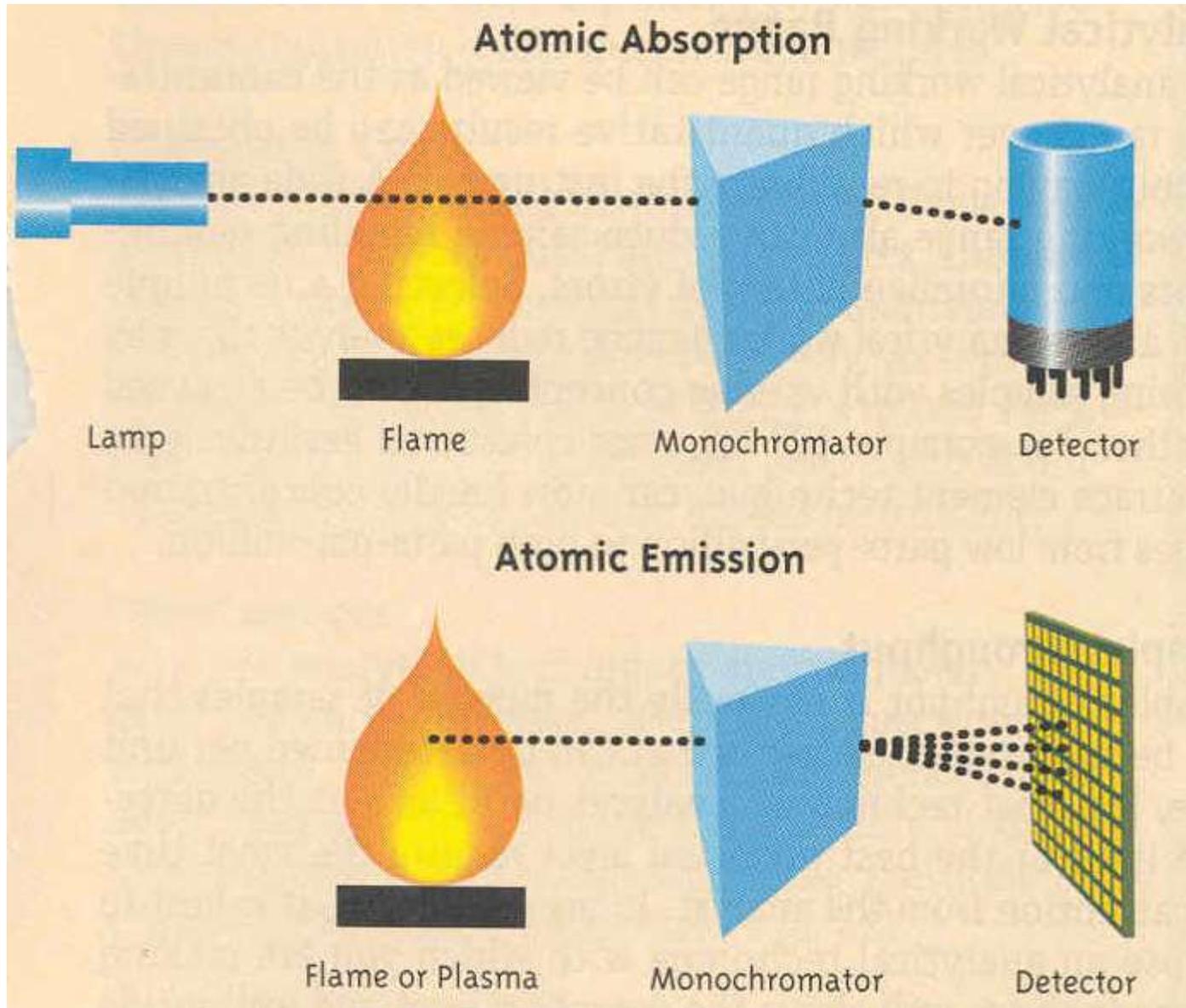


Chapter 8
Atomic Absorption
Spectrophotometry

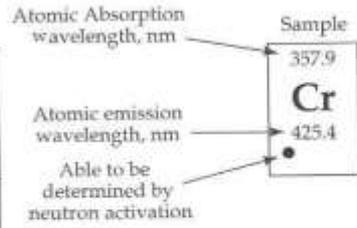
Atomic Spectroscopy

- **Methods that deal with absorption and emission of EMR by gaseous atoms**
- **The methods deal mainly with the free atoms (not ions)**
- **Line spectra are observed**
- **Specific spectral lines can be used for both qualitative and quantitative analysis of elements**

Principle components of Atomic absorption and atomic emission techniques



H															He			
670.8 Li 670.8	234.9 Be 234.9											249.7 B 518.0*	C	N	O	F	Ne	
589.0 Na 589.0 •	285.2 Mg 285.2 •											396.2 Al 396.2 •	251.6 Si 251.6 •	NA P 526.0*	NA S 392.0	Cl	Ar	
766.5 K 766.5 •	422.7 Ca 422.7 •	391.2 Sc 402.4 •	364.3 Ti 399.8 •	318.4 V 437.9 •	357.9 Cr 425.4 •	279.5 Mn 403.1 •	248.3 Fe 372.0 •	240.7 Co 345.4 •	232.0 Ni 352.5 •	324.7 Cu 324.7 •	213.9 Zn 481.1 •	287.4 Ga 417.2 •	265.2 Ge 265.2 •	193.7 As 193.7 •	196.0 Se NA •	Br	Kr	
780.0 Rb 780.0 •	460.7 Sr 460.7 •	410.2 Y 597.2*	360.1 Zr 360.1 •	405.9 Nb 405.9 •	313.3 Mo 390.3 •	Tc	349.9 Ru 372.8 •	343.5 Rh 343.5 •	274.6 Pd 363.5 •	328.1 Ag 328.1 •	228.8 Cd 326.1 •	303.9 In 451.1 •	224.6 Sn 284.0 •	217.6 Sb 252.8 •	214.3 Te 238.3 •	I	Xe	
852.1 Cs 455.5 •	553.5 Ba 553.5 •	550.1 La 441.8*	307.3 Hf 531.2 •	271.5 Ta 474.0 •	400.9 W 400.9 •	346.0 Re 346.0 •	305.9 Os 442.0 •	284.9 Ir 550.0*	265.9 Pt 265.9 •	242.8 Au 267.6 •	253.7 Hg 253.7 •	276.8 Tl 535.1 •	217.0 Pb 405.8 •	223.1 Bi 223.1 •	Po	At	Rn	
Fr	Ra	Ac																
			NA Ce 494.0	495.1 Pr 495.1	463.4 Nd 492.5	Pm	429.7 Sm 476.0	459.4 Eu 466.2	368.4 Gd 622.0	432.7 Tb 534.0*	421.2 Dy 404.6	410.4 Ho 410.4	400.8 Er 400.8	371.8 Tm 371.8	398.8 Yb 398.8*	331.2 Lu 451.9		
			NA Th 492.0 •	Pa	358.5 U 544.8 •	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw		

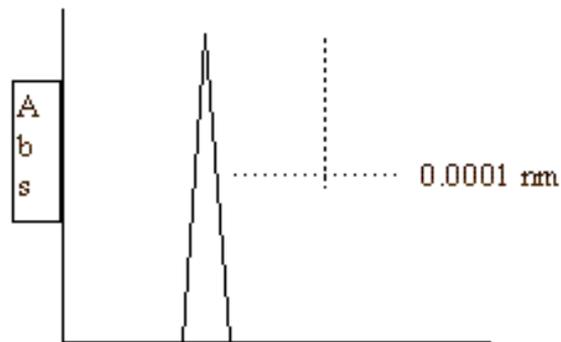
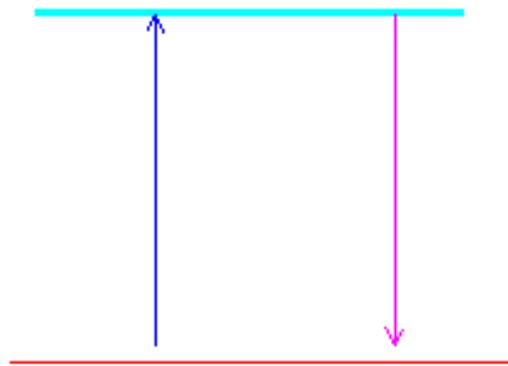


Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.

H												He																																	
670.8 Li 670.8	234.9 Be 234.9	<p>Atomic Absorption wavelength, nm → 357.9</p> <p>Atomic emission wavelength, nm → 425.4</p> <p>Able to be determined by neutron activation →</p> <p>Sample</p>										249.7 B 518.0*	C	N	O	F	Ne																												
589.0 Na 589.0	285.2 Mg 285.2											396.2 Al 396.2	251.6 Si 251.6	NA P 526.0*	NA S 392.0	Cl	Ar																												
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Fr	Ra	Ac	<table border="1"> <tr> <td>NA Ce 494.0</td> <td>495.1 Pr 495.1</td> <td>463.4 Nd 492.5</td> <td>Pm</td> <td>429.7 Sm 476.0</td> <td>499.4 Eu 466.2</td> <td>368.4 Gd 622.0</td> <td>432.7 Tb 594.0*</td> <td>421.2 Dy 404.6</td> <td>410.4 Ho 410.4</td> <td>400.8 Er 400.8</td> <td>371.8 Tm 371.8</td> <td>368.8 Yb 398.8*</td> <td>331.2 Lu 451.9</td> </tr> <tr> <td>NA Th 492.0</td> <td>Pa</td> <td>368.5 U 544.8</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lw</td> </tr> </table>															NA Ce 494.0	495.1 Pr 495.1	463.4 Nd 492.5	Pm	429.7 Sm 476.0	499.4 Eu 466.2	368.4 Gd 622.0	432.7 Tb 594.0*	421.2 Dy 404.6	410.4 Ho 410.4	400.8 Er 400.8	371.8 Tm 371.8	368.8 Yb 398.8*	331.2 Lu 451.9	NA Th 492.0	Pa	368.5 U 544.8	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
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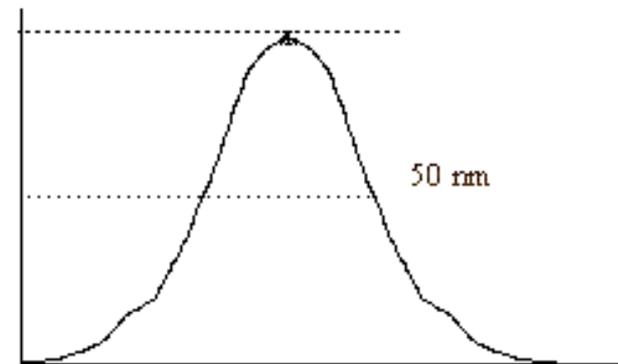
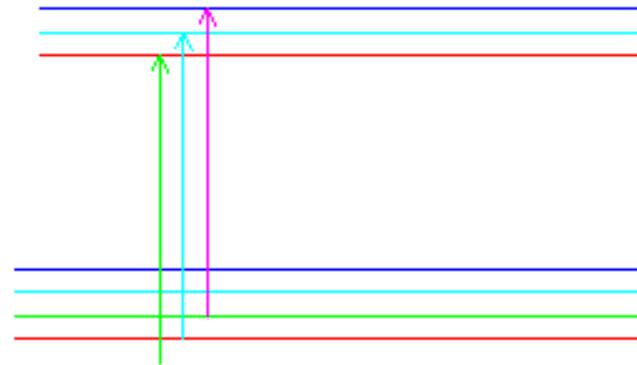
Molecular and Atomic Spectra

Atomic Transition



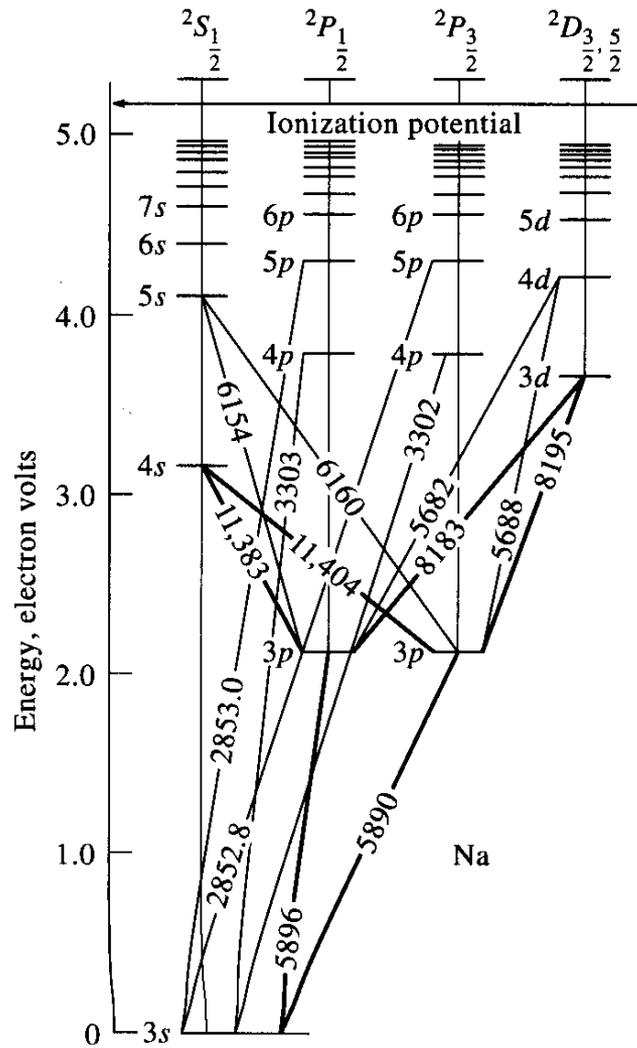
Atomic spectral line

Molecular transition

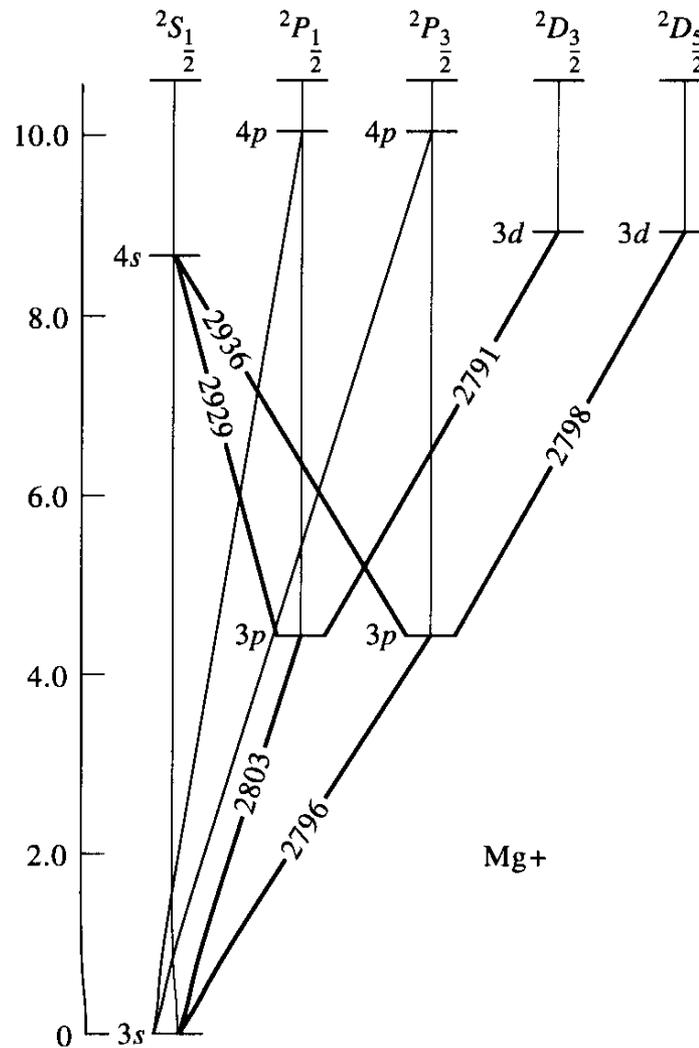


Molecular spectral line

Energy level diagrams (Na atom and Mg⁺ ion)



(a)



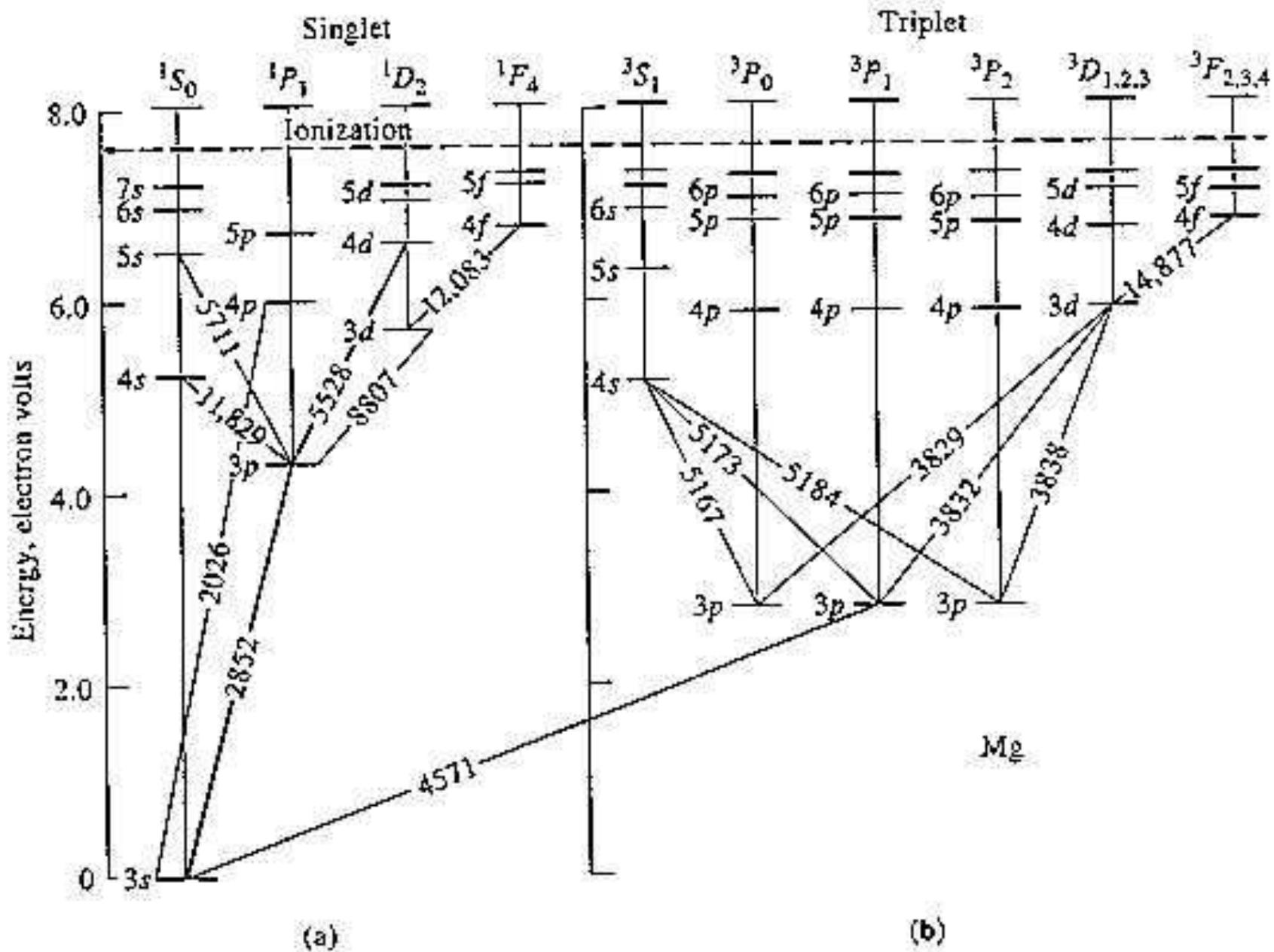
(b)

Energy Level Diagrams

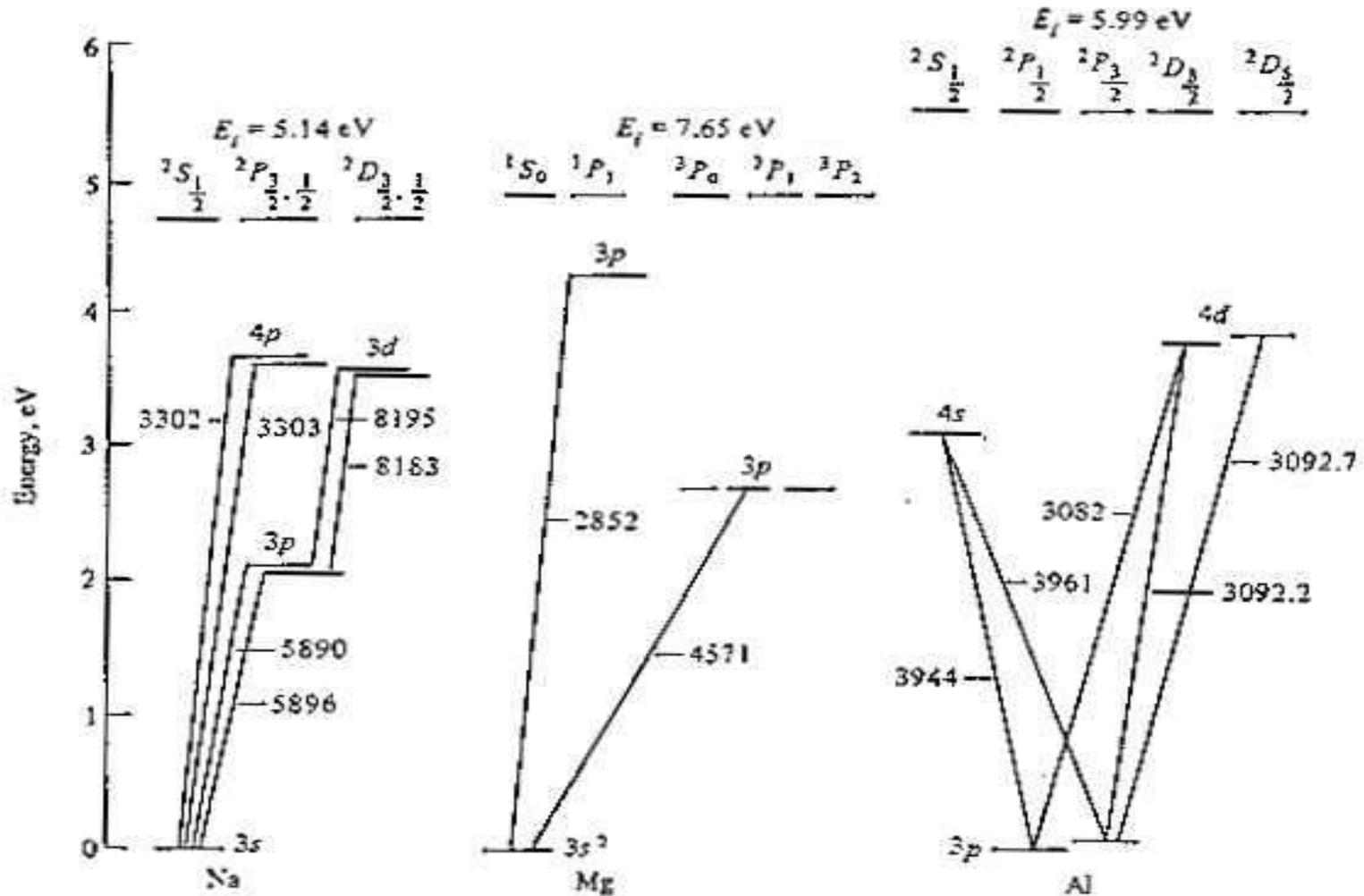
Energy Level Diagrams

- **Note similarity in patterns of lines, for monovalent ions but not wavelengths**
- **The spectrum of an ion is significantly different from that of its parent atom**

Energy level diagram (Mg atom)



Energy Level Diagrams for lower states of Na, Mg, Al



Ionic spectra versus atomic spectra

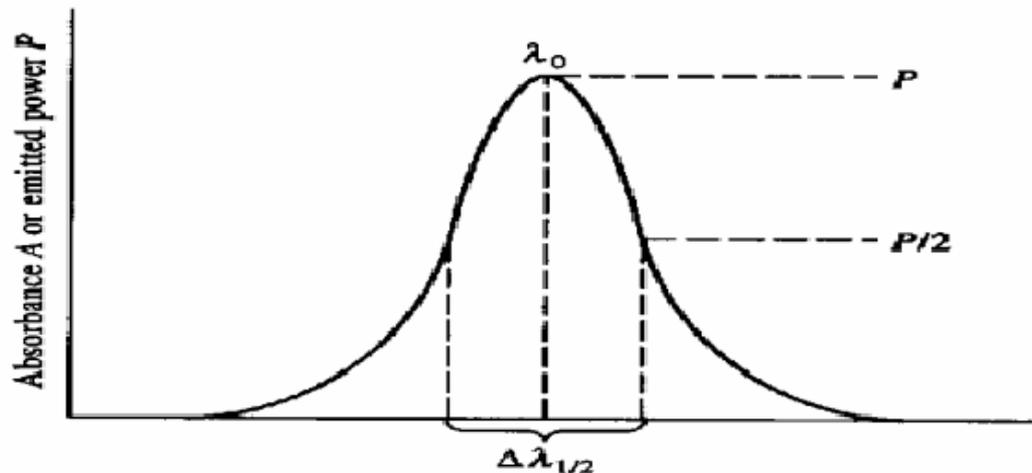
- Spectra of excited atoms differ from those of excited ions of the same atoms
- Spectrum of singly ionized atom is similar to the atomic spectrum of the element having an atomic number of one less e.g.:
 - spectrum of Mg^+ is similar to that of Na atom
 - spectrum of Al^+ is similar to that of Mg atom
- Ionic spectra contain more lines than atomic spectra; however the intensity of ionic spectra is much less than that of atomic spectra

Absorption and Emission Line Profile

Spectral Line width

- Narrow line desirable for absorption and emission work to reduce possibility of interference due to overlapping spectra.
- Theoretically atomic lines should have a zero line width but this does not exist
- The natural line should have a width of 10^{-5} nm

Atomic Line Widths



- **Experimentally: spectral lines have definite width and characteristic form**
- **Actual line width is $\sim 10^{-3}$ nm. That is the energy emitted in a spectral line is spread over a narrow wavelength range reaching a maximum at λ_o , for example:**

Element	λ_o	$\Delta \lambda$, nm
Ca	422.7	0.0032
Ag	328.1	0.0016
Mn	403.1	0.0026
Cs	455.5	0.0030

- **Why do we study the line profile?**
Resolution is limited by the finite width of the lines

Line Broadening

1) Uncertainty Effect

– due to finite lifetime of transition states. (10^{-4} A)

2) Doppler Broadening

– atoms moving toward radiation absorb at higher frequencies; atoms moving away from radiation absorb at lower frequencies.

3) **Pressure Effects** – due to collisions between analyte atoms with foreign atoms (like from fuel).

4) **Electric and Magnetic Field Effects.**

The largest two problems:

1. Doppler broadening

2. Pressure broadening

Doppler broadening

During atomization/ionization, our species may move towards or away from the detector.

This will result in a Doppler shift in the resulting line.

Spectral lines that should be about 1-5nm can end up being 100 times wider.

There is not much you can do about it except recognize that ~~is~~ it occurs.

it

Pressure Broadening

- **The effect that arise from the collision of the sample atoms with themselves or with other species causing some energy to be exchanged**
- **This effect is greater as the temperature increases**

Distribution of atomic population

The Effect of Temperature on Atomic Spectra

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp -(E_j/kT)$$

where N_j : # atoms excited state

N_o : # atoms ground state

k : Boltzmann constant

P_j & P_o : statistical factors determined by
of states having equal energy at
each quantum level

E_j : energy difference between energy
levels

The ratio of Ca atoms in the excited state to ground state at
(a) 2000 K and (b) 3000 K.

for Ca atoms: $P_j/P_o = 3$

$E_j = 2.93$ ev for 4227 D line

(a) 2000 K

$$\frac{N_j}{N_o} = 3 \exp - \frac{(2.93 \text{ ev})(1 \text{ erg}/6.24 \times 10^{11} \text{ ev})}{(1.38 \times 10^{-16} \text{ erg/K})(2000 \text{ K})}$$

$$= 1.23 \times 10^{-7}$$

(b) 3000 K

$$\frac{N_j}{N_o} = 3 \exp - \frac{(2.93 \text{ ev})(1 \text{ erg}/6.24 \times 10^{11} \text{ ev})}{(1.38 \times 10^{-16} \text{ erg/K})(3000 \text{ K})}$$

$$= 3.56 \times 10^{-5}$$

% Increase in the excited atoms =

$$(3.56 \times 10^{-5} - 1.23 \times 10^{-7}) / 1.23 \times 10^{-7} = 288 \text{ time}$$

- **Atomic population of Na atoms for the transition $3s \rightarrow 3p$**

$$N_{\text{excited}} / N_{\text{ground}} = 1 \times 10^{-5} = 0.001\%$$

- **That is 0.001% of Na atoms are thermally excited**
- **Thus 99.999% of Na atoms are in the ground state**
- **Atomic emission uses **Excited atoms****
- **Atomic absorption uses **Ground state atoms****

Table 4.1 Ratio of excited-to ground-state atoms for lines with varying excitation energies at increasing temperature.

Element	Line (nm)	g_i/g_0	E_i (J)	Ratio of excited- to ground-state atoms							
				2000 K	3000 K	4000 K	5000 K	6000 K	7000 K	8000 K	
Cs	852.1	2	2.34×10^{-19}	4.19×10^{-4}	7.06×10^{-3}	2.90×10^{-2}	6.75×10^{-2}	1.19×10^{-1}	1.78×10^{-1}	2.41×10^{-1}	
Na	589.1	2	3.38×10^{-19}	9.65×10^{-6}	5.71×10^{-4}	4.39×10^{-3}	1.49×10^{-2}	3.38×10^{-2}	6.05×10^{-2}	9.37×10^{-2}	
Ca	422.7	3	4.66×10^{-19}	1.40×10^{-7}	3.88×10^{-5}	6.47×10^{-4}	3.50×10^{-3}	1.08×10^{-2}	2.41×10^{-2}	4.41×10^{-2}	
Zn	213.9	3	9.13×10^{-19}	1.30×10^{-14}	7.99×10^{-10}	1.98×10^{-7}	5.40×10^{-6}	4.90×10^{-5}	2.36×10^{-4}	7.70×10^{-4}	

Conclusions about atomic population

- **Number of excited atoms is very temperature dependent. Temp. should be carefully controlled**
- **Number of ground state atoms is insensitive to temp.; but subject to flame chemistry which is dependent on temp., as well as type of the flame**
- **Most atoms are in ground state (resonance state). Resonance absorption lines are the most sensitive**
- **The fraction of excited atoms is very dependent on the nature of element and temperature**
- **Which of the two techniques (AA or AE) is more sensitive? Why?**

Choice Of Absorption Line

- **Resonance line is the best**
- **Resonance line is always more intense than other lines i.e., more sensitive for analysis**
- **Resonance line is used always for small concentrations**
- **Most elements require from 6-9 electron volts for ionization to occur. $1\text{eV} = 1.6 \times 10^{-19}\text{ J}$. Thus using appropriate excitation, the spectra of all metals can be obtained simultaneously**

- **Are all elements, including nonmetals, accessible on the AA or FE instruments?**
- **Yes for metals; no for nonmetals**
- **Excitation of nonmetals e.g., Noble gases, Hydrogen, Halogens, C, N, O, P, S necessitates the application of special techniques**

Self Absorption and Self Reversal of Spectral lines

- **When sample concentration increases, there would be an increase in the possibility that the photons emitted from the hot central region of the flame collide with the atoms in the cooler outer region of the flame and thus be absorbed**
- **Curvature of the calibration curves at high concentrations would be observed**
- **The effect is minimal with ICP until very high atom concentrations are reached**

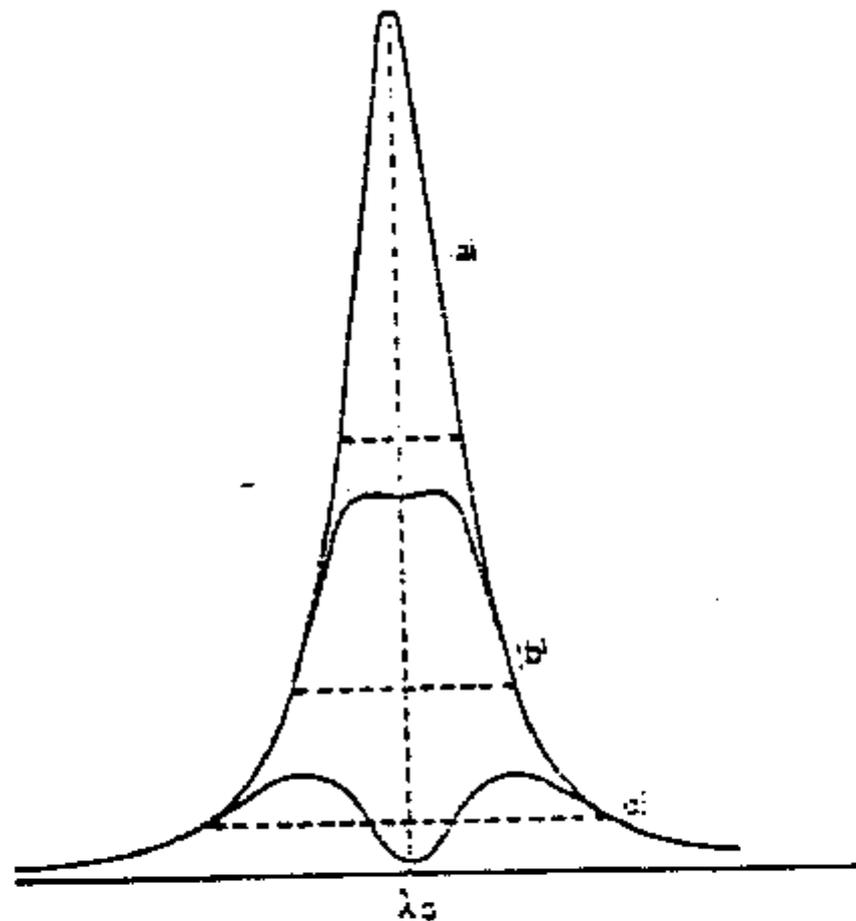


Fig. 6 Self-absorption of a resonance line (diagrammatic). (A) Line without self-absorption. (B) Reversed line

Self reversal

- **It occurs when emission line is broader than the corresponding absorption line**
- **Resonance line suffers the greatest self absorption**
- **The center of the resonance line will be affected more than the edges**
- **The extreme case of self absorption is: self reversal**

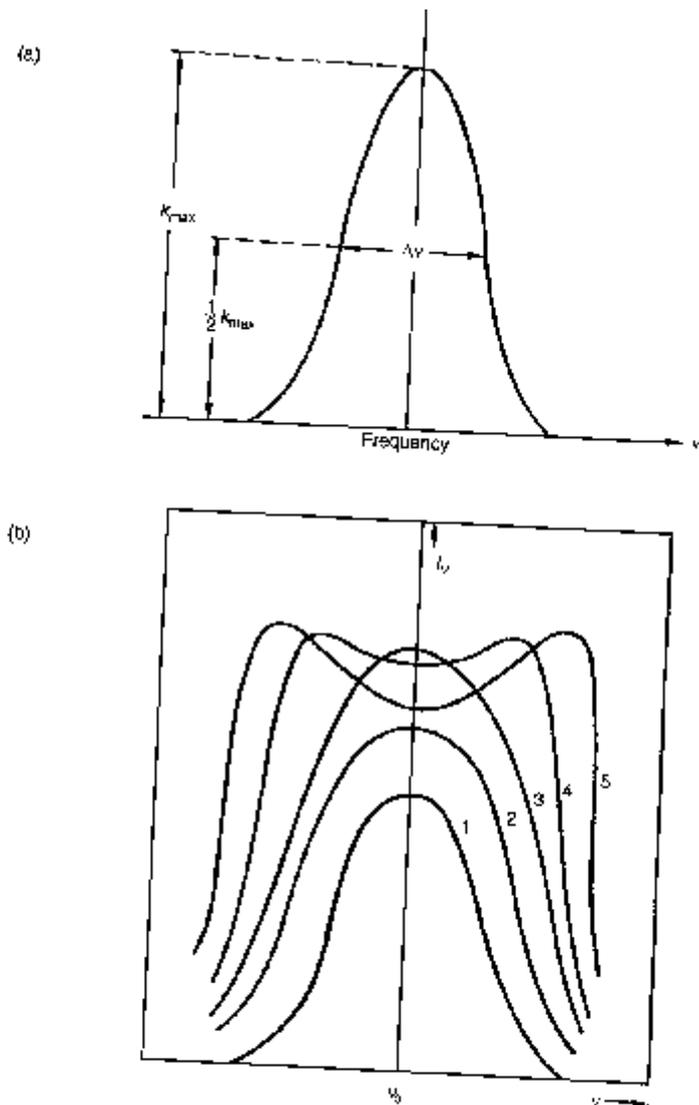


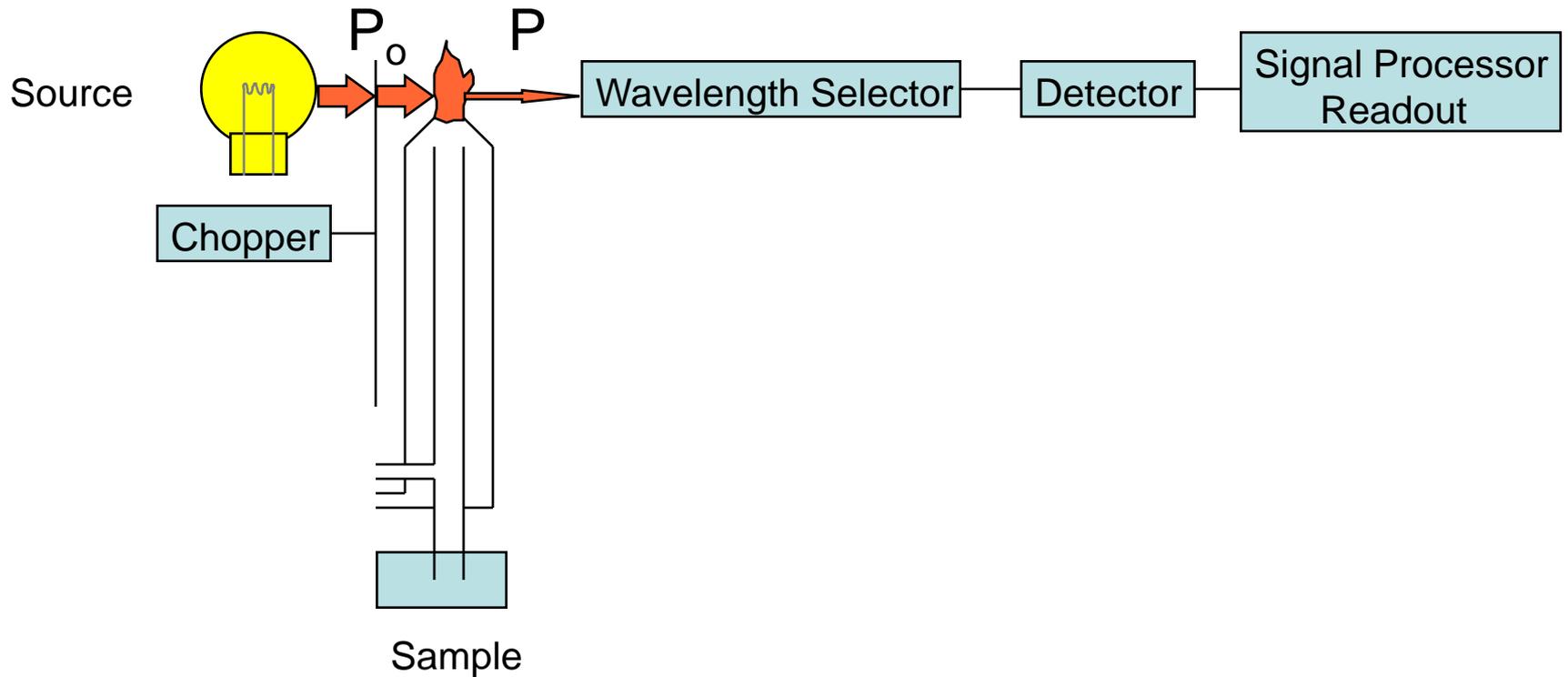
Figure 4.2 Profile of an atomic line: (a) the half width $\Delta\nu$ is the width of the line when $k_\nu = 1/2 k_{\max}$; (b) the effect of self-absorption as the concentration of atoms increases from 1 to 5.

Effect of self absorption and self reversal on measurements

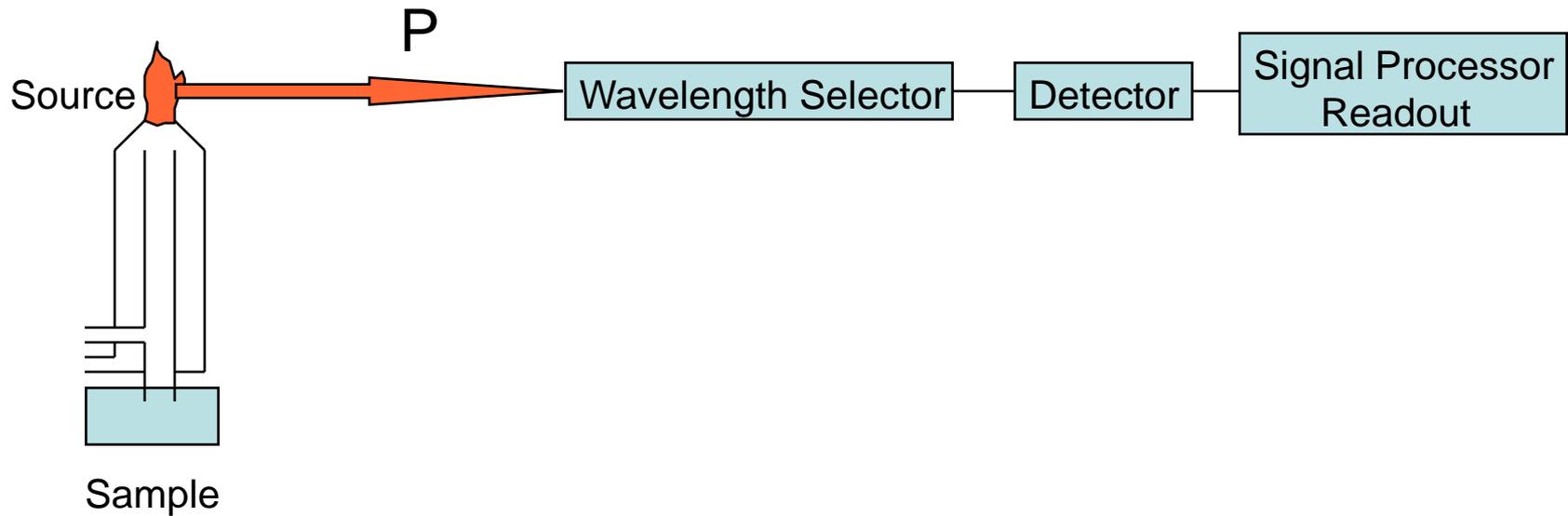
- **When self absorption occurs**
 - Line intensity interpretation becomes difficult and inaccurate
 - Thus non-resonance line is selected for analysis or **concentration is reduced**

Basic Principles of Atomic Spectrometers

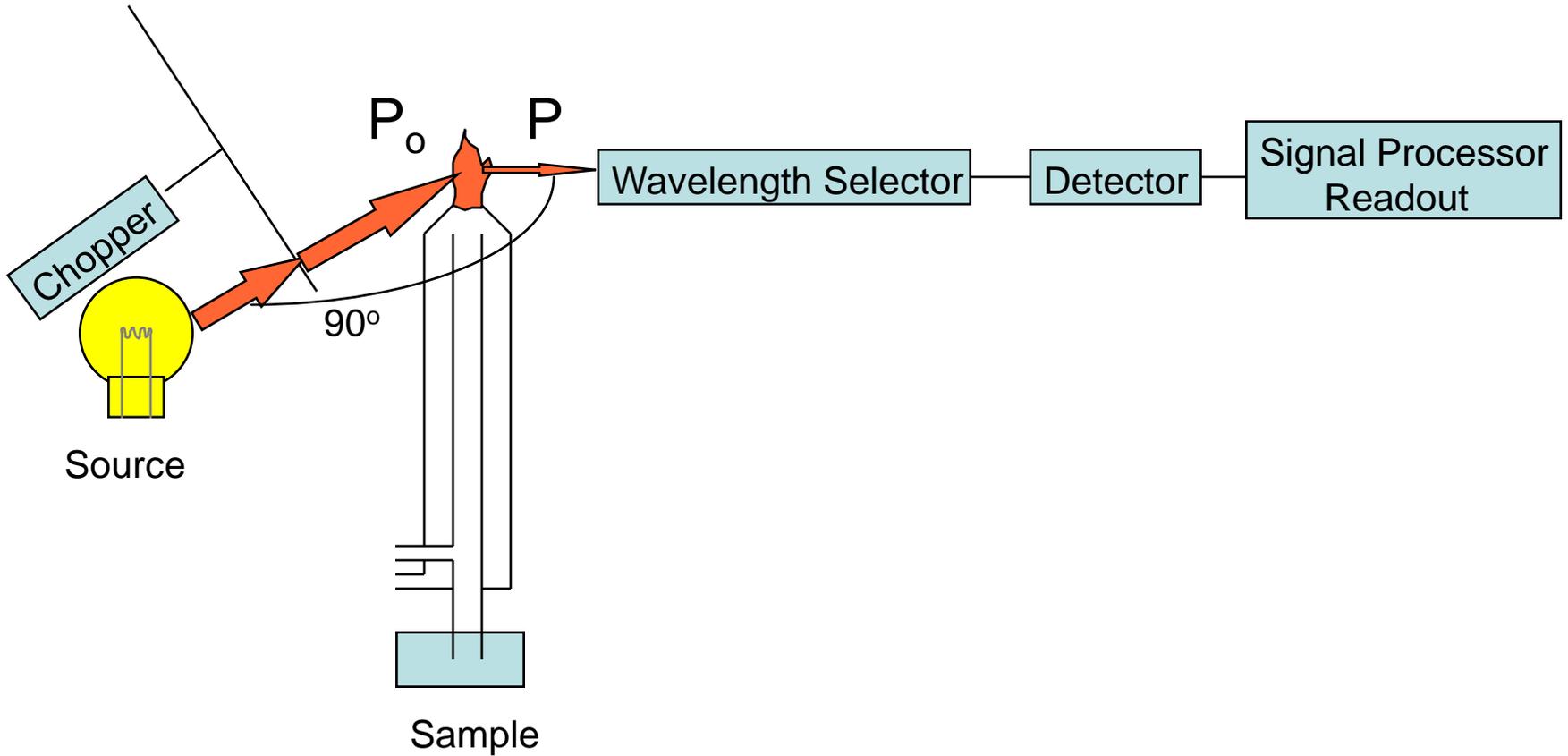
Flame Atomic Absorption Spectrometer



Emission Flame Photometer



Fluorescence Spectrometer



Relationship Between Atomic Absorption and Flame Emission

- **Flame Emission:** it measures the radiation emitted by the excited atoms that is related to concentration.
- **Atomic Absorption:** it measures the radiation absorbed by the unexcited atoms that are determined.
- **Atomic absorption** depends only upon the number of unexcited atoms, the absorption intensity is not directly affected by the temperature of the flame.
- **The flame emission** intensity in contrast, being dependent upon the number of excited atoms, is greatly influenced by temperature variations.

Measured signal and analytical concentration

1. Atomic Emission

Signal = Intensity of emission = $KN_f = K'N_a = K''C$

N_f = number of free atoms in flame

N_a = number of absorbing atoms in flame

C = concentration of analyte in the sample

K , K' and K'' depend upon:

- Rate of aspiration (nebulizer)
- Efficiency of aspiration (evaporation efficiency)
- Flow rate of solution
- Solution concentration
- Flow rate of unburnt gas into flame
- Efficiency of atomization (effect of chemical environment).
 - **This depends upon**
- Droplet size
- Sample flow rate
- Refractory oxide formation
- Ratio of fuel/oxygen in flame
- Temperature effect (choice of flame temperature)

2. Atomic absorption

$$\text{Signal} = I_{\text{absorbed}} = \text{Absorbance} = A = k I C$$

- For the measurement to be reliable k must be constant; k should not change when a change in matrix or flame type takes place.
- K depends upon same factors as those for the atomic emission spectroscopy

Atomizers in emission techniques

<u>Type</u>	<u>Method of Atomization</u>	<u>Radiation Source</u>
Arc	sample heated in an electric arc (4000-5000°C)	sample
Spark	sample excited in a high voltage spark	sample
Flame	sample solution aspirated into a flame (1700 – 3200 °C)	sample
Argon plasma	sample heated in an argon plasma (4000-6000°C)	sample

Atomizers in absorption techniques

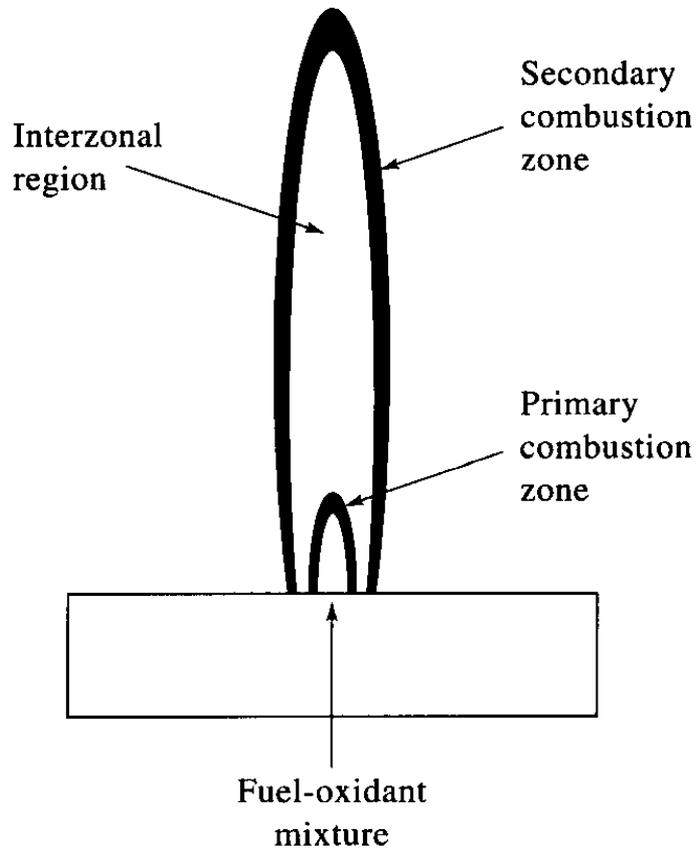
<u>Type</u>	<u>Method of Atomization</u>	<u>Radiation Source</u>
Atomic (flame)	sample solution aspirated into a flame	HCL
atomic (nonflame) (Electrothermal)	sample solution evaporated & ignited (2000 -3000 °C)	HCL
Hydride generation	Vapor hydride generated	HCL
Cold vapor	Cold vapor generated (Hg)	HCL

Atomizers in fluorescence techniques

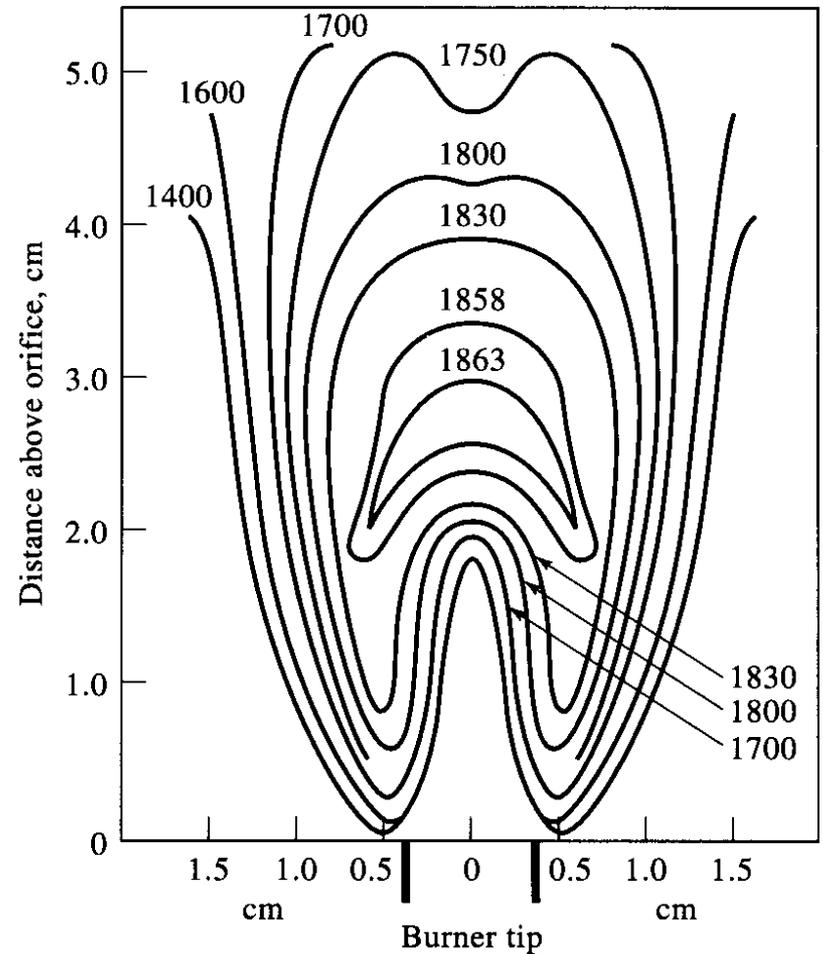
<u>Type</u>	<u>Method of Atomization</u>	<u>Radiation Source</u>
atomic (flame)	sample aspirated into a flame	sample
atomic (nonflame)	sample evaporated & ignited	sample
x-ray fluorescence	not required	sample

Flames

Regions in Flame



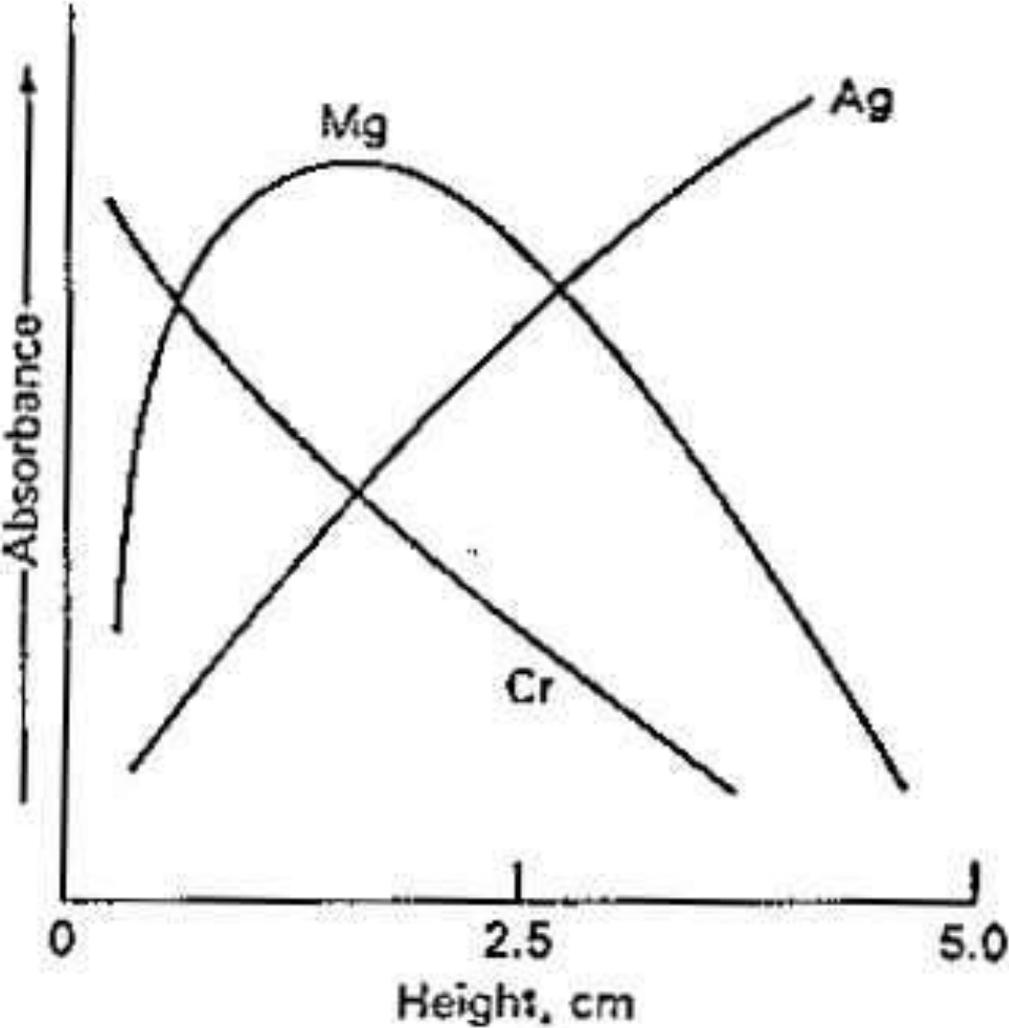
Temperature Profile



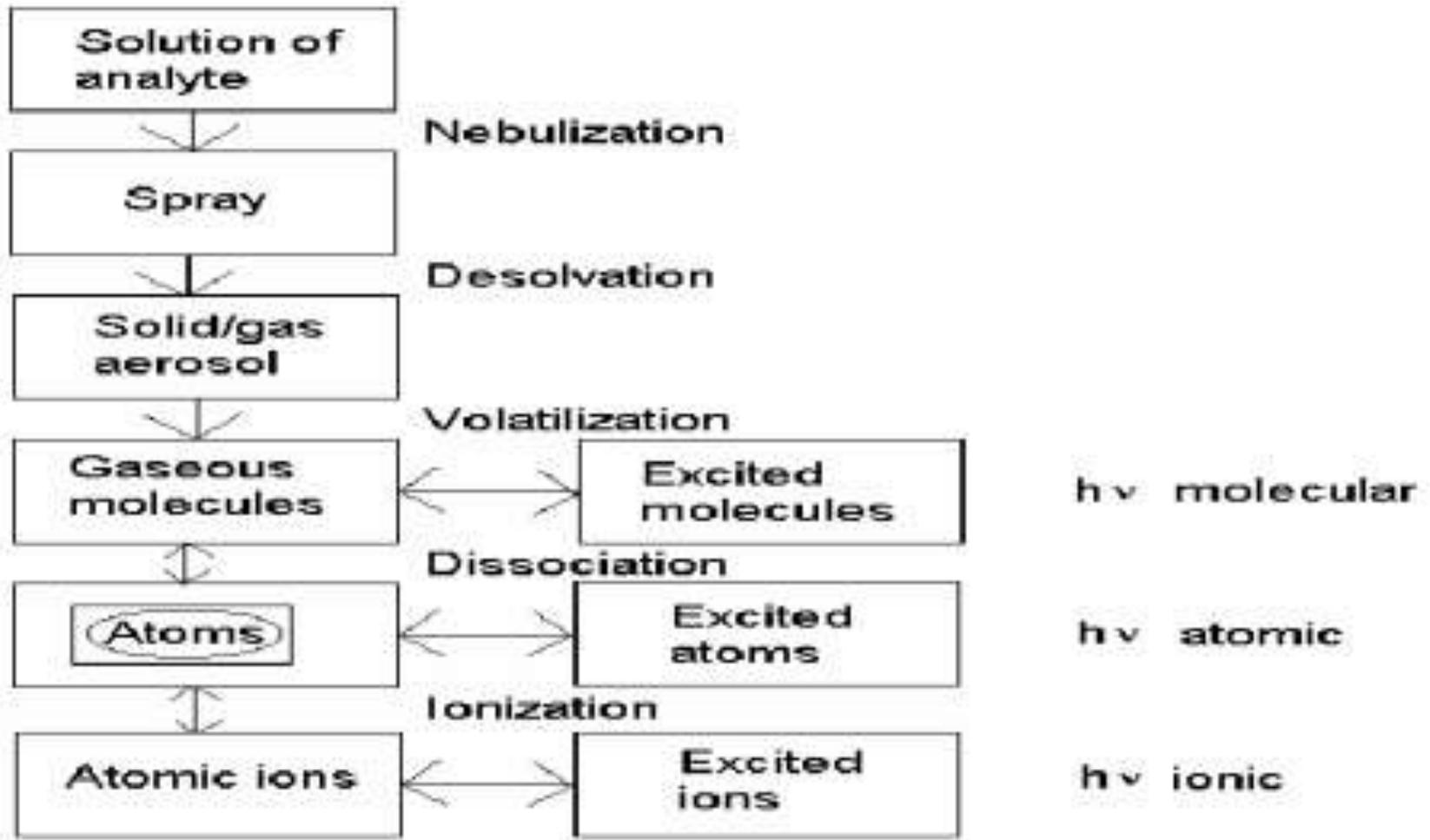
Properties of Flames

Fuel	Oxidant	Temp. °C	Burn Velocity (cm/s)
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

Flame absorbance profile for three elements



Processes that take place in flame or plasma



Sample introduction techniques

Solutions

- Pneumatic nebulization
- Ultrasound nebulization
- Electrothermal vaporization
- Hydride generation

Solids

- Electrothermal vaporization
- Direct insertion
- Laser ablation
- Spark or arc ablation

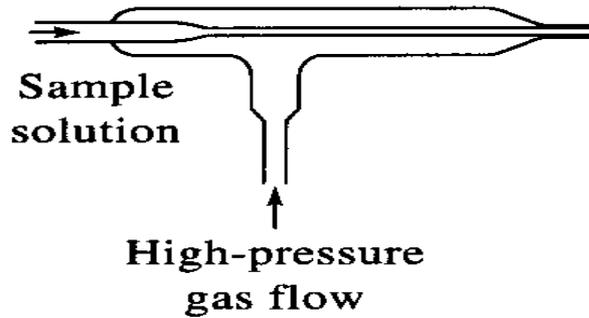
Methods of Sample Introduction in Atomic Spectroscopy

Method	Type of Sample
Pneumatic nebulization	Solution or slurry
Ultrasonic nebulization	Solution
Electrothermal vaporization	Solid, liquid, solution
Hydride generation	Solution of certain elements
Direct insertion	Solid, powder
Laser ablation	Solid, metal
Spark or arc ablation	Conducting solid
Glow discharge sputtering	Conducting solid

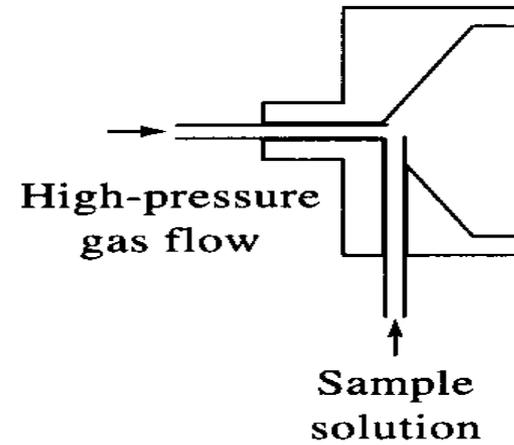
Nebulization

- **Nebulization** is conversion of a sample to a fine mist of finely divided droplets using a jet of compressed gas.
 - The flow carries the sample into the atomization region.
- **Pneumatic Nebulizers** (most common)
Four types of pneumatic nebulizers:
- **Concentric tube** - the liquid sample is sucked through a capillary tube by a high pressure jet of gas flowing around the tip of the capillary (Bennoulli effect).
 - This is also referred to aspiration. The high velocity breaks the sample into a mist and carries it to the atomization region.

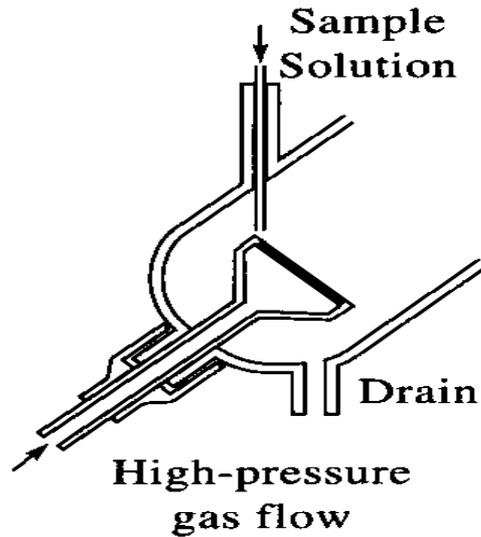
Types of pneumatic nebulizers



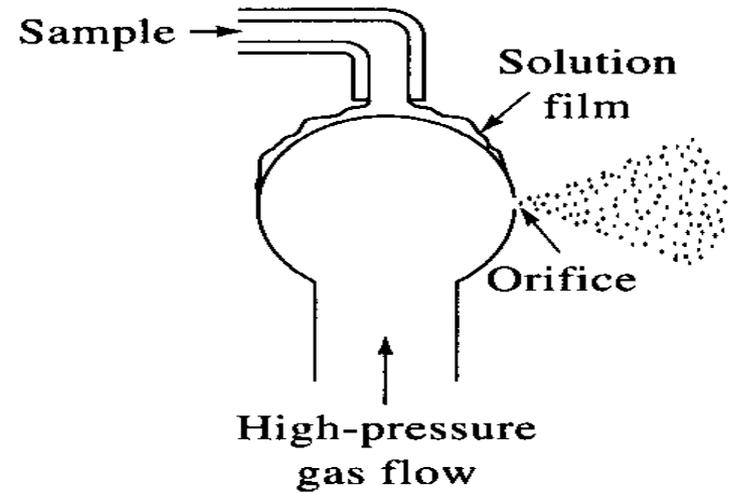
(a) **Concentric tube; Cross flow**



(b) **Concentric tube; Cross flow**



(c) **Fritted disk**



(b) **Babington**

- **Cross-flow**

The jet stream flows at right angles to the capillary tip. The sample is sometimes pumped through the capillary.

- **Fritted disk**

The sample is pumped onto a fritted disk through which the gas jet is flowing. Gives a finer aerosol than the others.

- **Babington**

Jet is pumped through a small orifice in a sphere on which a thin film of sample flows. This type is less prone to clogging and used for high salt content samples.

- **Ultrasonic Nebulizer**

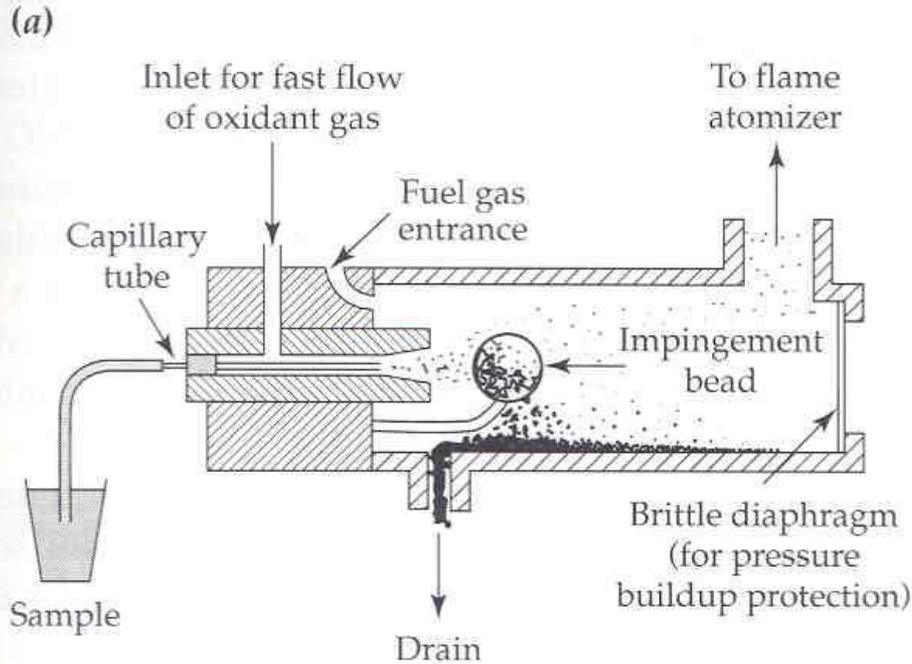
- The sample is pumped onto the surface of a vibrating piezoelectric crystal.

- The resulting mist is denser and more homogeneous than pneumatic nebulizers.

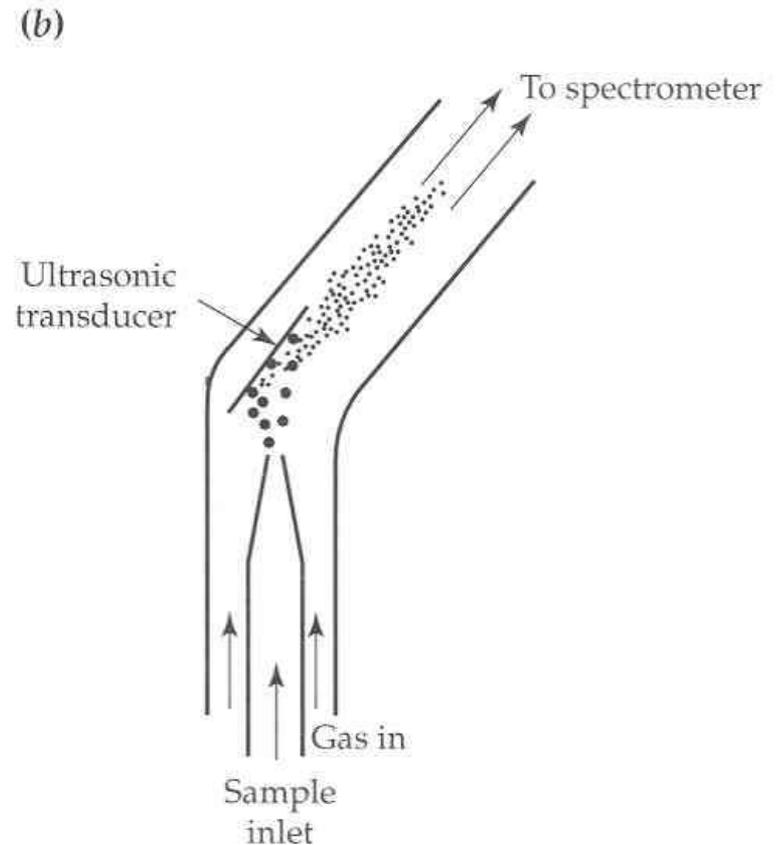
- **Electro-thermal Vaporizers (Etv)**

An electro thermal vaporizer contains an evaporator in a closed chamber through which an inert gas carries the vaporized sample into the atomizer.

Liquid samples introduced to atomizer through a nebulizer



Pneumatic nebulizer



Ultrasonic-Shear Nebulizer

Atomization Atomizers

Flame

Electrothermal

Special

Glow Discharge

Hydride Generation

Cold-Vapor

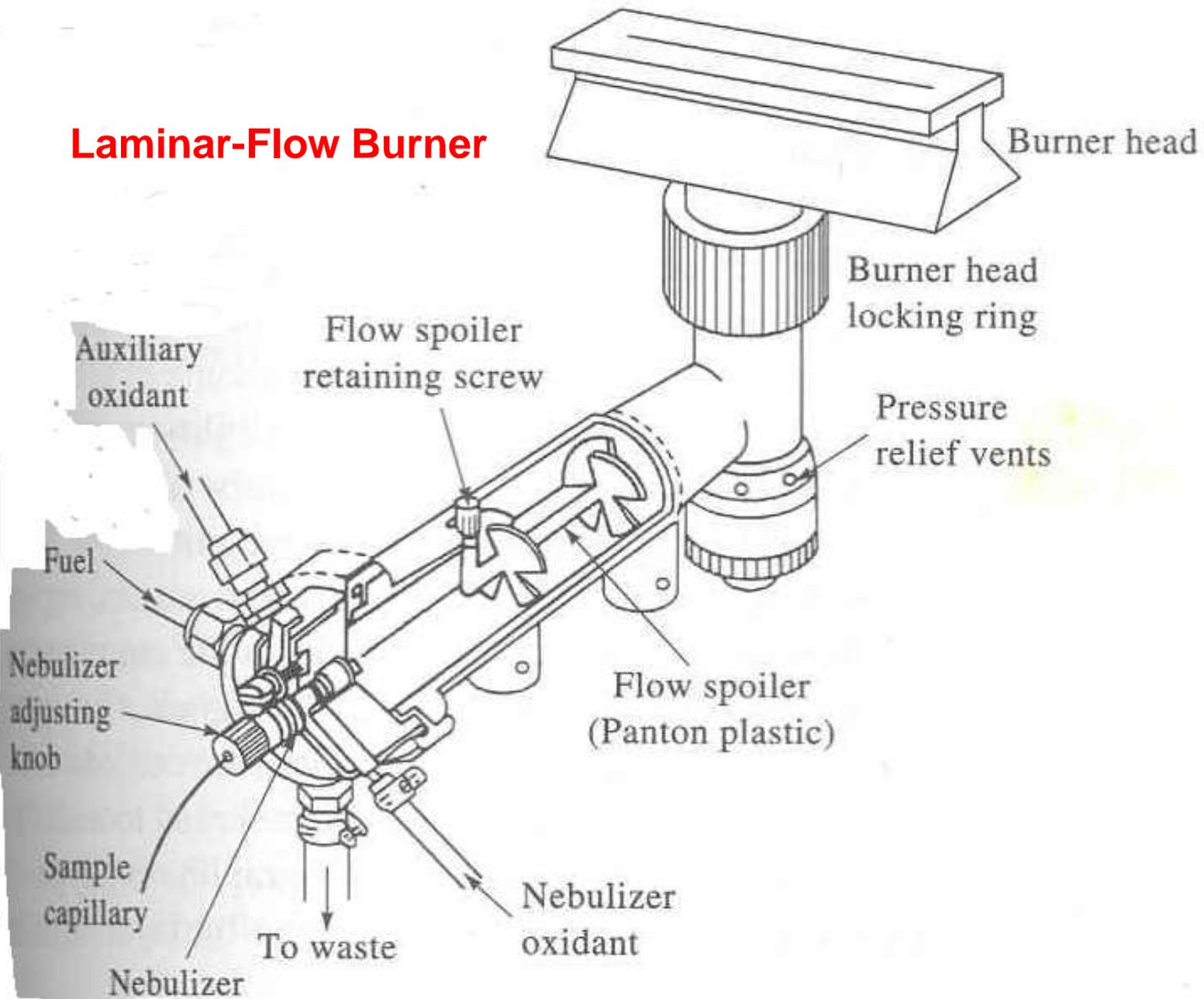
Different Atomization Sources for Atomic Spectroscopy

Source Type	Typical Source Temperature
Combustion Flame	°3150 - 1700C.
Electrothermal Vaporization (ETV) on graphite platform	°3000 - 1200C
Inductively coupled plasma (ICP)	°8000- 5000C
Direct-current plasma (DCP)	°1000-6000C
Microwave induced plasma (MIP)	°3000-2000C
Glow Discharge plasma (GDP)	non-thermal
Spark Sources (dc or ac Arc)	°40,000 ~C(?)

Flame Atomizers

- **Superior method for reproducible liquid sample introduction for atomic absorption and fluorescence spectroscopy.**
- **Other methods better in terms of sampling efficiency and sensitivity.**
- **The simplest type is the “Total consumption burner” that is used usually with the simple flame photometers**
- **The one that is widely used for AA instruments is the “laminar flow burner”.**

Laminar-Flow Burner



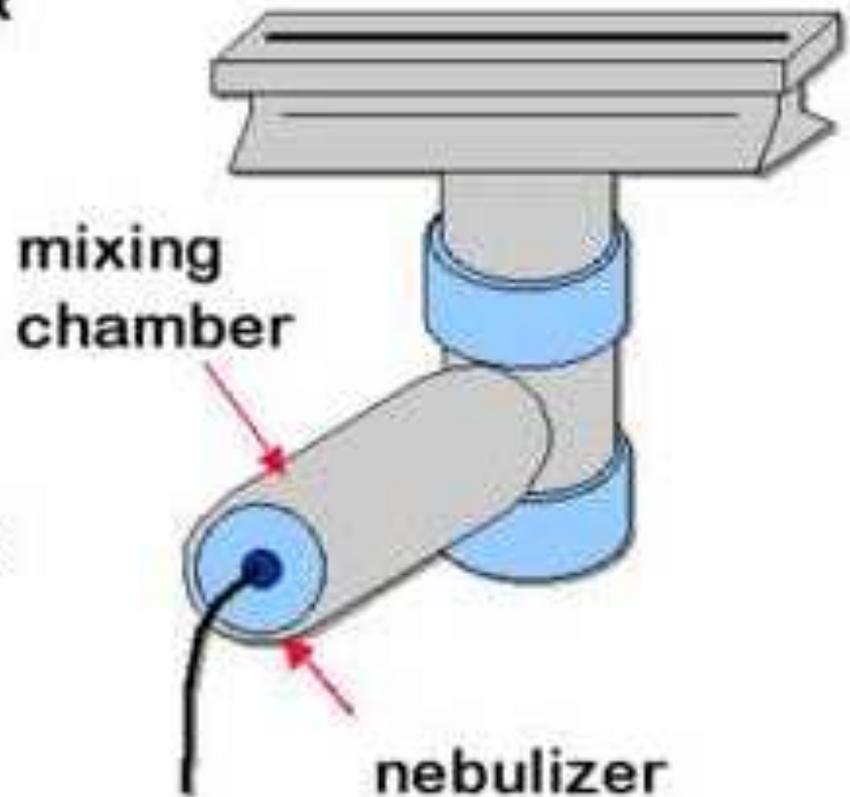
Laminar flame atomizer

A flame atomizer will usually have a long, narrow burner head that serves as a sample path (b).

Sample is introduced via aspiration.

The nebulizer controls sample flow, producing a mist.

The mixing chamber assures that the sample mixes with the oxidant and fuel prior to entry into the flame.



Flame atomization

The most common fuel to use is acetylene.

Either air or nitrous oxide are used as oxidants, with N_2O producing a hotter flame.

	Temperature, °C
C_2H_2/Air	2100 - 2400
C_2H_2/N_2O	2600 - 2800

N_2O also tends to produce a noisier flame.

Flame atomization

Flame atomization tends to produce stable signals in the ppm range for most metals.

It is a dynamic method

Sample is constantly being consumed.

Large sample size (>1 ml).

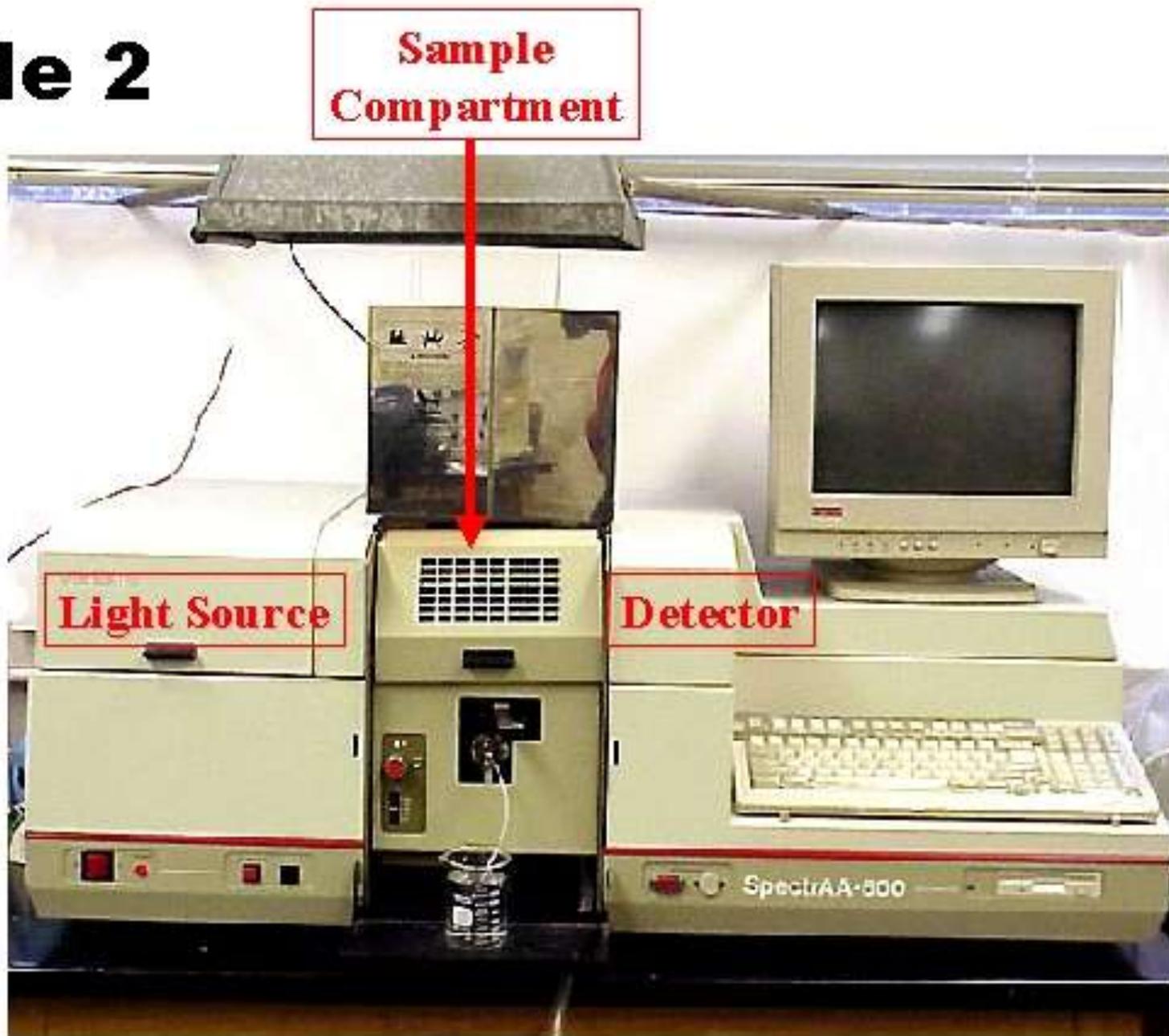
Your sample must be a fluid.

The detection limits are relatively high since only a small portion of your sample is present in the flame at any given time.

Slide 1



Slide 2

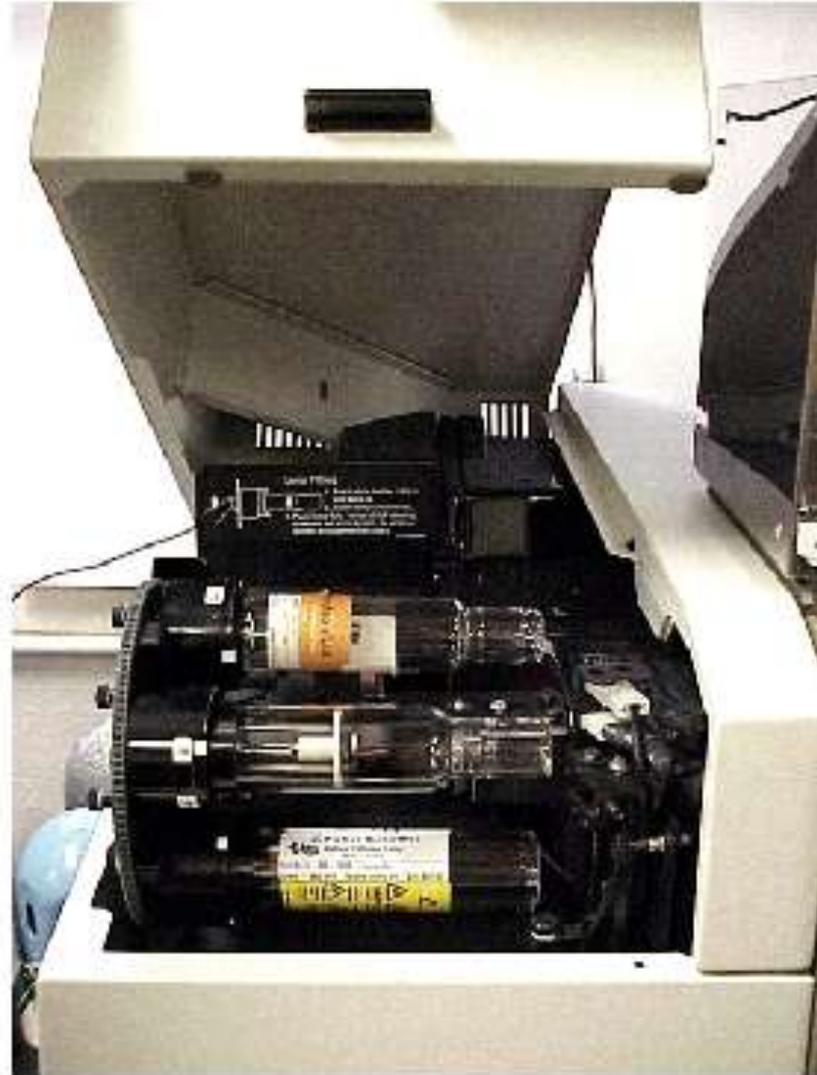


Slide 3

Light Path



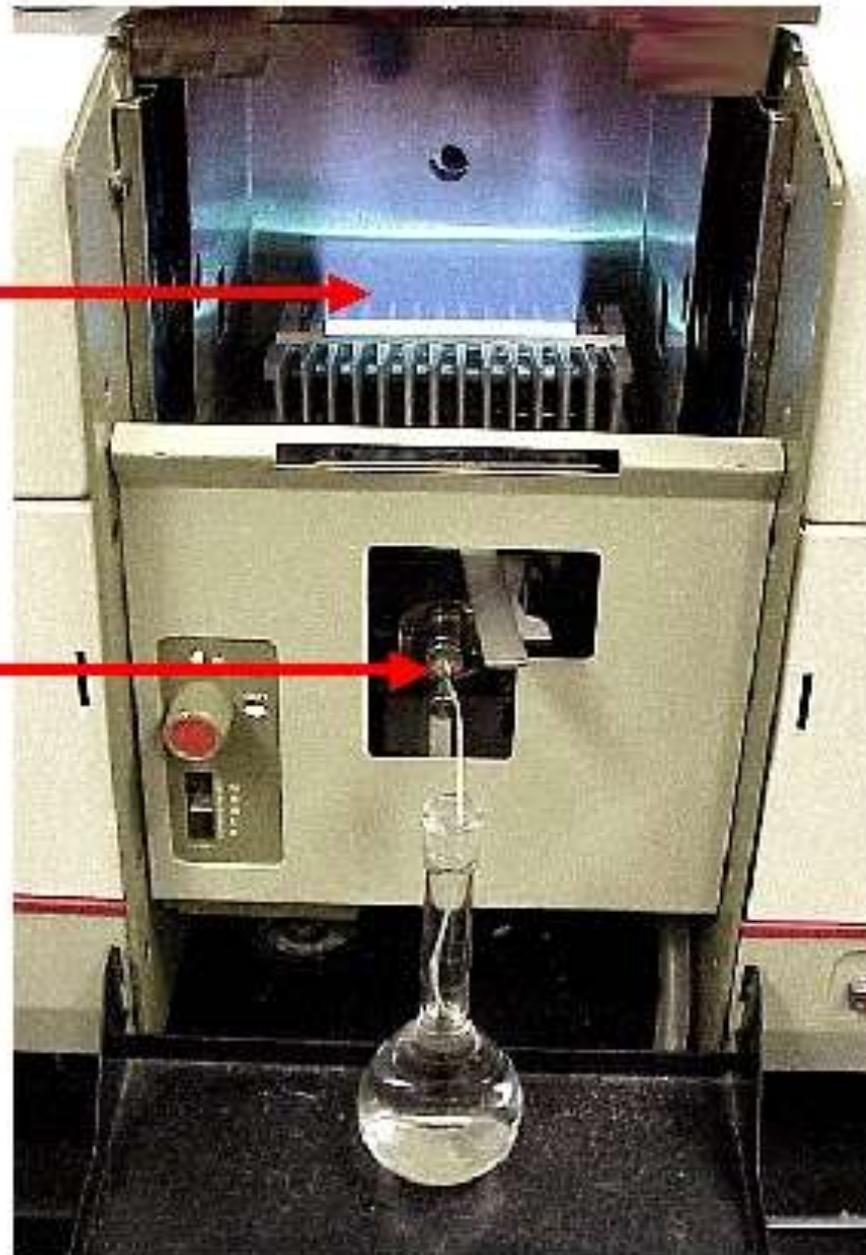
Slide 5



Slide 10

Sample is
vaporized
in the flame.

Aspirator
tube sucks the
sample into the
flame in the
sample
compartment.



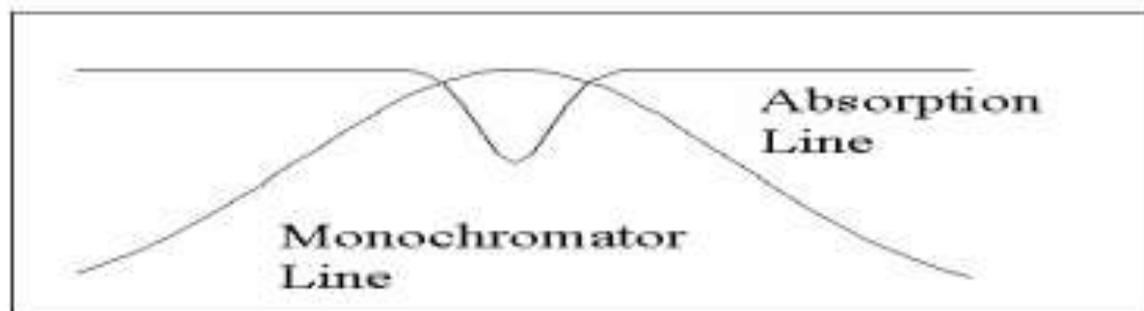
Atomic Absorption Spectrophotometry

Light source used for AA

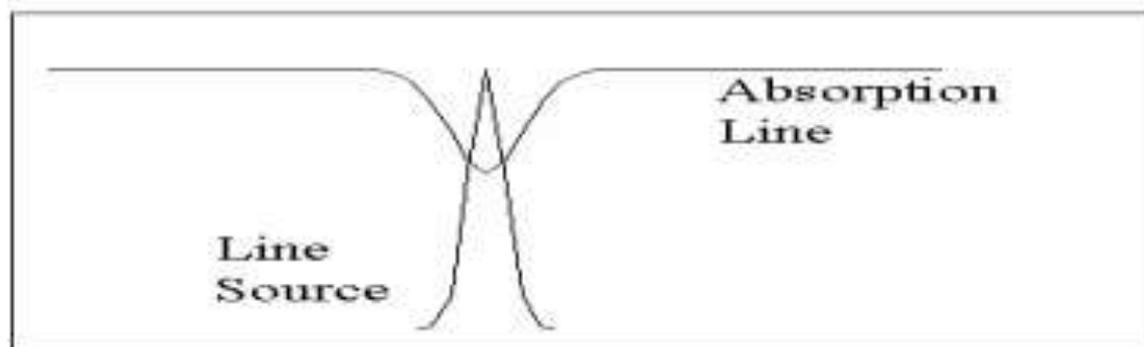
- **What light source do we use with AA?**
- **Would it be a continuous light source or a line light source?**
- **A line light source is used for AA**

Why a line source and not a continuous source?

- Continuous source with monochromator:



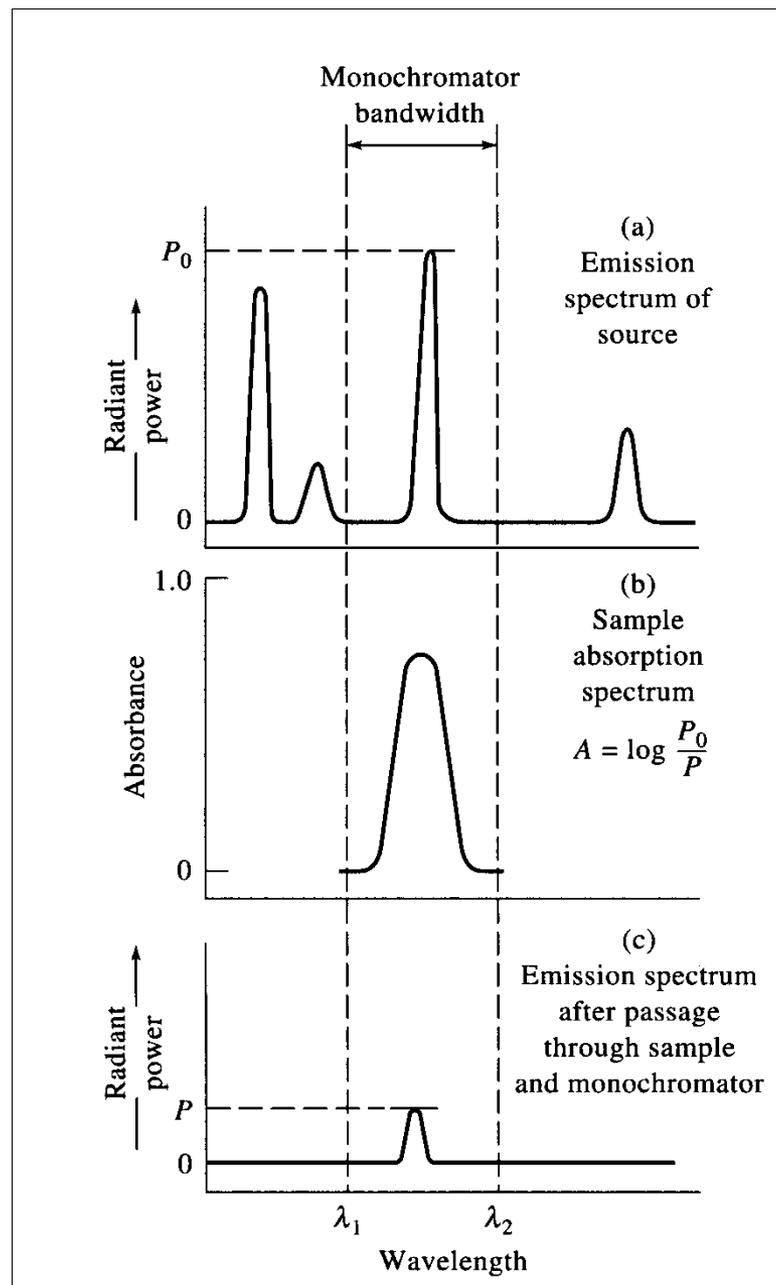
- Line source:



Why a line source and not a continuous source?

- With a monochromator band from a continuous source, the relative amount of incident light absorbed is much smaller. This gives lower sensitivity, and a curved calibration curve.
 - absorption linewidth
 - $\sim 10^{-3}$ nm from both pressure and Doppler broadening
 - monochromator linewidth
 - $\sim 10^{-2}$ nm
 - hollow cathode lamp linewidth
 - $\sim 10^{-4}$ nm

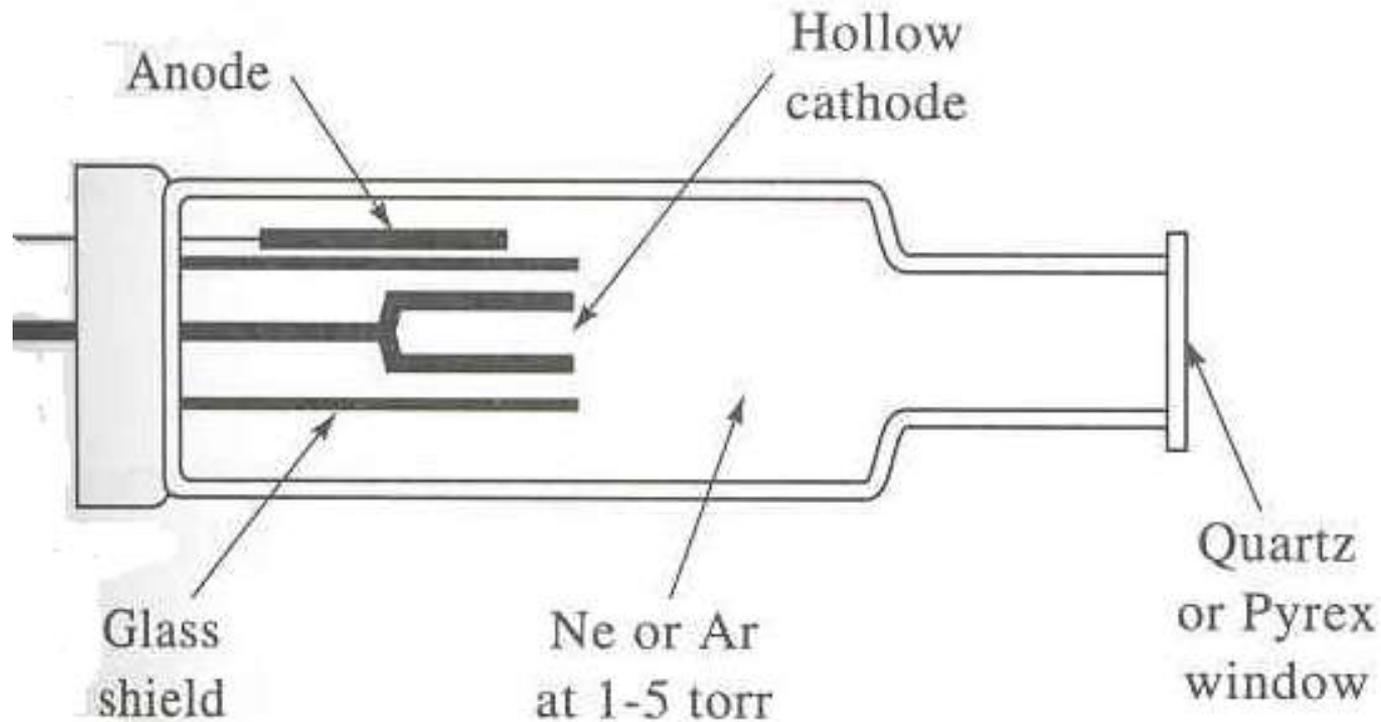
Absorption of resonance line from vapor lamp



Hollow-Cathode Lamp, HCL

- The hollow cathode lamp (HCL) uses a cathode made of the element of interest with a low internal pressure of an inert gas.
- A low electrical current (~ 10 mA) is imposed in such a way that the metal is excited and emits a few spectral lines characteristic of that element (for instance, Cu 324.7 nm and a couple of other lines; Se 196 nm and other lines, etc.).
- The light is emitted directionally through the lamp's window, a window made of a glass transparent in the UV and visible wavelengths.

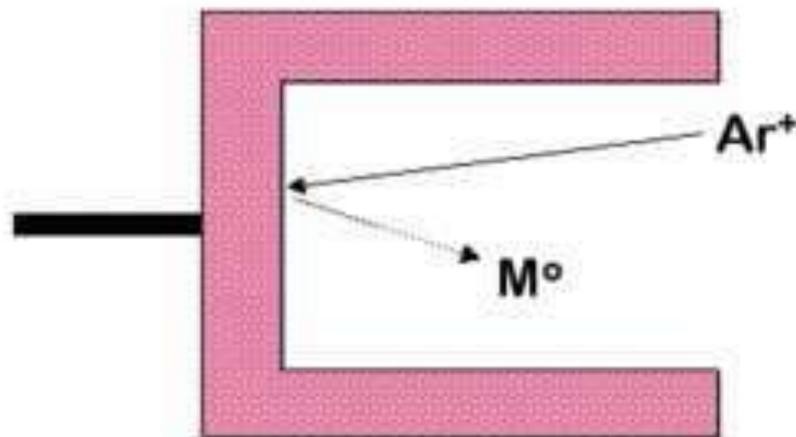
Hollow Cathode Lamp



- **Most common source for AA.**
- **Ionization of inert gas at high potential.**
- **Gaseous cations cause metal atoms at cathode to sputter, emitting characteristic radiation.**

Hollow cathode lamp

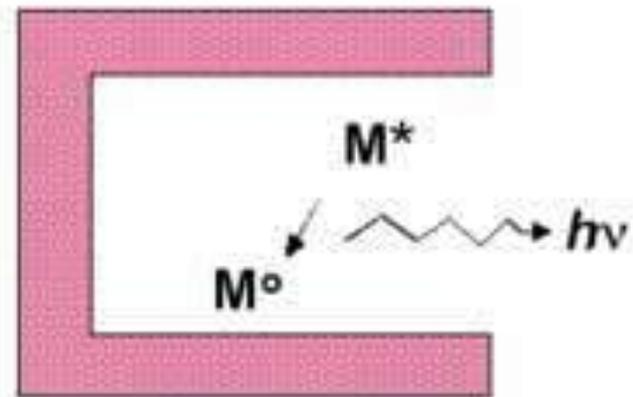
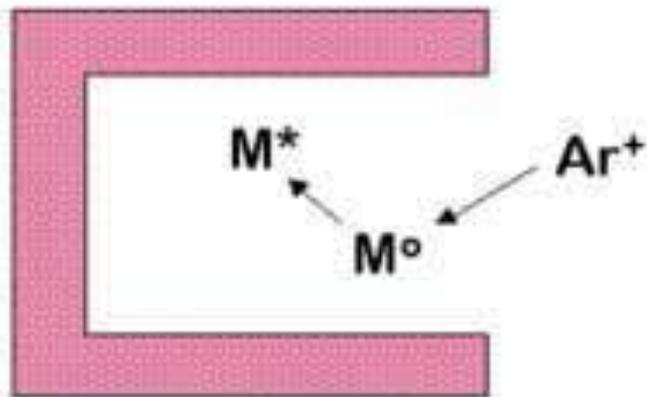
The lamp is filled with an inert gas like argon or neon.
When a potential is applied, it causes the gas to become excited and it is driven towards the cathode.



Metal atoms are then sputtered off the surface of the cathode.

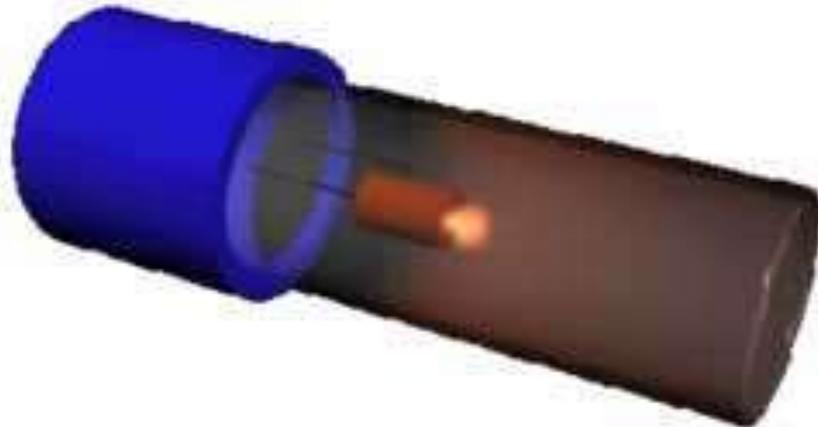
Hollow cathode lamp

Repeated bombardment of the metal atom by the gas causes it to be excited. It ultimately relaxes, producing specific atomic emission lines.



Hollow cathode lamp

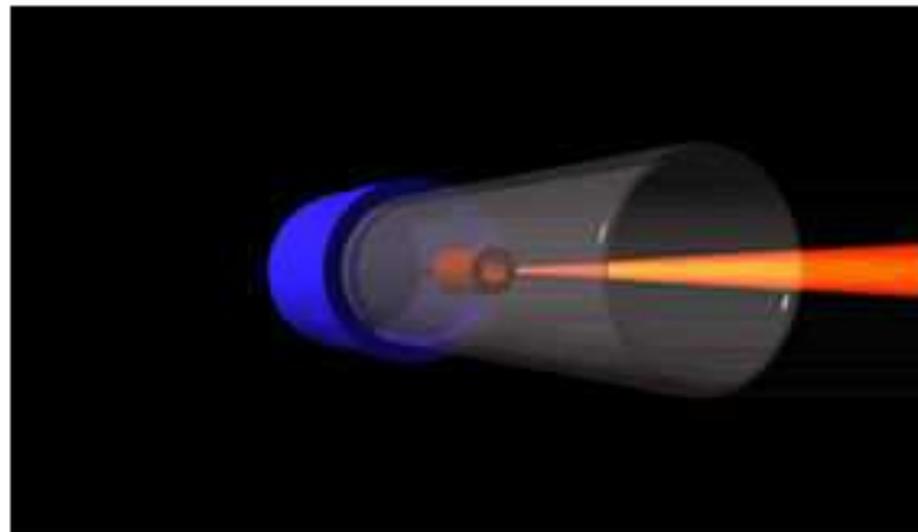
This source produces emission lines specific for the element used to construct the cathode.



The cathode must be capable of conducting a current for it to work.

Hollow cathode lamp

This source produces emission lines specific for the element used to construct the cathode.

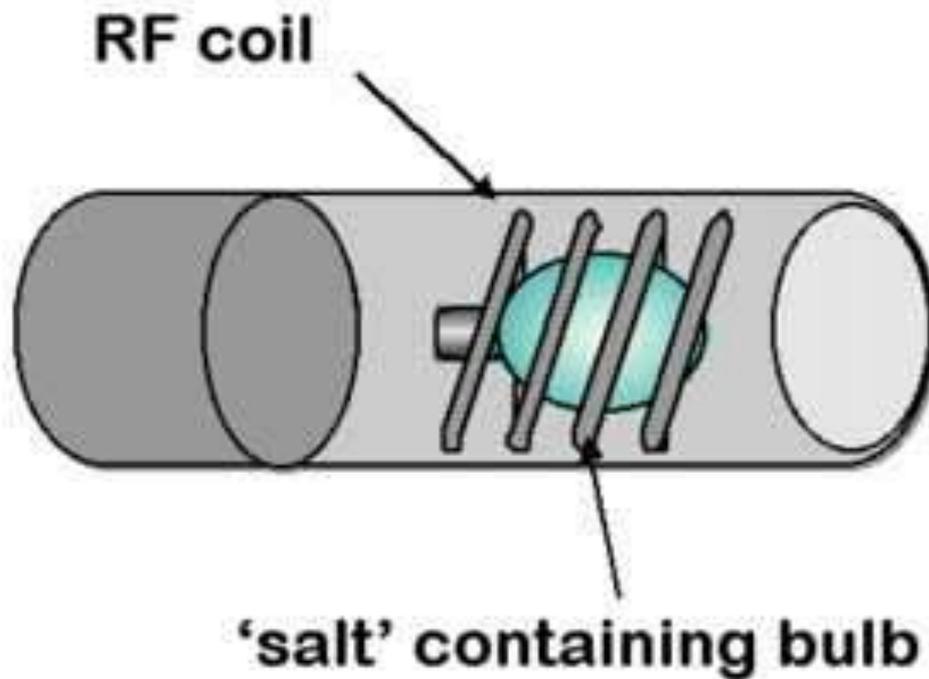


The cathode must be capable of conducting a current.

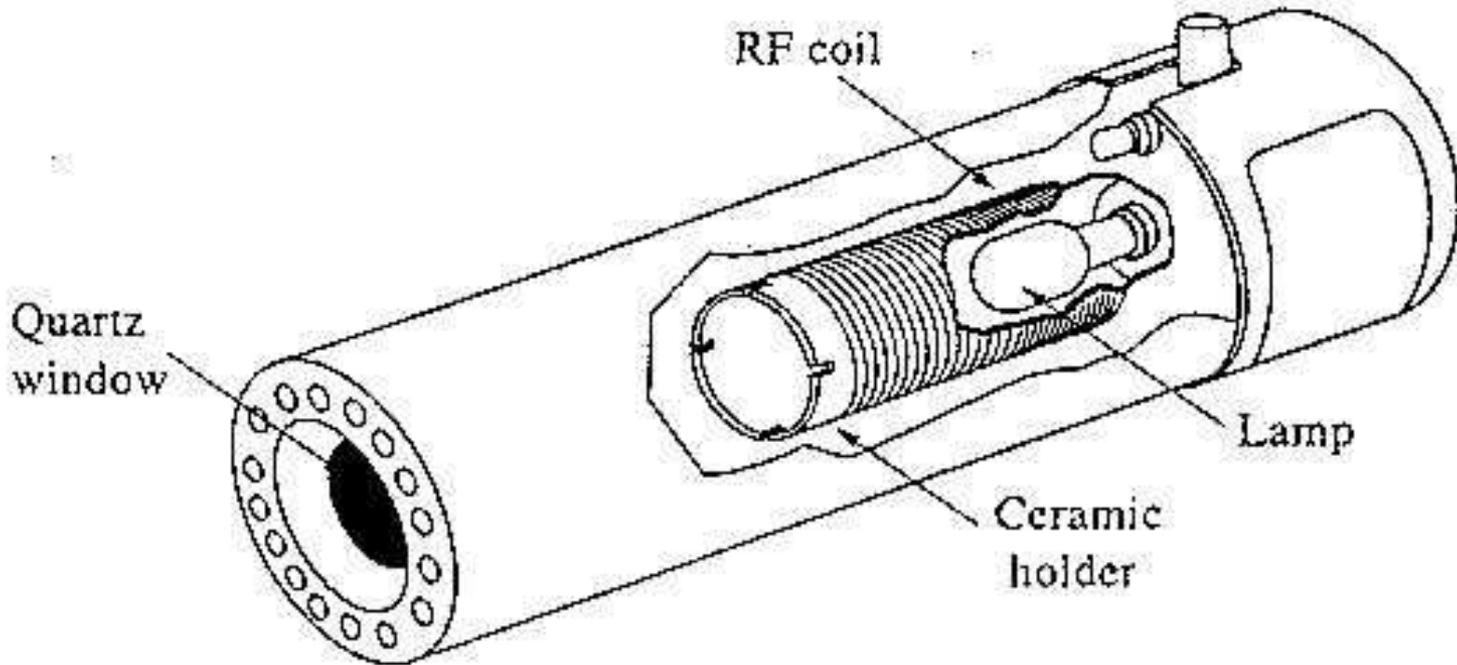
Electrodeless discharge lamps

- A salt containing the metal of interest is sealed in a quartz tube along with an inert gas
- Discharge lamps, such as neon signs, pass an electric current through the inert gas .
- The electrons collide with inert gas atoms, ionizing them and accelerating their cations to collide with the metal atoms which then will be excited and decay to lower levels by emitting electromagnetic radiation with wavelengths characteristic to the element.
- Low-pressure lamps have sharp line emission characteristic of the atoms in the lamp, and high-pressure lamps have broadened lines superimposed on a continuum.
- Common discharge lamps and their wavelength ranges are:
 - hydrogen or deuterium** : 160 - 360 nm
 - mercury** : 253.7 nm, and weaker lines in the near-uv and visible
 - Ne, Ar, Kr, Xe discharge lamps** : many sharp lines throughout the near-uv to near-IR
 - xenon arc** : 300 - 1300 nm
- Deuterium lamps are the Uv source in Uv-Vis absorption spectrophotometers.
- The sharp lines of the mercury and inert gas discharge lamps are useful for wavelength calibration of optical instrumentation. Mercury and xenon arc lamps are used to excite fluorescence.

Electrodeless discharge lamp



Electrodeless Discharge Lamp



- They sometimes provide superior performance to HCL.
- Their useful lifetime is longer than HCL
- They provide light intensity 10-100 times more than that of HCL.
- They are less stable than HCL

Instruments for atomic absorption spectroscopy

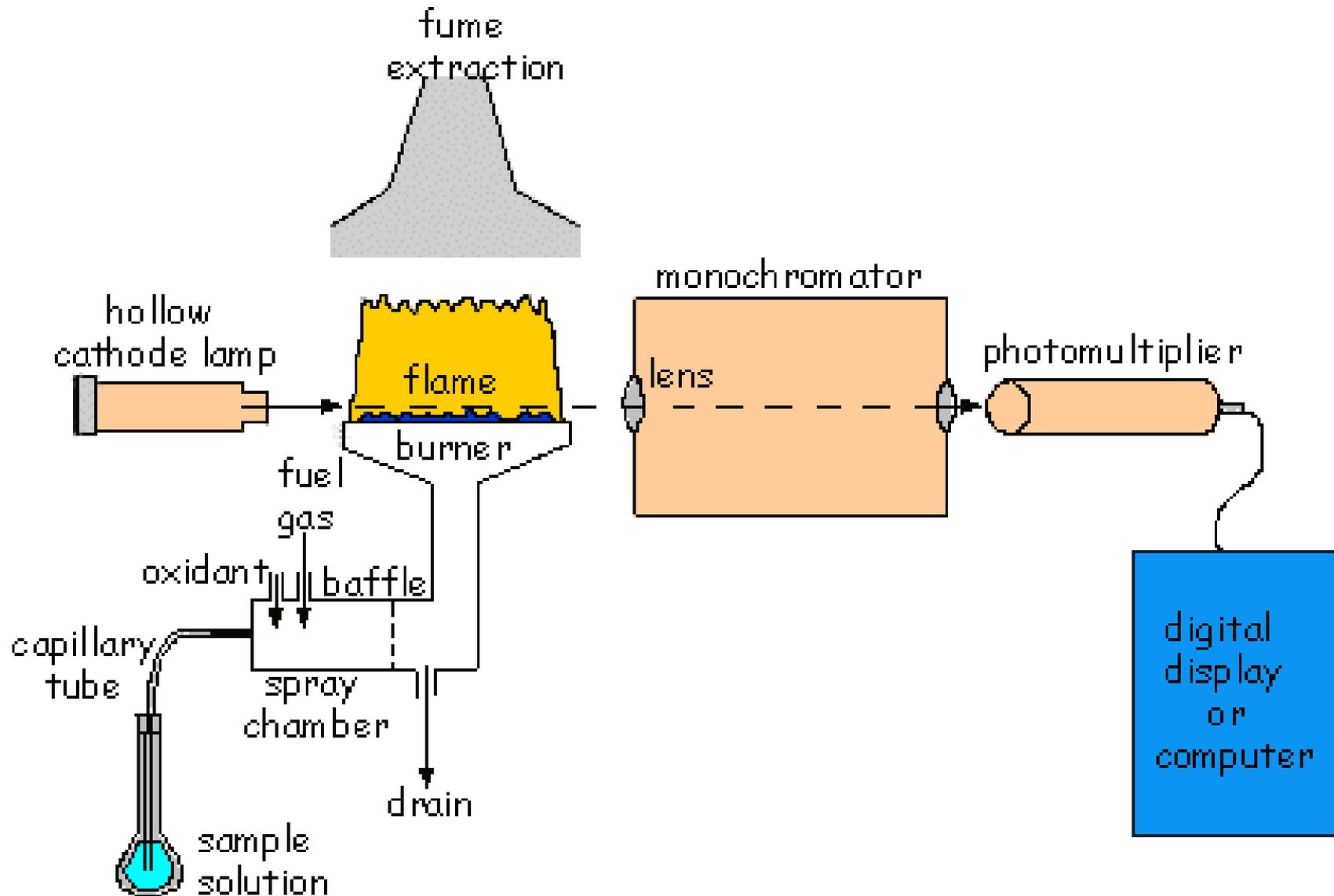
Typical flame spectrophotometers:

(a) single-beam design

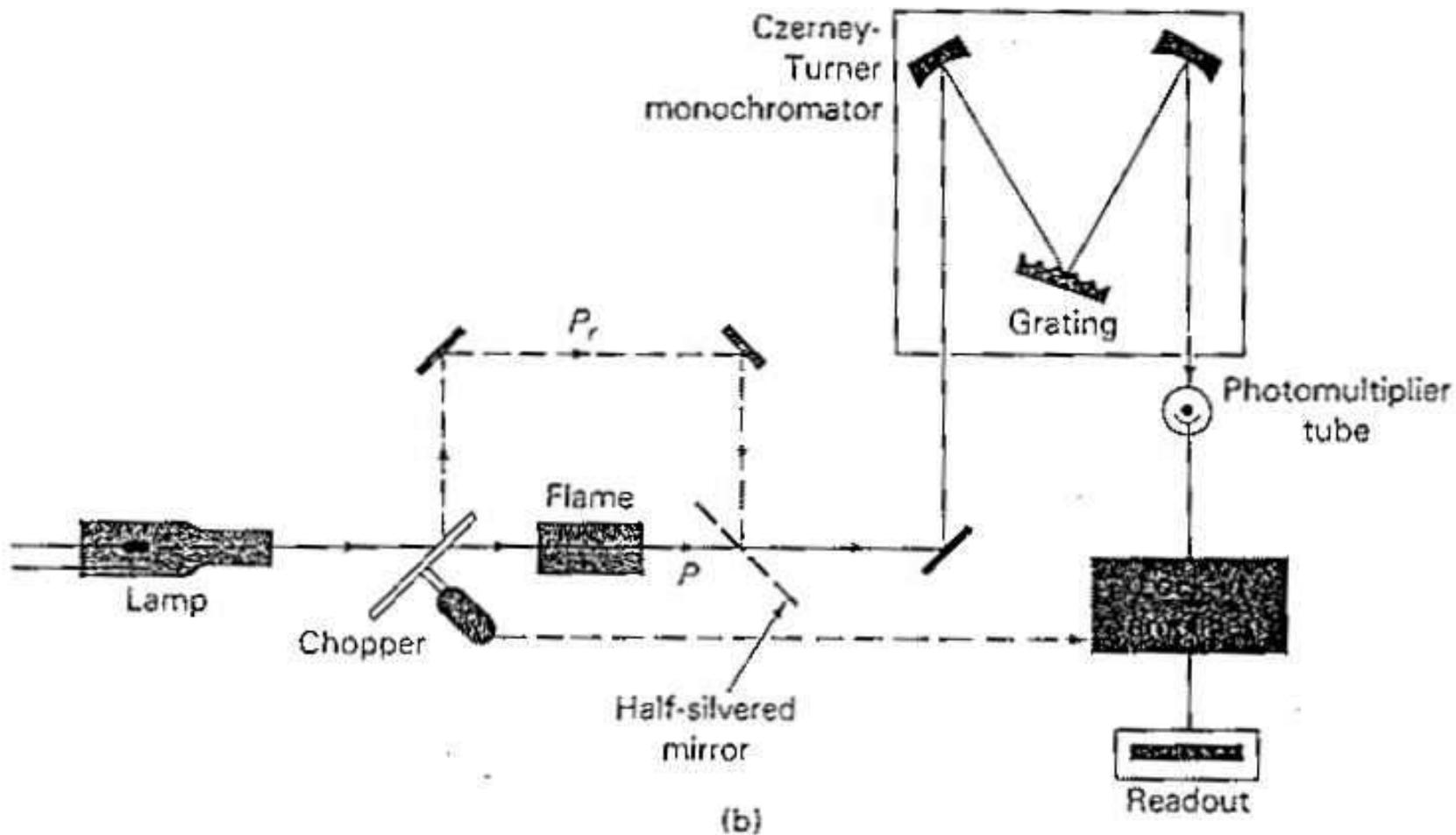
(b) double-beam design."

Flame atomic absorption spectrophotometer

Single beam design



Double Beam Design



Chopper

A chopper is used to provide signal modulation - in conjunction with a lock-in amplifier.

Its not practical to have two separate cells, so the light is simply split, with half being sent around the atomization source.

This reduces some noise from the atomization source and accounts for instrumental variations.

Monochromator

Sample

Source

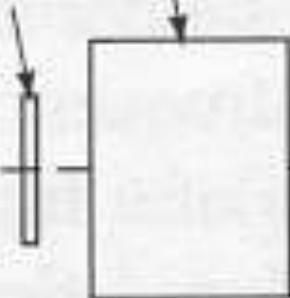
Signal
detector

v_s

V_s

Motor

Chopper



Source

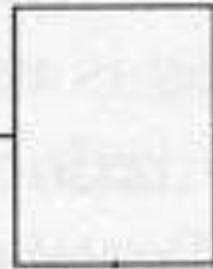
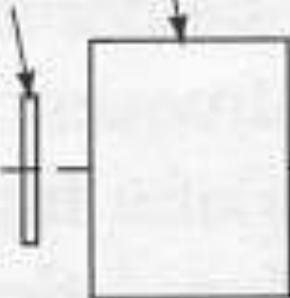
Signal
detector

v_s

V_s

Motor

Chopper



Signal chopping in spectroscopic methods

- **Take atomic absorption spectroscopy as an example, low frequency fluctuations inherent in flames and other atomization sources constitute the majority of noise.**
- **With a mechanical chopper, the signal generated in the transducer is a square-wave electrical signal whose frequency depends upon the size of the slots and the rate of which the chopper rotates.**
- **Noise inherent in flames and other atomization devices is usually of low frequency and can be significantly reduced by the use of high-pass filter prior to amplification of the transduced electric signal.**
- **Finally , a RC filter can be used to smooth the signal and produce an amplified dc output.**

Only noise that arises after chopping is removed, so the chopper should be placed as close to the source as possible

Modulation and demodulation

- Low frequency or dc signals from transducers are often converted to a higher frequencies (by the process of modulation).
- After amplification, the modulated signal can be freed from amplifier $1/f$ noise by filter with a high-pass filter. Demodulation and filtering with a low-pass filter recover the amplified dc

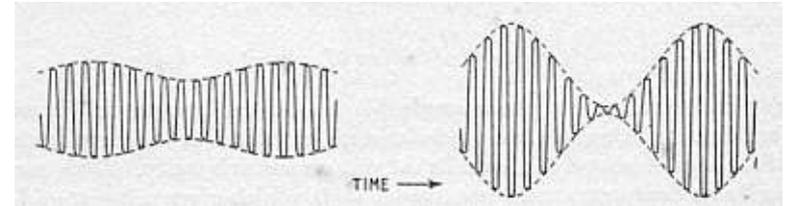


Carrier wave can be a synthesized waveform with a known frequency or an effect created by a mechanical modulator working at a known frequency

Types of Modulation

A. Amplitude modulation (AM)

Source output power to the detector is changed periodically, e.g. with a mechanical chopper.



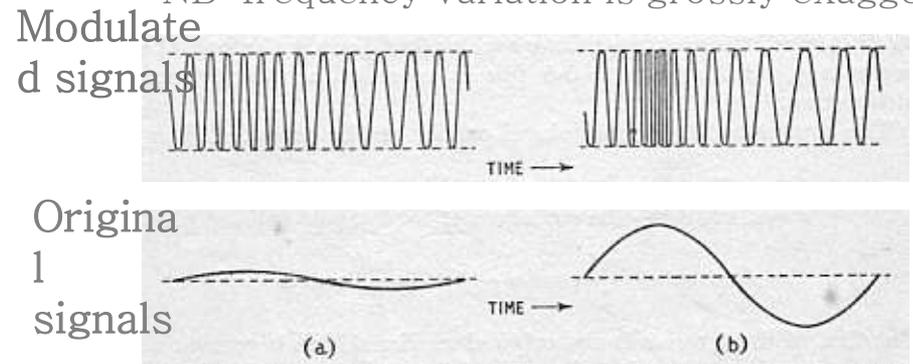
B. Frequency modulation (FM)

Source output frequency to the detector is modulated, i.e. the frequency of the *carrier wave* is swung above and below the unmodulated value at the frequency of the modulating signal. The extent of the frequency swing is proportional to the amplitude of the modulating signal.

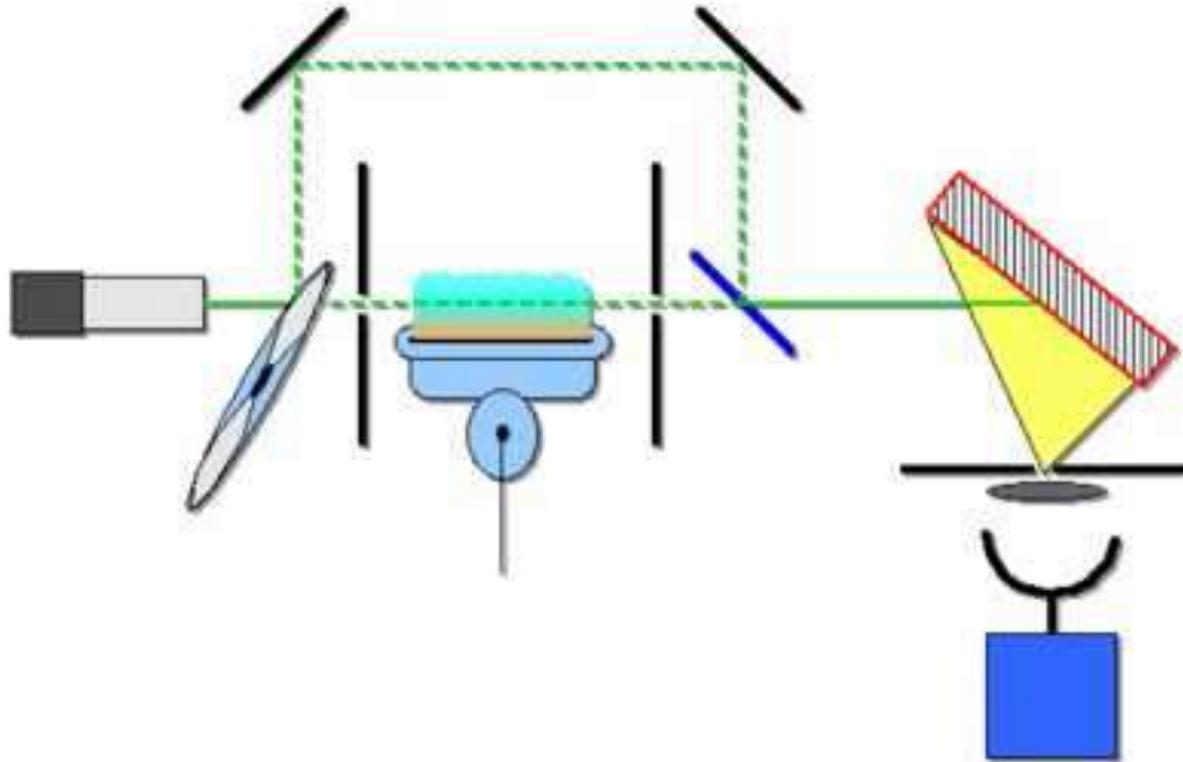
NB: frequency variation is grossly exaggerated

C. Phase modulation (PM)

The phase angle (ϕ) of the *carrier wave* is swung above and below its average of unmodulated value at the frequency of the modulating signal. The extent of the phase swing is proportional to the amplitude of the modulating signal.



Source Signal modulation



Monochromator

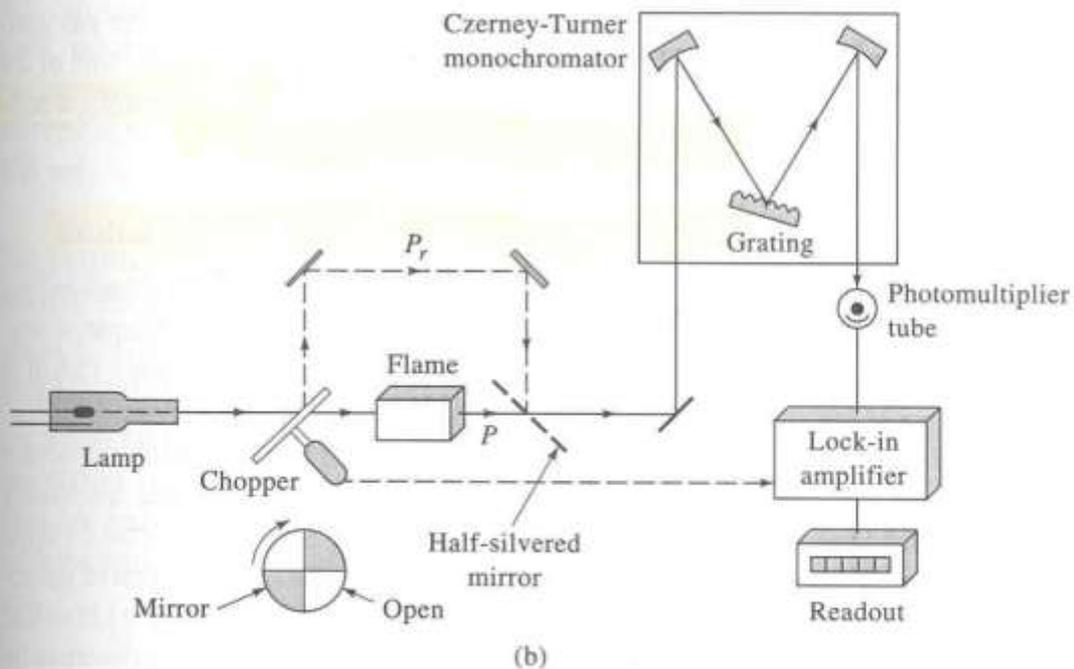
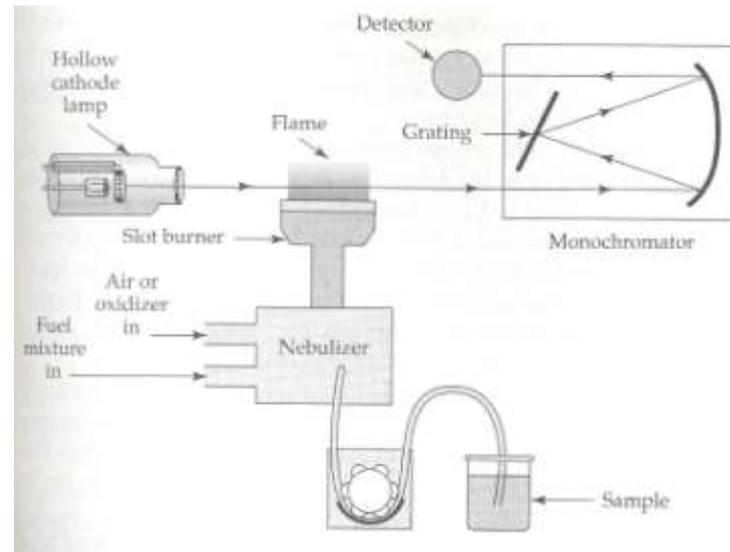
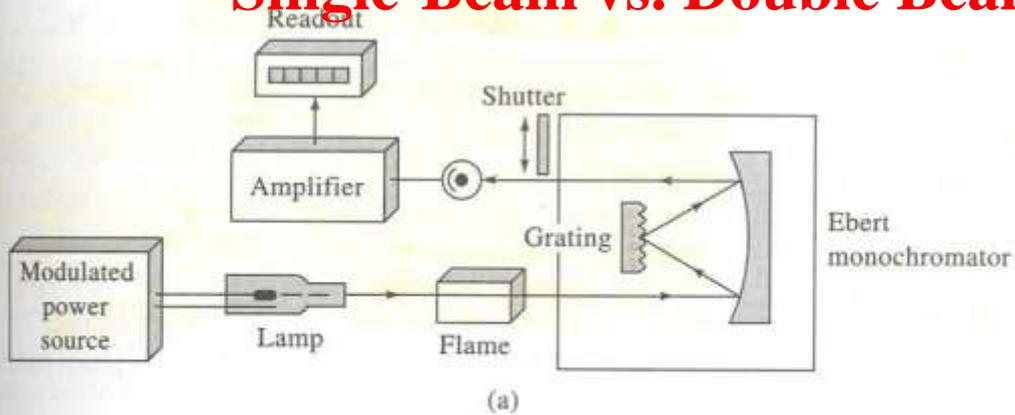
- Usually UV/VIS grating monochromator
- its purpose is to isolate the resonance line of interest
- It separates the spectral line of interest from others
- Usually, spectral lines with different wavelengths are emitted by the hollow-cathode lamp.
- Generally, most of the instruments are equipped with two gratings with the goal to cover a wavelength range from 189 to 851 nm which is used in atomic absorption.
- Use beam chopper to distinguish (only alternating signal is measured) two sources of radiation attenuated beam from lamp and excited atoms from the flame

Detector

Photomultiplier tube (PMT) - converts radiant energy into electrical signal (analog or digital)

Readout device

Single-Beam vs. Double Beam AA Spectrometers



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Source: Rubinson and Rubinson, *Contemporary Instrumental Analysis*, Prentice Hall Publishing.

Interferences in Flame Atomic Absorption Technique

Interferences

- **Interference** is the influence of one or more elements on the signal to be analyzed. This causes an error in determination
- **Interferent** is substance present in the sample, standards, or blank which affects the signal of the analyte
- Interference is termed “**Matrix error**” that is : Effect of complex chemical environment on the element to be determined
- Blank interference (**mostly spectral**)
- Blank signal measured for the sample is different from that measured for standards.
 - It arises due to species present in the sample but not in the standards or vice versa

- **Ideally: N (#atoms in flame) = kC**
- **If k varies with group of measurements, interference occurs.**
- **Interference effect is responsible for:**
 - a decrease in sensitivity
 - lowering the precision
 - causing higher detection limit

Checking interference problem

- **How do we check the presence of an interferent?**
“Carry out a quality control program”
- **Analyze samples of known composition (reference materials) along with the unknowns**
- **Matrix of reference materials should match the sample matrix and both should have similar concentration range of the analyte elements**
- **Quality control experiments will vary with:**
 - **Sample type**
 - **Required precision and accuracy**
 - **Penalty anticipated if errors exceed certain level**

Source of reference materials

- **Reference materials with numerous certified trace elements concentrations are obtained from:**
 - **US national institute of standards & Technology (NBS)**
 - **US environment protection agency**
 - **International atomic energy agency**
 - **Bureau of analyzed samples, ltd, UK**
 - **National research council of Canada**
 - **Several commercial firms: Spex, Alcoa, Dow chemical, Jhonson ,etc.**

How do we solve the interference problem?

- **Follow the literature solution for similar cases**
- **Match the matrix in the unknown, standards and blank**
- **Add an excess amount of the interferent species to unknown, standards and blank**
- **Use the external standard addition technique or internal standard addition technique**
- **Remove the interferent chemically before analysis**

Interferences in flame atomic absorption

1. Chemical:

Due to the formation of a compound which cannot be decomposed in the flame. The results will always be low.

a. General rule for suspecting chemical interferences

A chemical interference may exist if analyzing a polyvalent cation in the presence of a polyvalent oxyanion or or fluoride containing substance.

b. Note the possibility of amphoteric element acting as polyvalent anion, e.g., aluminum, silicon, boron, chromium, iron, vanadium, molybdenum, etc.

2. Physical:

Variations in viscosity or surface tension between samples and standards. Unequal rates of delivery of material to flame.

3. Ionization:

Caused by ion formation in the flame. Lack of recognition and control of this problem can produce either positive or negative errors in an analysis. This effect is responsible for anomalous curvature in the calibration curve

- a. All of the alkali metals show this interference in the acetylene-air flame.
- b. Most elements show this interference in the acetylene-nitrous oxide flame.

4. Background Absorption or Scatter:

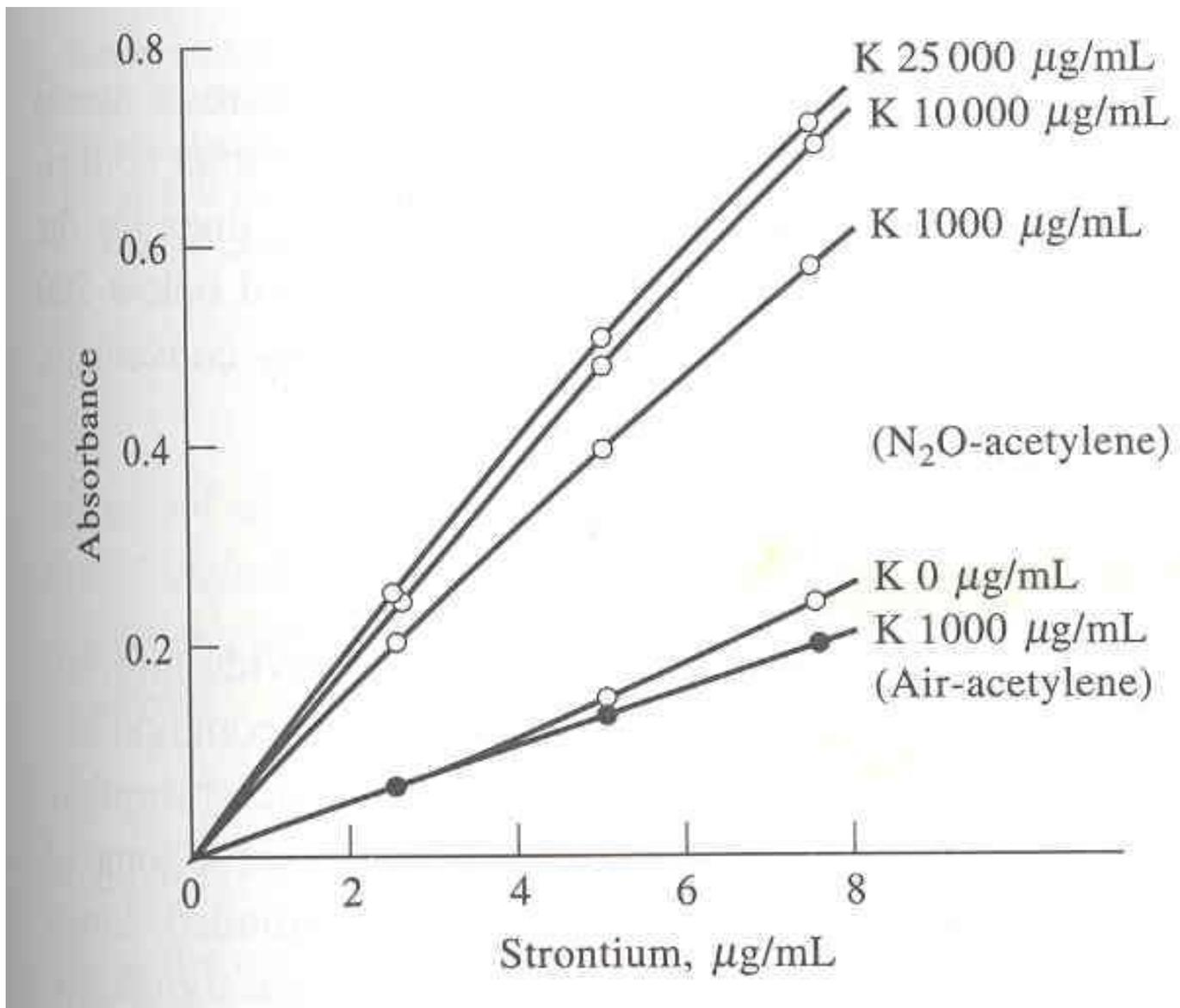
Caused by molecular absorption at resonance wavelength or by light scatter due to very small, unvolatilized particles in the flame. This phenomenon is wavelength dependent (greater at short wavelength) and always gives a positive error in the analysis.

Interference due to ionization equilibria

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.



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

5. Spectral Interferences

Spectral interferences arise when the absorption or emission of an interfering species either overlaps or lies so close to the analyte absorption or emission that resolution by the monochromater becomes impossible.

Remedy for Interferences

- **Chemical Interferences** - Use of a releasing or protecting agent
 - a. Tie up the interference chemically. Add between 0.1 and 0.2% lanthanum chloride to samples and standards.
 - b. Tie up the element to be analyzed with EDTA. This reaction is pH dependent so not as frequently used as lanthanum chloride.

Note:

- High purity La_2O_3 or LaCl_3 , specified for AA must be used.
- EDTA should be recrystallized from acid several times before use.
 - c. Use the acetylene-nitrous oxide flame. Few chemical interferences are ever found in this flame.
 - d. Isolate the element to be analyzed by extraction, precipitation, or volatilization from the interfering agent.

- **Physical Interferences**

- a. Dilution of samples and standards with a common solvent, commonly used for oil analysis.
- b. Calibration by the method of standard additions.

- **Ionization Interference**

Use of an ionization suppressor. Add Between 0.1 and 0.2% of an alkali metal salt to all samples and standards.

- **Background Interference**

- a. Deuterium arc background correction (continuum source).
- b. Non-absorbing line (or two-line) method.

Electrothermal atomization
Flameless atomization
Graphite furnace atomization

Samples are placed in a carbon tube which is heated electrically - graphite furnace

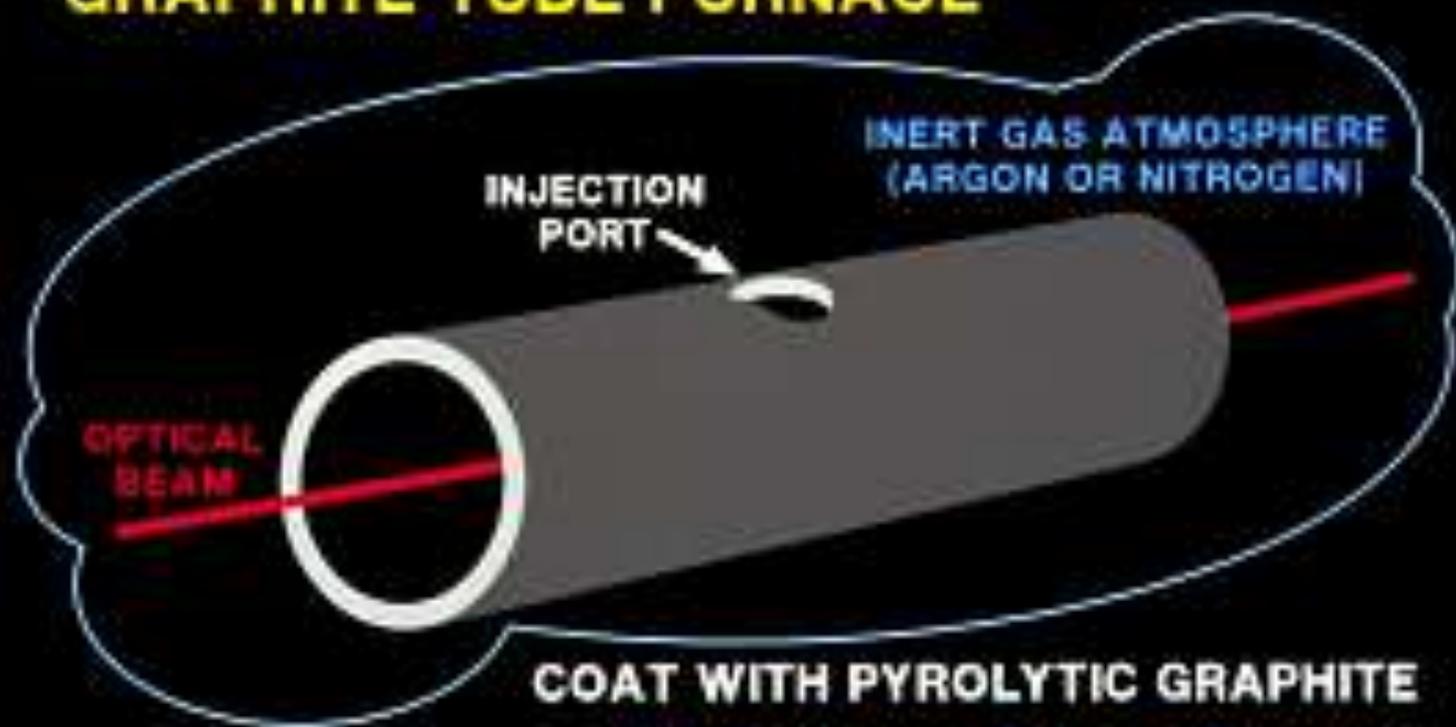
Sample residence time is greater so you have improved detection limits and sensitivity.

Solid samples can also be assayed.

Electrothermal atomization
Flameless atomization
Graphite furnace atomization

- ◆ **Samples are placed in carbon tubes which is heated electrically (graphite furnace)**
- ◆ **A technique to minimize dilution during atomization of the analyte prior to its determination with atomic absorption spectrometry**
- ◆ **A technique with more interferences than the more reliable flame atomization**
- ◆ **A technique with high sensitivity and very good detectability but not so good throughput and precision**

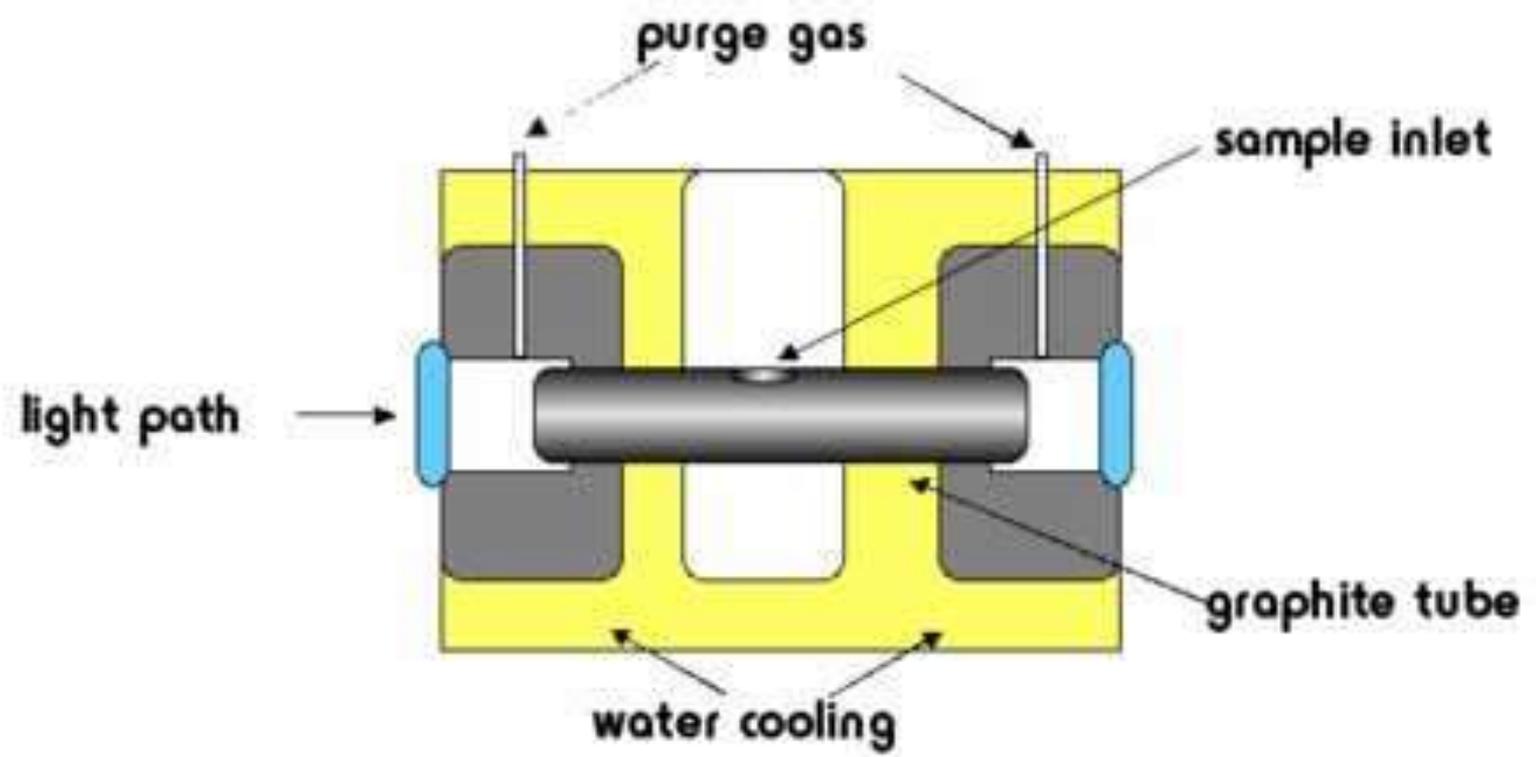
GRAPHITE TUBE FURNACE



COAT WITH PYROLYTIC GRAPHITE

- MINIMIZES CARBIDE FORMATION
- PROLONGS TUBE LIFE

Flameless atomization





Advantages of GFA

- Increase in the **residence time** thus more sensitivity will be obtained
- Possibility of analyzing samples of **various matrices**
- Analyzing **small size** samples even on the microliter scale
- Avoiding the formation of **refractory oxides** that cause serious interference sources

Why do we use an inert gas with Flameless atomization?

Argon is often used as a purge gas to:

Remove excess material during the dry and char phases and after atomization

Reduce oxidation of the tube.

Provides a protective blanket during atomization since high temperature carbon will react with nitrogen to produce cyanogen - you should always vent to a hood anyway.

Atomization Process

You can't simply heat your sample to atomization temperatures or the sample will splatter.

We use a temperature program to ensure reproducible atomization.

A three stage program is the most common.

Steps in graphite furnace atomization

- **The steps of a GF atomization**
- **5-100 μ l sample**
 - **drying**
 - **ashing**
 - **atomization**
 - **burnout**
 - **cool**

Steps in GF atomization

- The sample introduction
 - The sample is injected, usually between **5-30 μ l** but sometimes the range could be extended to **100 μ l**.
 - The solution is preferably made up of dilute nitric acid as matrix
 - sometimes solid samples are introduced

- **The drying step**

- to volatilize the sample solvent

- use some degrees above the solvents boiling point (for water use 110°C) and about the same time in seconds as the injected volume in μl

- **Ashing of the sample**
 - May be the most important step
 - **Remove** sample **matrix** without losing the analyte
 - Highly dependent on both the **analyte and sample matrix**
 - Conditions for every new sample type should be optimized
 - Inorganic matrix more difficult, because higher temperatures are needed
 - Temp may be in the range 200-500°C
 - Drying and ashing may take about 30-90 sec.

- **The atomization step**
 - Temp is in the range of 2000 to 3000 °C
 - It takes 3-5 sec.
 - This step is to vaporize and atomize the analyte
 - the vaporization pressure of the analyte dominate the supply of analyte atoms inside the tube
 - rapid heating is necessary for good sensitivity

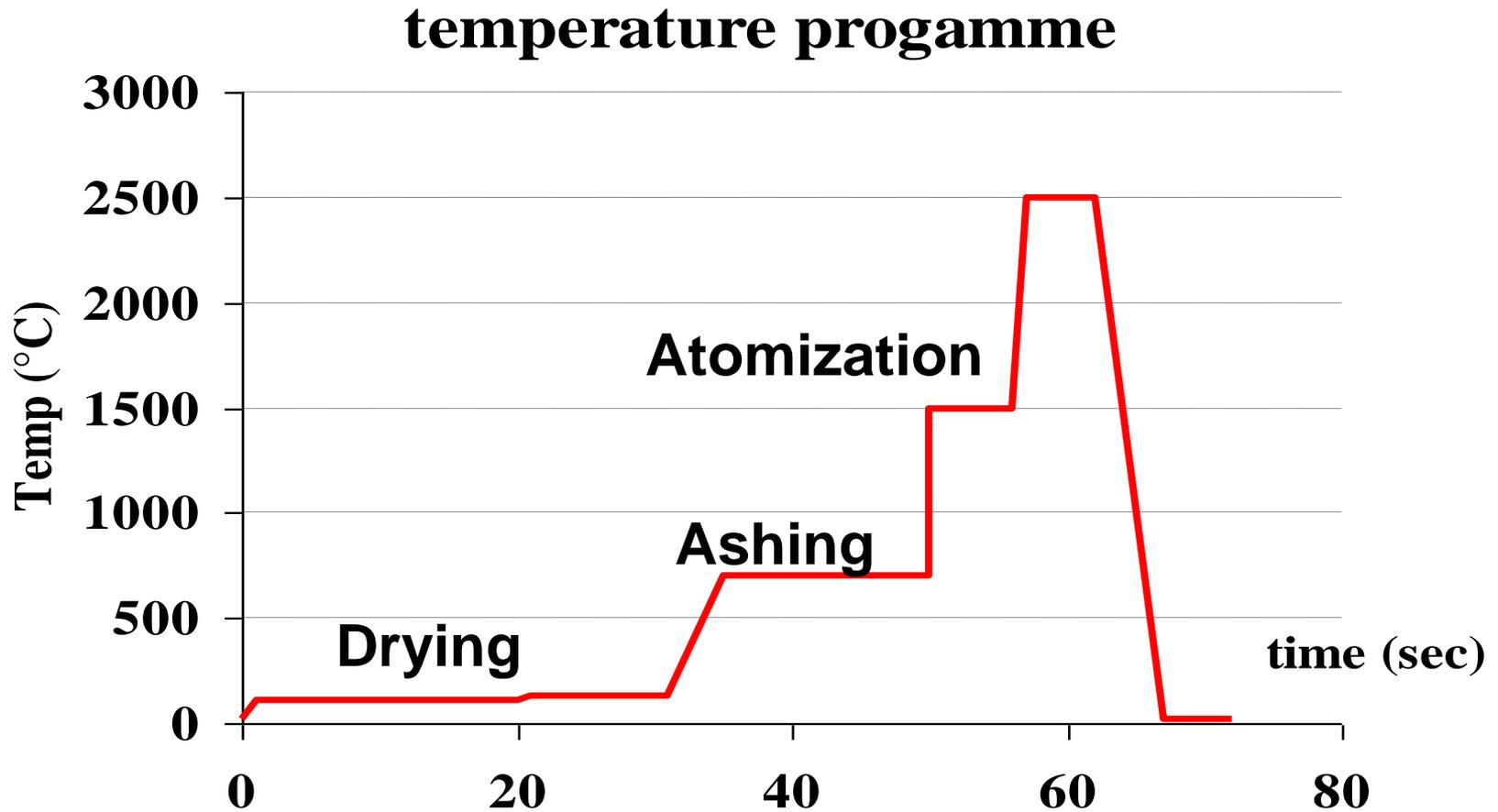
- **The burnout step**

- it is used for taking away parts of the sample not completely volatilized during atomization
- temperatures in the range 2700-3000°C is most often used
- if vaporization of the sample is achieved, completely, the sensitivity will slowly decrease and the imprecision increase

- **Cooling step**

- its purpose is to cool down the furnace before next sample is added

Steps in GF atomization



Interferences with graphite furnace and its control

- **In the early days this technique was accepted as a highly interference technique**
- **Later, new instrumental and analytical procedures were developed which avoided the conditions found to be the source of interference problems**

Interferences in GFAAS

- The graphite furnace atomization technique is much more affected by interferences than the flame which depends on higher concentrations of non-analytes
 - physical**
 - change in surface properties of the graphite tube influences the atomization rate
 - Spectral**
 - molecular absorption by molecules or atoms other than the analyte atoms
 - light scattering
 - non spectral or chemical**
 - molecular binding between analyte and matrix
 - formation of less volatile compound
 - reactions with the graphite tube

Interference removal

Spectral interferences

- **Emission interference**
- **Non-analyte absorption and scattering**

1. Emission interference

- Radiation emitted by the hot graphite tube or platform that covers a wide range of wavelengths (250-800 nm)
- Following elements will be obscured:
 - Zn 213.9 nm; **might be ok**
 - Cr 357.9 nm
 - Ca 422.7 nm
 - Ba 553.7 nm mostly affected
- **This effect is eliminated by removing the graphite tube wall or platform from the view of the detector. This is achieved by one of the following arrangements:**

- Setting a **narrow** monochromator slit
- Furnace alignment
- Cleaning graphite tube and windows to prevent light scattering
- Atomization temperature should not be higher than required

2. Non-analyte absorption and scattering

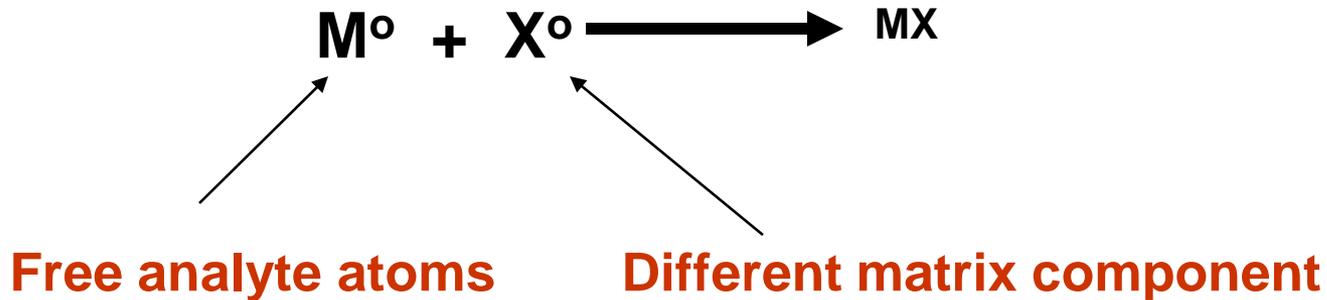
- It is considered as a background absorption
- It is the most severe spectral interference problem
- It occurs as a non specific attenuation of light at the analyte wavelength due to matrix components in the sample
- It leads to having a broad band covering 10-100's nm due to molecular absorption caused by “undissociated sample matrix” components in the light path at atomization

Remedy?

- Matrix modification
- Furnace control procedures
- Background correction as with flame techniques

Chemical Interference

- It occurs when other components of the sample matrix inhibit the formation of free analyte atoms



Interference Removal

1. Ashing with the optimal temperature

– **matrix modification** (mentioned above)

- **Delay of analyte release to furnace allows time for a constant furnace temperature**
- **thermal stabilization of analyte (to hold the analyte on the graphite surface to a higher temperature) and vaporization of interference during the ashing step**
 - Thus, volatility of interfering matrix compound is increased
- **On the other hand volatility of interfering compound is decreased and selective vaporization during the atomization step takes place**

2. Use of pyrolytically coated Tubes and Platforms

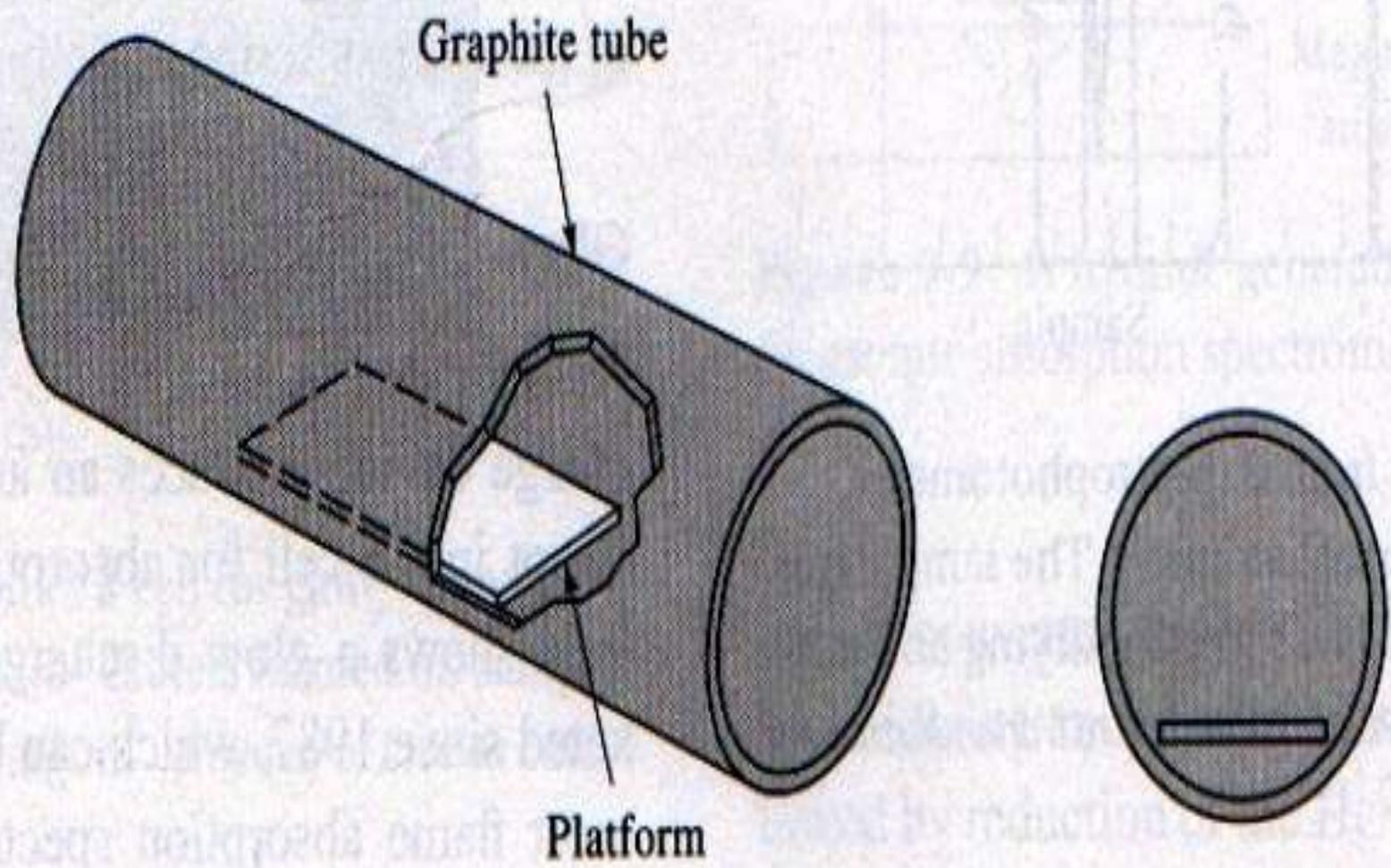
- Ordinary graphite has a **porous surface** thus it forms with the analyte a **carbide that is nonvolatile**
- The tubes are more or less always fabricated from pyrolytic carbon or covered with a **pyrolytic carbon layer**. It's a **more inert** form of the graphite. It is more dense surface and **less absorption**
- Tubes could sometimes be coated with **tungsten or tantalum** for prolonged lifetime or other special applications
- The **platform technique** is used to vaporize the analyte into a **more uniform** and **higher temperature** than the release from the wall. **The analyte vaporizes after the tube wall and gas phase reach a steady state**



Tubes and Platforms

- The tubes are more or less always fabricated from pyrolytic carbon or covered with a pyrolytic carbon layer. It's a more inert form of the graphite.
- Tubes could sometimes be coated with tungsten or tantalum for prolonged lifetime or other special applications
- The platform technique is used to vaporize the analyte into a more uniform and higher temperature than the release from a wall will give.

- **L'vov Platform - Tray inserted into tube with flat trough**
 - **L'vov barely contacts sides of tube**
- **Heated more uniformly by air**



Functions of the platform

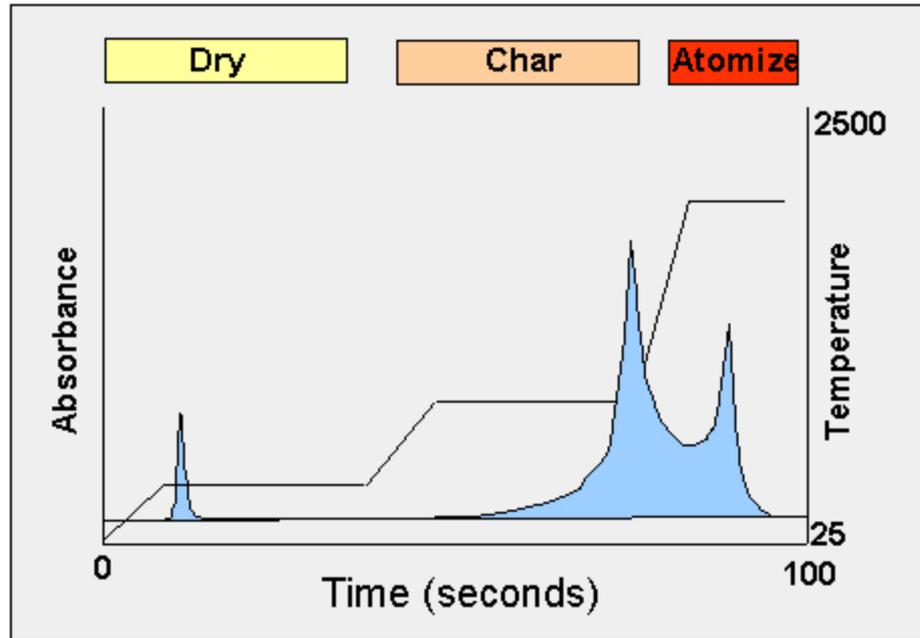
- **It resists tendency for sample to soak into surface before or during drying**
- **It tolerates high acid concentration**
- **It gives bigger signal and less background**
 - **It is heated gradually by radiation from walls**
 - **When atomization step is reached the temperature of the sample and furnace environment will be similar**
 - **No chance for sudden cooling and recombination forming molecular species inhibiting atomization**

Matrix Modifiers

- **Thermal stabilization of analyte**
 - Ni(NO₃)₂ or Mg salt to keep Se or As (highly volatile components) and make it possible to increase ashing temperature (800°) without loss of Se or As
- **Increased volatility of interfering compound**
 - ammonium-sulfate or ammonium-nitrate to increase volatility of chloride
 - $$\text{NaCl} + \text{NH}_4\text{NO}_3 \rightarrow \text{NaNO}_3(\text{s}) + \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$$

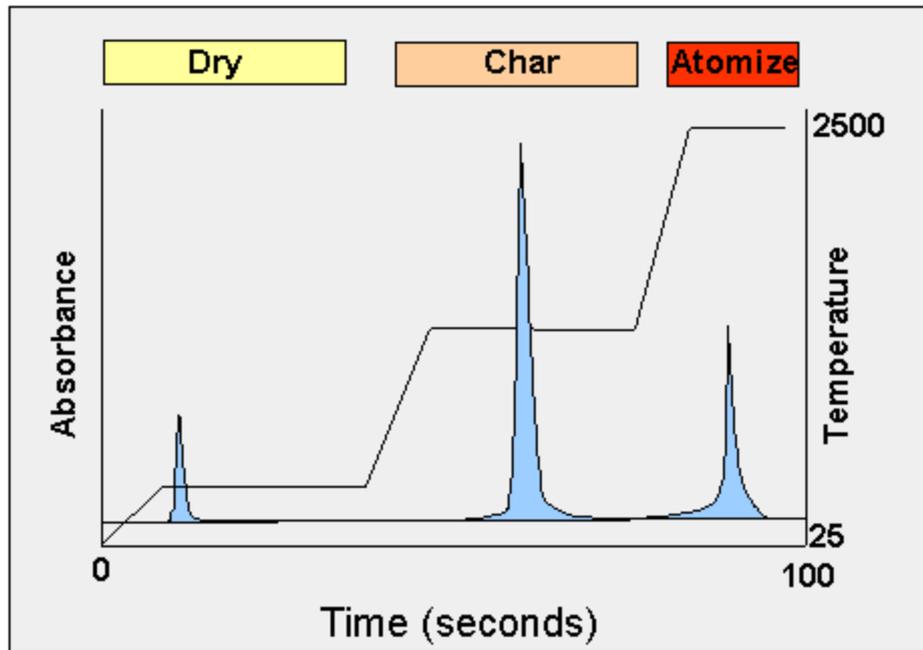
(non-volatile matrix) (Modifier) (More volatile components)
- **Decreased volatility of interfering compound**
 - La to make sulfate stable and not interfere with arsenic

**Effects of Matrix Modifier on analyte with low atomization temp.
No matrix modifier - molecular interference**



analyte atomizes at a temp. so low it doesn't separate from char components

- **Adding matrix modifier allows raising of char and atomizer temps.**



Temporal separation of analyte and interfering molecules

- **Converting the analyte element into a less volatile (if it is too volatile) component using a modifier e.g., Ni (NO₃)₂ for Se determination.**
- **Se is a highly volatile component**
- **With the modifier Se form nickel selenide. Thus, Se can be heated up to 900 °C without loss. Consequently the matrix would be removed without affecting Se.**

Disadvantages of Graphite Furnace

- Prone to interferences, poor precision
- Must take Step to control Precision:
 1. Autosamplers vs. Manual Injection - more precise
 2. Duplicate analyses for all samples (repeat if poor agreement)
 3. Standard addition method - making standards up in sample
 4. Background correction for Molecular Absorption)
 1. D_2
 2. Zeeman Background Correction
 3. Matrix Modifiers to control atomization

Background and Background Correction

Background correction

- **continuously deuterium lamp**
- **Zeeman**
- **Smith Hieftje or the source self reversal method**

What is a background?

- It is the signal observed when the **element sought is absent**
- The light at a specific wavelength (Analyte wavelength) is attenuated by the effect of **flame components** or **matrix components** in the sample
- Thus measured **absorbance** and analyte concentrations are **too high**
- If problem from flame, **blank aspiration will correct for it**
- It is more serious at short wavelengths (< 430 nm) and with graphite furnace

Sources of Background in atomic absorption

- 1. Absorption by flame itself (Serious at λ below 220 nm; e.g., As, Se, Zn)**
 - Water blank can compensate for this flame absorption**
 - In flame absorption, background interference is insignificant at $\lambda > 230$ nm**

- 2. Absorption by concomitant molecular species originating from the matrix like NaX or solvents containing X (halogen) like CCl₄.**
 - **Halides absorb at $\lambda < 300$ nm**

- 3. Scattering of radiation from the particulate material in the flame**
 - **Particulate material: Unevaporated droplets; unevaporated refractory salt particles**
 - **Scattering is more serious at short λ**
 - **2 and 3 are most common with electrothermal atomizer**

Specific Applications Require background correction

- 1. Graphite furnace**
- 2. Flame determination of low concentrations of an element in the presence of high concentrations of dissolved salts**
- 3. Flame analysis where sample matrix may show molecular absorption at λ of the resonance line**
- 4. Flame determination of an element at λ where flame absorption is high**

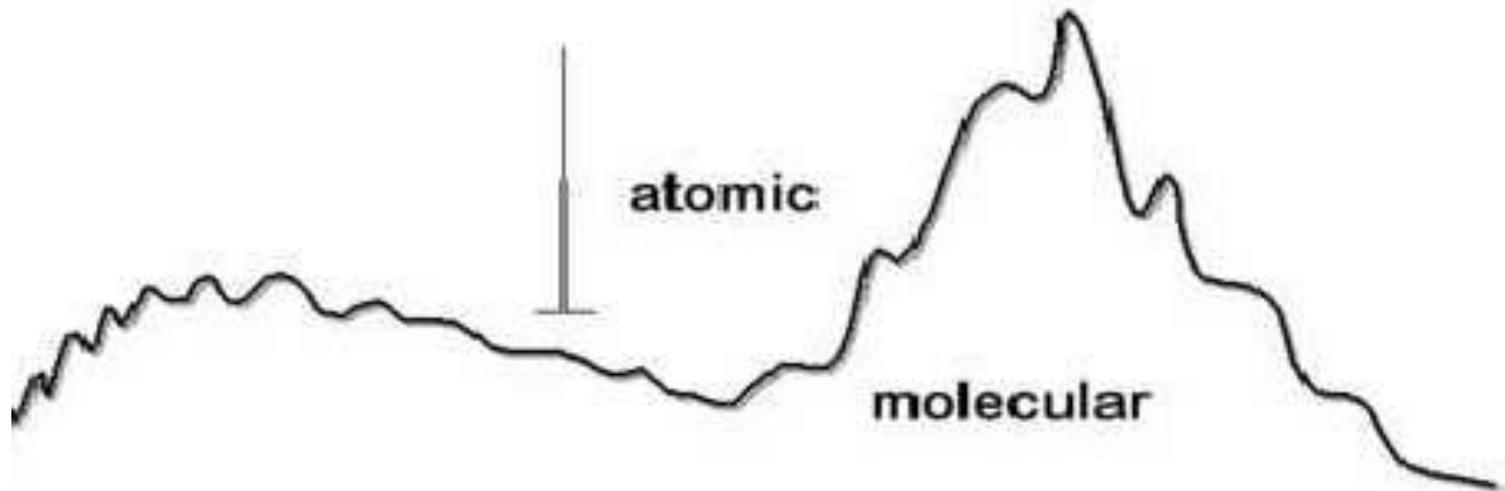
Background correction methods

1. Using a blank

- **Measure the absorbance of the metal resonance line by both flame & blank (flame system)**
- **Measure the absorbance of the metal resonance line by sample and flame system (flame + blank)**
- **A is the difference**

The main two methods used for background correction:

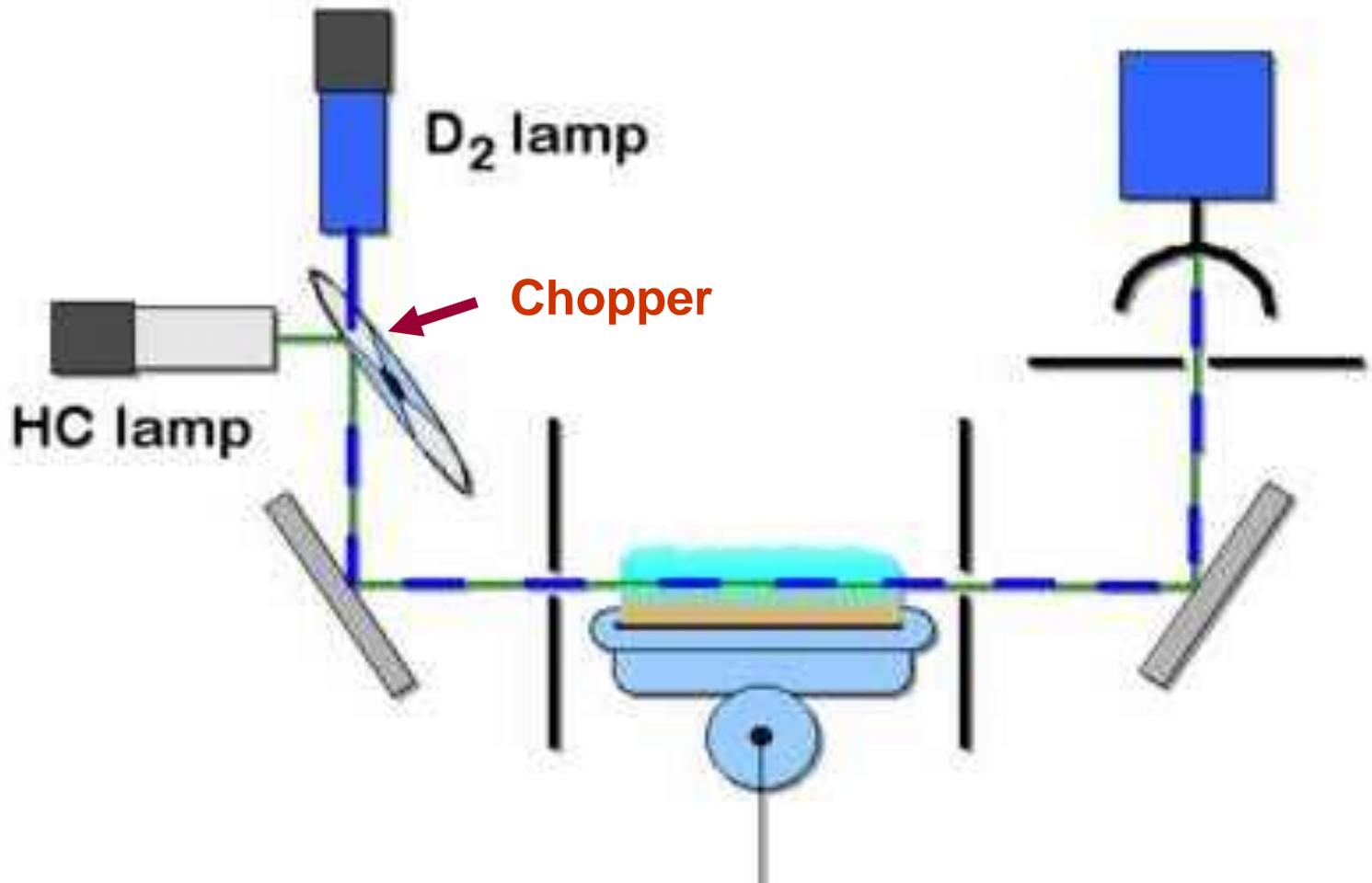
1. Continuous source correction method
 2. Zeeman effect correction method
- These two methods are based on the fact that
 - Atomic bands are very narrow
 - Background bands are molecular in nature thus they are broad bands



2. The continuous-source correction method

- This method is an available option with most instruments
- Deuterium lamp is used in conjunction with the HCL lamp
- The two lamps are observed by detector alternatively in time
- Background usually absorb radiation from D₂ lamp and HCL
- Absorption of the analyte from D₂ lamp is negligible
- The lamps may be pulsed at different frequencies, thus the signal processing electronics can distinguish and process separate absorption signals
- Thus
$$A_{\text{corrected}} = A_{\text{HCL}} - A_{\text{D}_2}$$

The continuous-source correction method



Background correction

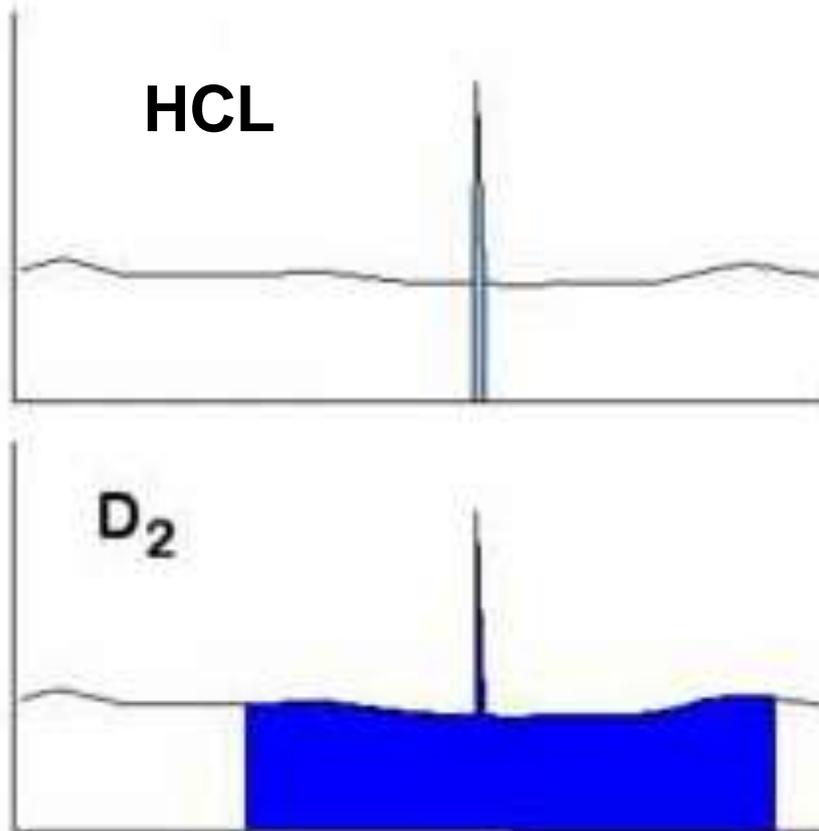
D_2 background correction

A continuous-source correction method.

Light from both the AA source lamp and a D_2 lamp alternately pass through the sample.

Because the spectral slit width is significantly larger than the AA source line, the D_2 lamp sends a much broader band of light through the sample.

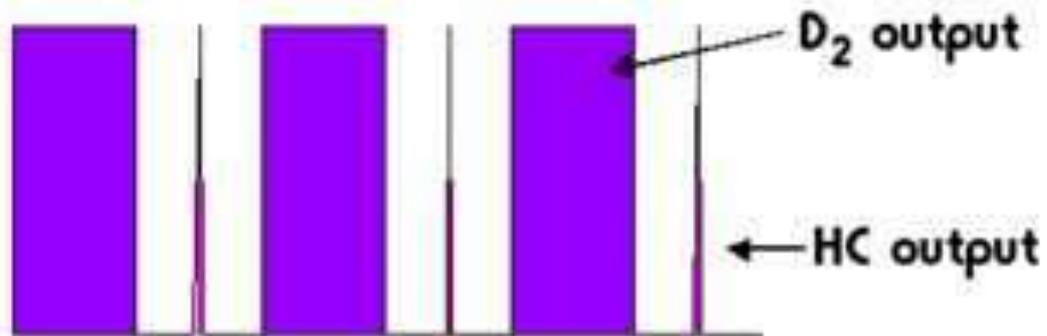
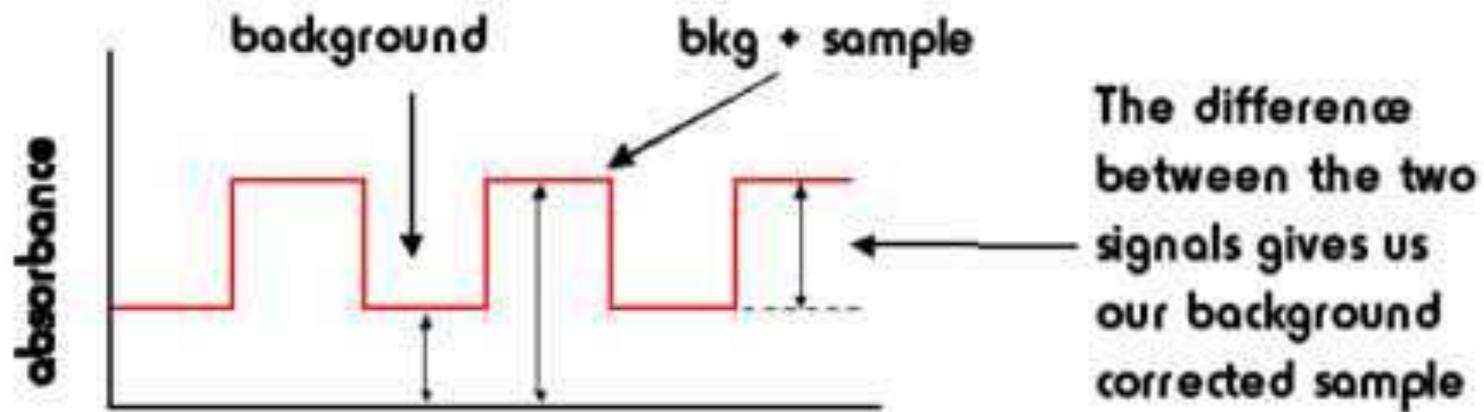
Background correction by continuous source correction method



With the HCL , we measure absorption of our element and background over a very narrow bandwidth.

With the D_2 lamp, we measure absorption over a much larger bandwidth. Because the elemental line is so narrow, we mostly measure background.

Background correction



Disadvantages of the continuous source correction method

- **Correction may degrade detection limit. The current of HCL is reduced to match the D_2 lamp**
- **The correction may be in error if the backgrounds (sample and standards) are not the same**
- **Alignment of the two sources to pass through the same area of atomizer is tedious**
- **Beam splitter reduces the intensity of radiation which may affect the limit of detection**
- **Additional light source and electronics are needed**

Zeeman effect correction method

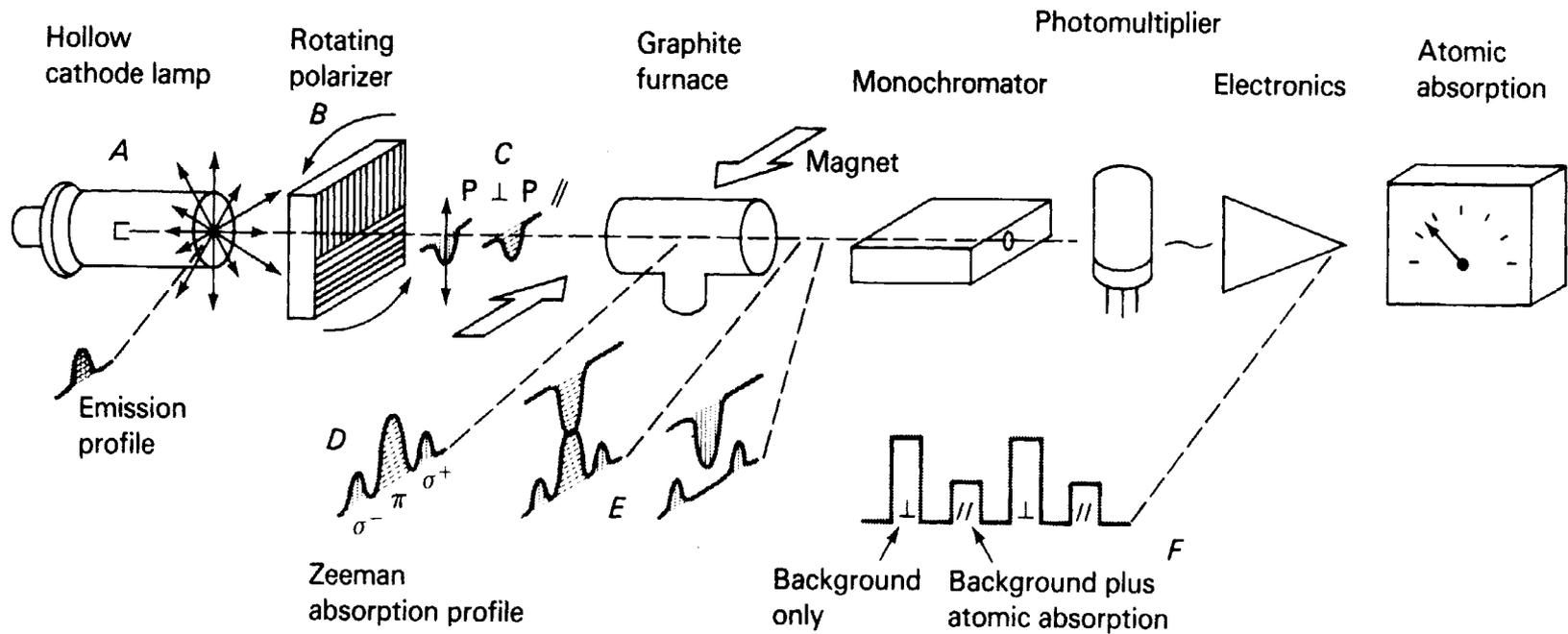


FIGURE 10-23 Schematic of an electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect. (Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)

Zeeman effect correction method

An alternate approach is to make use of the Zeeman effect.

When an atomic vapor is exposed to a strong magnetic field (1 - 10kG), there is a splitting of the atoms electronic energy levels.

This essentially moves our absorption away from the emission lines.

The magnetic field is applied to the sample.

- Under the magnetic field, atomic spectral line (emitted or absorbed) splits into three or more polarized components
- Two components will be displaced at equal wavelength intervals higher and lower than the original line.
- The original line is polarized in plane parallel to the magnetic field and the other lines are polarized perpendicular to the magnetic field
- The **original line** is absorbed by **both background and analyte**. However, the other lines are absorbed by **background only**
- The signal corresponding to the analyte is the difference

Advantages of Zeeman method

- **Only a single lamp is required**
- **Problems of alignment of two beams is eliminated**
- **It provides more accurate correction for background than other methods**
because the background absorbance is measured at or very near the wavelength that the analyte absorbance is measured

Disadvantages of Zeeman method

- The implementation is rather complex and expensive
- The original and the split bands may overlap causing an increase in the background signal
- This causes a curvature in the calibration curve
- The **instrument is bulky because** of the magnet
- Spectral lines for some elements may undergo more complex splitting. Thus sensitivity will be reduced (It gave good results for 44 elements)
- It is more difficult to engineer with flames

Source self reversal background correction method Smith-Hieftje technique

- It is based on self-reversal of the HCL spectral lines at high current
- At high current, many free atoms are generated causing an increase in the number of **unexcited atoms** that absorb the center of the emitted line causing the self reversal
- Specially good for correcting for high molecular absorption for that by phosphate on Se and As
- A total is measure

- Hollow cathode lamps normally operate at currents of 3-15 mA.
- If the applied power is raised to several hundred mA, they exhibit a phenomenon called self-reversal.
- This giant pulse of current changes the nature of the analyte absorption line so it will only measure the background absorbance.
- A_{total} is measured during the low current period.
 $A_{\text{background}}$ is measured during the high current period
- The low current (6-20 mA) is pulsed at 100-500 mA

**Corrected signal = Signal before the pulse
–Signal After the pulse**

Advantages of Smith-Hieftje technique

- Only a single source is used
- It offers all the advantages of other methods at low cost
- It does not lose radiation like in Zeeman but this method with the Zeeman one are less sensitive than the D_2 one
- **Drawbacks**
 - less sensitivity
 - lamp life decreased

Background in atomic emission

- **Sources**

1. **Emission from flame**

2. **Emission from the sample matrix**

Advantages and disadvantages of atomic absorption

Advantages

- **sensitive (GFAA)**
- **selective**

Disadvantages

- **intended for metallic/metalloid atomic species, not nonmetals or intact molecular species**
- **lamps - one element at a time**
- **not easy for solids**
- **calibration curves nonlinear above $A = 0.5$**
- **more costly and less widely applicable than UV vis**
- **matrix effects - easy for some metals to be masked**

Sample Preparation

- **Many materials of interest, such as soils, animal tissues, plants, petroleum products, and minerals are not directly soluble in common solvents, and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization.**

Organic Solvents

- **Leaner fuel/oxidant ratios must be employed with organic solvents in order to offset the presence of the added organic material.**

Calibration Curves

- **In theory, atomic absorption should follow beer's law with absorbance being directly proportional to concentration.**

Standard Addition Method

- **The standard addition method is widely used in atomic absorption spectroscopy in order to partially or wholly counteract the chemical and spectral interferences introduced by the sample matrix.**

Applications of Atomic Absorption Spectrometry

- **Atomic absorption spectrometry is a sensitive means for the quantitative determination of more than 60 metals or metalloid elements. The resonance lines for the nonmetallic elements are generally located below 200 nm, thus preventing their determination by convenient, nonvacuum spectrophotometers.**

Atomic fluorescence

A modification of the normal AA setup will permit atomic fluorescence to be done.

The HC lamp is placed at a right angle to the detector.

Any atoms that fluoresce can be measured.

Not as common as AA or plasma emission.

Atomic fluorescence

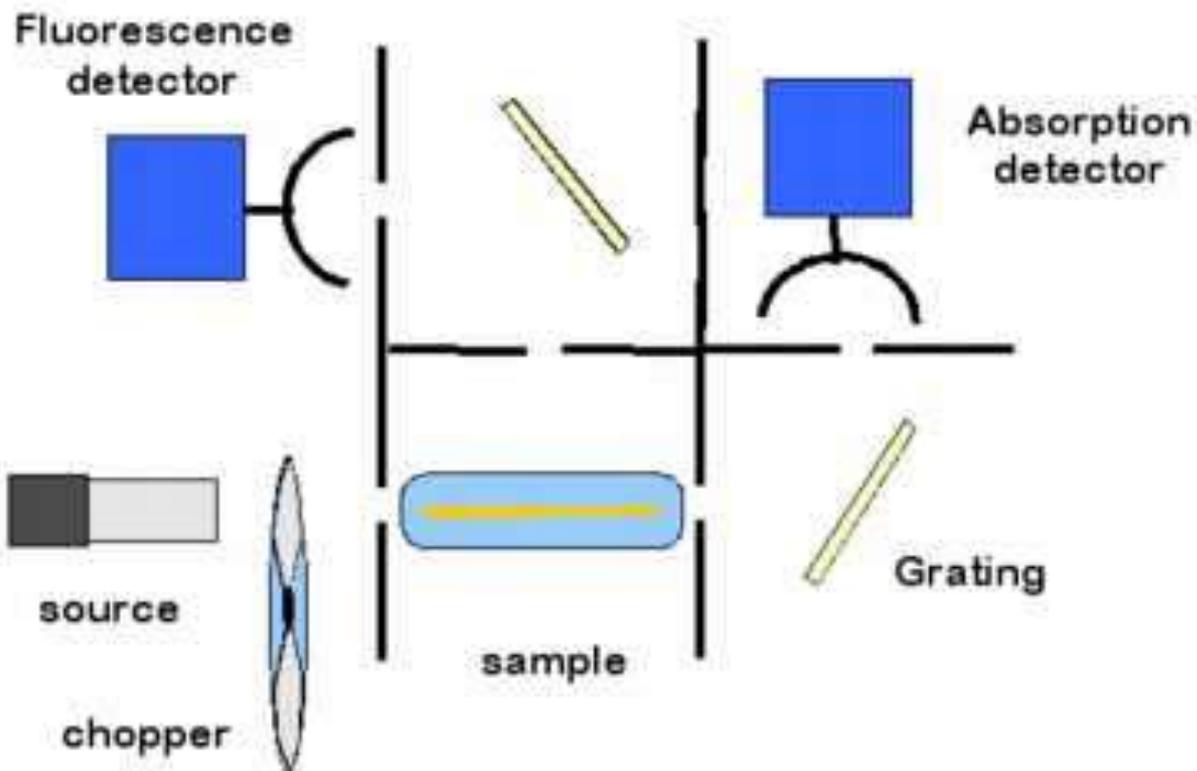
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Atomic fluorescence



Instrumentation

Sources

- **In the early work on atomic fluorescence, conventional hollow cathode lamps often served as excitation sources. In order to enhance the output intensity without destroying the lamp, it was necessary to operate the lamp with short pulses of current that were greater than detector, of course, was gated to observe the fluorescent signal only during pulses.**

Dispersive instruments

- **A dispersive system for atomic fluorescence measurements is made up of a modulated source, an atomizer, a monochromator or an interference filter system, a detector, and a signal processor and readout.**

Nondispersive Instruments

Advantages of such a system

- (1) simplicity and low-cost instrumentation**
- (2) ready adaptability to multielement analysis**
- (3) high-energy throughput and thus high sensitivity, and**
- (4) Simultaneous collection of energy from multiple lines, also enhancing sensitivity.**

Interferences

- **Interferences encountered in atomic fluorescence spectroscopy appear to be of the same type and of about the same magnitude as those found in atomic absorption spectroscopy.**

Applications

- **Atomic fluorescence methods have been applied to the analysis of metals in such materials as lubricating oils, seawater, biological substances, graphite, and agricultural samples.**