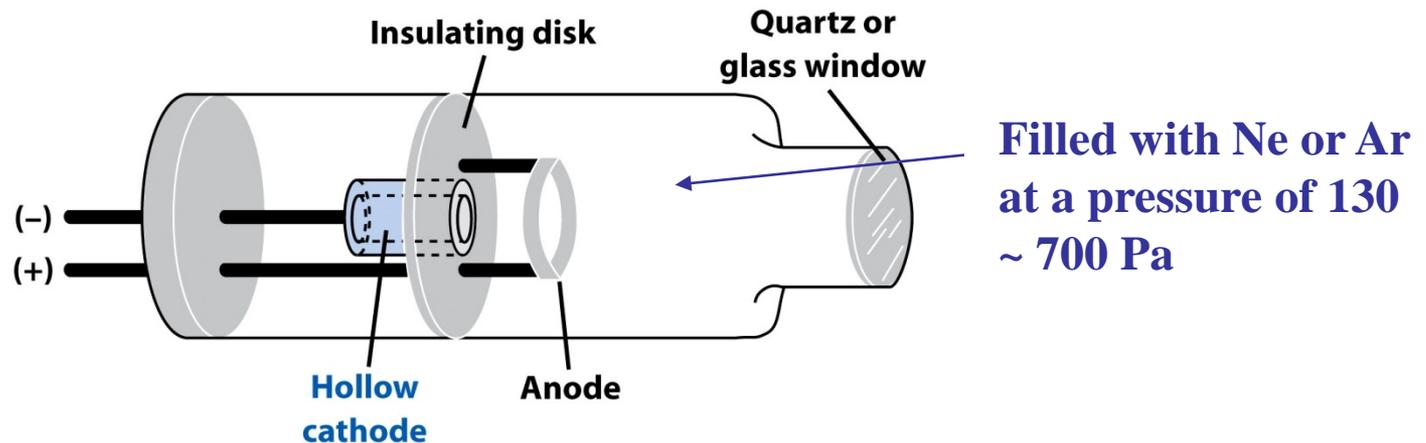


Figure 21-16
Quantitative Chemical Analysis, Seventh Edition
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High voltage ($\sim 300\text{V}$) is applied between the anode and cathode

→ Filler gas is ionized and positive ions are accelerated toward the cathode

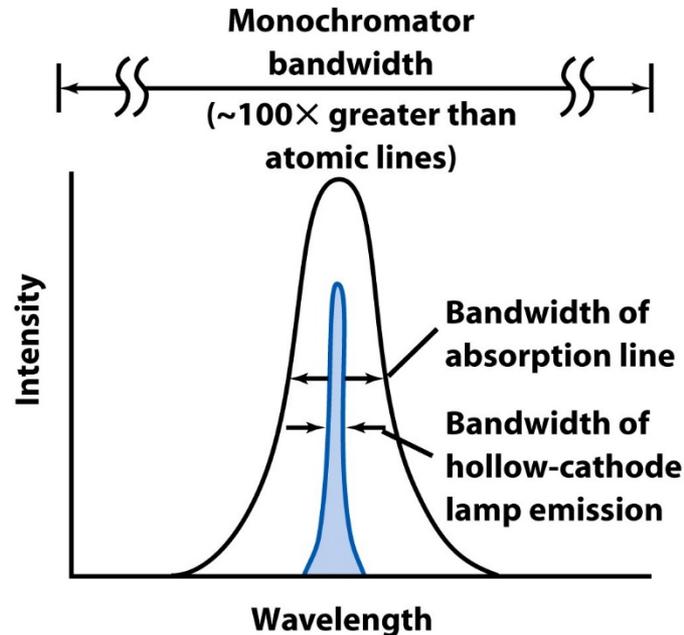
→ Accelerated positive ions strike the cathode with enough energy to **sputter** metal atoms from the cathode into the gas phase

→ Free atoms are excited by collisions with high-energy electrons: photon emission

Atomic radiation has the same frequency as that absorbed by the analyte atoms

Hollow Cathode Lamp in AAS

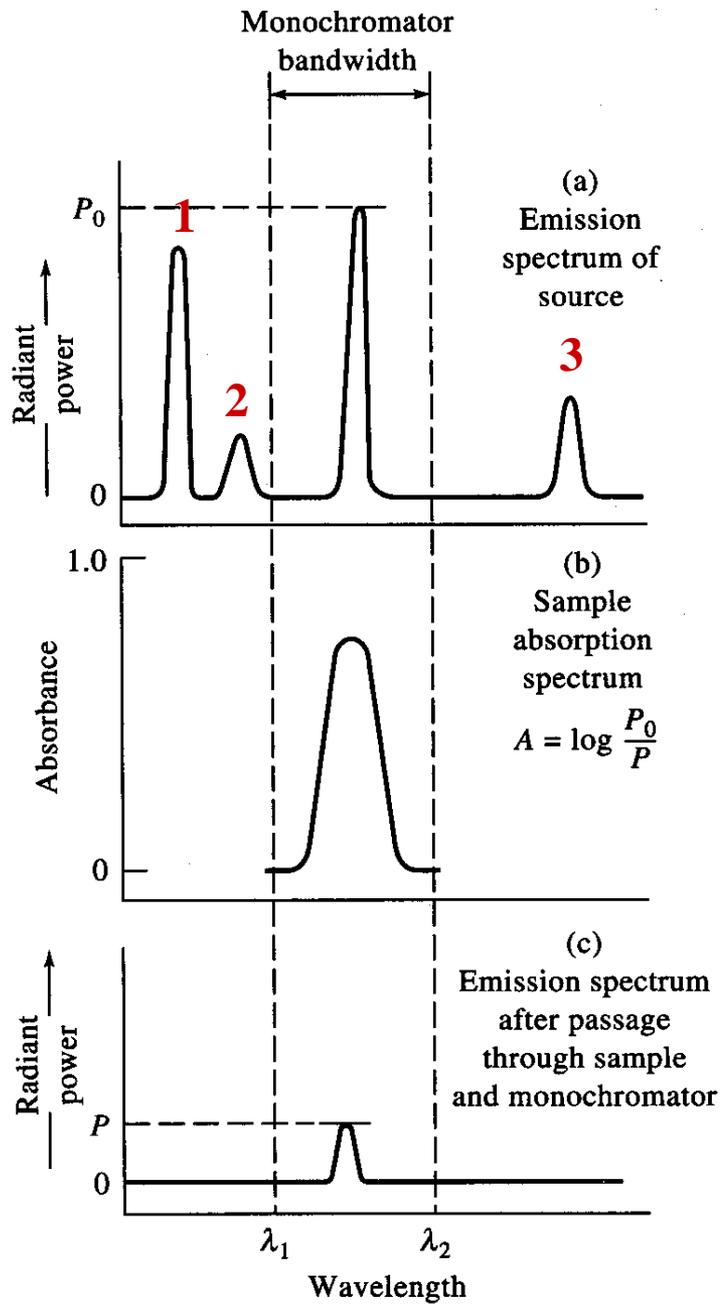
- The linewidth in hollow cathode lamp is sufficiently narrow



Atoms in lamp are cooler than atoms in a flame → lamp emission is narrower than the absorption bandwidth in the flame

Figure 21-17
Quantitative Chemical Analysis, Seventh Edition
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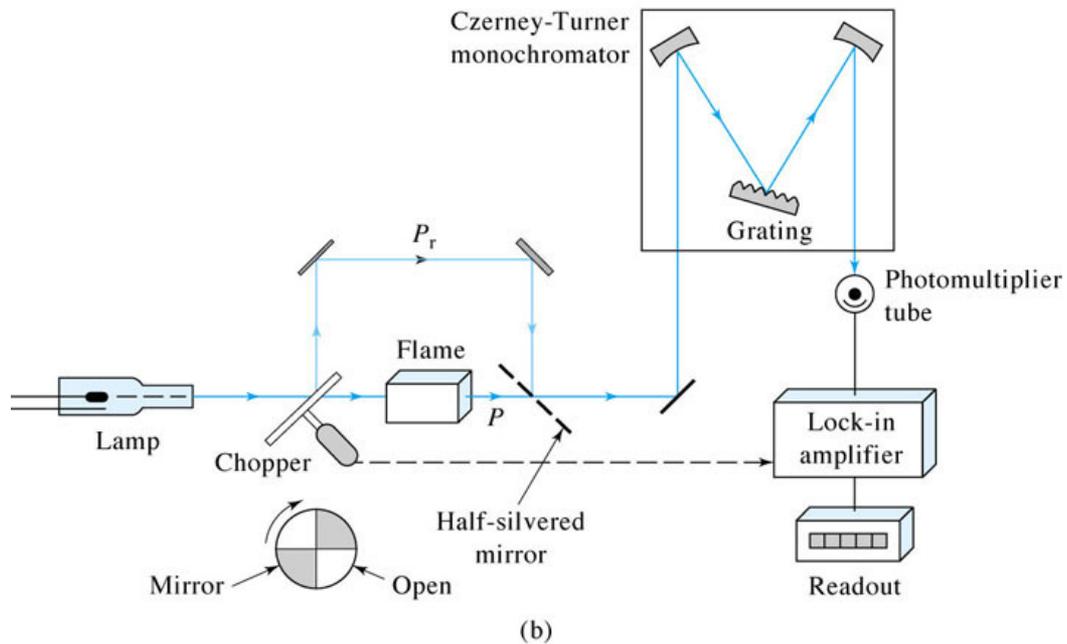
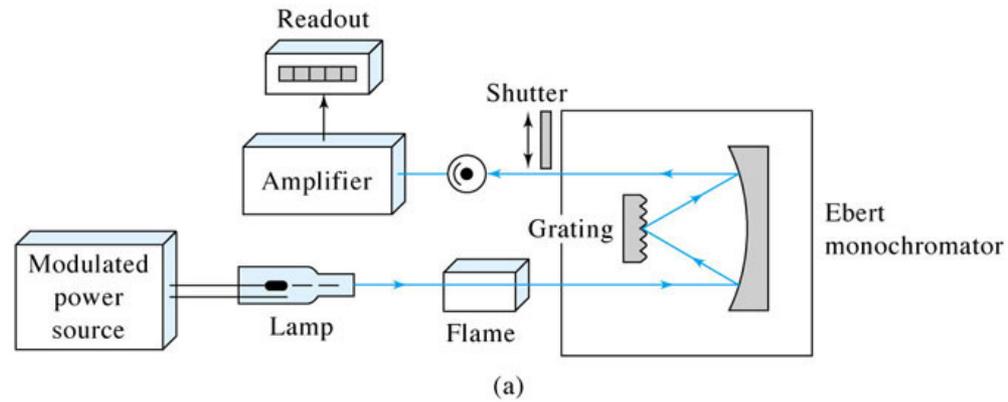
- A different lamp is required for each element
- Some lamps are made with more than one element in the cathode
- The purpose of a monochromator in atomic spectroscopy:
 - 1) to select one line from hollow cathode lamp (usually filter)
 - 2) to reject as much emission from the flame or furnace as possible



1,2,3:
 removed by filter or
 monochromator

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

Flame Spectrophotometers in AAS



Atomic Emission Spectrometry

Inductively Coupled Plasma

- Exclusively for emission (not absorption) or mass spec.
- 6000-10000K in ICP
- (higher and more stable temp than flame)

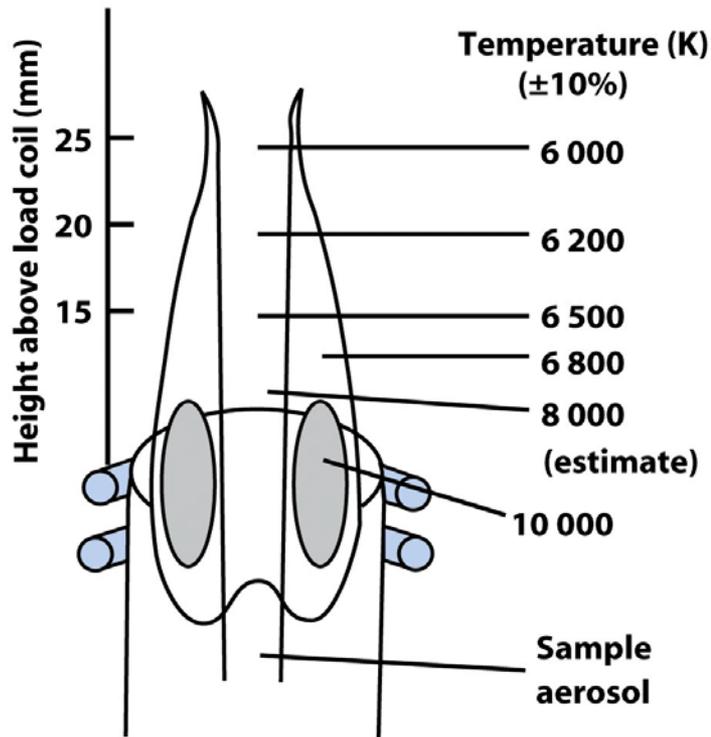


Figure 21-11
Quantitative Chemical Analysis, Seventh Edition
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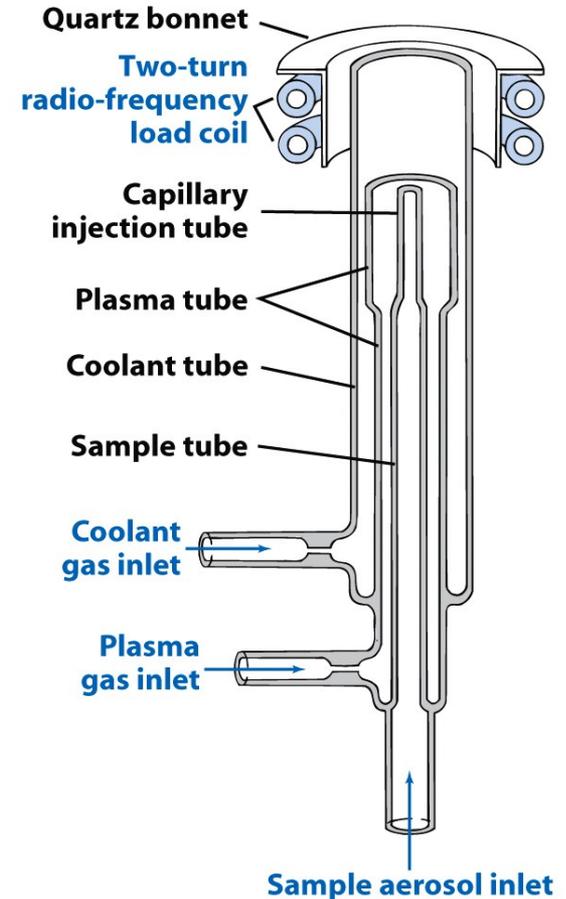
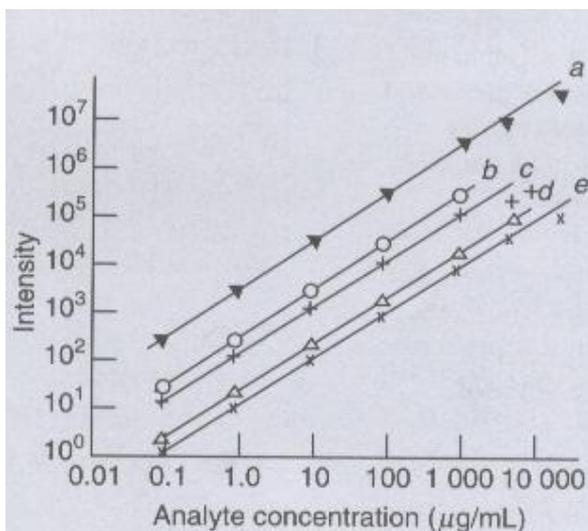


Figure 21-12
Quantitative Chemical Analysis, Seventh Edition
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- Tesla coil ionize Ar gas \rightarrow Free electron is accelerated and oscillated in rf induction coil
- Accelerated free electrons collide with Ar atom and transfer energy \rightarrow Joule Heating

Virtues of ICP in AES

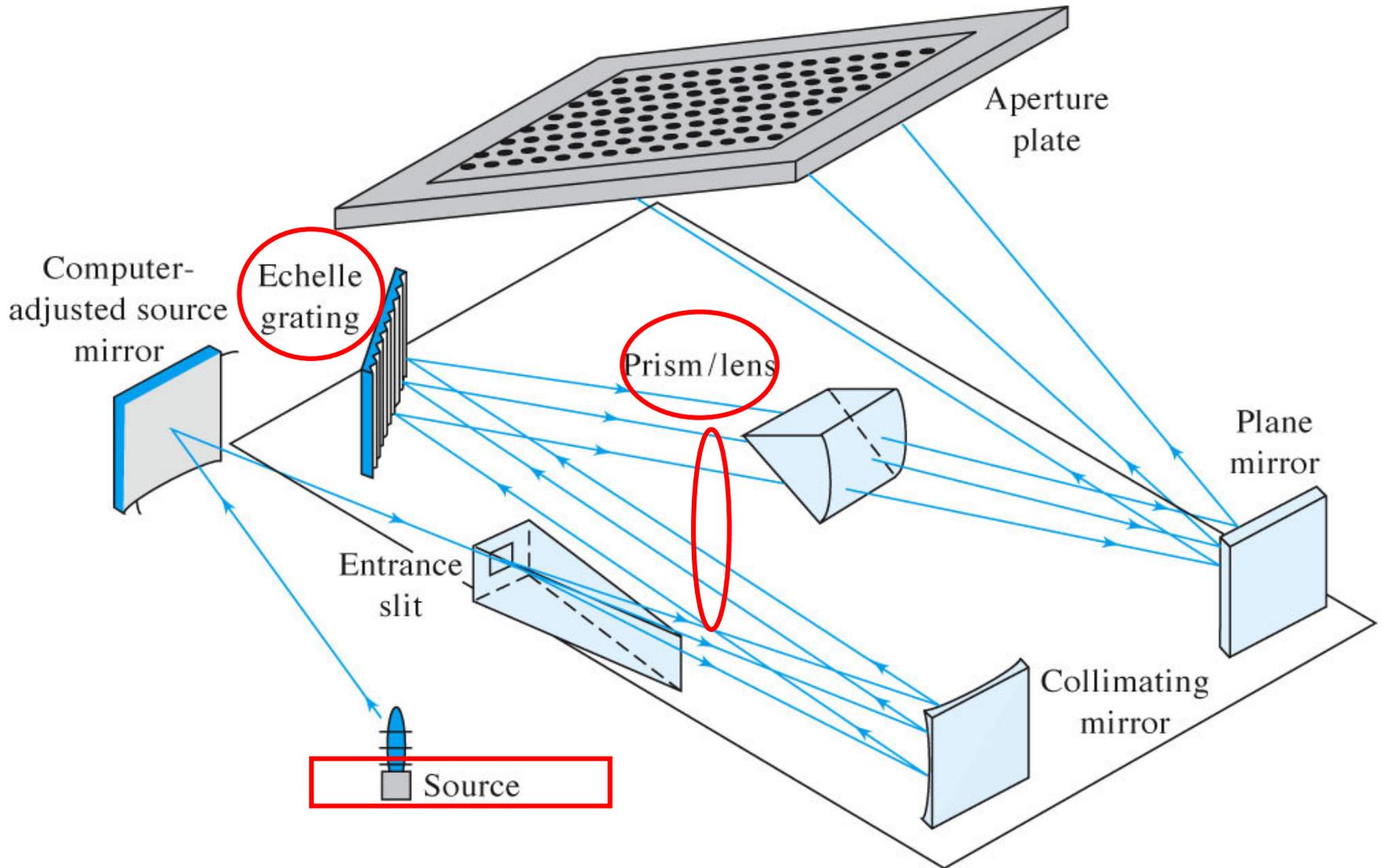
1. ICP is twice as hot as a conventional flame
2. The residence time of analyte in the plasma is twice as long
 - Atomization is more complete
 - Signal is enhanced
 - Formation of oxides and hydroxides are negligible
3. ICP is free of background radiation
4. The temperature in ICP is more uniform → almost no self-absorption



Linear dynamic range, ICP: 5 orders
Flames and Furnaces: 2 orders

Figure 22-25 Analytical calibration curves for emission from (a) Ba⁺, (b) Cu, (c) Na, (d) Fe, and (e) Ba in an inductively coupled plasma. Note that both axes are logarithmic. [From R. N. Savage and G. M. Hieftje, *Anal. Chem.* **1979**, *51*, 408.]

Echelle Monochromator in AES



Echelle Monochromator

Two dispersion elements
arranged **in series**
: higher dispersion and
resolution
than an echellette of the same
size

Used in
atomic emission spectroscopy

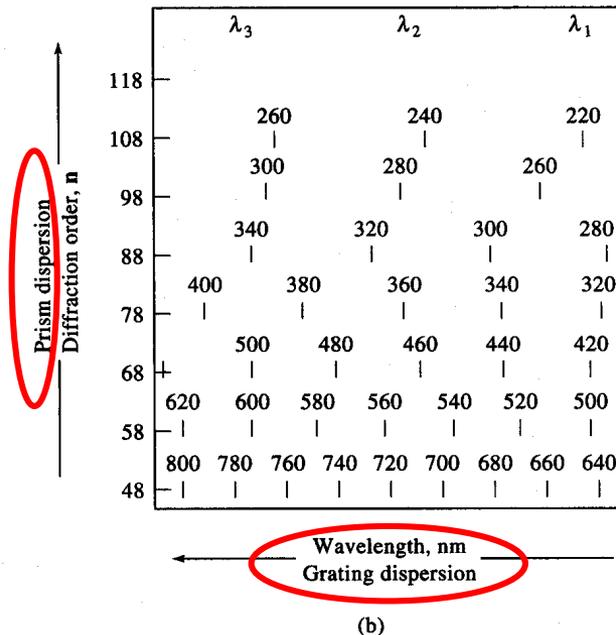
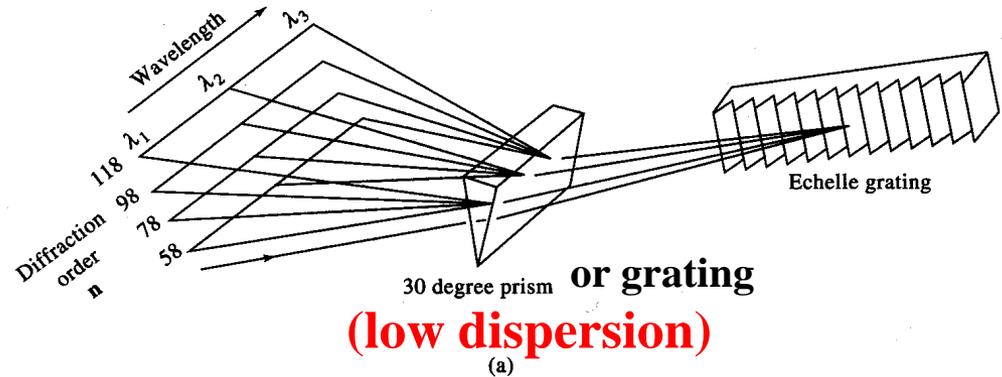


Figure 7-21 An echelle monochromator: (a) arrangement of dispersing elements, and (b) schematic end-on view of the dispersed radiation from the point of view of the transducer.

ICP-AES

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

Atomic Mass Spectrometry

Advantages of atomic mass spectrometry over atomic optical spectrometry

- (1) Good detection limit: 3 orders of magnitude better**
- (2) Simple spectra; unique and easily interpretable**
- (3) The ability to measure atomic isotope ratio**

Disadvantages

- (1) High instrument costs: 2-3 times**
- (2) Certain types of interference effects**

Atomic Mass Spectrometry

TABLE 11-1 Types of Atomic Mass Spectrometry

Name	Acronym	Atomic Ion Sources	Typical Mass Analyzer
Inductively coupled plasma	ICPMS	High-temperature argon plasma	Quadrupole
Direct current plasma	DCPMS	High-temperature argon plasma	Quadrupole
Microwave-induced plasma	MIPMS	High-temperature argon plasma	Quadrupole
Spark source	SSMS	Radio-frequency electric spark	Double-focusing
Thermal ionization	TIMS	Electrically heated plasma	Double-focusing
Glow discharge	GDMS	Glow-discharge plasma	Double-focusing
Laser microprobe	LMMS	Focused laser beam	Time-of-flight
Secondary ion	SIMS	Accelerated ion bombardment	Double-focusing

Components of Atomic Mass Spectrometer

- (1) Atomization
- (2) Ionization

ICP

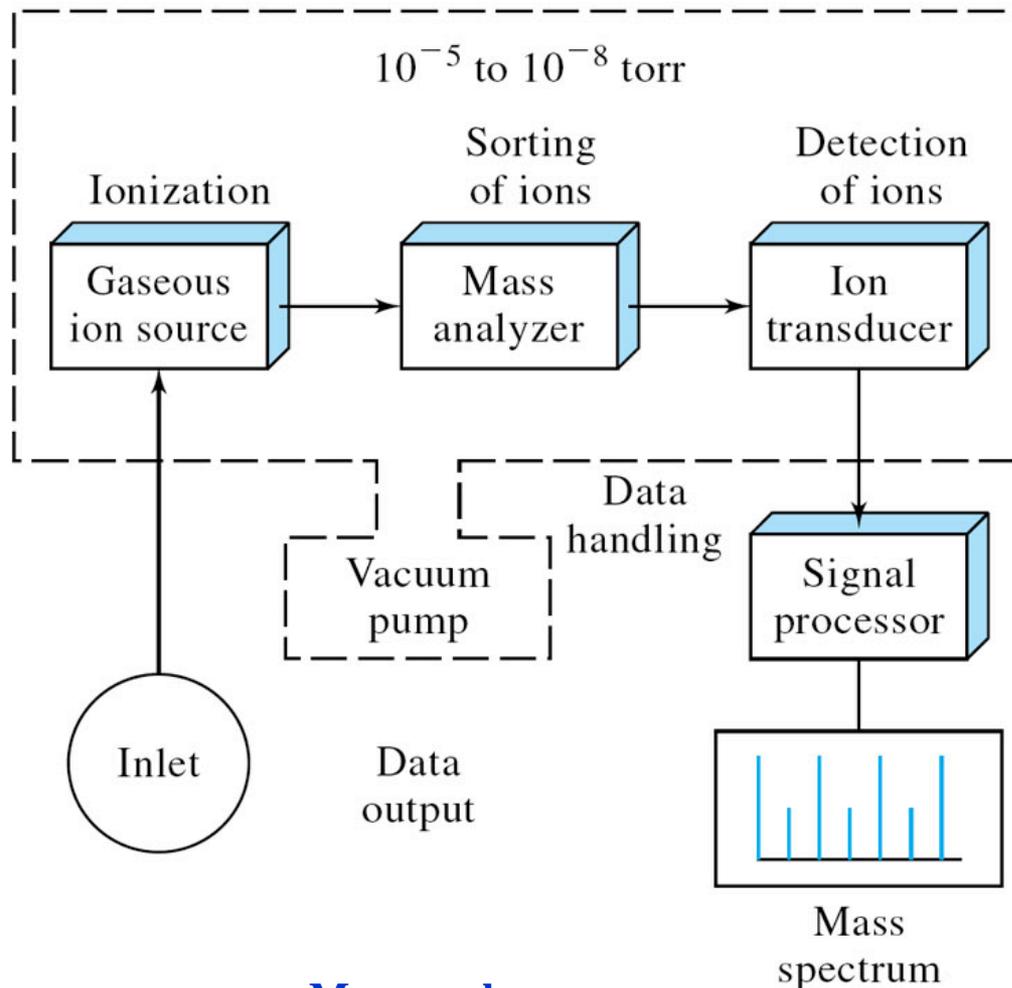
Same technique as in atomic optical spectrometry

Reason for Vacuum in MS

10^{-6} to mid 10^{-5} Torr

: ions to reach detector without colliding with other gaseous molecules

(Such collision: reduce the resolution and sensitivity of the instrument (fragmentation))



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Mass analyzer:
Separation are based on m/z ($z = 1$ for most ions, $m/z = z$)

Transducer for Mass Spectrometry

Electron Multiplier

- Rugged
- reliable
- high current gains
- nanosecond response time

Discrete-dynode e.m. (similar to PMT)

: 20 dynodes ($G = 10^7$)

Continuous-dynode e.m.

- A potential of 1.8 ~ 2KV is applied across the length of the transducer
- Gain: 10^5 - 10^8

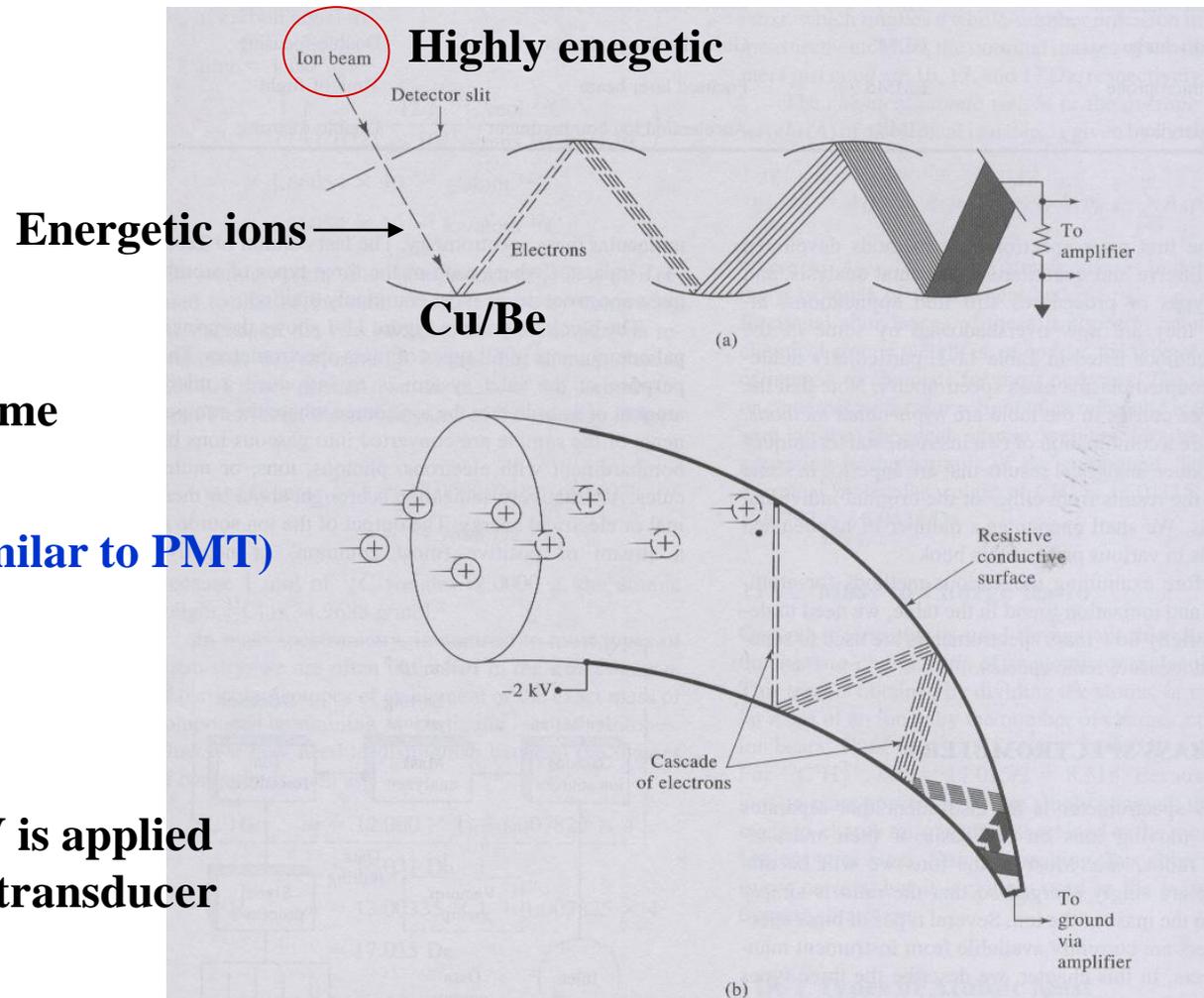


Figure 11-2 (a) Discrete dynode electron multiplier. Dynodes are kept at successively higher potentials via a multistage voltage divider. (b) Continuous dynode electron multiplier. (Adapted from J. T. Watson, Introduction to Mass Spectrometry, p. 247. New York: Raven Press, 1985. With permission.)

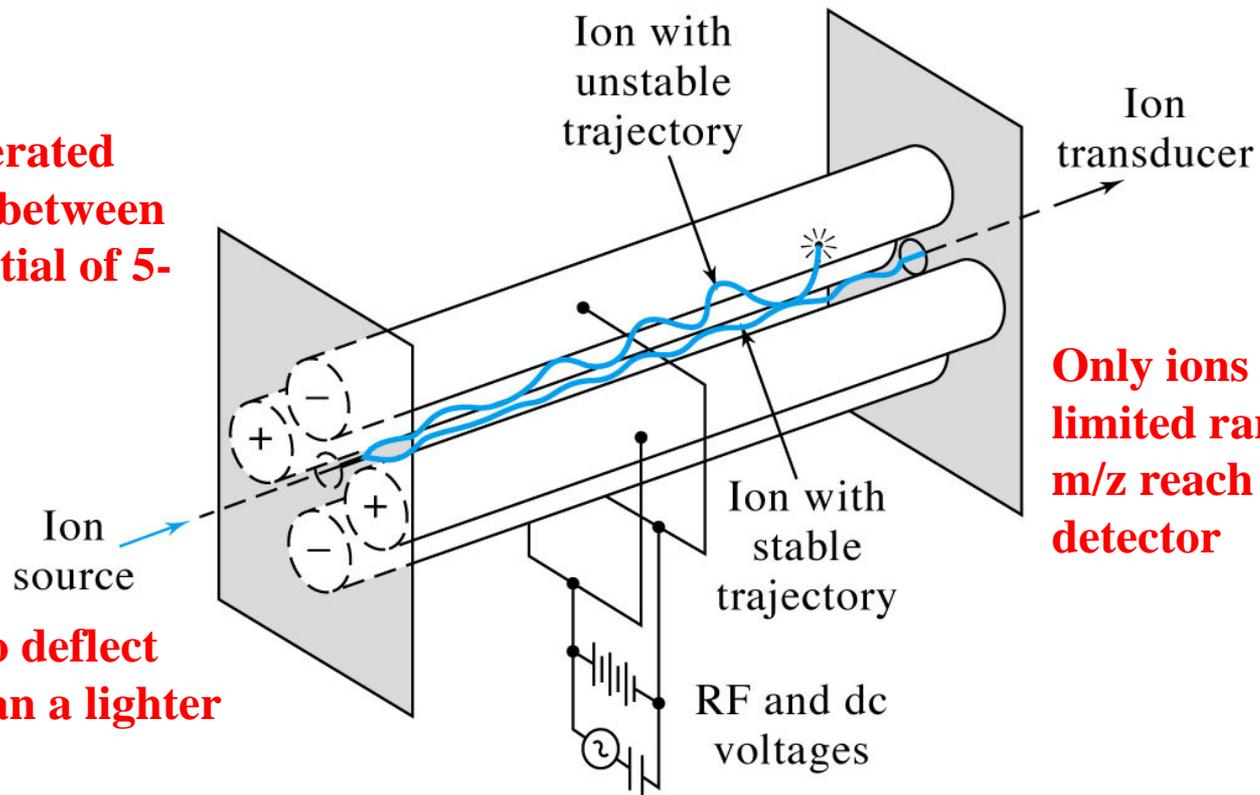
Mass Analyzer for Mass Spectrometry

Quadrupole Mass

- More compact, more rugged, less expensive than magnetic sector mass spec
- high scan rate (less than 100 ms)

Ions are accelerated into the space between rod by a potential of 5-10 V

It is difficult to deflect heavier ion than a lighter ion



Only ions having a limited range of m/z reach the detector

ICP-Mass Spectrometer

- Most important techniques for elemental analysis
- Mass range: 3-300
- Ability to resolve ions differing in m/z by 1
- 90% elements in periodic table can be determined
- Detection limits; 0.1 – 10 ppb
- RSD: 2 ~ 4%
- Dynamic range: 6 orders
- Fast analysis: 10 s for 1 elements

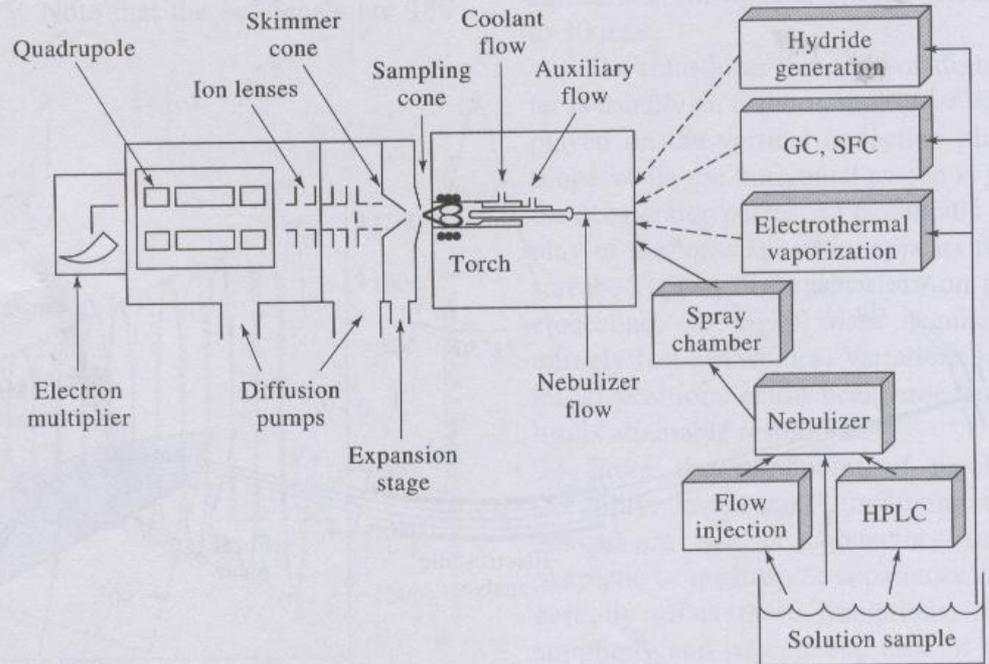


Figure 11-10 Schematic of an ICPMS system. Dotted lines show introduction of gaseous samples; solid lines shown introduction of liquid samples. (From N. P. Vela, L. K. Olson, and J. A. Caruso, *Anal. Chem.*, 1993, 65, 587A. With permission.)

ICP-Mass Spectrometer

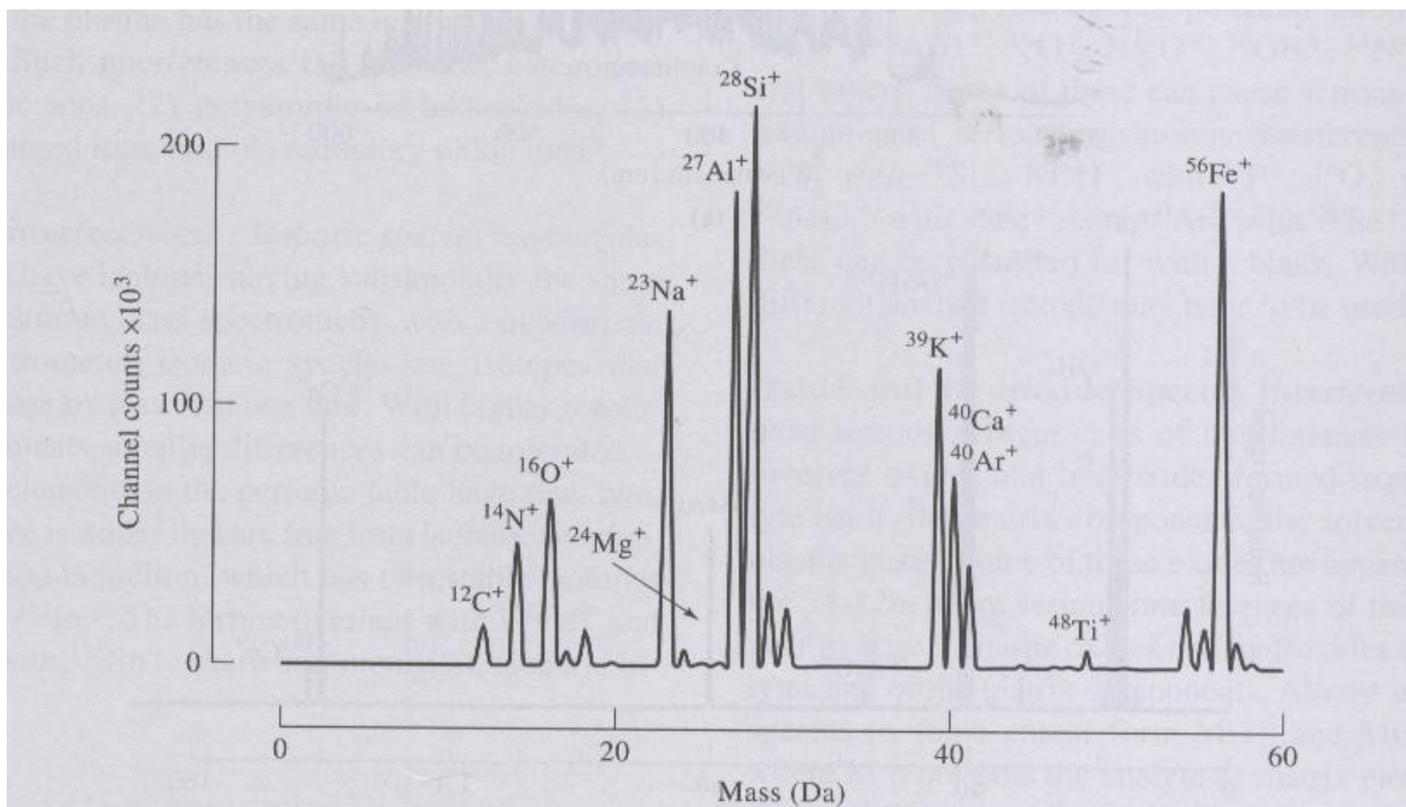
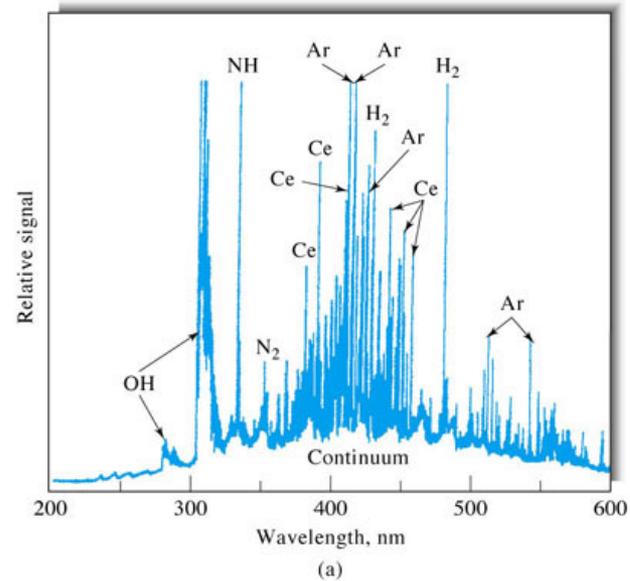


Figure 11-11 Spectrum of a standard rock sample obtained by laser ablation/ICPMS. Major components (%): Na, 5.2; Mg, 0.21; Al, 6.1; Si, 26.3; K, 5.3; Cu, 1.4; Ti, 0.18; Fe, 4.6. (From *Inorganic Mass Spectrometry*, F. Adams, R. Gijbek, and R. Van Grieken, Eds., p. 297. New York: Wiley, 1988. With permission.)

ICP-Mass Spectrometer

ICP-Emission
: complex spectra



ICP-Mass
: simple spectra

