

Atomic Absorption Spectrometry (Chapter 9)

- AAS intrinsically **more sensitive** than AES
- **similar atomization techniques** to AES
- addition of **radiation source**
- high temperature for **atomization necessary**
flame and electrothermal atomization
- very high temperature for **excitation not necessary**
generally no plasma/arc/spark AAS

Flame AAS:

- **simplest** atomization of gas/solution/solid
- laminar flow burner - **stable** "sheet" of flame
- flame atomization best for **reproducibility** (precision) (<1%)
- relatively **insensitive** - incomplete volatilization, short time in beam

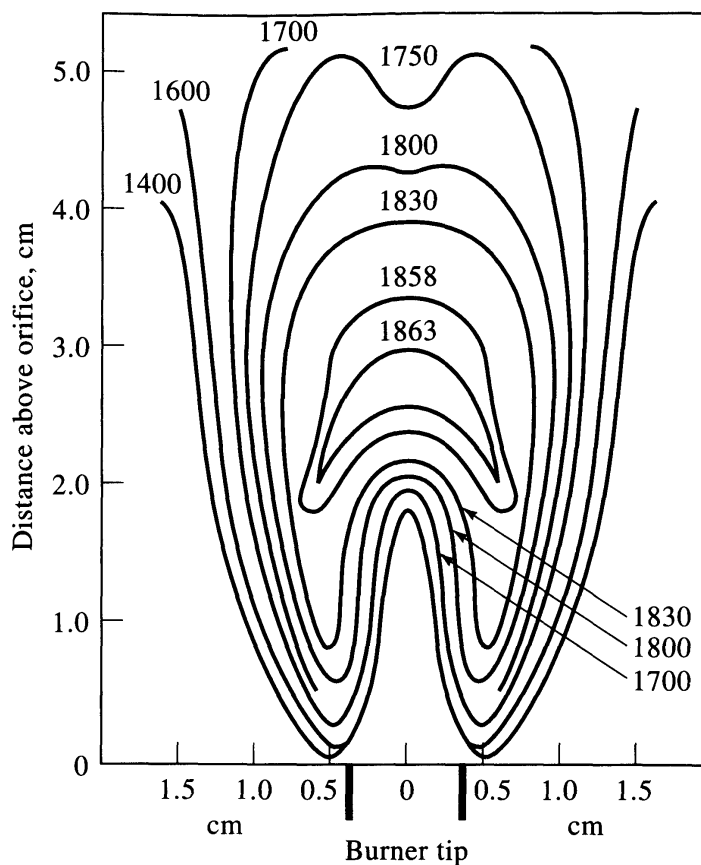


Fig 9-3

Primary combustion zone - initial decomposition, molecular fragments, cool

Interzonal region - hottest, most atomic fragments, used for emission/fluorescence

Secondary combustion zone - cooler, conversion of atoms to stable molecules, oxides

- element rapidly oxidizes - largest [atom] near burner
- element poorly oxidizes - largest [atom] away from burner

most sensitive part of flame for AAS varies with analyte

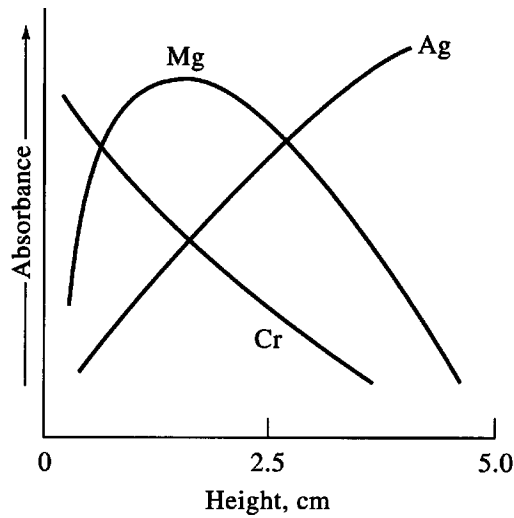


Fig 9-4

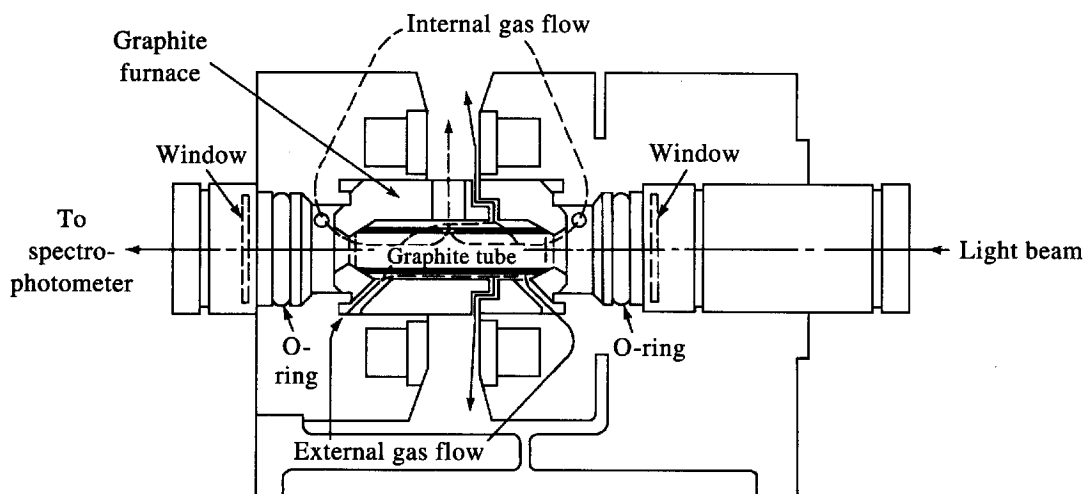
Consequences?

- sensitivity varies with element
- must maximize burner position
- makes multielement detection difficult

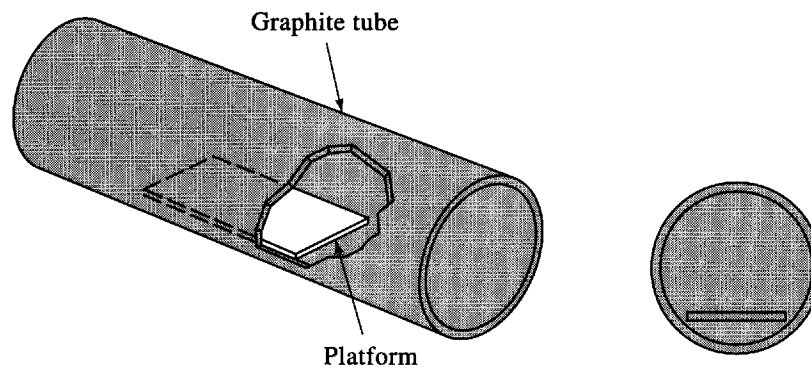
Electrothermal Atomizers:

- entire sample **atomized short time** (2000-3000 °C)
- sample spends up to **1 s in analysis volume**
- superior **sensitivity** (10^{-10} - 10^{-13} g analyte)
- **less reproducible** (5-10 %)

Graphite furnace ETA (Fig 9-6)



(a)



(b)

- **external** Ar gas prevents tube destruction
- **internal** Ar gas circulates gaseous analyte

Three step sample preparation for graphite furnace:

- (1) **Dry** - evaporation of solvents (10->100 s)
- (2) **Ash** - removal of volatile hydroxides, sulfates, carbonates (10-100 s)
- (3) **Fire/Atomize** - atomization of remaining analyte (1 s)

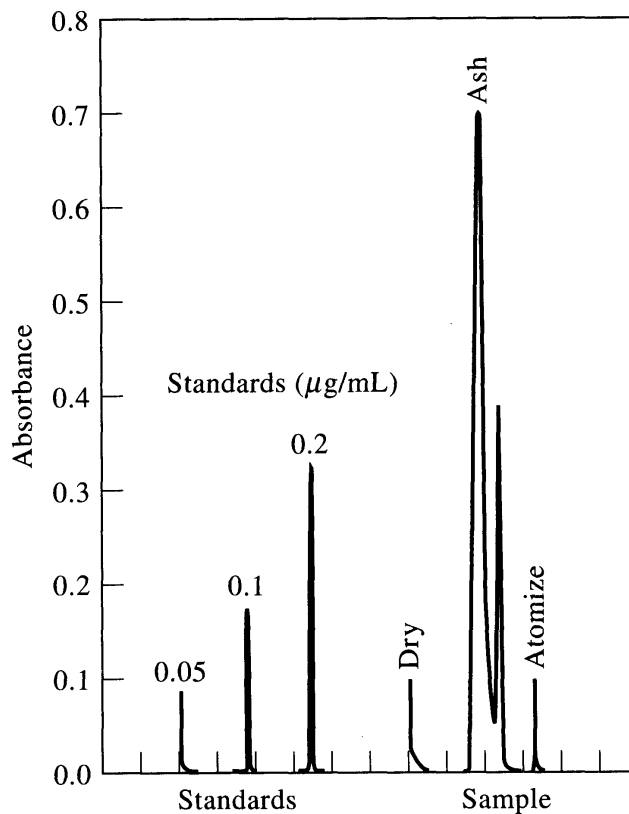


Fig 9-7

Atomic Absorption Instrumentation:

- AAS should be **very selective** - each element has different set of energy levels and lines very narrow
- BUT for linear calibration curve (Beers' Law) need bandwidth of absorbing species to be broader than that of light source
difficult with ordinary monochromator

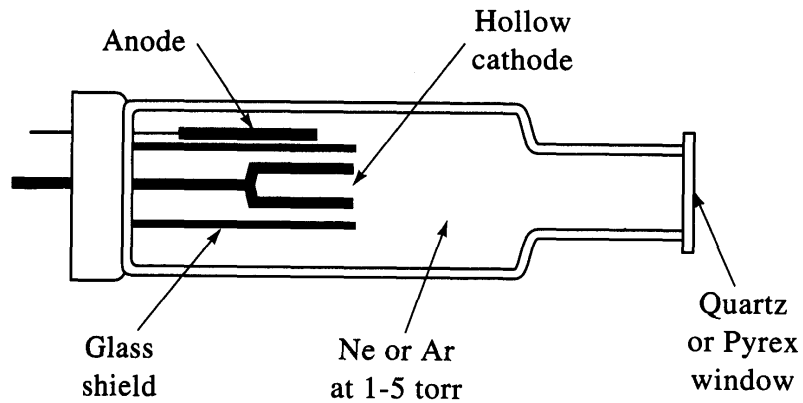
Solved by using **very narrow line radiation sources**

- minimize Doppler broadening
- pressure broadening
- lower P and T than atomizer

and using resonant absorption

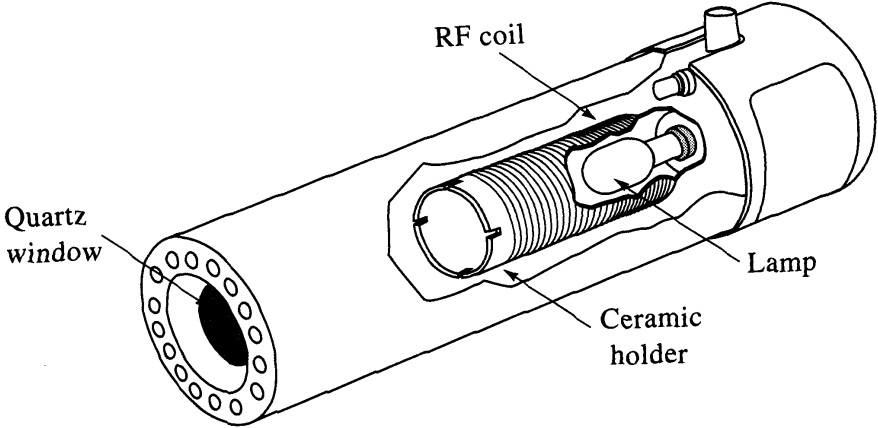
- Na emission $3p \rightarrow 2s$ at 589.6 nm used to probe Na in analyte

Hollow Cathode Lamp: (Fig 9-11)



- 300 V applied between anode (+) and metal cathode (-)
- Ar ions bombard cathode and sputter cathode atoms
- Fraction of sputtered atoms excited, then fluoresce
- Cathode made of metal of interest (Na, Ca, K, Fe...)
 - different lamp for each element
 - restricts multielement detection
- Hollow cathode to
 - maximize probability of redeposition on cathode
 - restricts light direction

Electrodeless Discharge Lamp: (Fig 9-12)



AAS Spectrophotometers:

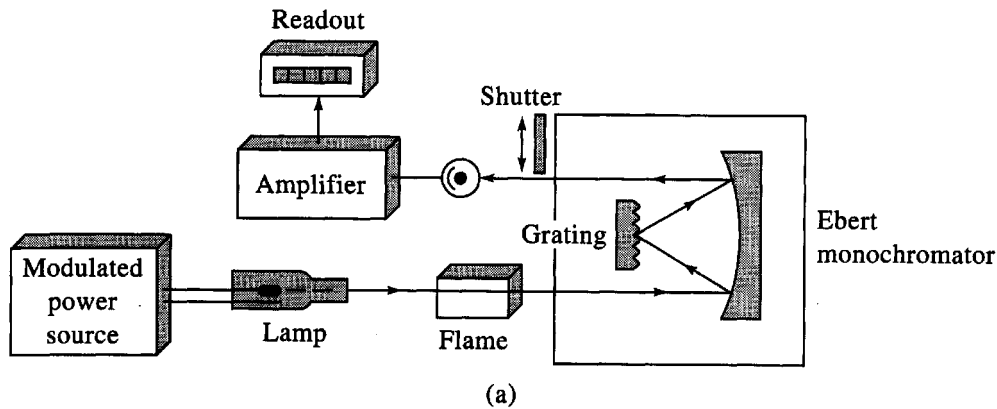


Fig 9-13(a)

Signal at one wavelength often contains luminescence from **interferents** in flame

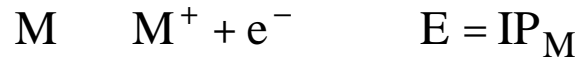
Chemical interference:

- (i) reverses atomization equilibria
- (ii) reacts with analyte to form low volatility compound

releasing agent - cations that react preferentially with interferent - Sr acts as releasing agent for Ca with phosphate

protecting agent - form stable but volatile compounds with analyte (metal-EDTA formation constants)

(iii) ionization



$$N_{M^+} = N_M \exp\left(\frac{-IP_M}{kT}\right)$$

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.

hotter atomization means:

more ionization

emission from interferents

Spectral interference - emission or absorption from interferent overlaps analyte

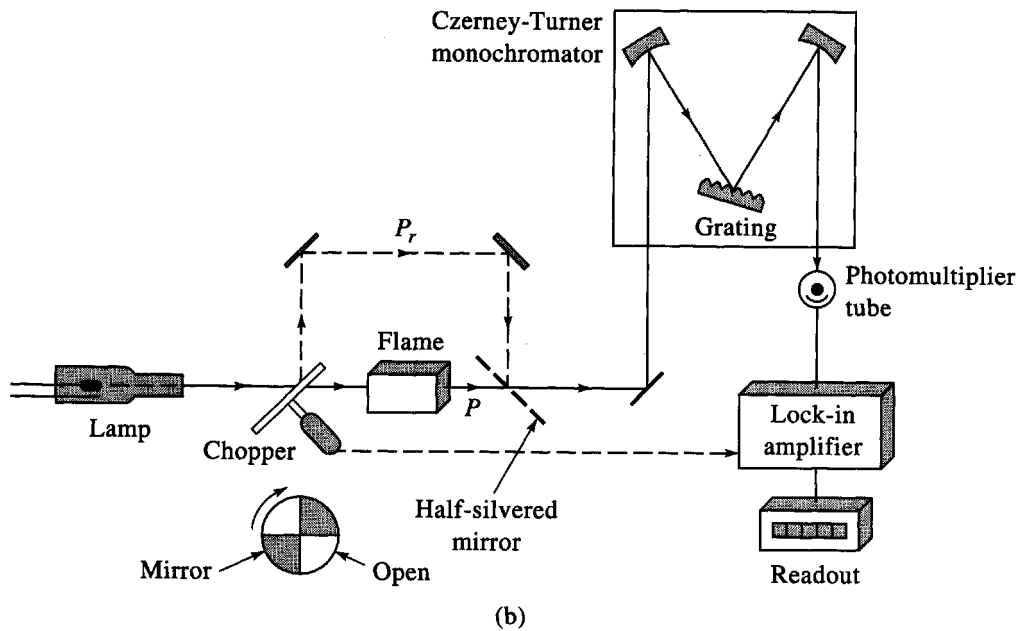
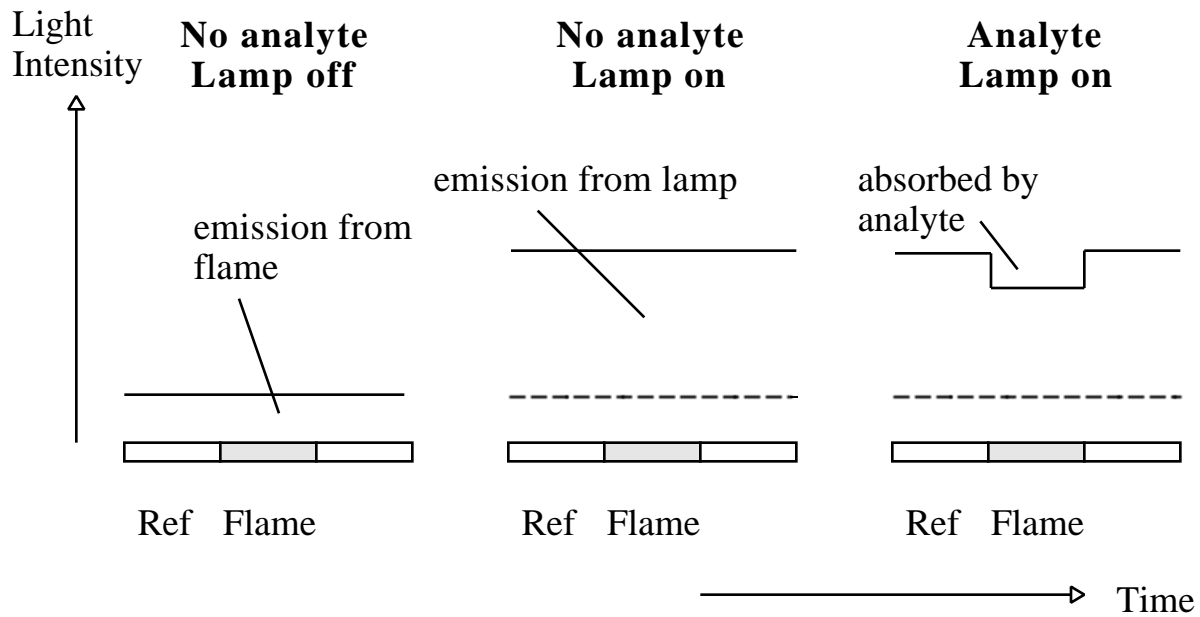


Fig 9-13(b)

Beam usually *chopped* or *modulated* at known frequency

Signal then contains constant (background) and dynamic (time-varying) signals



Detection limits for AAS/AES?

- AA/AE **comparable** (ppb in flame)
- AAS less suitable for
 - weak absorbers** (forbidden transitions)
 - metalloids** and **non-metals** (absorb in UV)
 - metals with **low IP** (alkali metals)

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