Atomic Absorption And Atomic Fluorescence Spectrometry

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Atomic Spectroscopy Methods

- Atomic spectroscopy methods are based on light absorption and emission (via electronic transitions, all in the UV-VIS domain) of atoms in the gas phase.

- The goal is elemental analysis - identity and determine concentration of a specific element in the sample.

- Chemical and structural information are lost.

- The sample is destroyed.

Atomic Spectroscopy Methods

- Atoms in the gas phase have very well defined electronic energy levels for the electrons.

- Consequently light is absorbed by a ground state atom or emitted by an excited atom at very precise wavelengths, resulting in line spectra.

- In the UV-VIS domain, each element has hundreds to thousands of absorption/emission lines.

- The bandwidth of each line is extremely narrow (ca. 0.002 to 0.005 nm; bandwidth increases with temperature and pressure).

- Consequently, it is possible to selectively detect and quantify one specific element by carefully setting the observation wavelength and keeping the observation bandpass very small.

- Certain electronic transitions have the highest probability. The corresponding absorption/emission lines are called resonance lines, and have the best wavelengths for analysis of that element.

Atomic Absorption Spectroscopy

- Atomic absorption spectroscopy is probably the most widely used method for the determination of *single elements* in analytical samples.

- A quantitative method of analysis is based on the absorption of light by atoms in the free atomic state.

- The method relies on the Beer-Lambert relationship - calculations are the same as with molecular absorption methods.

- There are two commonly used methods for achieving this goal: flames and electrothermal methods.
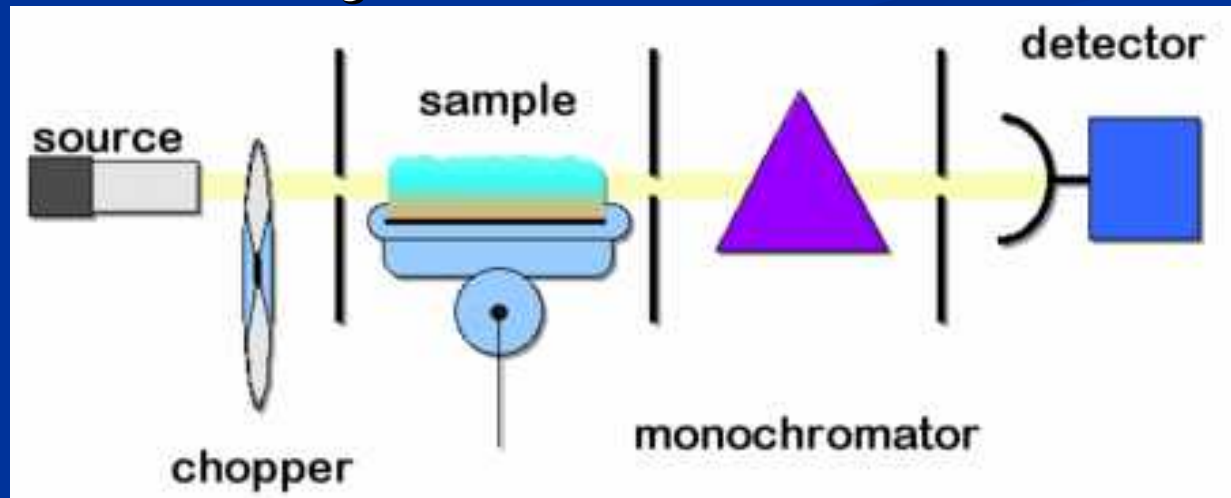
Basis of Method

- With electrical or flame excitation, most atoms remain in the unexcited state.

- A sample is atomized and the atomic absorbance is measured.
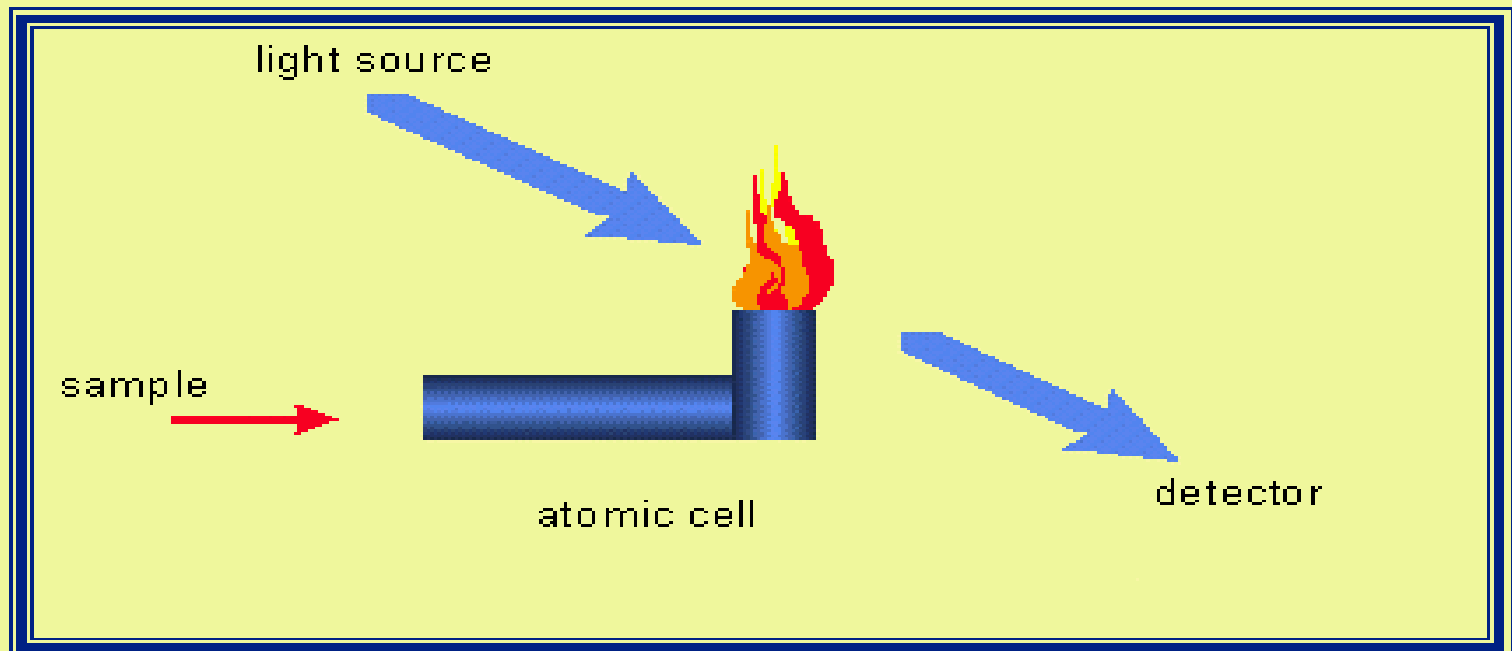
Atomic Absorption Instrumentation

- Radiation source.

- A flame will serve as the sample holder, containing gaseous atomized sample.

- A wavelength selector.

- Detector.

- Signal process and digital readout.

In its simplest form, an AAS resembles a single beam spectrophotometer.

Radiation Source

- The atomic absorption lines are very narrow.

- For Beer's law to be valid, the bandwidth of the source must be narrow relative to the width of an absorption peak.

- We can't approach this narrow line width even with a good monochromator.

- Therefore we use a radiation source that emits the same line spectra of the element which we are trying to detect.

  - Want to look for lead? Then use a lead lamp.

 - Want to look for copper? Then use a copper lamp.

Light Sources

- A molecular spectrophotometer relies on a broad band light source.

- With atomic absorption, a line source is required to reduce interferences from other elements and background.

- Two basic types
  - Hollow cathode lamp.
 - Electrodeless discharge lamp.

Hollow Cathode Lamp

- The hollow cathode lamp consists of an anode and a cylindrical cathode sealed in a glass tube that is filled with an inert gas (Ne or Ar) at a pressure of 1 - 5 torr.

- The cathode is constructed of the element that is to be analyzed (Na, Ca, K, Fe...).

- A large potential is applied across the electrodes which ionizes the inert gas.

Insulating disk

Quartz or glass window

(−)
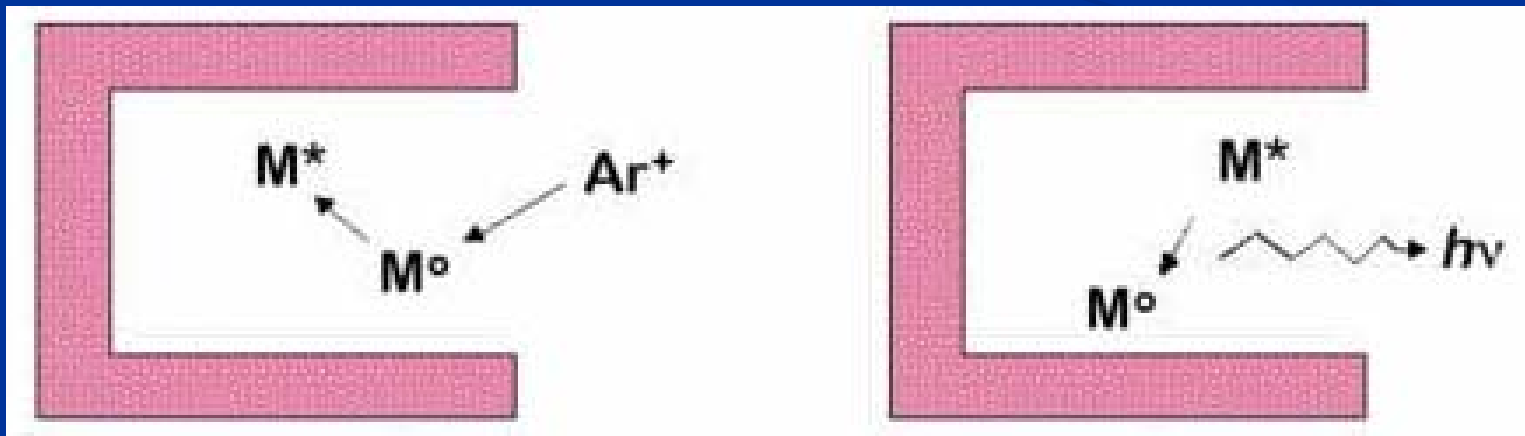
(+)

Hollow cathode

Anode
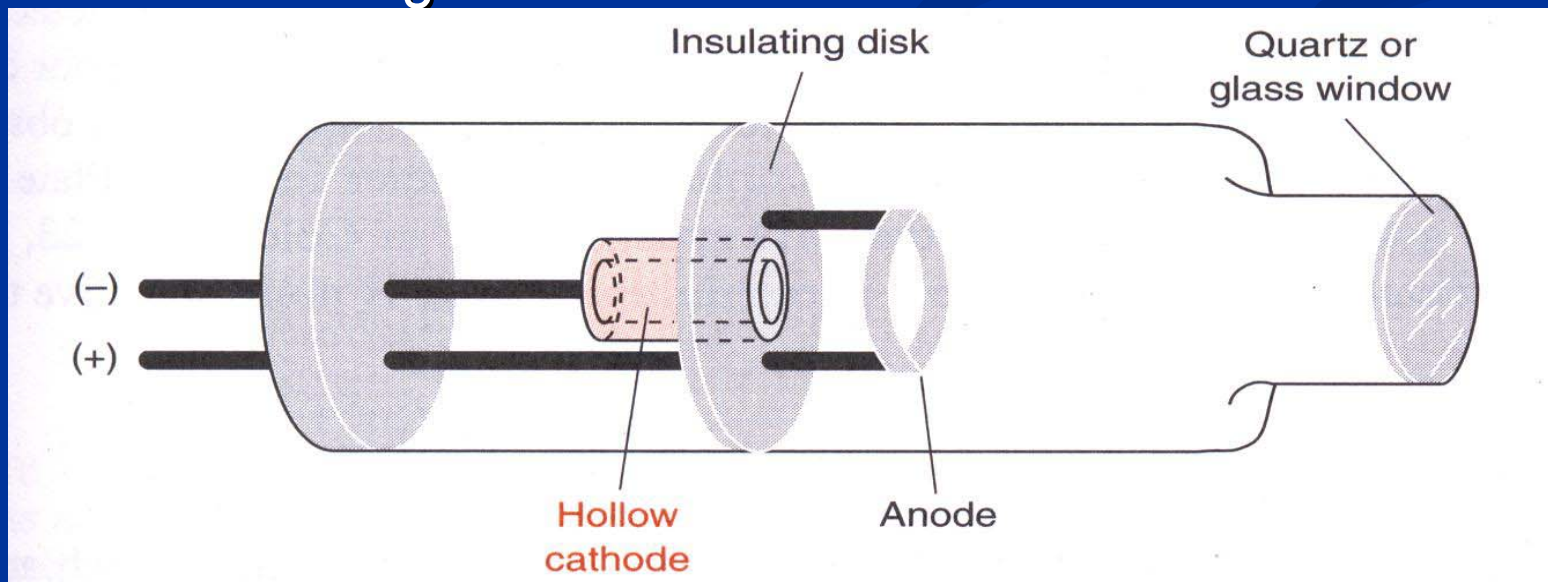
Hollow Cathode Lamp

- Ar ions bombard cathode and sputter cathode atoms.
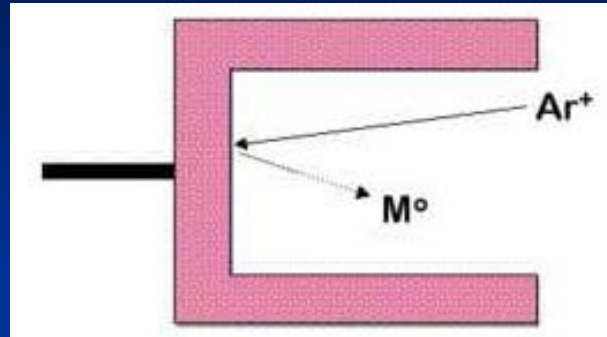
- Repeated bombardment of the metal atom by the gas causes it to be excited. It ultimately relaxes, producing specific atomic emission lines. The metal atoms eventually diffuse back to the cathode surface.

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.

- A window that is transparent to the emitted radiation is fused to the end of the cylinder.

Hollow Cathode Lamp

- The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the tube and also enhances the probability that redeposition will occur.

- High potentials lead to greater intensities.
  - Doppler broadening becomes a problem.
  - Greater currents produce an increased number of unexcited atoms in the cloud that can absorb the emitted radiation.
  - This self-absorption leads to lowered intensities, particularly at the center of the emission band.

- A different cathode lamp is needed for each element, although there are some lamps that can be used to determine three or four different elements if the cathode contains all of them.

- Each time a lamp is changed, proper alignment is needed in order to get as much light as possible through the flame, where the analyte is being atomized, and into the monochromator.

Hollow Cathode Lamp

- An hollow cathode lamp will only produce the emission lines for the cathode element.

- Multi-element hollow cathode lamps are available but are limited.

- Not all metals will make suitable cathodes.

  - Metal is too volatile.

  - A good cathode can't be produced.

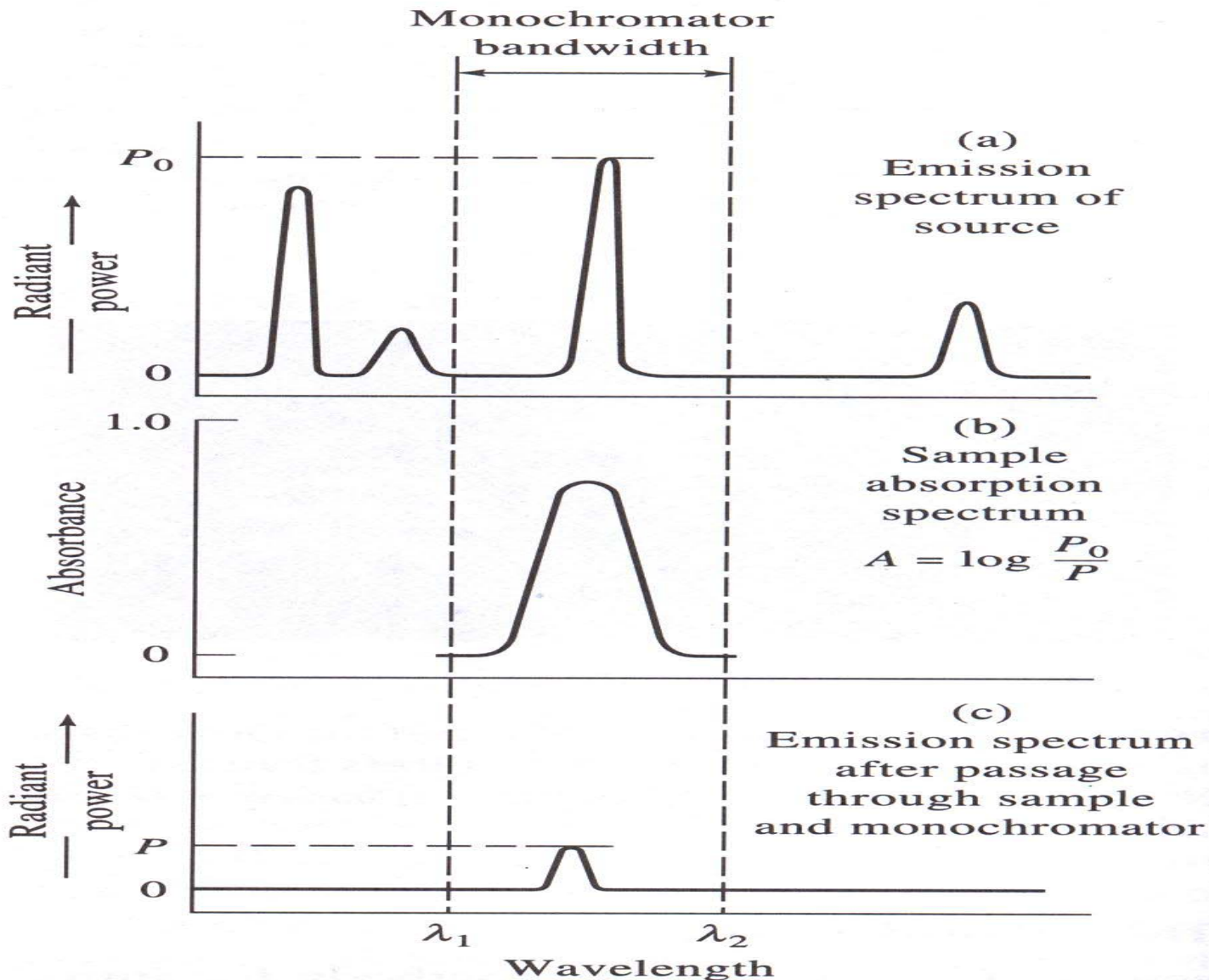 - The metal may not be good conductors.
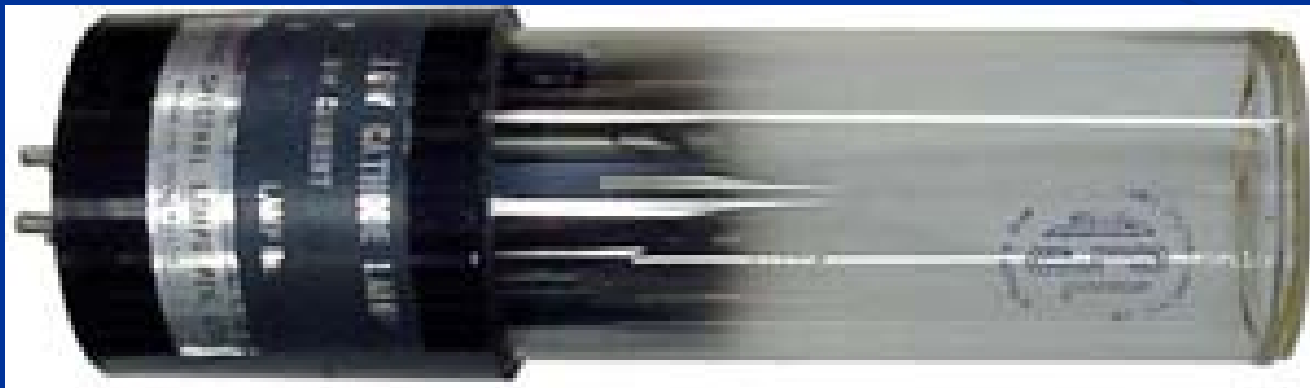
Electrodeless Discharge Lamps

- They are useful sources of atomic line spectra.
- They provide radiant intensities that are usually one to two orders of magnitude greater than hollow cathode lamps.
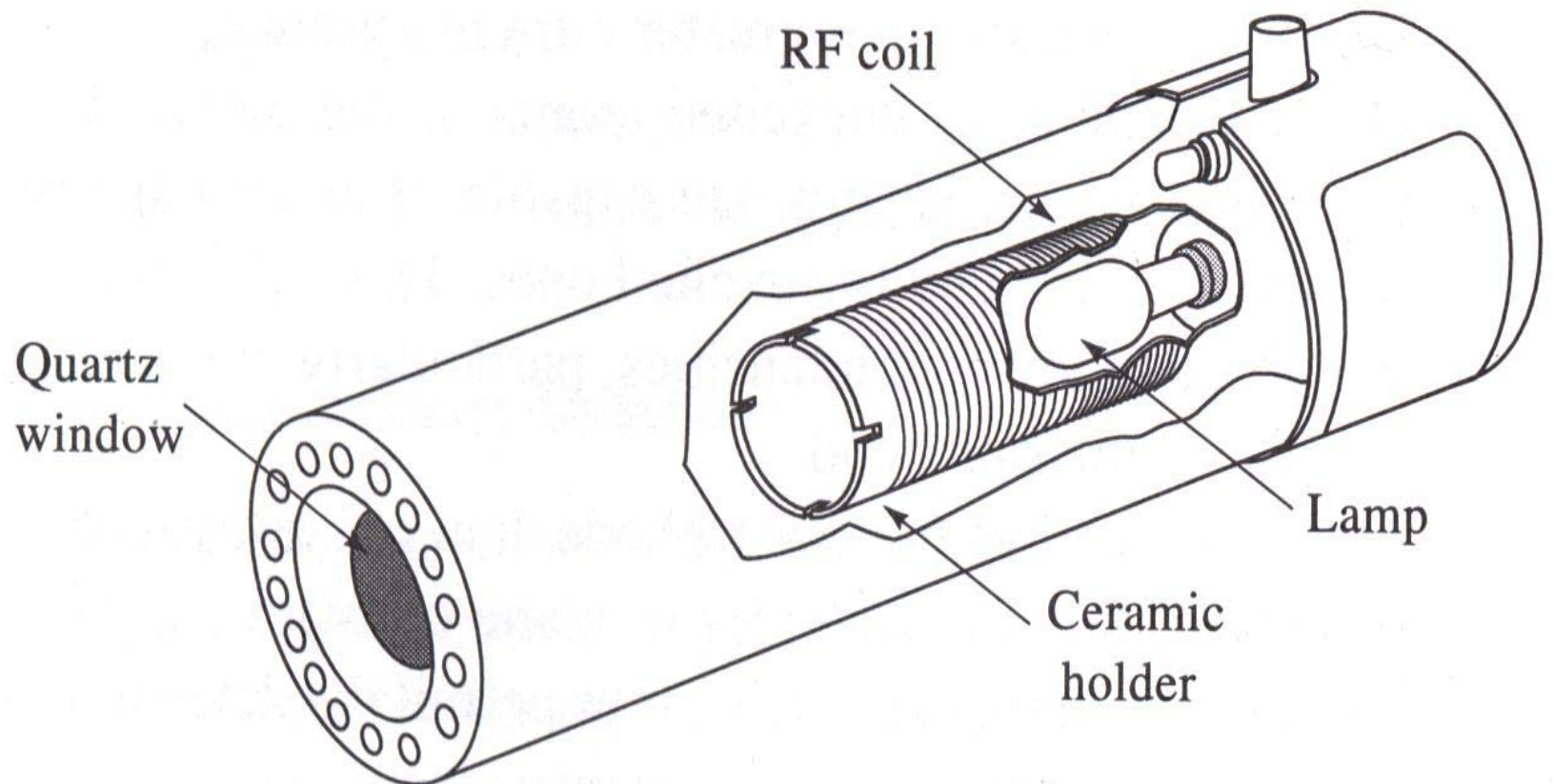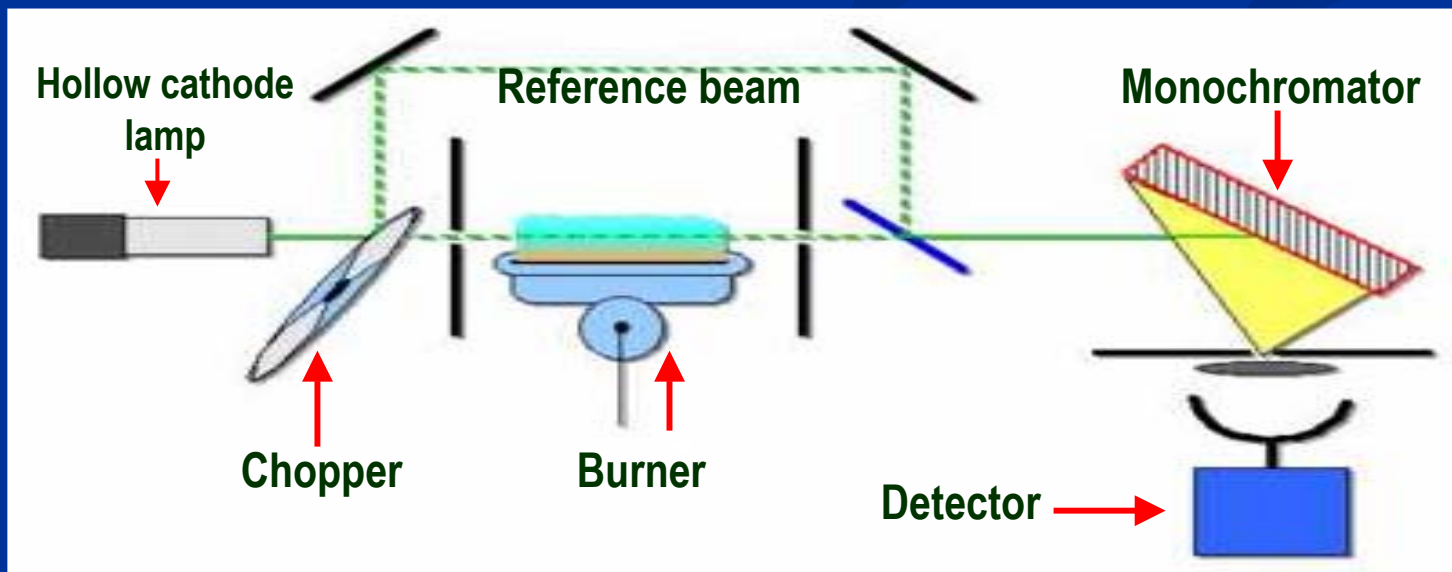
Absorption of a Resonance line by Atoms

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.
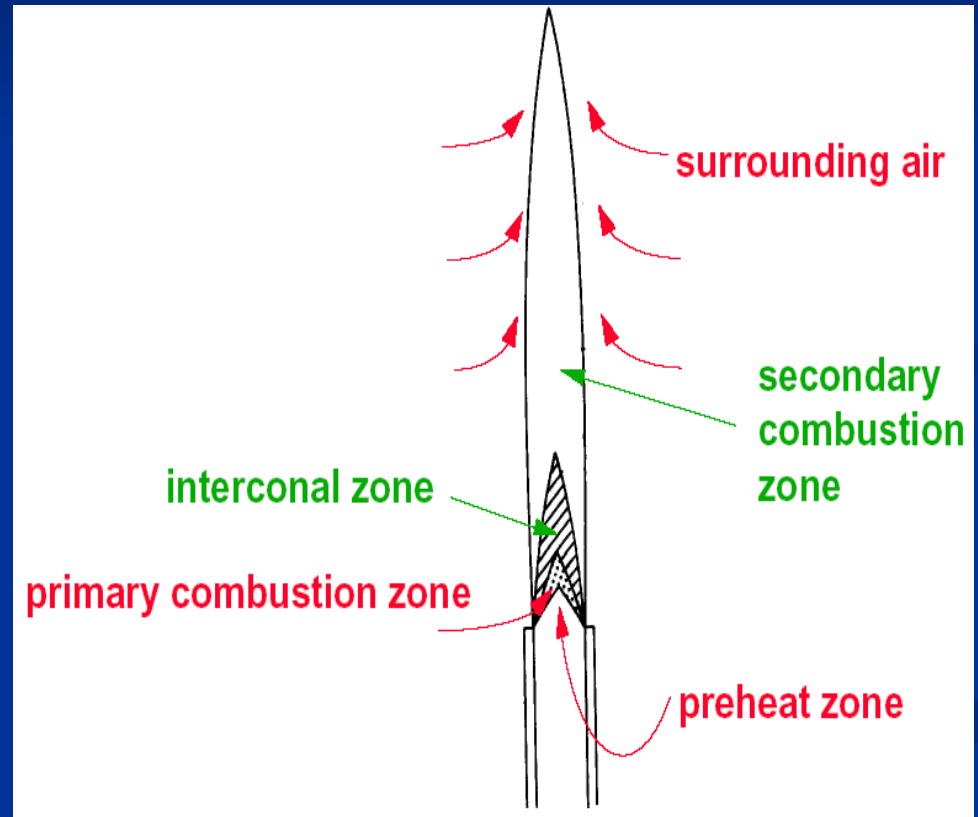
Atomization Source

- We need to be able to convert our sample to free atoms. Two approaches are used.
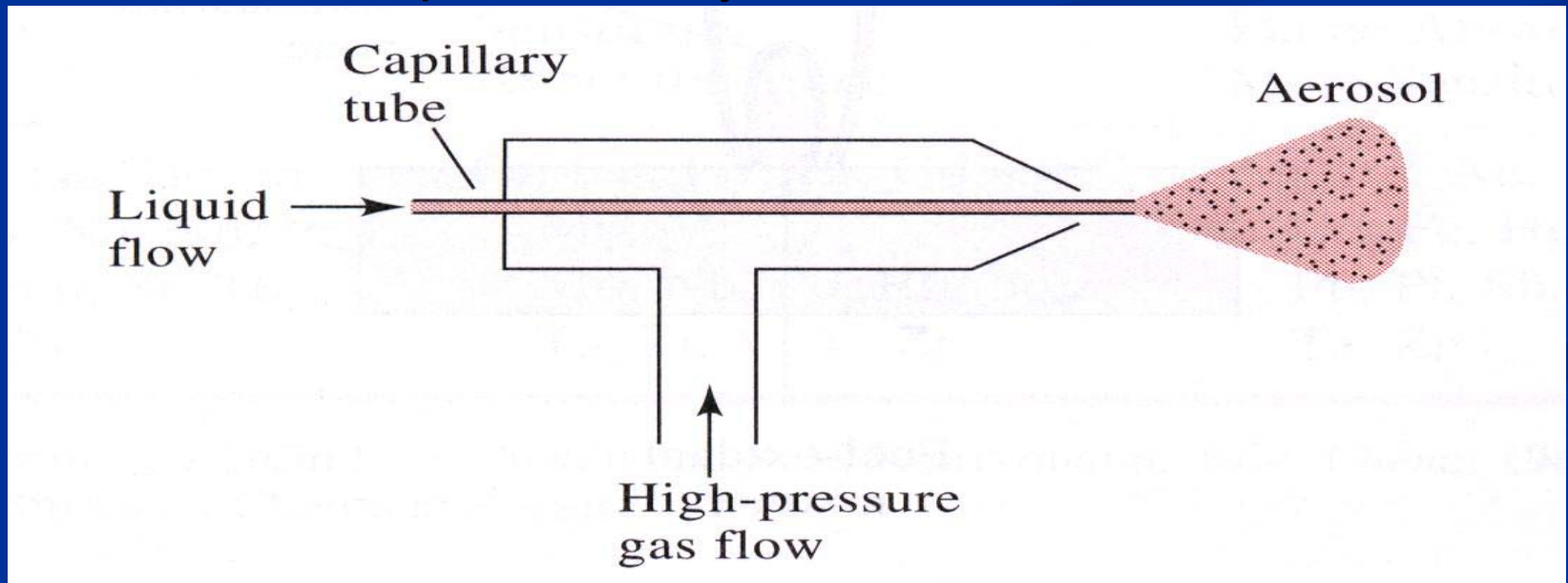 - ❖ Flame atomization
    - ❑ Liquids and gases

  - ❖ Flameless atomization
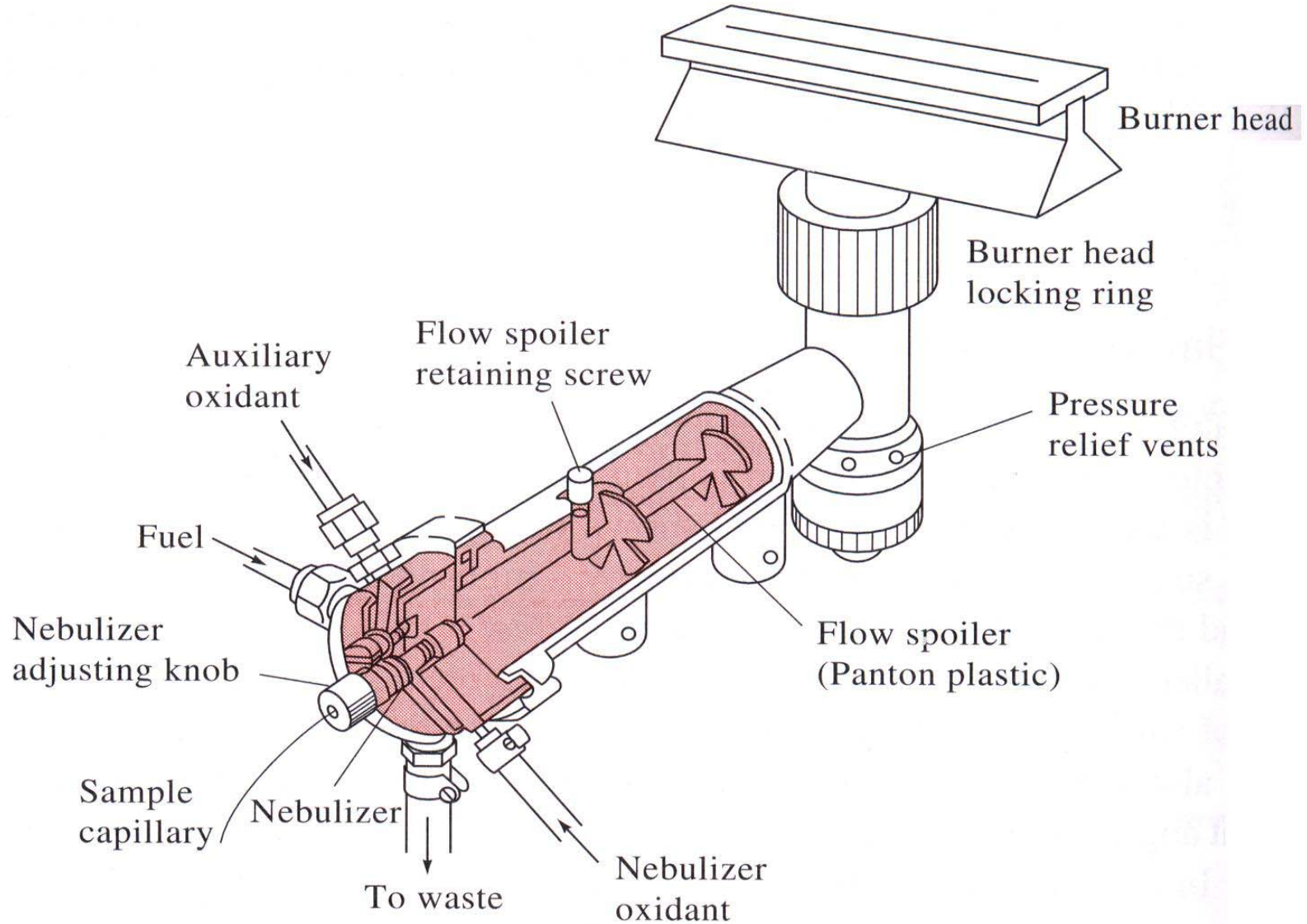   - ❑ Graphite furnace
    - ❑ Liquids and solids

Flame Atomization

- 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 assure that the sample mixes with the oxidant and fuel prior to entry into the flame.
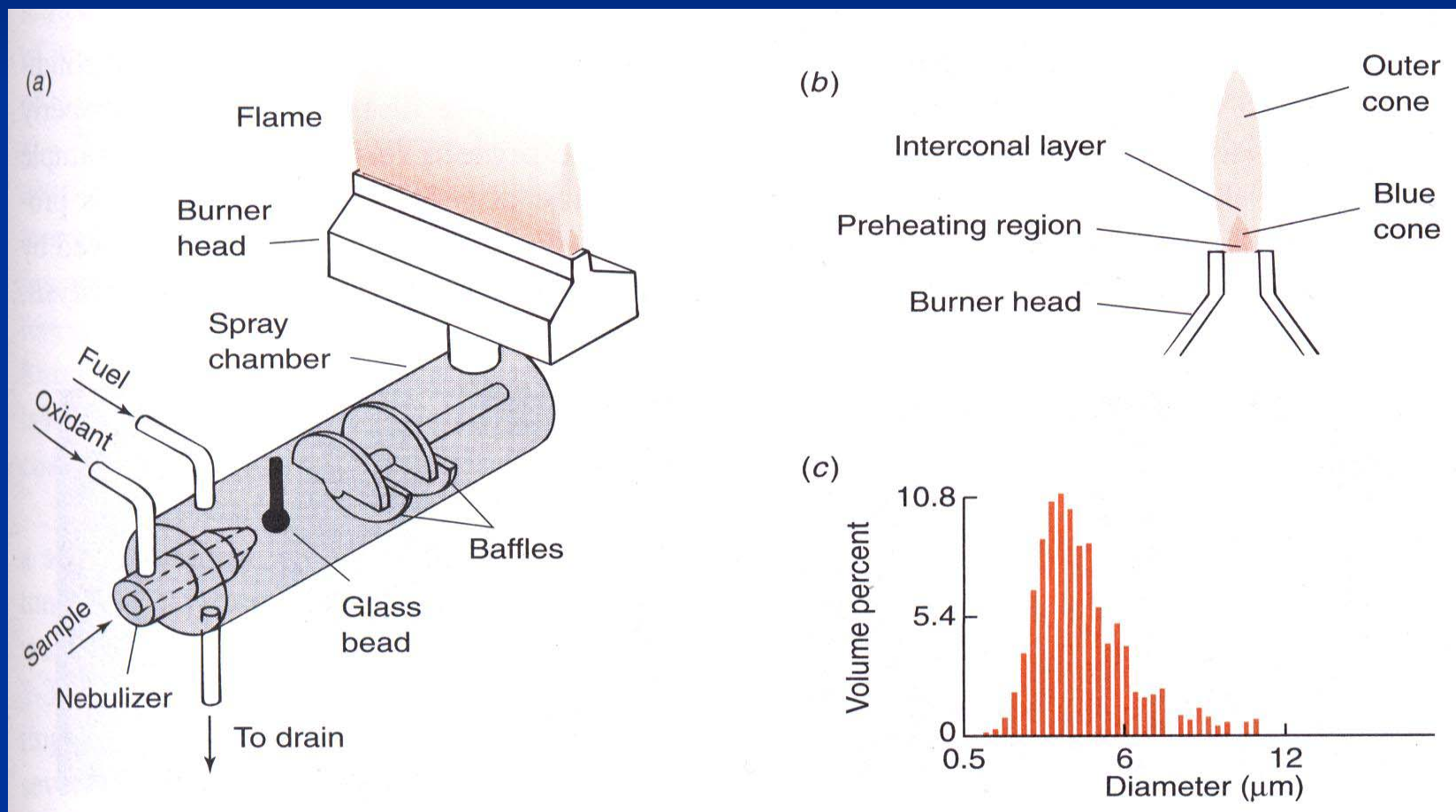
Flame Atomization

- A solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs.

Flame Atomizer

	Max. flame speed (cm/s)	Max. temp. (^{o}C)
Air-coal gas	55	1840
Air-propane	82	1925
Air-hydrogen	320	2050
Air-50% oxygen-acetylene	160	2300
Oxygen-nitrogen-acetylene	640	2815
Oxygen-acetylene	1130	3060
Oxygen-cyanogen	140	4640
Nitrous oxide-acetylene	180	2955
Nitric oxide-acetylene	90	3095
Nitrogen dioxyde-hydrogen	150	2660
Nitrous oxide-hydrogen	390	2650

Flame Atomizer

- The fuel to oxidant ratio is adjusted to give a stable flame.
  - Too high flow rate will cause the flame to blow off the burner.
  - Too low flow rate will cause the flame to propagate back into the burner, giving a flashback.
  - Every fuel will require different flow rates.

Steps of Flame Atomization

➢ The solution is *desolvated* by evaporating the solvent to produce a finely divided solid *molecular* aerosol.

➢ Most of these molecules are *dissociated* leading to an atomic gas.

➢ Some atoms are ionized to give cations and electrons.

➢ Other molecules and atoms are also produced as a result of interaction with the fuel and oxidant.

➢ A fraction of the atoms, molecules, and ions are excited by the flame giving an emission spectra.

Therefore, the flame is the most important variable.

Steps of Flame Atomization
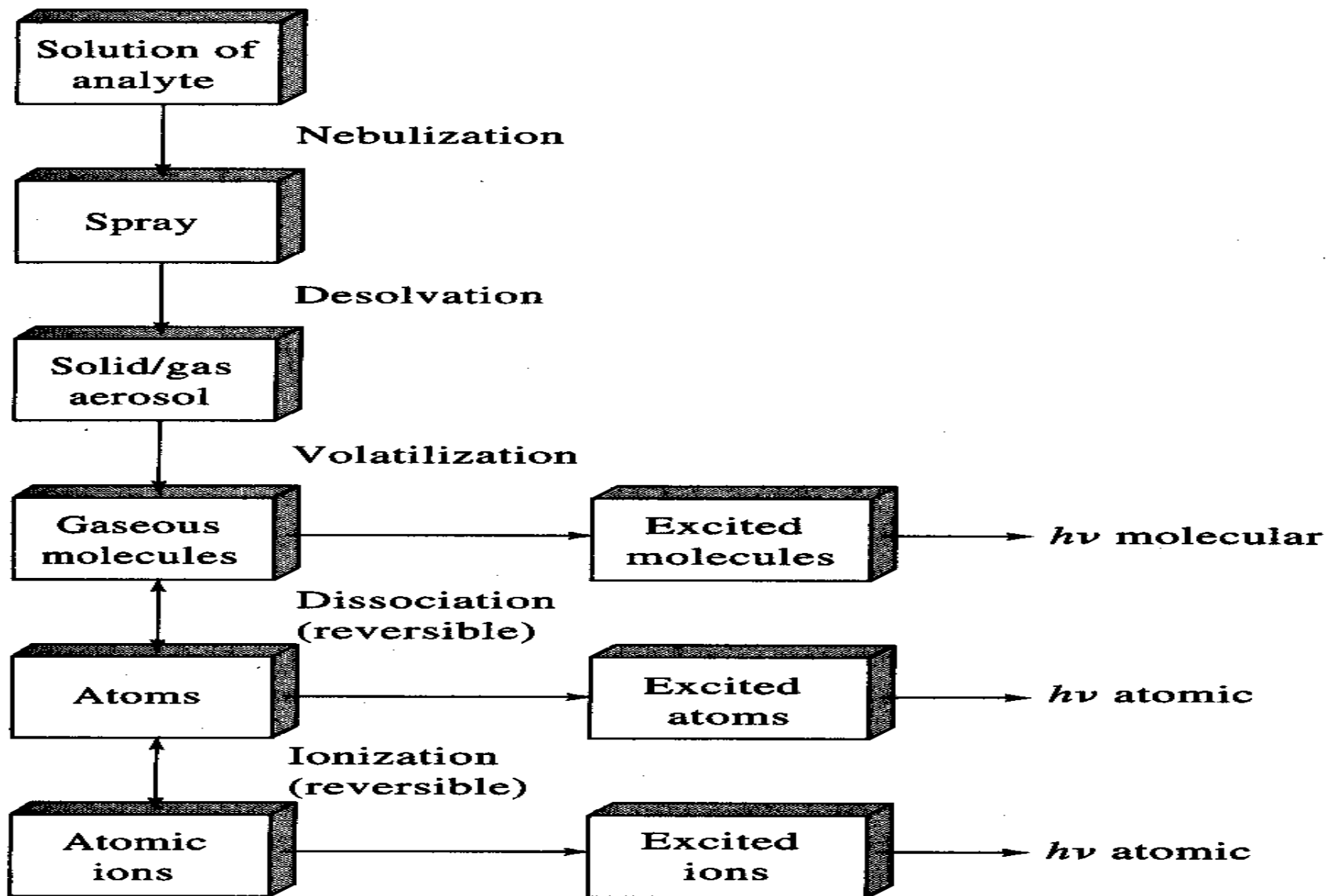
Flame Structure

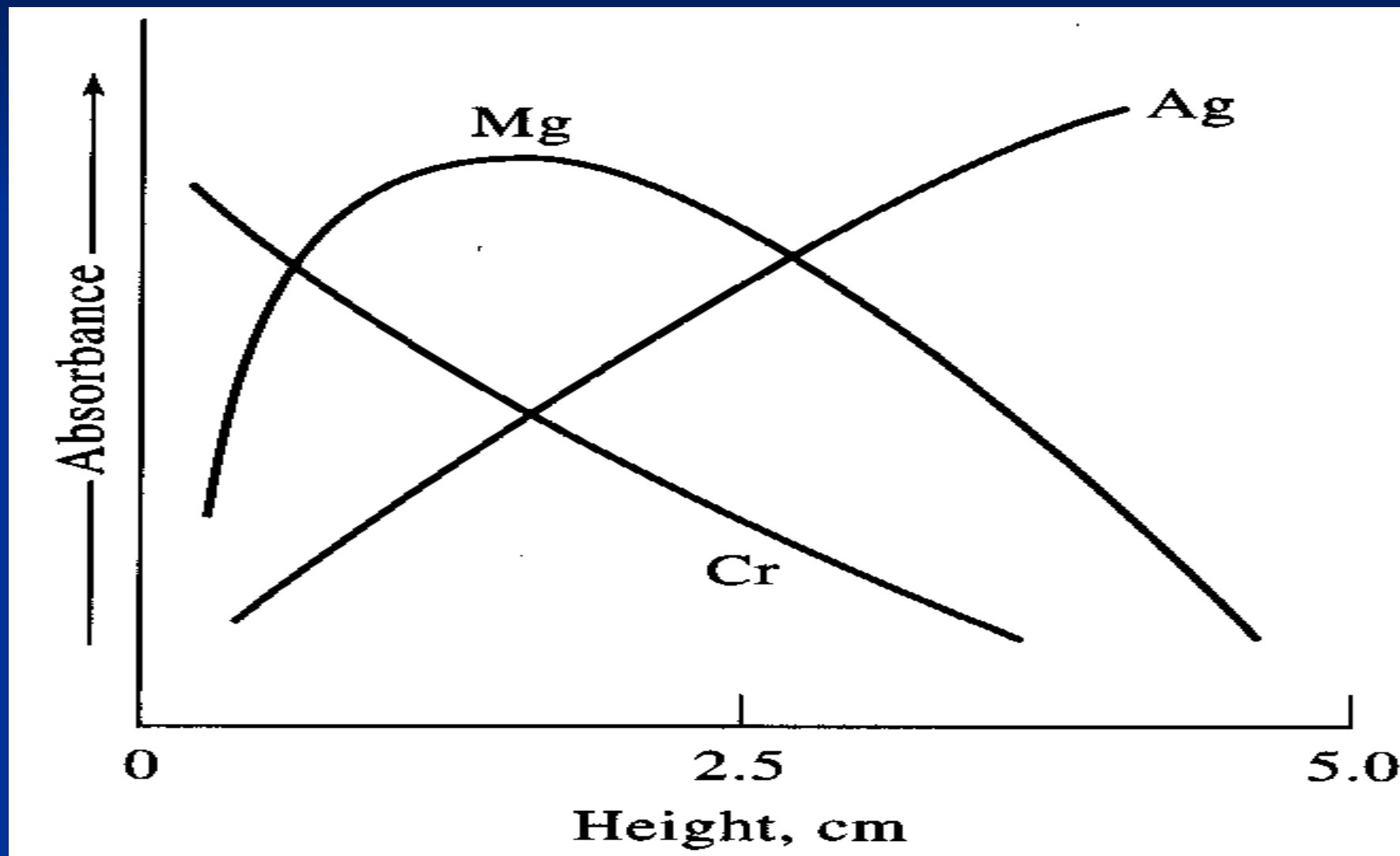- Primary combustion zone - initial decomposition, molecular fragments, cool

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

- Secondary combustion zone - cooler, conversion of atoms to stable molecules, oxides.
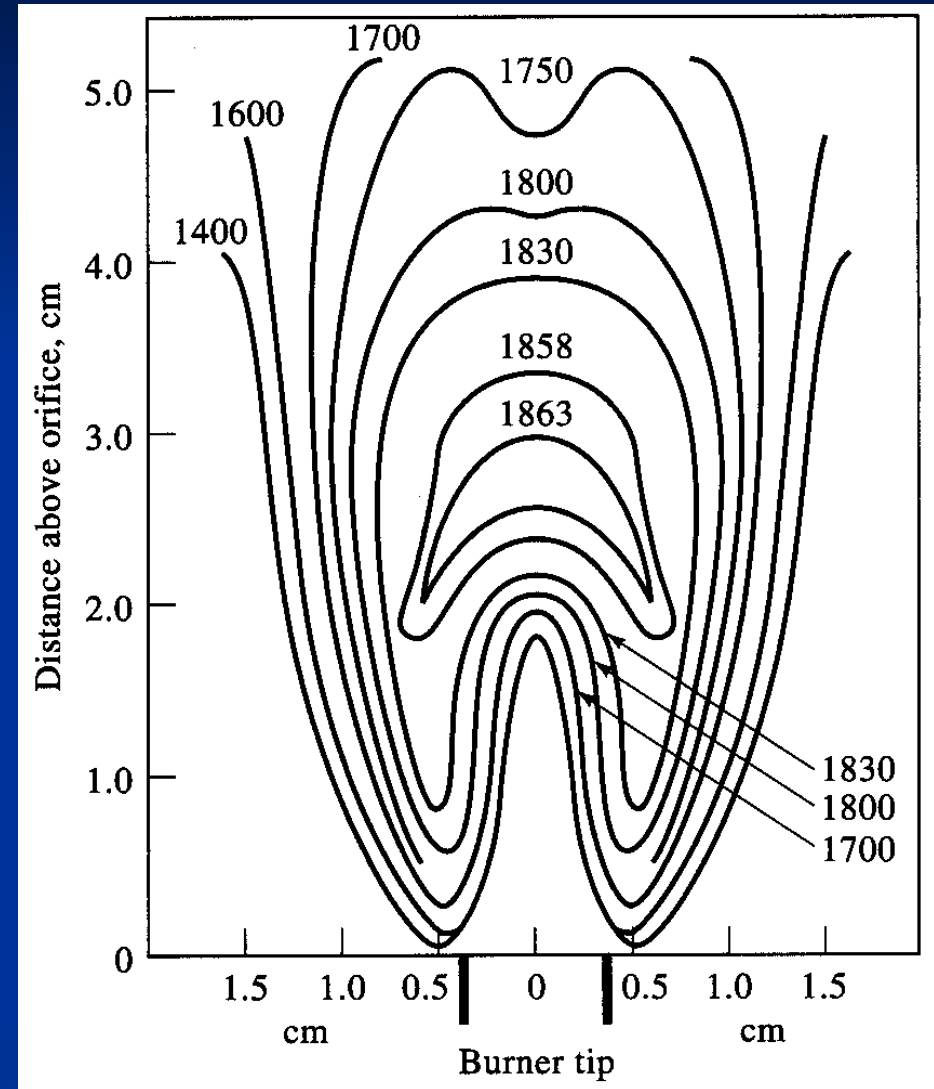
Flame Absorbance Profiles

Different elements have different absorption profiles in the flame.

Flame Absorbance Profiles

- **Magnesium**
  - ❖ The initial increase in absorbance as the distance from the flame base increases is due to the longer exposure to the heat causing more magnesium atoms to be formed.
  - ❖ The absorption decreases if the magnesium is exposed even longer because oxides are formed which absorb at a different wavelength.
- **Silver**
  - ❖ No stable oxides form so a continuous increase in absorbance is seen.
- **Chromium**
  - ❖ Forms very stable oxides so there's a continuous decrease in absorbance as it rises above the burner tip.

Flame Absorbance Profiles

- From the last slide, we see that a different portion of the flame should be used for the analysis of each element.

- To obtain the maximum analytical sensitivity, the flame is moved up and down with respect to the beam until a maximum absorbance is obtained.

- Don't forget to do this!!!
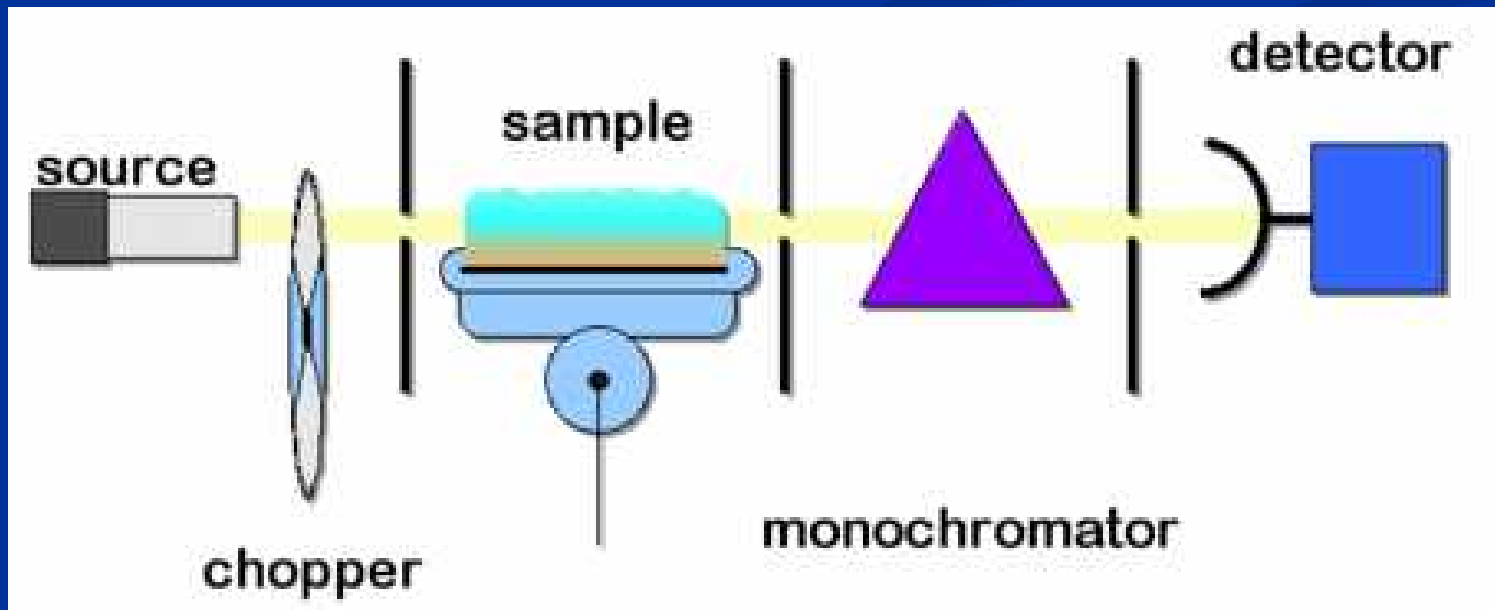
Electrothermal Atomizers

- 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.
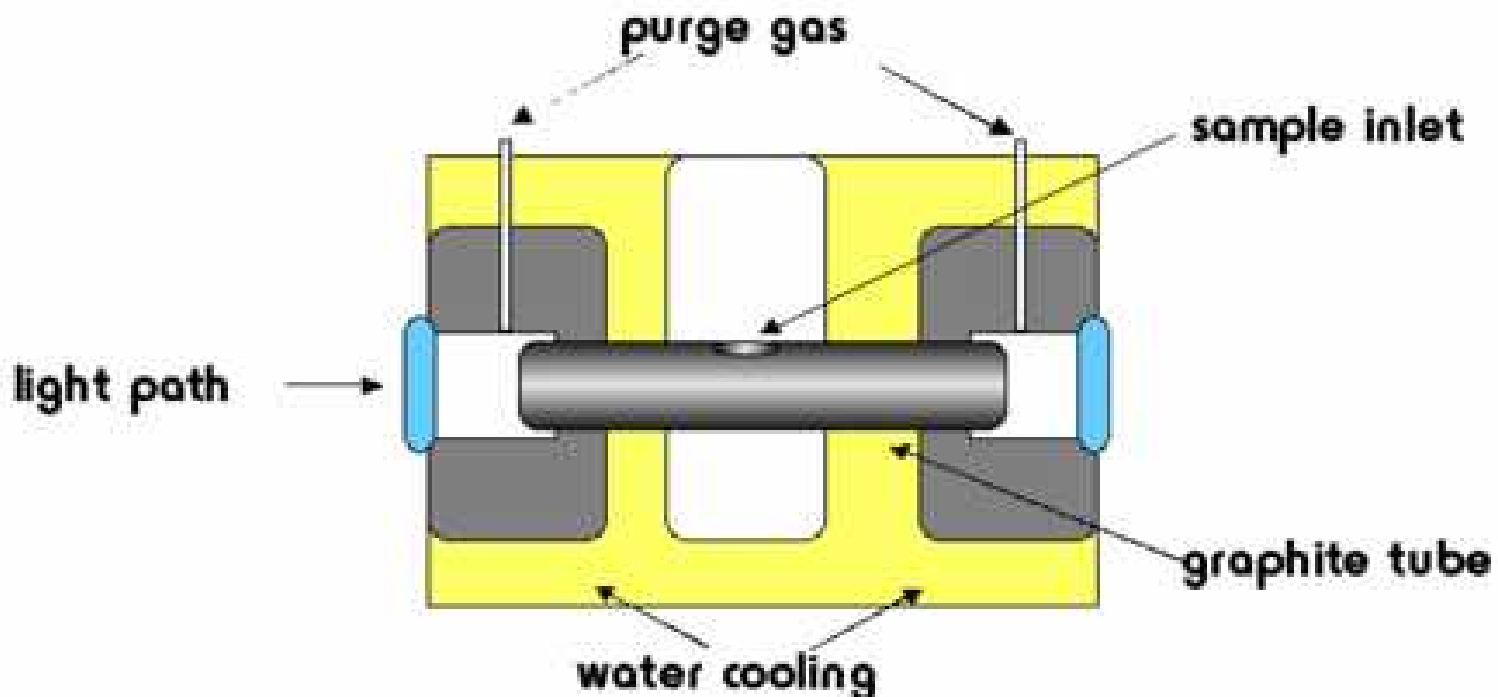
Electrothermal Atomizers

- Graphite furnace
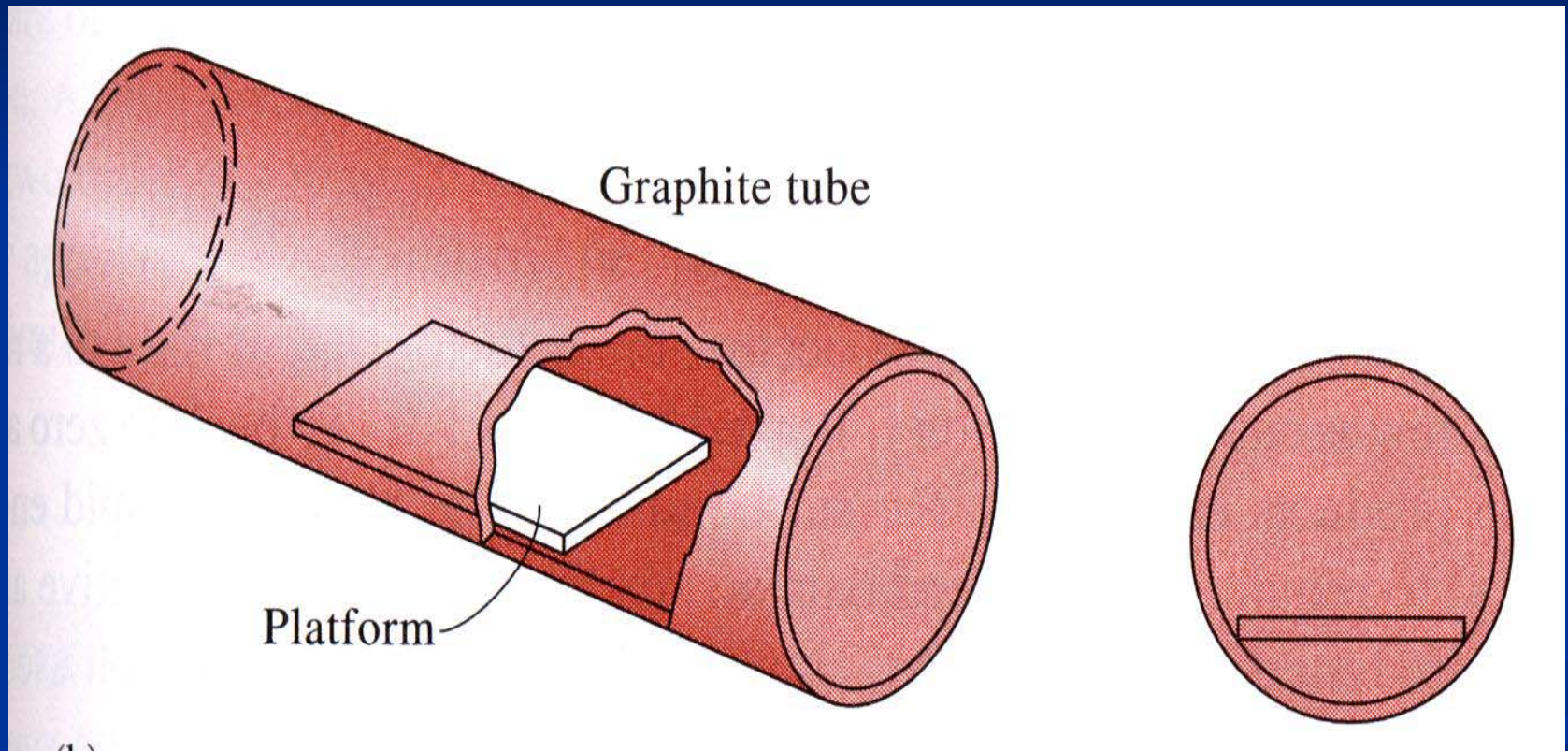
- External Ar gas prevents tube destruction.
- Internal Ar gas circulates gaseous analyte.

Electrothermal Atomizers

- Entire sample is atomized in short time (2000-3000 °C).

- Sample spends up to 1 s in analysis volume.

- Superior sensitivity (10^{-10} - 10^{-13} g of analyte).

- Less reproducible (5-10 %).

Internal gas flow

Graphite tube

Graphite furnace

Window

Window

To spectro-photometer

Light beam

O ring

O ring

External gas flow
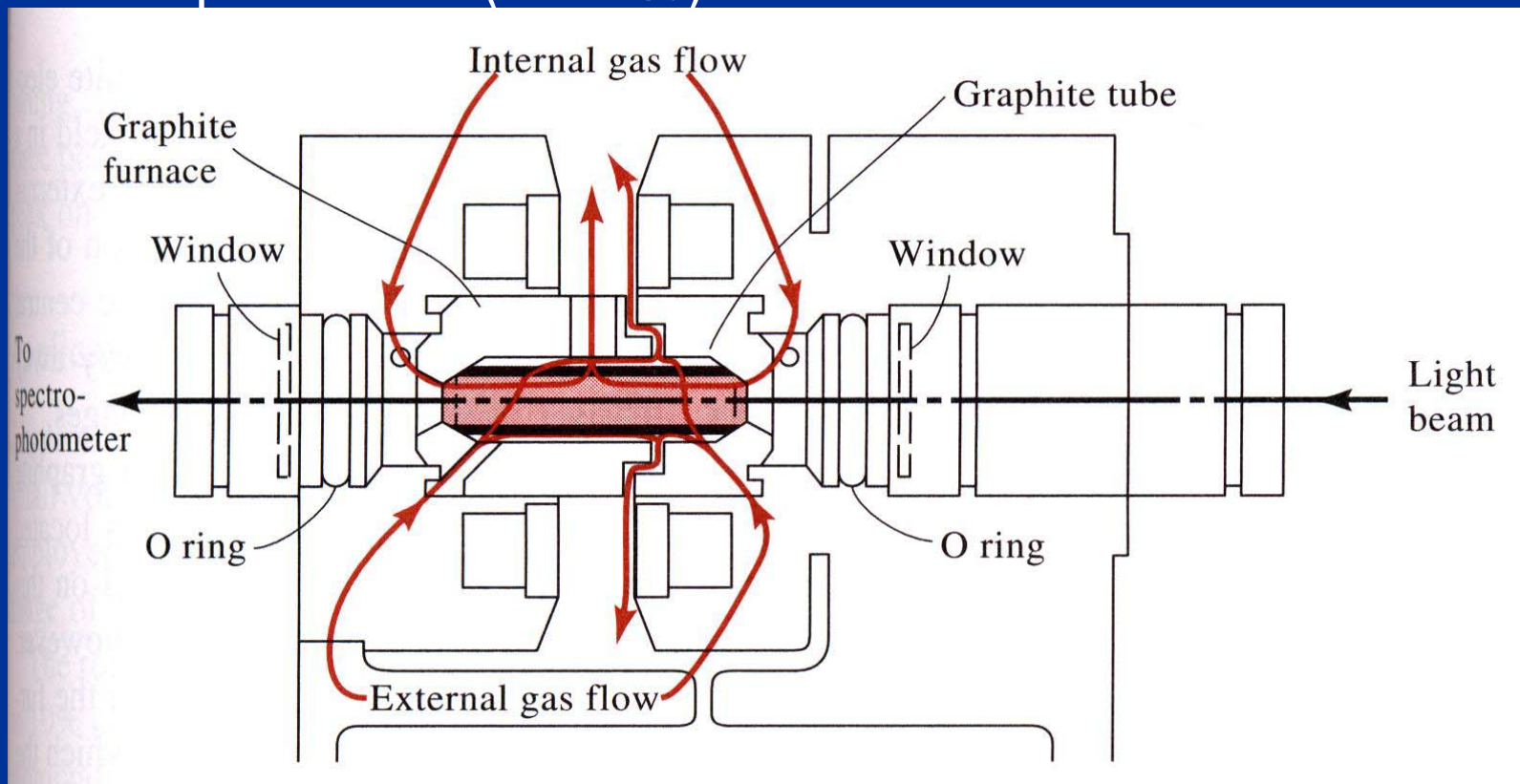
Electrothermal Atomizers

- 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.

Electrothermal Atomizers

- Three-step sample preparation for graphite furnace:
  - Dry – a fixed temperature and time is used to remove your solvent (50 – 200 ^{0}C)
  - Ash – A second temperature/time used to decompose your matrix (200 - 800 ^{0}C)
  - Atomization – A rapid increase to 2000 – 3000 ^{0}C for just a few seconds – when you collect your data.
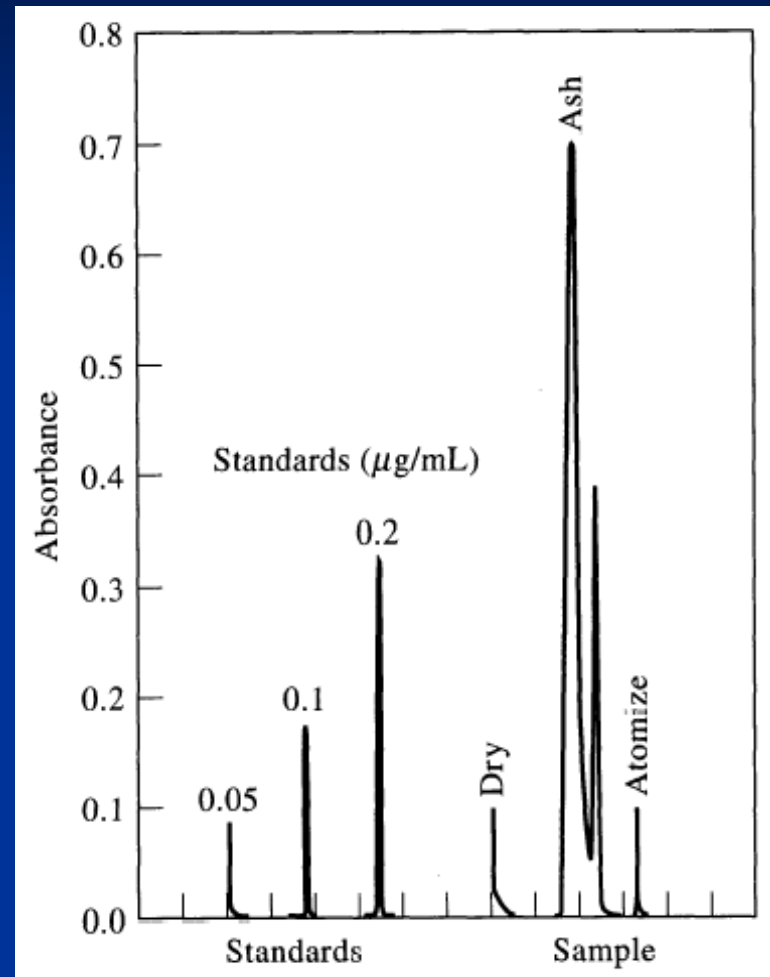
Flameless Atomization

Argon is often used as a purge gas to:

- ❖Remove excess material during the dry and ash phases and after atomization.

- ❖Reduce oxidation of the tube.

- ❖Provide a protective blanket during atomization since high temperature carbon will react with nitrogen to produce cyanogen.

AAS Spectrophotometers

- Signal at one wavelength often contains luminescence from interferents in flame.
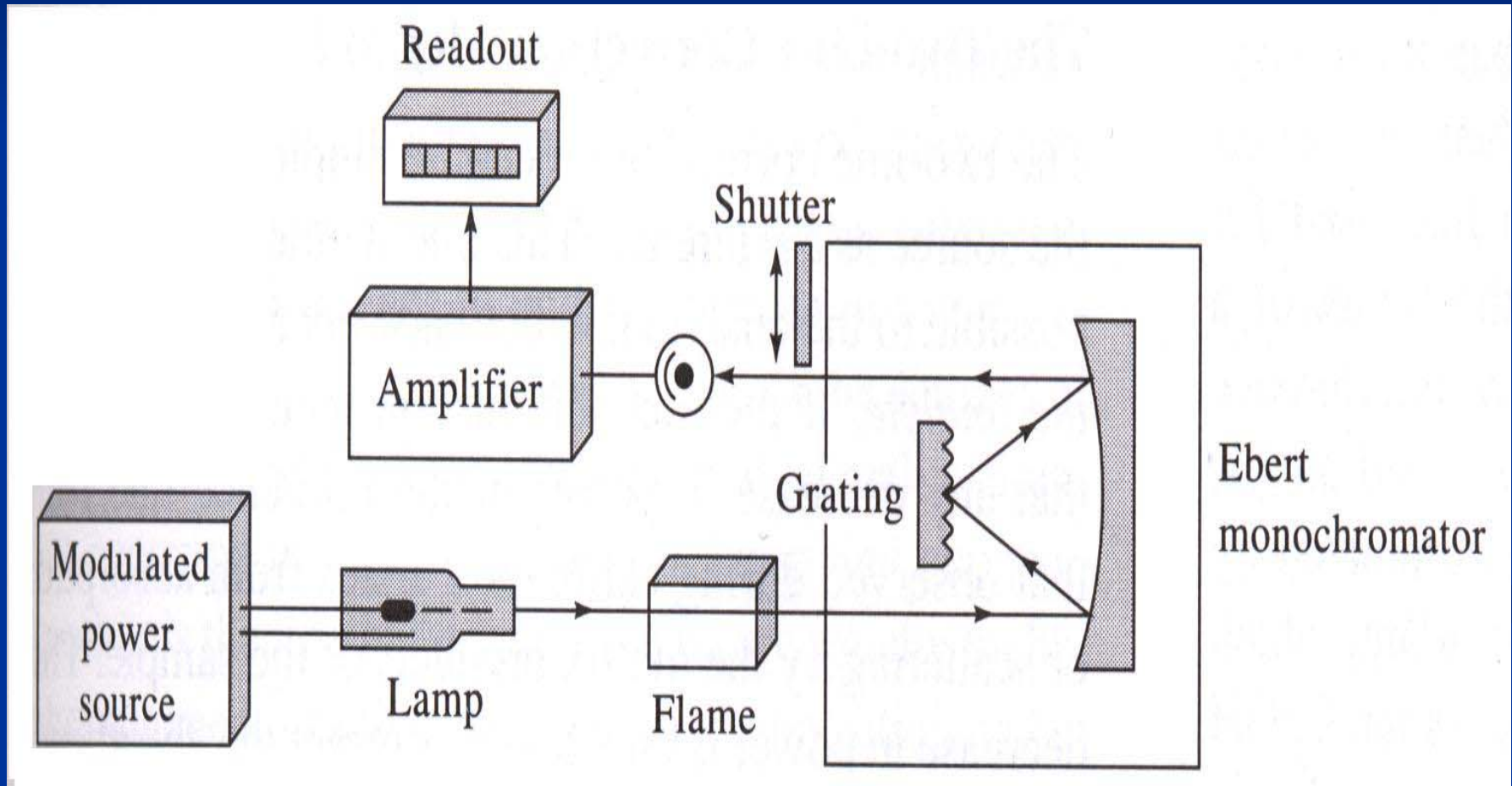
Spectral Interference

- Spectral interference - emission or absorption from interferents which overlap analyte.
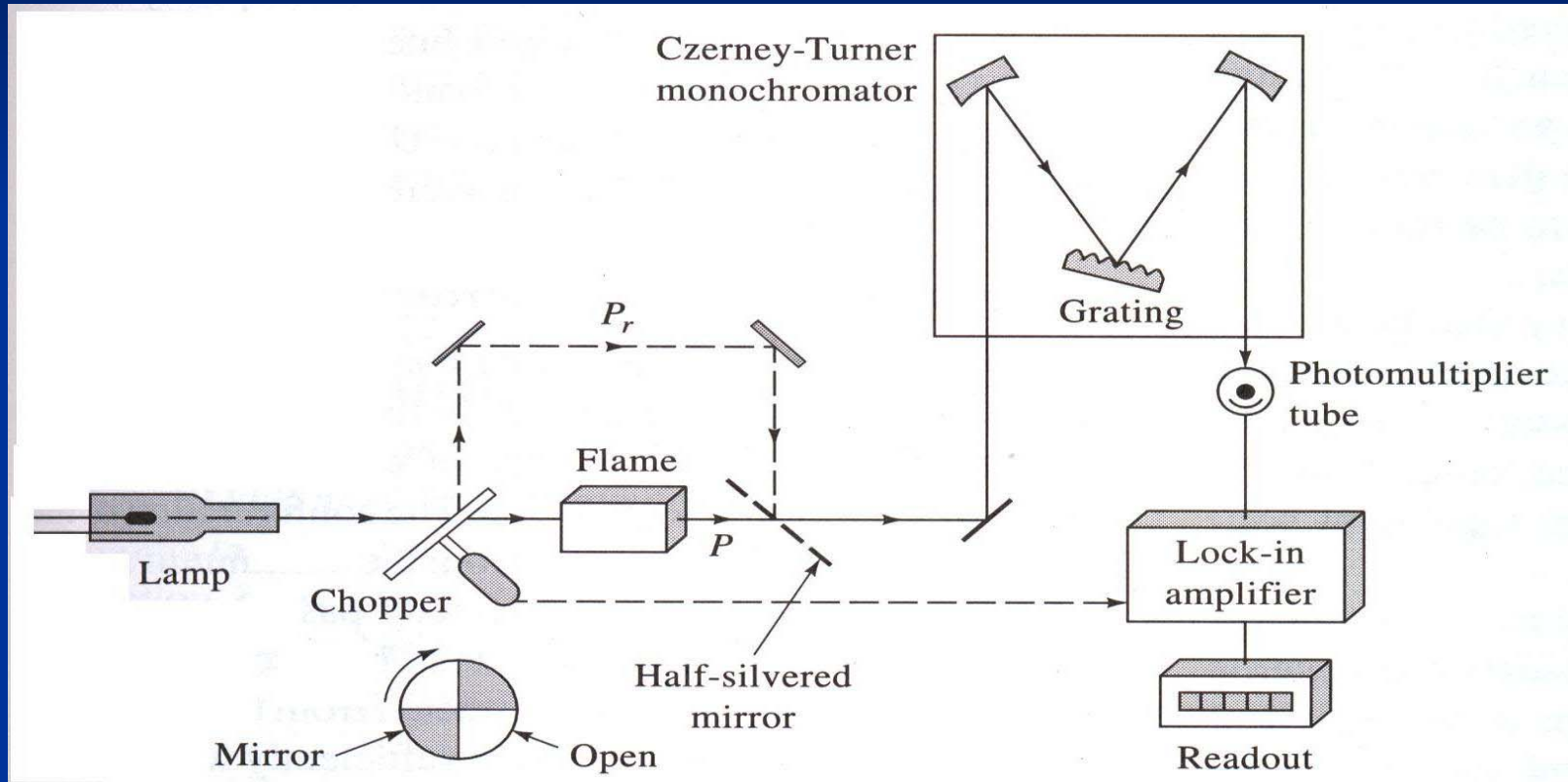
- ❖ Beam usually *chopped* or *modulated* at known frequency.
- ❖ Signal then contains constant (background) and dynamic signals.

Monochromator and Detector

- A high resolution, holographic grating is used to resolve your lines. It is not designed to be used in 'scan' mode.

- The typical detector is a photomultiplier tube.

- An additional component that is very common is a method of background correction.

Types of Interferences
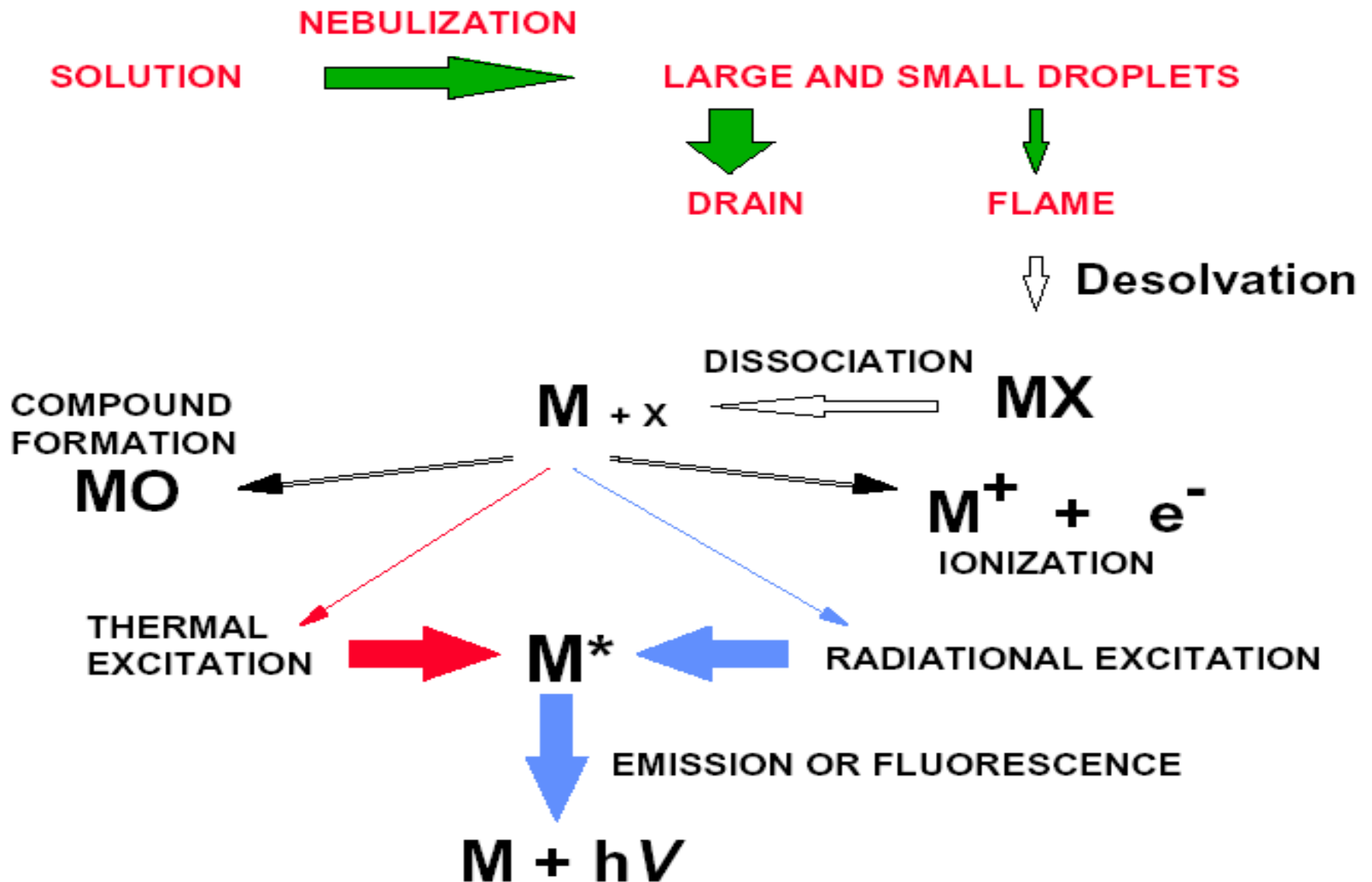
Background Correction

- Modulation of your signal (using a chopper) is an easy way to account for instrumental variations and 'flame flicker'.

- It is not very good at accounting for background absorption or emission.

- Two approaches commonly used are D_2 or Zeeman correction.

- These methods rely on that:
  - Atomic line is very narrow.
  - Background is typically molecular broad band.

D$_2$ Background Correction

- A continuous-source correction method.

- Light from both hollow cathode lamp and a D$_2$ lamp alternately passes through the sample.

- Because the spectra slit width is significantly larger than the AAS source line, the D$_2$ lamp sends a much broader band of light through the sample.

D$_2$ Background Correction

Hollow cathode lamp

D$_2$
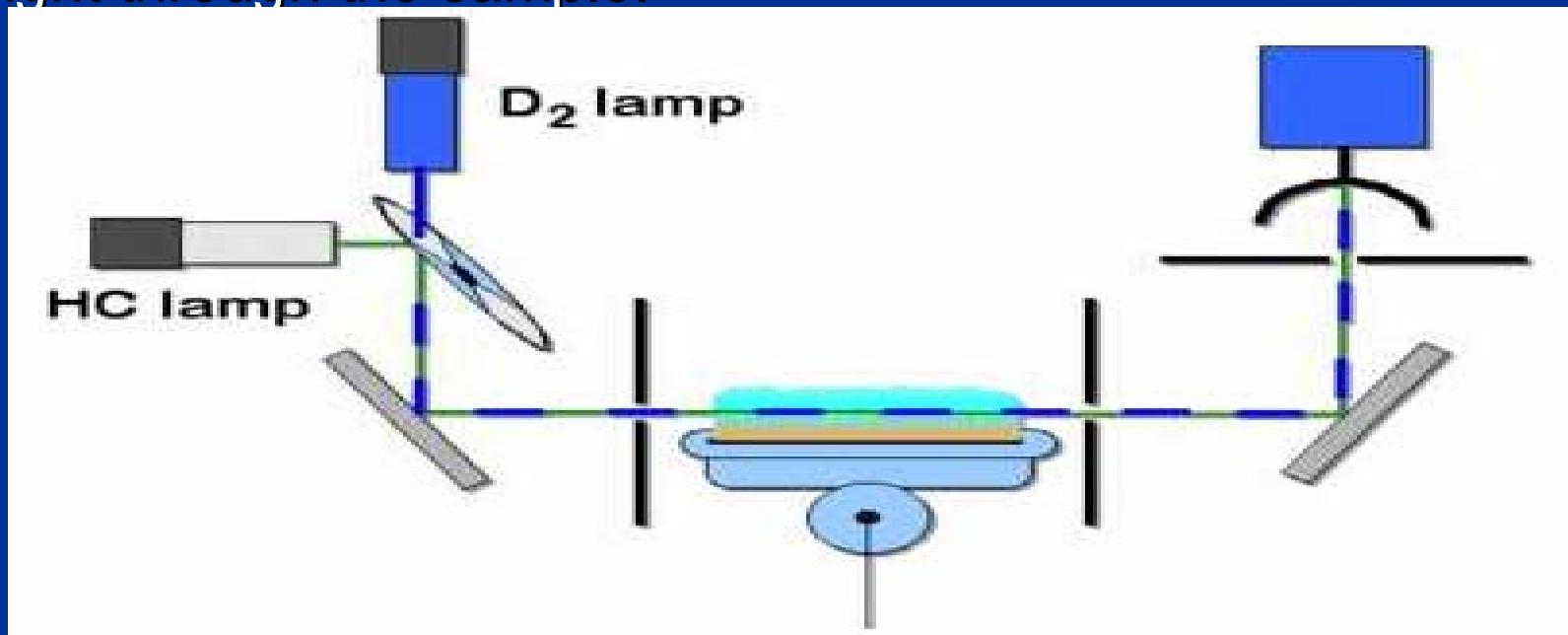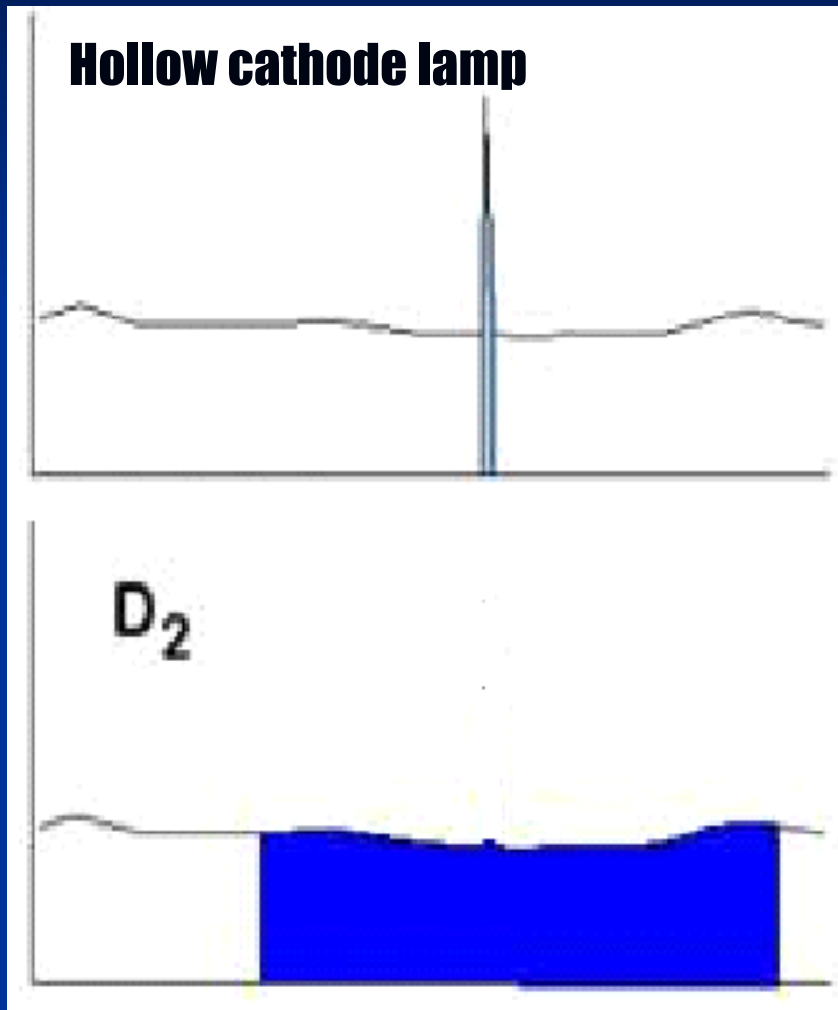
- With the hollow cathode lamp, we measure absorption of our element and background over a very narrow bandwidth.

- 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

The difference between the two signals gives us our background corrected sample.
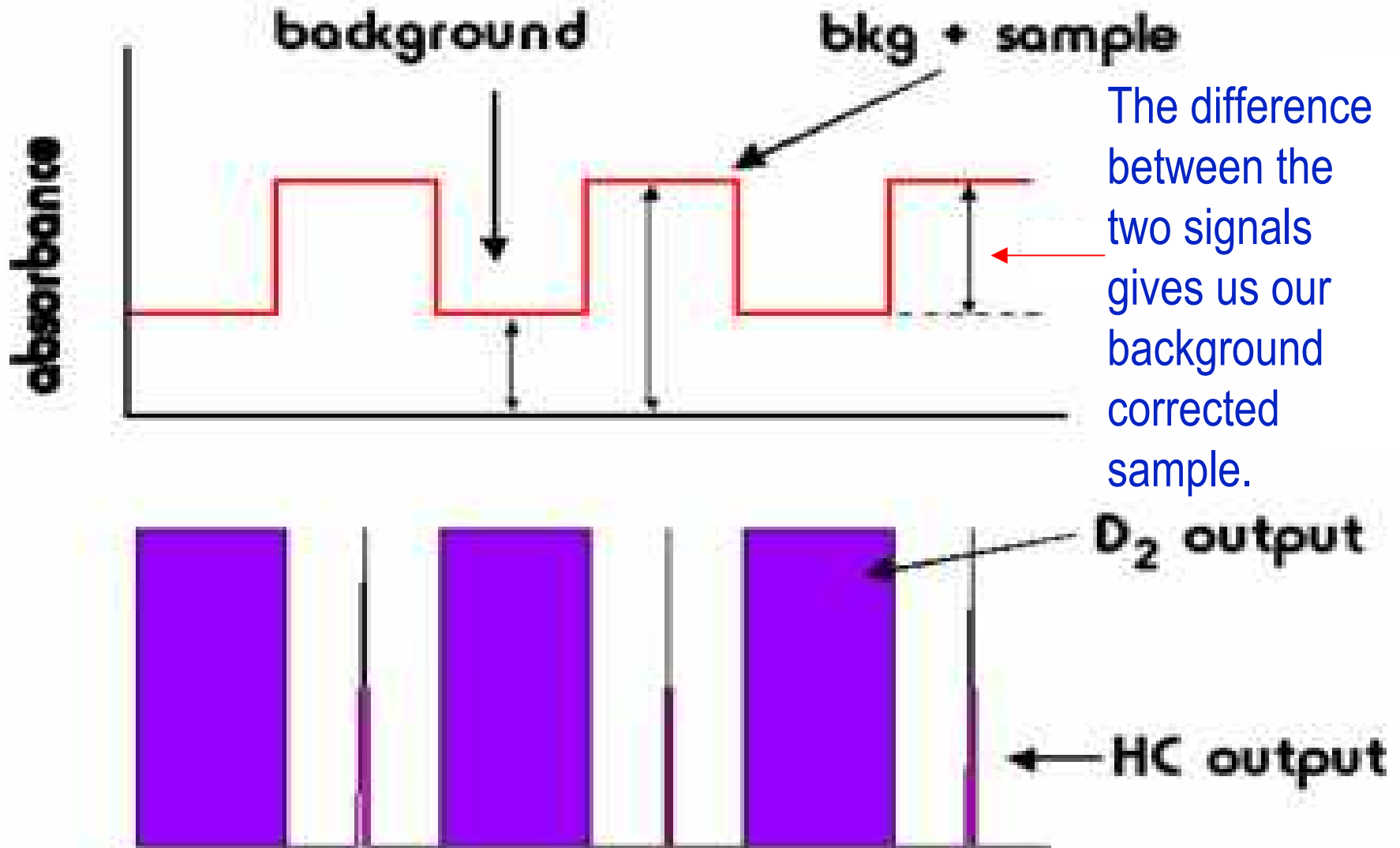
D$_2$ Background Correction

- Limitations of D$_2$ correction
  - Either undercorrection or overcorrection can occur based on sample.
- Background may be around line.
- Composition of background can differ based on position in flame – requires good alignment of hollow cathode and D$_2$ lamps.
- D$_2$ output is not very good at > 350 nm.

Background Correction

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

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

- This essentially moves our absorption away from the emission lines.

- The magnetic field is applied to the sample.

Background Correction

- Using this method of correction, we can measure at a fixed and narrow wavelength.

- At regular intervals, we simply move our sample component out of the way.

- This allows us to directly measure background.

normal absorption line

split lines in presence of a strong magnetic field
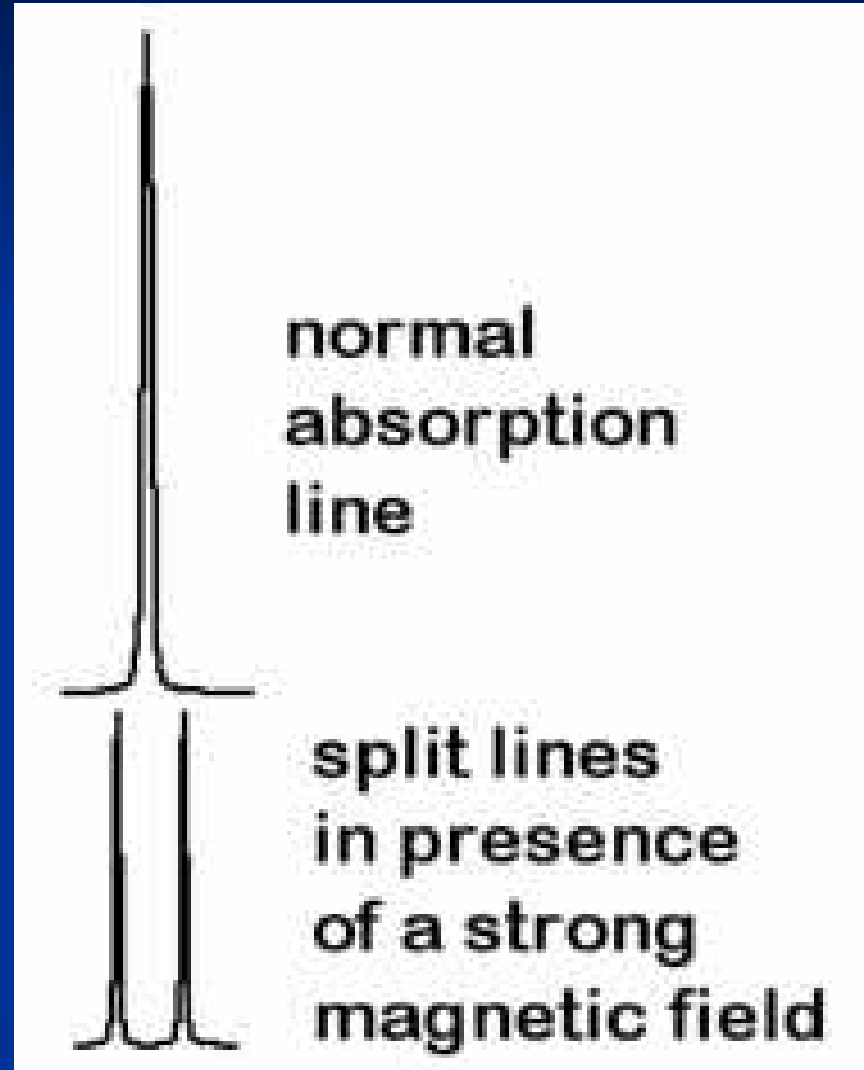
AAS Methods

- For each element, you must consider:
  - Which λ and slit width to use.
  - Determines sensitivity and linear range.
- For flame AAS
  - Flame type.
  - Method of sample mixing.
- For flameless AAS
  - Optimum temperatures to use.

AAS Methods

- Fortunately, AAS is a reasonably well worked out technique.

- Standard conditions for all elements that can be measured by AAS are available.

- If you have a computer based system, it will even help set up the proper conditions.

Flame AAS Example - Mn

λ	Relative Noise	Sensitivity (mg/l)	Linear range (mg/l)
279.5	1.0	0.052	2.0
279.8	0.77	0.067	3.0
280.1	0.88	0.11	5.0

Other conditions   Air/C_2H_2 flame - lean, blue

Slit width of 0.2 nm

Flow spoiler

0.2% $CaCl_2$ can be added to overcome interference from presence of Si.

Matrix	Aqueous
λ	279.5 nm
Slit width	0.2 nm
Temperatures	
Maximum Char	1100°C
Optimum Atomization	2700°C
Sensitivity	4 pg / 0.0044A
Linear range	200 pg

Atomic Fluorescence

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

- The hollow cathode lamp is placed at a right angle to the detector.

- Any atoms that fluoresce can be measured.

- Not as common as AAS or plasma emission.

Atomic Fluorescence
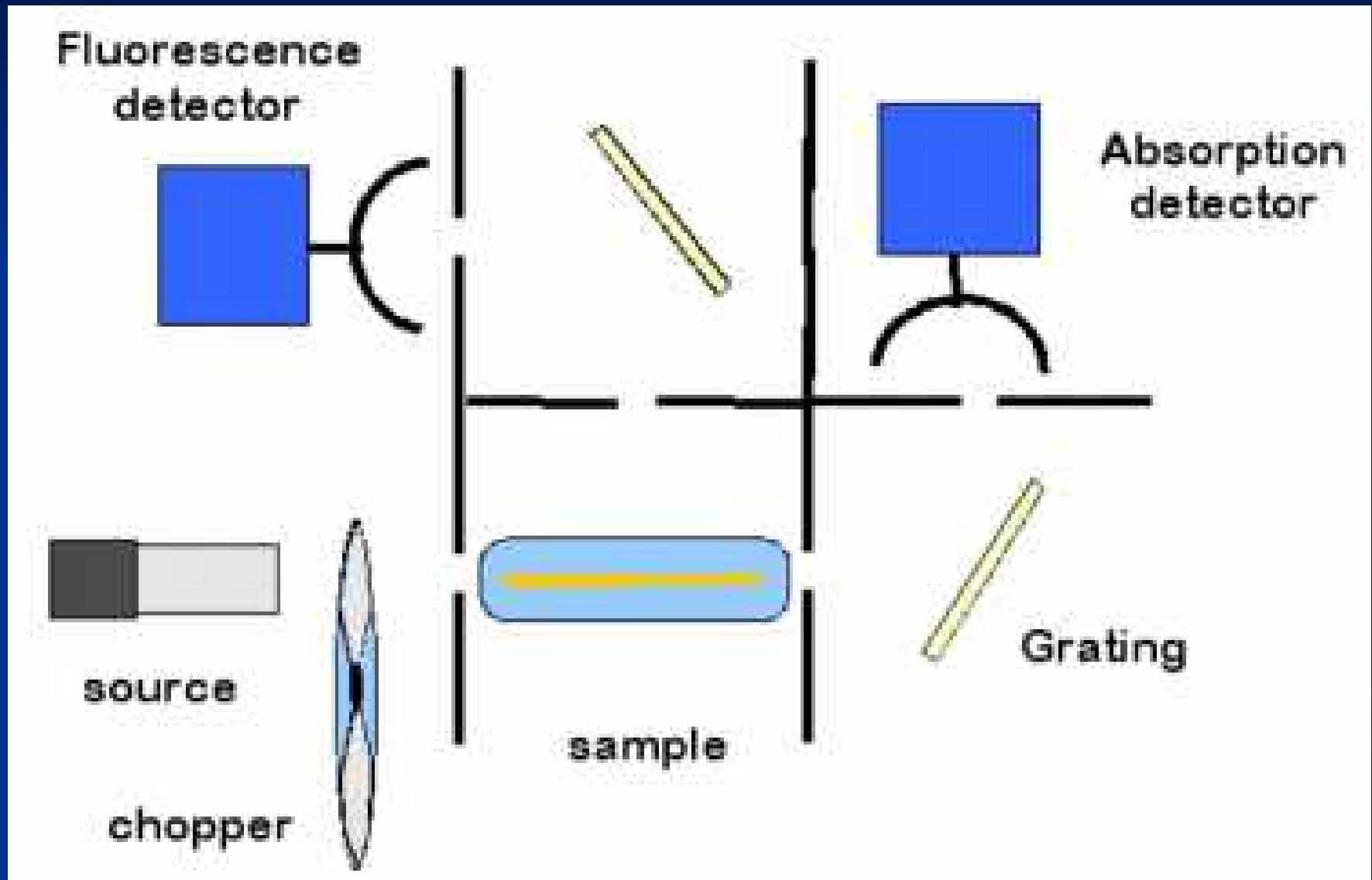
Spectral Interferences

- The presence of combustion products
  - ❖ Often exhibit a broadband absorption.
  - ❖ Can form particulate products that scatter radiation.
  - ❖ We have to correct these effects by making absorbance measurements of a blank to set our base-line.
- Samples containing metal oxide particles can cause scattering of the incident beam.

Spectral Interferences

- *Spectral interferences* occur when the absorption or emission of an interfering species overlaps with the analyte absorption or emission.

  - ❖ An easy way to overcome this problem is to choose another wavelength.

  - ❖ For example, vanadium absorbs at 3082.11 angstroms which interferes with an analysis based upon the aluminum absorption line at 3081.15 angstroms.

  - ❖ We can avoid the interference by employing the aluminum line at 3092.7 angstroms.

Chemical Interferences

- Formation of less volatile compounds reduces the rate at which the analyte is atomized.

  - For example, the absorbance of calcium is reduced in the presence of high concentrations of sulfate or phosphate.

  - Aluminum causes low results in the determination of magnesium due to the formation of a heat-stable aluminum/magnesium compound.

- Higher flame temperatures is one solution to this problem.

- Adding *releasing agents* that will react with the interferent, preventing its interaction with the analyte, is another solution.

- *Protective agents* prevent interference by forming stable but volatile species with the analyte.

Chemical Interferences

- Dissociation and association reactions lead to conversion of the metallic constituents.

  - These constituents all have different absorption profiles.

- Ionization of atoms and molecules can occur in higher temperature flames where oxygen or nitrous oxide serves as the oxidant.

  - The ionization equilibrium can be suppressed by adding an ionization suppressor which will yield a high concentration of electrons to the flame.

Chemical interferences

➢ Ionization

M ---→ M$^+$ + e-

❖ Hotter atomization means:

■ more ionization

■ emission from interferents.

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

What to do

- The instrument comes with a manual that describes the best conditions for measuring each element.
  - ❖ Interference problems are addressed.
  - ❖ Fuel/oxidant.
  - ❖ Wavelength.
  - ❖ Detection limits are given.
- Basically, you just decide what you want to look for, open the book, and follow the recipe.
  - ▪ Of course you'll have to put the appropriate lamp in the instrument and adjust the flame to the proper height.
  - ▪ You'll also have to line up the lamp to give maximum response at the detector.

What to do

- Although old, the instrument has the capability to do a Beer's law analysis for you.

  - You just make two standards and tell the instrument what the concentration of each standard is.

  - It will measure the absorbance of each and fit with a straight line.

  - All you have to do is put in your unknown and its concentration will be readout on the display.

Standard Addition Method

- **Standard addition method** is used in many techniques in analytical chemistry.

- A sample mixture is analyzed for the analyte of interest by adding a specified amount of this analyte to the sample, thus increasing its concentration.

- Successive standard amounts of the analyte are then added, each sample standard mixture being analyzed and the areas recorded.

Standard Addition Method

- A graph of peak area versus concentration is drawn and the amount of analyte in the sample obtained by projection of the calibration line to intersect the abscissa.