Chapter 9:

Atomic Absorption and Atomic Fluorescence Spectrometry

9 A- Sample Atomization Techniques

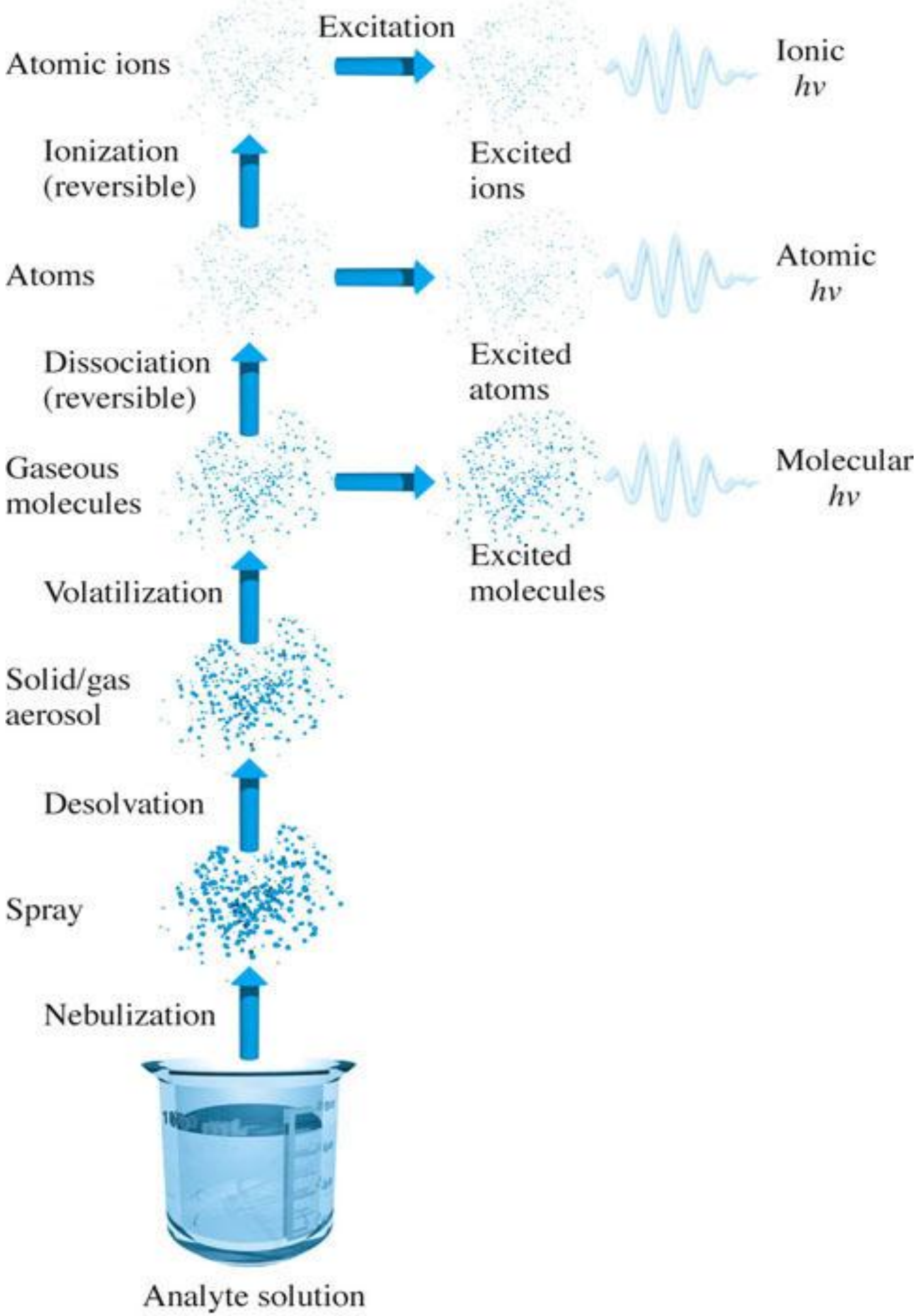
- The two most common methods of sample atomization encountered in AAS and AFS,
  - *Flame atomization and*
  - *Electrothermal atomization,*
- Three specialized atomization procedures
  - *Glow-Discharge Atomization*
  - *Hydride Atomization*
  - *Cold-Vapor Atomization*

used in both types of spectrometry.

9A-1 Flame Atomization:

In a flame atomizer, 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. The following processes then occur in the flame.

- *Desolvation: Solvent evaporates to produce a finely divided solid molecular aerosol.*
- *The aerosol is then volatilized to form gaseous molecules.*
- *Dissociation (leads to an atomic gas)*
- *Ionization (to give cations and electrons)*
- *Excitation (giving atomic, ionic, and molecular emission)*



© 2007 Thomson Higher Education

Types of Flames:

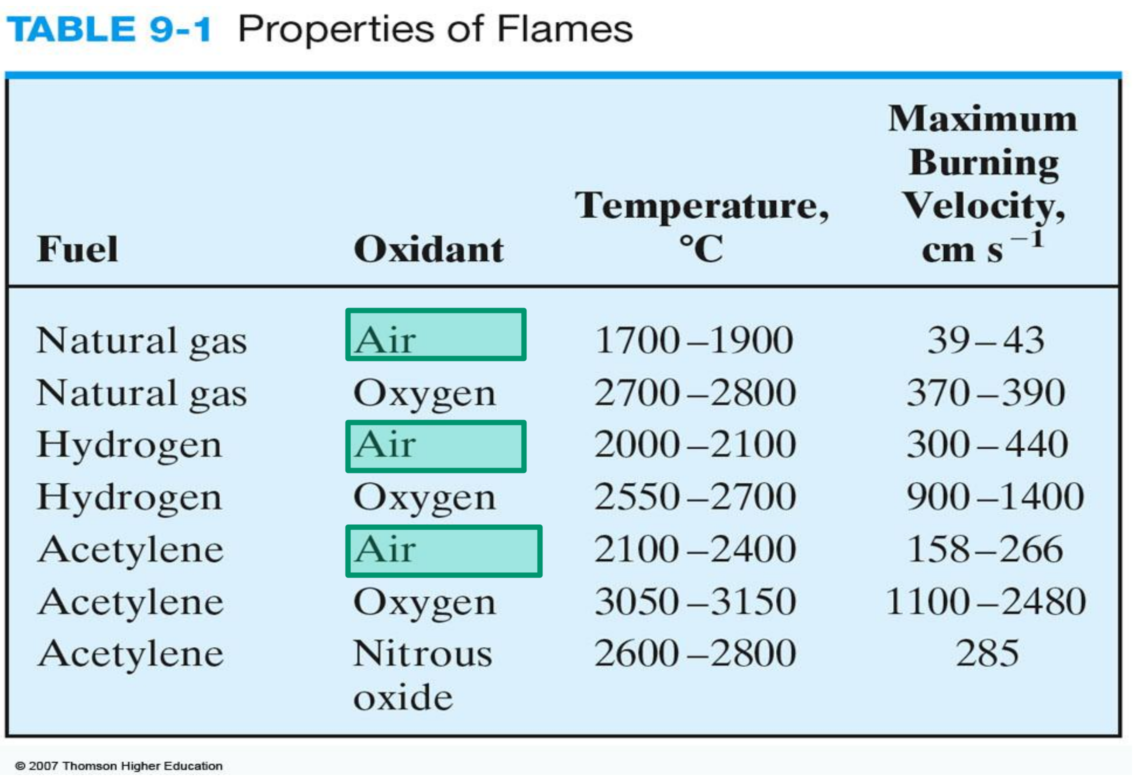


TABLE 9-1 Properties of Flames

Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, cm s^{-1}
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

Several common fuels and oxidants can be employed in flame spectroscopy depending on temperature needed.

- Temperatures of 1700°C to 2400°C are obtained with the various fuels when *air serves as the oxidant*. At these temperatures, only easily decomposed samples are atomized.
- For more refractory samples, *oxygen or nitrous oxide* must be employed as the oxidant. With the common fuels these oxidants produce temperatures of 2500°C to 3100°C.

Burning Velocity:

- The burning velocities are important because flames are stable only in certain ranges of gas flow rates.
- If the gas flow rate does not exceed the burning velocity, the flame propagates itself back in to the burner, giving *flashback.*
- As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. This region is where the flame is stable.

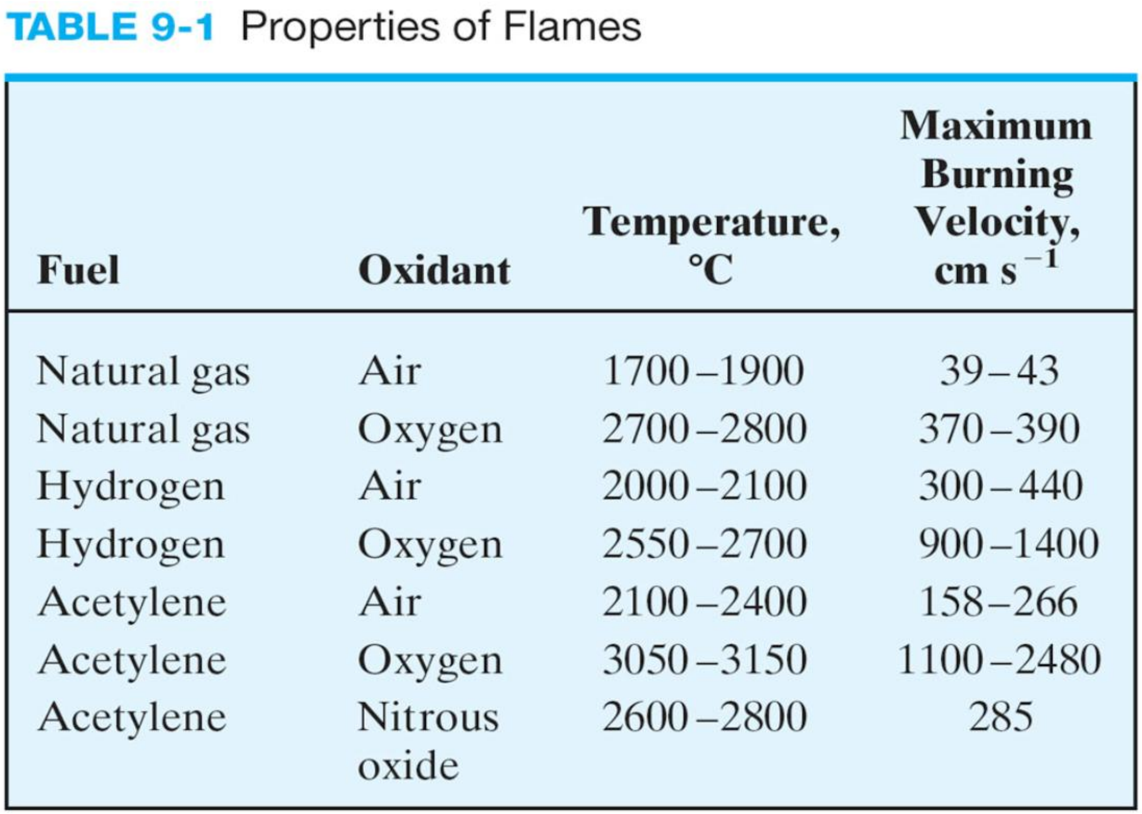


TABLE 9-1 Properties of Flames

Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, cm s^{-1}
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

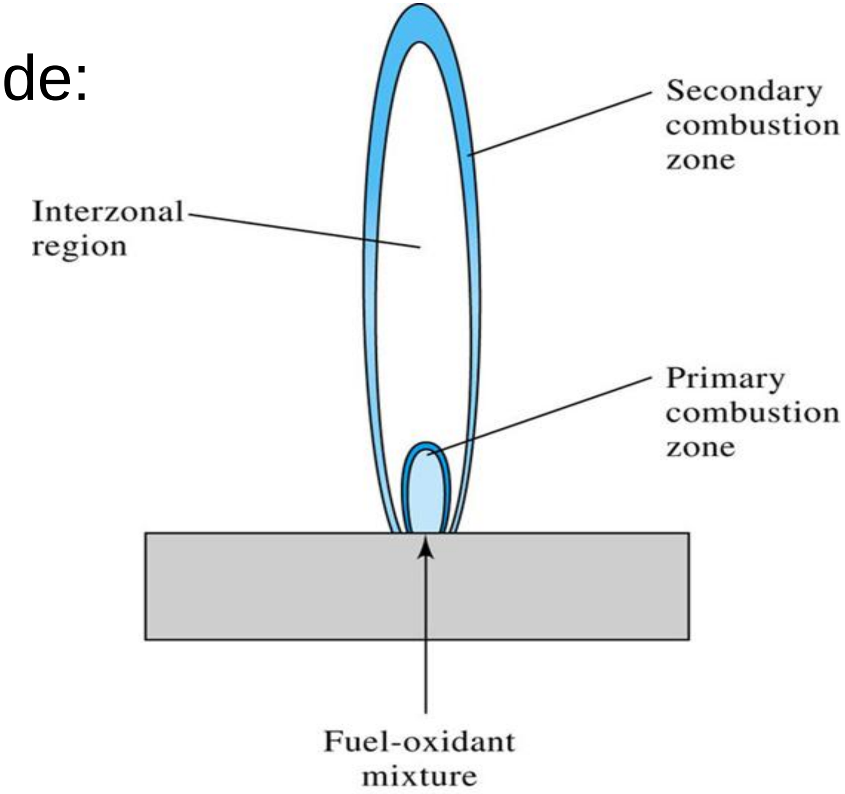
- At higher flow rates, the flame rises and eventually reaches a point where it blows off of the burner.
- With these facts in mind, it is easy to see why it is so important to control the flow rate of the fuel-oxidant mixture. This flow rate very much depends on the type of fuel and oxidant being used.

Flame Structure:

Important regions of a flame include:

1. *primary combustion zone*
2. *interzonal region*
3. *secondary combustion zone*

The *appearance and relative size* of these regions vary considerably with the *fuel-to-oxidant ratio* as well as with the *type of fuel and oxidant.*



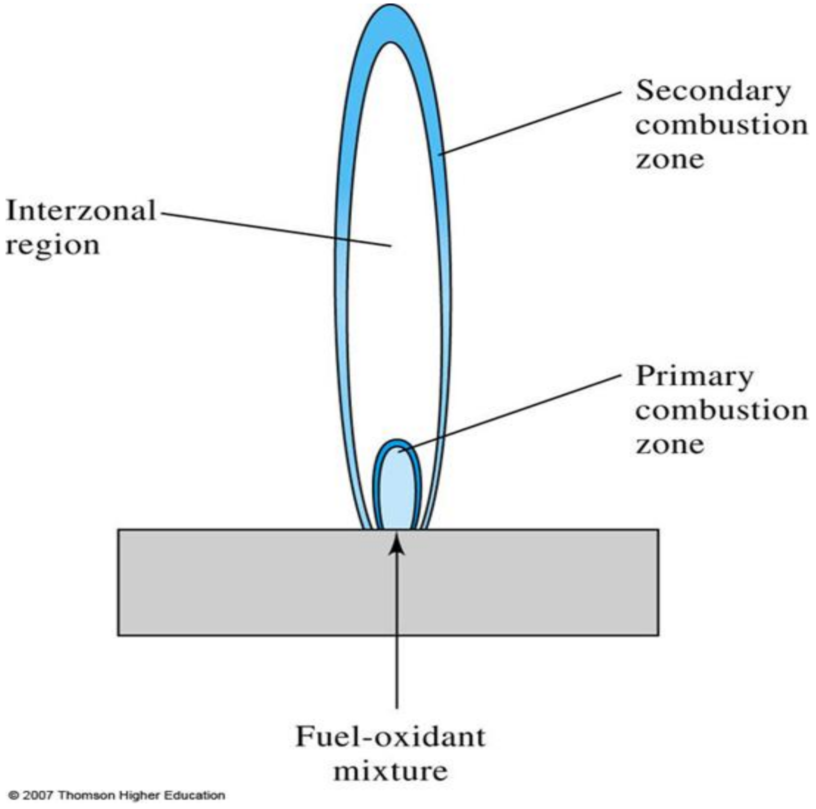
© 2007 Thomson Higher Education

1. Primary combustion zone:

➢ is recognizable by its blue luminescence arising from the band emission of C_2, CH and other radicals, in a hydrocarbon flame . Thermal equilibrium is usually not achieved in this region, and it is therefore, rarely used for flame spectroscopy.

2. Interzonal region:

- This area is relatively narrow in stoichiometric hydrocarbon flames, may reach *several centimeters in height* in fuel-rich acetylene-oxygen or acetylene-nitrous oxide sources.
- Since it is often rich in free atoms, it is the most widely used part of the flame for spectroscopy.

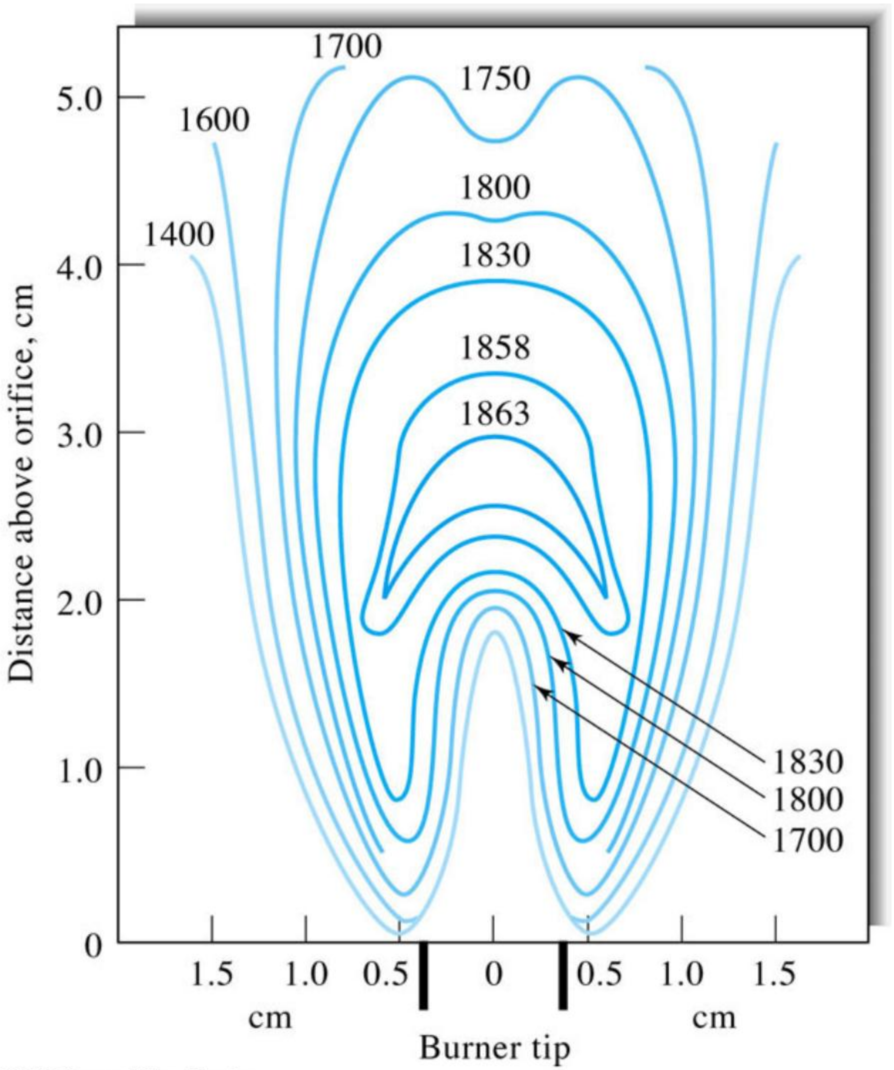


© 2007 Thomson Higher Education

3.Secondary combustion zone:

- In the secondary reaction zone, the products of the inner core are converted to stable molecular oxides that are then dispersed into the surroundings.

Temperature Profiles:



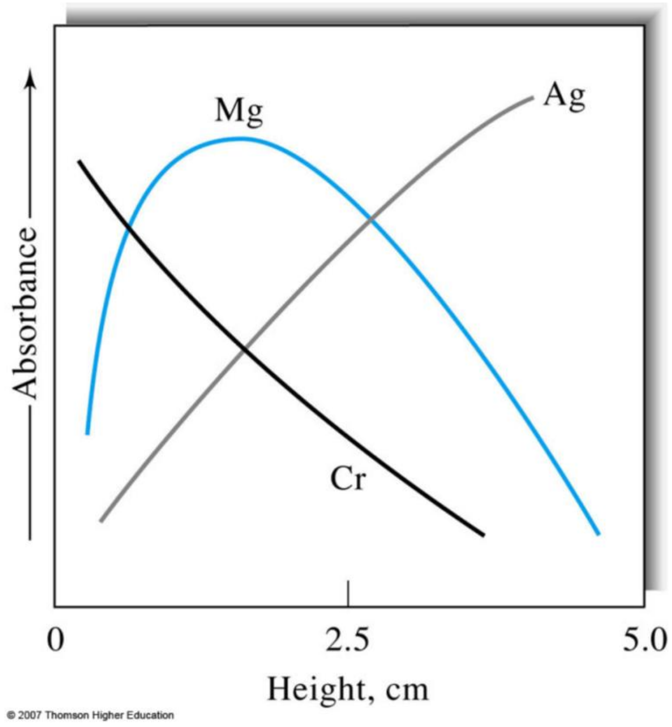
- The maximum temperature is located in the flame about 2.5 cm above the primary combustion zone.
- It is important– particularly for emission methods – to focus the same part of the flame on the entrance slit for all calibrations and analytical measurements.

Fig. 9-3. A temperature profile of a typical natural-gas air flame for atomic spectroscopy

Flame Absorption Profiles:

- Magnesium exhibits a maximum in absorbance at the middle of the flame. Then due to oxidation, a decrease in absorbance observed.
- The behavior of silver, which is not easily oxidized, is quite different. A continuous increase in the number of atoms, and thus the absorbance, is observed from the base to the periphery of the flame.
- Chromium, oxidizes readily and forms very stable oxides, shows a continuous decrease in absorbance beginning close to the burner tip.

These observations suggest that a different portion of the flame should be used for the determination of each of these elements.



© 2007 Thomson Higher Education

Fig. 9-4 Typical absorption profiles for three elements

To achieve maximum analytical sensitivity the flame must be adjusted up and down with respect to the beam until the region of maximum absorbance is located

Flame Atomizers:

- The aerosol formed by the flow of oxidant, is mixed with fuel and passes a series of baffles that remove all but the finest solution droplets.

- The baffles cause most of the sample to collect in the bottom of the mixing chamber where it drains to a waste container.

- The aerosol, oxidant, and fuel are then burned in a slotted burner to provide a 5- to 10-cm high flame.

- The quiet flame and relatively long-path length minimizes noise and maximizes absorption. These features result in reproducibility and sensitivity improvements for AAS

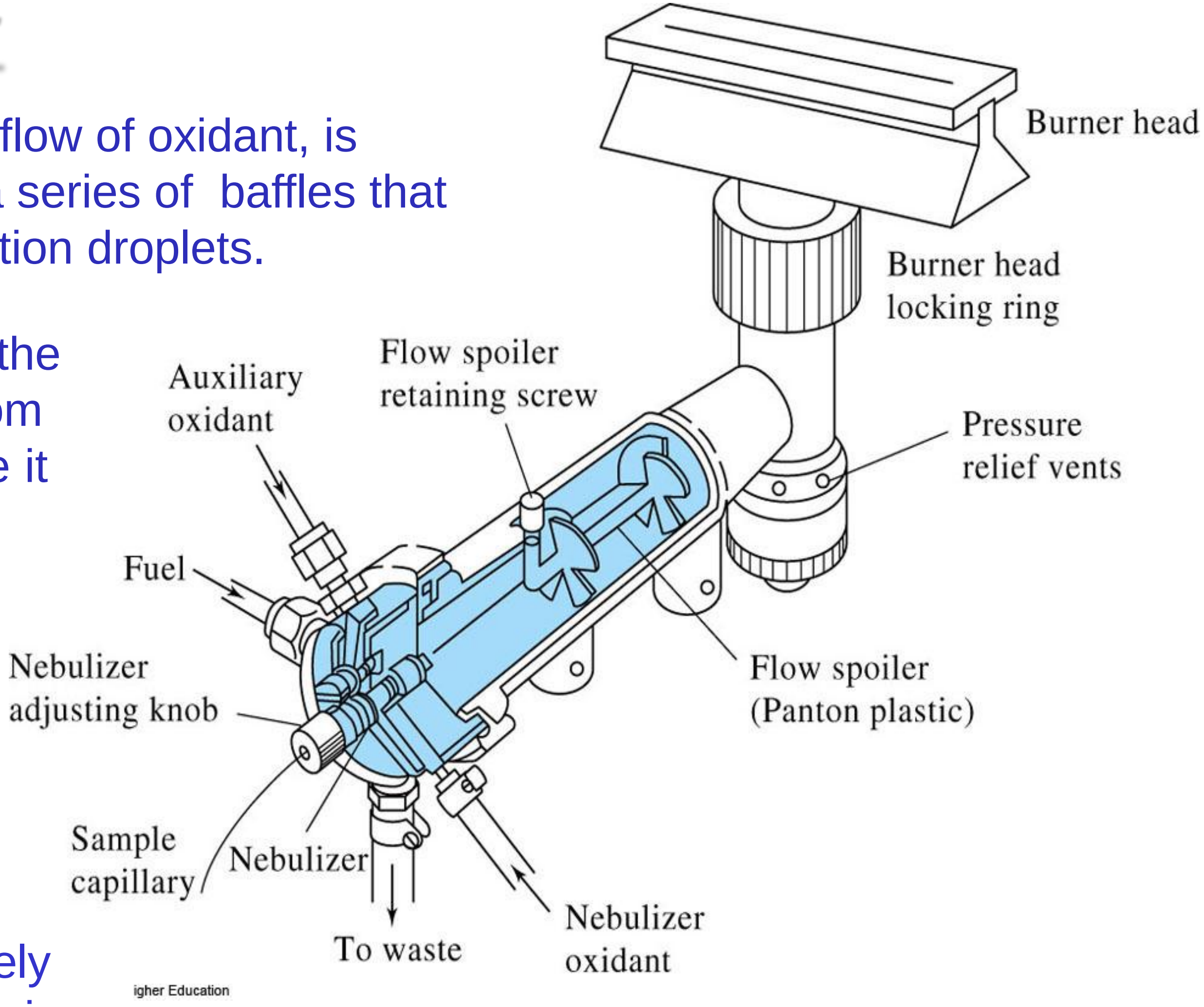


FIGURE 9-5 A laminar-flow burner.
(Courtesy of Perkin-Elmer Corporation, Norwalk, CT.)

Laminar-flow burners:

- produce a relatively quiet flame and a long path length for maximizing absorption.

- These properties tend to enhance sensitivity and reproducibility in AAS.

- The mixing chamber in this type of burner contains a potentially explosive mixture that can *flash back* if the flow rates are too low.
Note that the laminar-flow burner in Figure 9-5 is equipped with pressure relief vents for this reason.

- Other types of laminar-flow burners and turbulent-flow burners are available for atomic emission spectrometry and AFS.

Fuel and Oxidant flow-rate:

- It is desirable to be able to control the fuel and oxidant flow rate, over a broad range so that optimal atomization conditions can be achieved.
- Fuel and oxidant are usually combined in approximately stoichiometric amounts.
- For the determination of metals that form *stable oxides*, a flame that contains an excess of fuel is often desirable.
- Flow rates are usually controlled by means of double-diaphram pressure regulators followed by needle valves in the instrument housing.
- A widely used device for measuring flow rates is the rotameter. which consists of a tapered, graduated, transparent tube that is mounted vertically with the smaller end down. A lightweight conical or spherical float is lifted by the gas flow; its vertical position is determined by the flow rate.

Performance Characteristics Of Flame Atomizers

- In terms of reproducible behavior, flame atomization appears to be superior to all other methods for liquid sample introduction.

ADVANTAGES:

1. Uniform dropsize
2. Homogeneous flame
3. Quiet flame and a long path length

- In terms of sampling efficiency and thus sensitivity, however, other atomization methods are markedly better.

DISADVANTAGES:

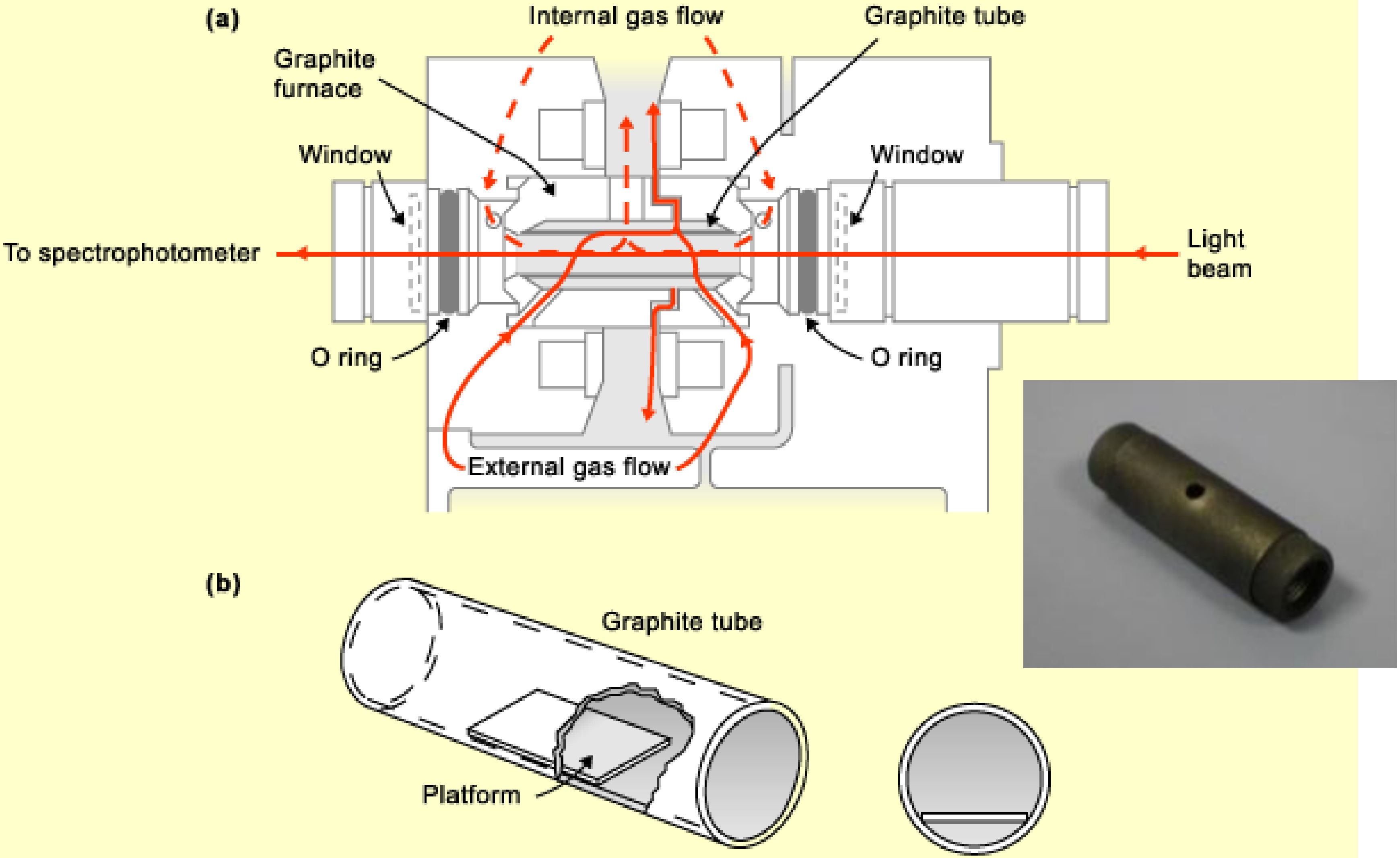
1. A large portion of the sample flows down the drain , ~90% of sample is lost
2. the residence time of individual atoms in the optical path in the flame is brief (~10^{-4}s).
3. Flash back, if $V_{burning} > V_{flow}$

9A-2 Electrothermal Atomization

Acc. To IUPAC recommendation

- An electrothermal atomizer is defined as a device which is heated to the temperature required for analyte atomization by the *passage of electrical current through its body*.
- This technique has largely been developed for use in atomic absorption spectrometry for which the terms electrothermal atomic absorption spectrometry, electrothermal AAS and the abbreviation ETAAS are defined.
- It has also been applied in optical emission and atomic fluorescence spectrometry, with appropriate analogous terms, such as electrothemal optical emission spectrometry, OES and electrothermal atomic fluorescence spectrometry, AFS being defined.

ElectroThermal AAS (ETAAS or GFAAS)



- The furnace goes through several steps…
  - Drying (usually just above 110 deg. C.)
  - Ashing (up to 1000 deg. C)
  - Atomization (Up to 2000-3000 C)
  - Cleanout (quick ramp up to 3500 C or so). Waste is blown out with a blast of Ar.
- The light from the source (HCL) passes through the furnace and absorption during the atomization step is recorded over several seconds. This makes ETAAS more sensitive than FAAS for most elements.

9A-2 Electrothermal Atomization

- Enhanced sensitivity due to
  - entire sample is atomized in a short period,
  - the average residence time of the atoms in the optical path is a second or more.
- A few microliters of sample are first evaporated at a low temperature and then ashed at a **s**omewhat higher temperature in an electrically heated graphite tube or in a graphite cup.
- Then the current is rapidly increased to several hundred amperes, which caused the temperature to soar to perhaps 2000^{o}C to 3000^{o}C; atomization of the sample occurs in a period of a few milliseconds to seconds.
- The absorption or fluorescence of the atomic vapor is then measured in the region immediately above the heated surface.

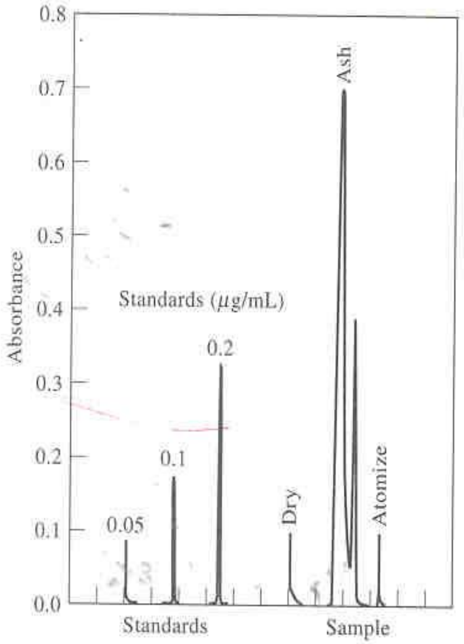
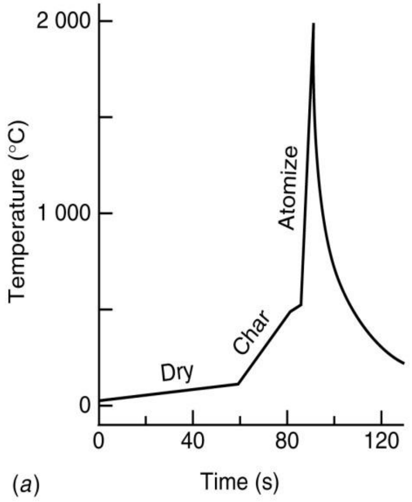


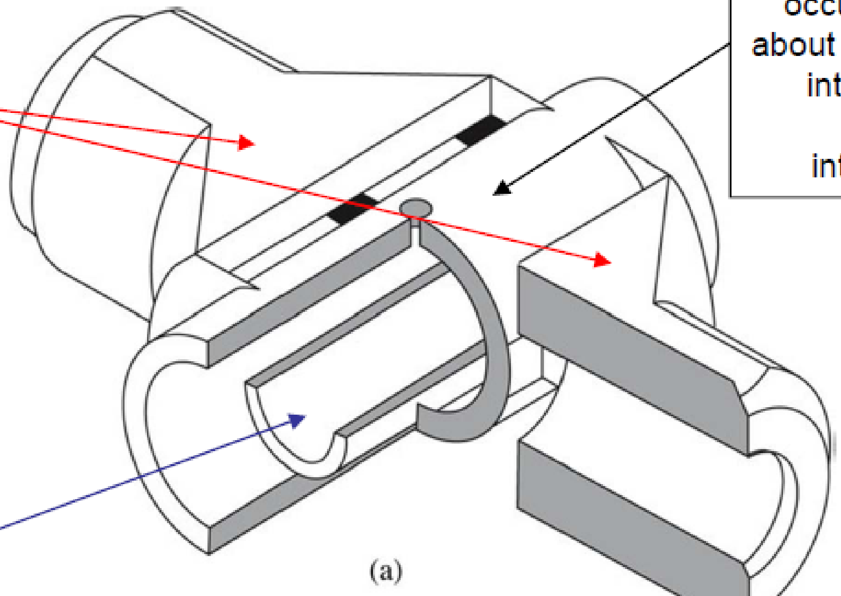
Figure 9-7 Typical output from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 μL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively. *(Courtesy of Varian Instrument Division, Palo Alto, CA.)*



Commercial electrothermal atomizer.

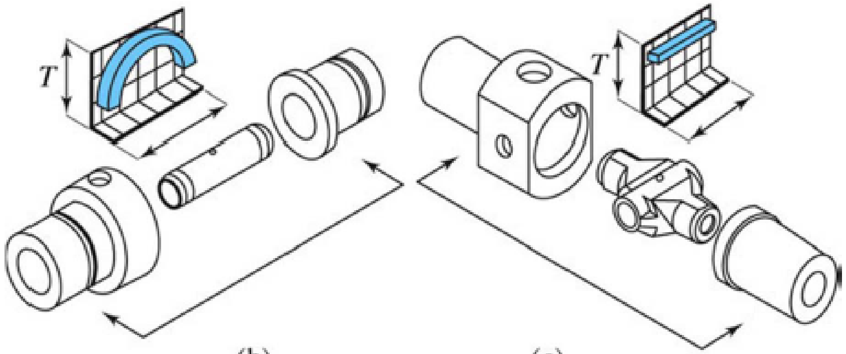
Cylindrical graphite electrical contacts. These contacts are held in a water-cooled metal housing.

L'vov platform. Made of graphite, sample is evaporated and ashed on this platform. Temperature on the platform does not change as fast as it changes in the walls of the furnace. Atomization occurs in an environment where temperature does not change so fast, which improves reproducibility of measurements. Facilitates furnace cleaning, which reduces memory effects.



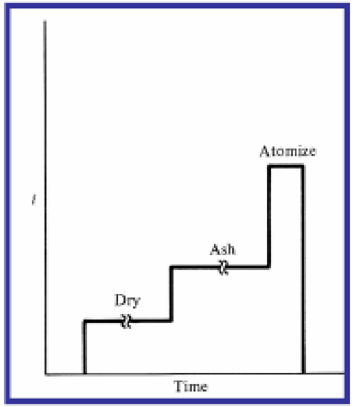
(a)

Cylindrical graphite tube where atomization occurs. Dimensions: about 5cm long and 1cm internal diameter. This tube is interchangeable.

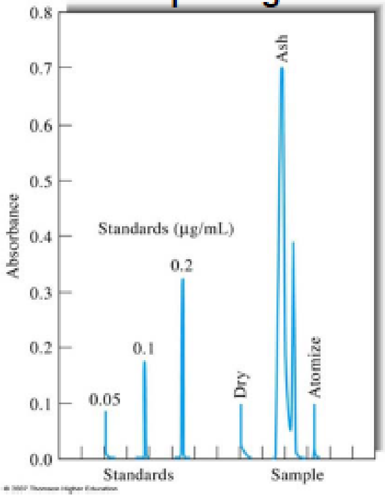


(b) (c)

Longitudinal (b) and transversal (c) furnace heating. Transversal mode is preferred because it provides a uniform temperature profile along the entire length of the tube and optical path.



Output signal



Pyrolytic coating of graphite tubes

-reducing the natural porosity of the graphite tube minimizes some sample matrix effects and poor reproducibility associated with graphite furnace atomization.

-During atomization, part of the analyte and matrix apparently diffuse into the surface of the tube, which slows the atomization process, thus giving smaller analyte signals.

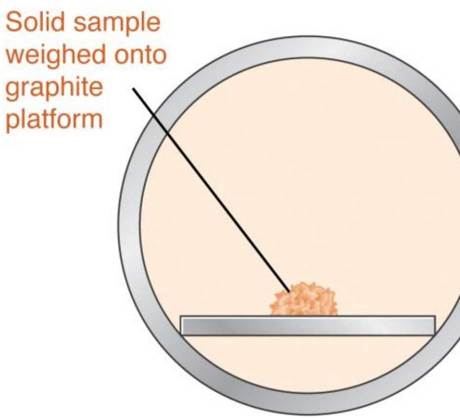
-To overcome this effect, most graphite surfaces are coated with a thin layer of pyrolytic carbon, which seals the pores of the graphite tube.

Performance Characteristics of Electrothermal Atomizers:

- Electrothermal atomizers offer the advantage of unusually high sensitivity for small volumes of sample. Typically, sample volumes between 0.5 and 10 μL are used;
- Absolute detection limits lie in the range of 10^{-10} to 10^{-13} g of analyte.
- The relative precision of electrothermal methods is generally in the range of 5% to 10% compared with the 1% or better that can be expected for flame or plasma atomization.
- Because of the heating-cooling cycles, furnace methods are slow; typically requiring several minutes per element.
- A final disadvantage is that the analytical range is low, being usually less than two orders of magnitude.

Analysis of solids by ETA

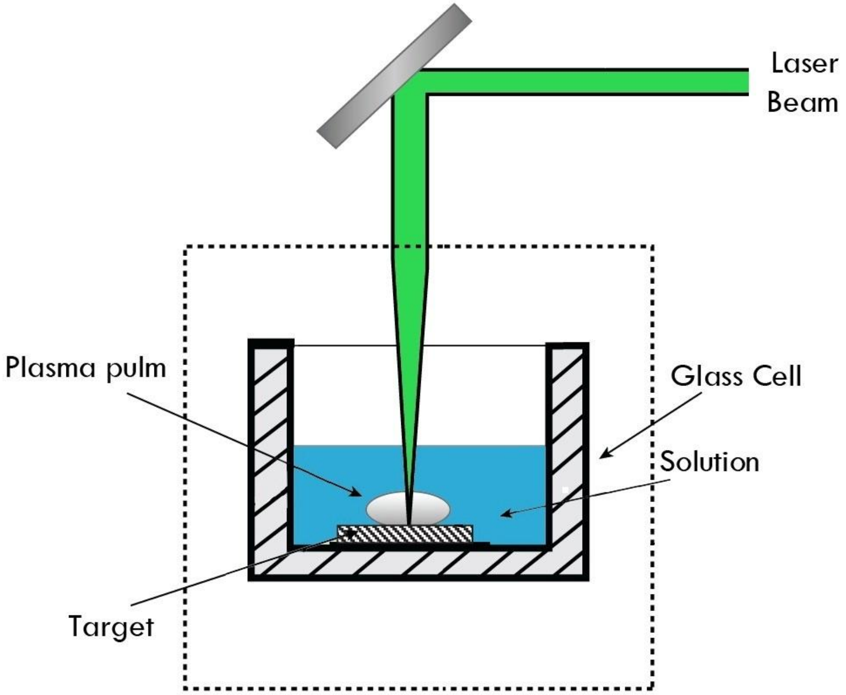
Direct solid sampling:



Direct solid sampling
— end view of furnace

Laser ablation :

process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimes. At high laser flux, the material is typically converted to a plasma.

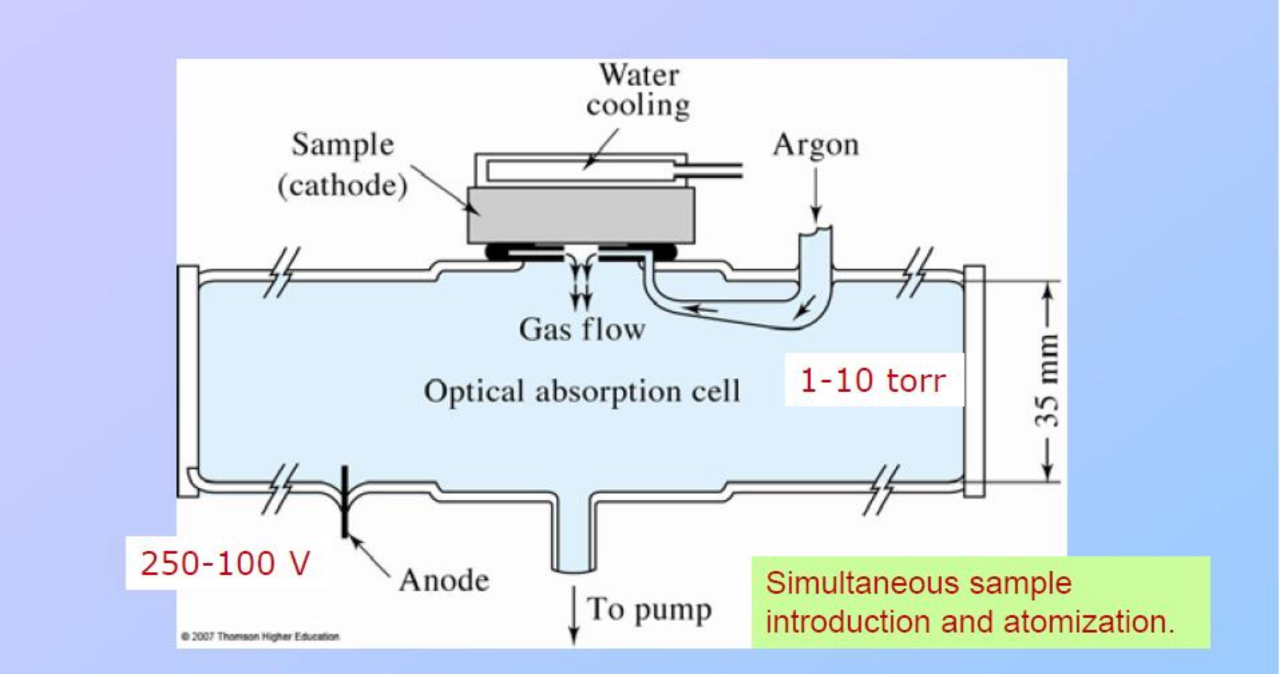


Slurry sampling:

- A second way is to prepare a slurry of the powdered sample by ultrasonic agitation in an aqueous medium. The slurry is then pipetted into the furnace for atomization.

Specialized Atomization Techniques

Glow Discharge Atomization:



Simultaneous sample introduction and atomization.

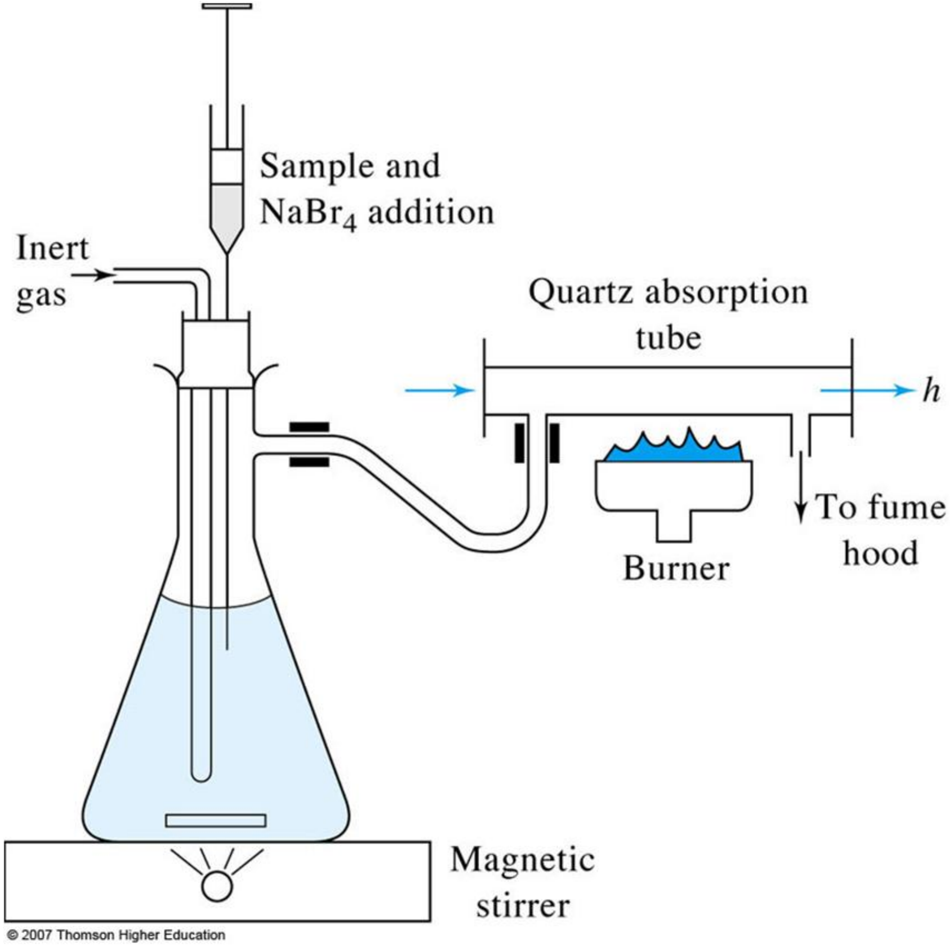
- A glow-discharge device(GD) serves as a versatile source, as it can simultaneously introduce and atomize the sample.
- The glow-discharge occurs in a low-pressure argon gas atmosphere between 1 and 10 torr.
- In this atmosphere lies a pair of electrodes applying a DCvoltage of 250 to 1000 V to break down the argon gas into positively charged ions and electrons.
- These ions, under the influence of the electric field, are accelerated into the cathode surface containing the sample, bombarding the sample and causing neutral sample atom ejection through the process known as *sputtering.*

Glow Discharge Atomization

- The atomic vapor is composed of ions, ground state atoms, and fraction of excited atoms.
- When the excited atoms relax back into their ground state, a low-intensity glow is emitted, giving the technique its name.
- The requirement for samples is that they are electrical conductors. Therefore GD atomizers are most commonly used in the analysis of metals and other conducting samples.
- However, with proper modifications, it can be utilized to analyze liquid samples as well as nonconducting materials by mixing them with a conductor (e.g. graphite).
- Detection limits are reported to be in the low ppm range for solid samples

Hydride Atomization:

- ∗The technique provides a means of introducing samples containing As, Sb, Sn, Se, Bi, and Pb into an atomizer in the gas phase.
- ∗ With these elements, hydride atomization enhances detection limits by a factor of 10 to 100 compared to alternative methods.
- ∗Hydride generation occurs by adding an acidified aqueous solution of the sample to a 1% aqueous solution of sodium borohydride, all of which is contained in a glass vessel.



© 2007 Thomson Higher Education

$$3BH_4^-(aq) + 3H^+(aq) + 4H_3AsO_4(aq) \rightarrow 3H_3BO_3(aq) + 4AsH_3(g) + 3H_2O\ (l)$$

- ∗The volatile hydride generated by the reaction that occurs is swept into the atomization chamber by an inert gas, where it undergoes decomposition.
- ∗ The chamber is usually a silica tube heated to several hundred degrees in a furnace or in a flame where atomization takes place.

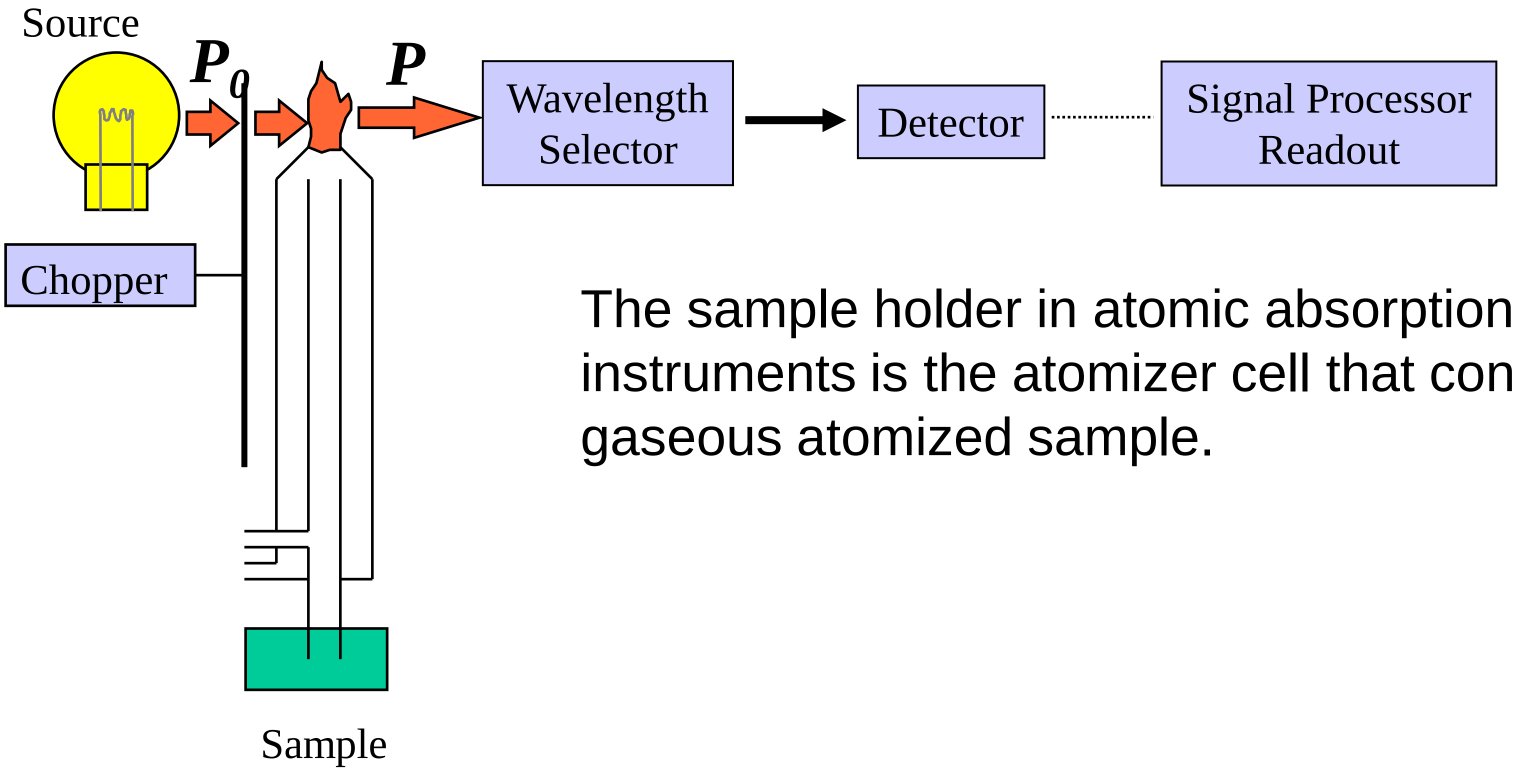
Cold-Vapor Atomization:

- The cold-vapor technique is an atomization method applicable only to the determination of mercurv because it is the only metallic element that has an appreciable vapor pressure at ambient temperature.
- mercury is converted to Hg^{+2} by treatment of samples with an oxidizing mixture of nitric and sulfuric acids followed by reduction of the Hg to the metal Hg^{0} with SnCl,.
- The elemental mercury is then swept into a long-pass absorption tube similar to the one shown in Figure 9-9 by bubbling a stream of inert gas through the reaction mixture.
- The determination is completed by measuring the absorbance at 253.7 nm. Detection limits in the parts-per-billion range are achieved.
- Several manufacturers offer automatic instruments for performing this determination.

ATOMIC ABSORPTION INSTRUMENTATION

Instruments for atomic absorption spectrometry (AAS) consist of:

- (1) Radiation source
- (2) Sample holder = atomizer
- (3) Wavelength selector
- (4) Detector
- (5) Signal processor and readout



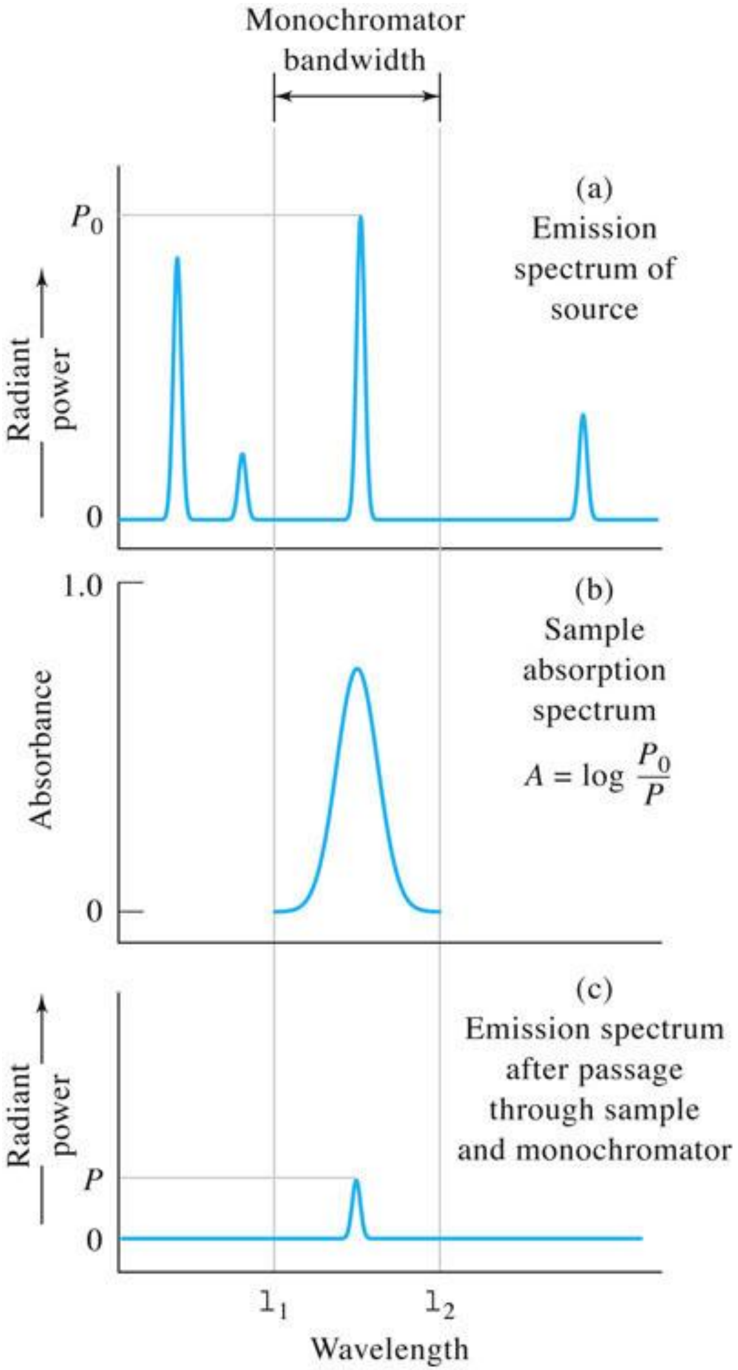
The sample holder in atomic absorption instruments is the atomizer cell that contains the gaseous atomized sample.

1. Radiation Sources:

-It is necessary that band width of the radiation source must be narrow relative to the width of an absorption line or band.

-Fig. 9-10a shows the emission spectrum of a typical atomic lamp source. With a suitable filter or monochromator, all but one of these lines are removed. Fig. 9-10b shows the absorption spectrum for the analyte between wavelengths λ_1 and λ_2. As shown in Figure 9-10c, passage of the line from the source through the flame reduces its intensity from P_0 to P; the absorbance is then given by $\log(P_o/P)$, which is linearly related to the concentration of the analyte in the sample.

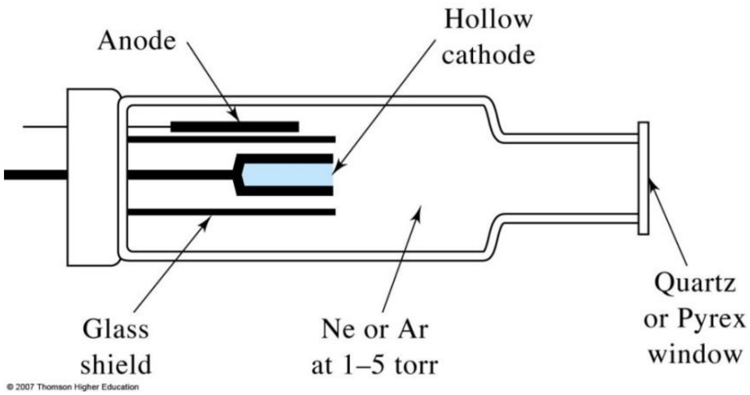
- The problem created by limited width of atomic absorption peaks has been solved by the use of line sources with bandwidths even narrower than absorption peaks. A disadvantage of the procedure is that separate lamp source is needed for each element.



© 2007 Thomson Higher Education

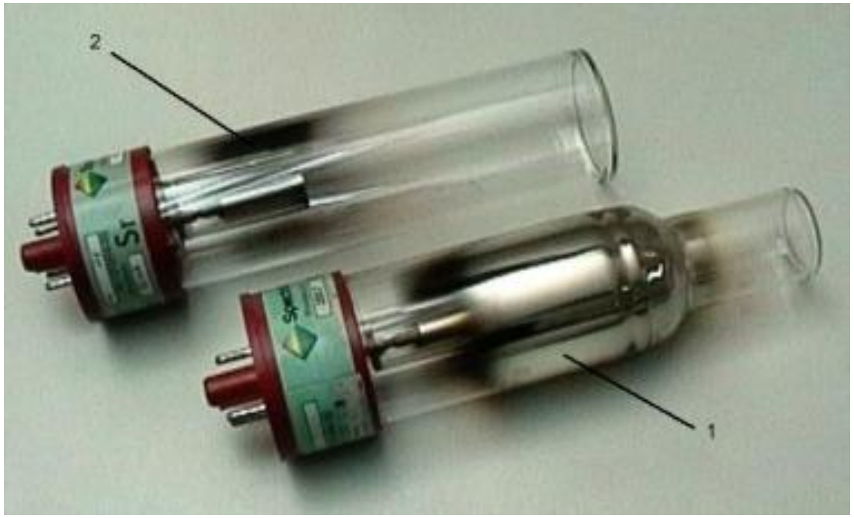
Hollow Cathode Lamps:

- The most common source for AAS.
- Consists of a tungsten anode and a cylindrical cathode sealed in a glass tube that is filled with *neon or argon at a pressure of 1 to 5 torr.*
- The cathode is constructed of the metal whose spectrum is desired.



© 2007 Thomson Higher Education

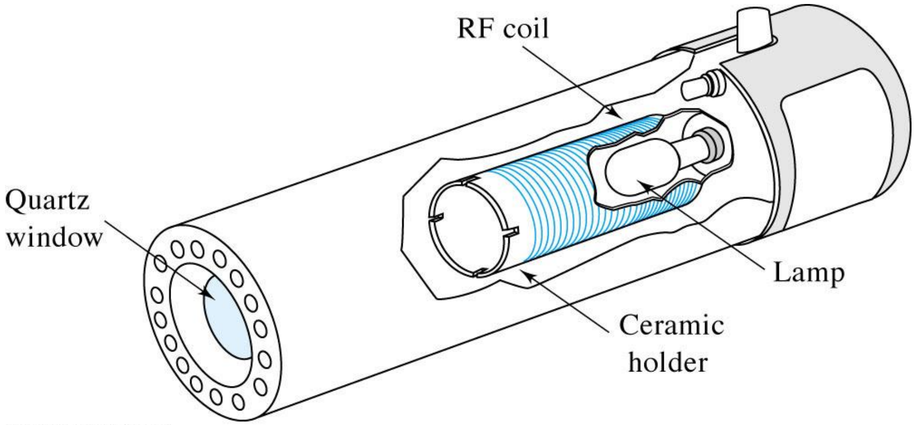
- Ionization of the inert **g**as occurs when a potential on the order of 300 V is applied across the electrodes, which generates a current of about 5 to 15 mA.
- If the potential is sufficiently large, the gaseous cation acquire enough kinetic energy to dislodge some of the metal atoms from the cathode surface and produce an atomic cloud in a process called *sputtering*.
- A portion of the sputtered metal atom are in excited states and thus emit their characteristic radiation as they return to the ground state.
- Eventually, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are redeposited.



- The efficiency of the hollow-cathode lamp depends on its geometry and the operating voltage.
- High voltages, and thus high currents, lead to greater intensities. This advantage is offset somewhat by an increase in Doppler broadening of the emission lines from the lamp.
- Furthermore, the greater currents produce an increased number of unexcited atoms in the cloud. The unexcited atoms, in turn, are capable of absorbing the radiation emitted by the excited ones. This *selfabsorption* leads to lowered intensities, particularly at the center of the emission band.

Electrodeless Discharge Lamps (EDLs):

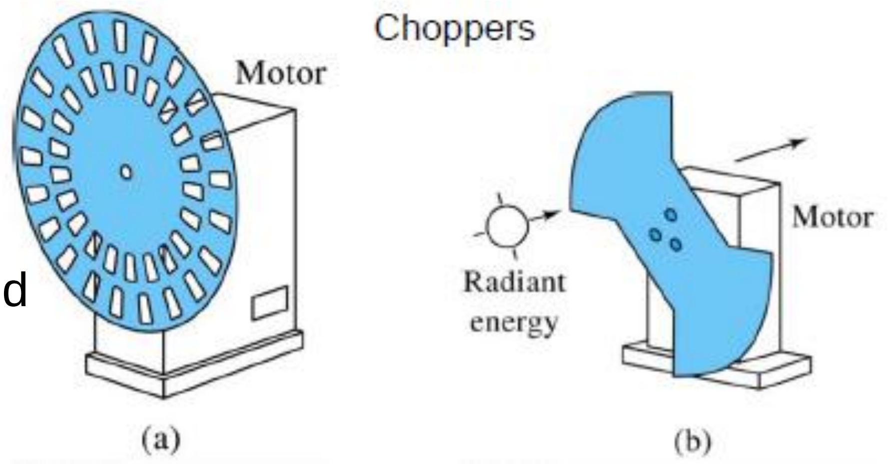
- These provide radiant intensities that are usually one to two orders of magnitude greater than hollow cathode lamps.
- A typical lamp is constructed from a sealed quartz tube containing a few torr of an inert gas such as argon and a small quantity of the metal (or its salt) whose spectrum is of interest.
- The lamp is energized by an intense field of radio-frequency or microwave radiation. Ionization of the argon occurs to give ions that are accelerated by the high-frequency component of the field until they gain sufficient energy to excite the atoms of the metal whose spectrum is sought. Electrodeless discharge lamps are available commercially for 15 or more elements.



© 2007 Thomson Higher Education

- EDLs exhibit better detection limits than do hollow-cathode lamps." This occurs because EDLs for these elements are more intense than the corresponding hollow-cathode lamps, and thus, EDLs are quite useful in determining these elements.

Source Modulation:



- to eliminate interferences caused by *emission of radiation by the flame*,

- the emission from the source is modulated with a chopper interposed between the source and the flame.

- As another alternative, the power supply for the source can be designed for intermittent or AC operation so that the source is switched on and off at the desired constant frequency.

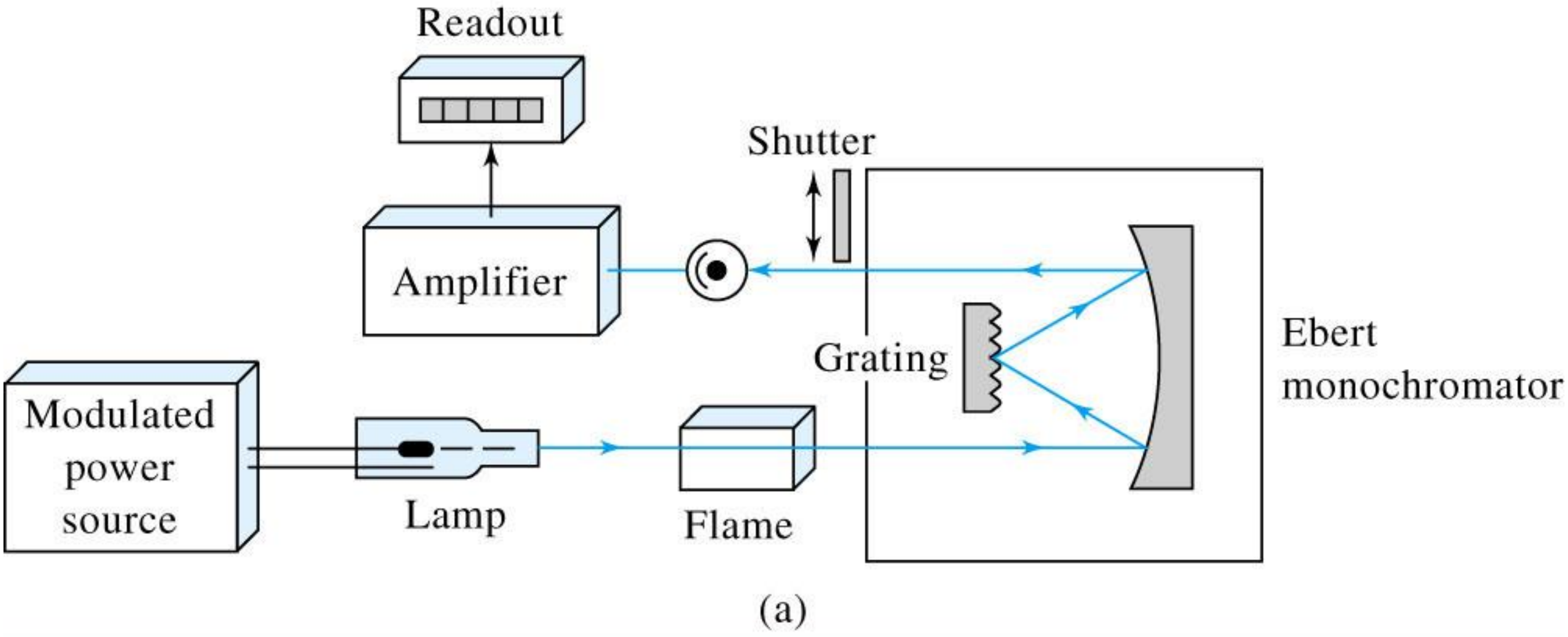
- The detector then receives two types of signal, an alternating one from the source and a continuous one from the flame. These signals are converted to the corresponding types of electrical response. A simple high-pass *RC filter can then be* used to remove the unmodulated DC signal and pass the AC signal for amplification.

Emission from the sample + emission from the flame

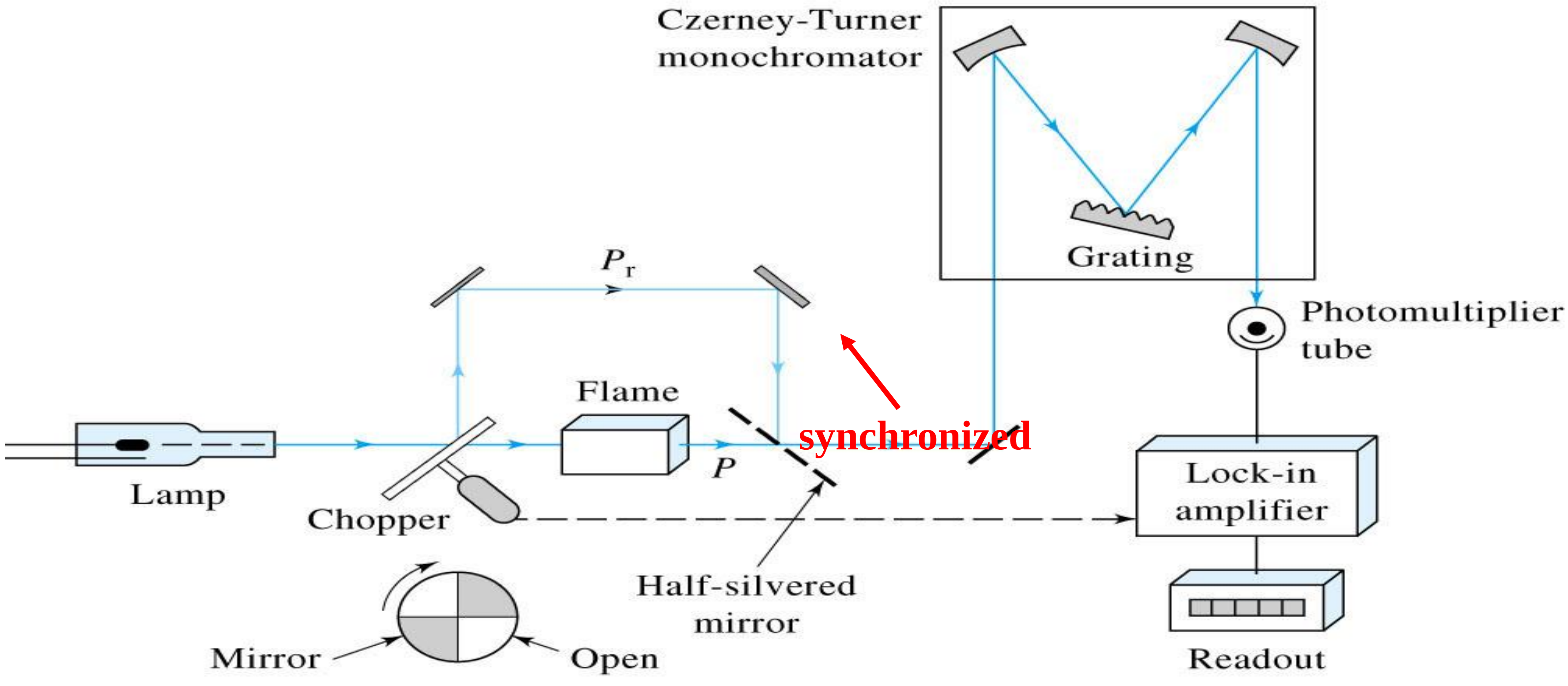
Monochromator is able to eliminate flame interference based on wavelength separation. However, when the wavelength of interference is the same as the analyte wavelength the monochromator is unable to eliminate interference.

9B-2 Spectrophotometers

Single-Beam Instruments: A typical single-beam instrument, consists of several hollow cathode sources, an atomizer, and simple grating spectrophotometer with a photomultiplier transducer. The 100% T adjustment is then made while a blank is aspirated into the flame. Finally, the transmittance is obtained with the sample replacing the blank.



Double-Beam Instruments: In double-beam instrument the beam from the hollow cathode source is split by a mirrored chopper, one half passing through the flame and the other half around it. The two beams are then recombined by a half-silvered mirror and passed into a grating monochromator; a photomultiplier tube serves as the transducer. The ratio between the reference and sample signal is then amplified and fed to the readout, which may be a digital meter or a signal recorder.



synchronized

(b)

Note: The Ref beam does not pass through the flame and thus does not correct for *loss of radiant power due to absorption or scattering by the flame itself.*

INTERFERENCES IN ATOMIC ABSORPTION SPECTROSCOPY

1. Spectral Interferences:

2. Chemical Interferences:

1. Spectral Interferences:

(I) Spectral line Interference:

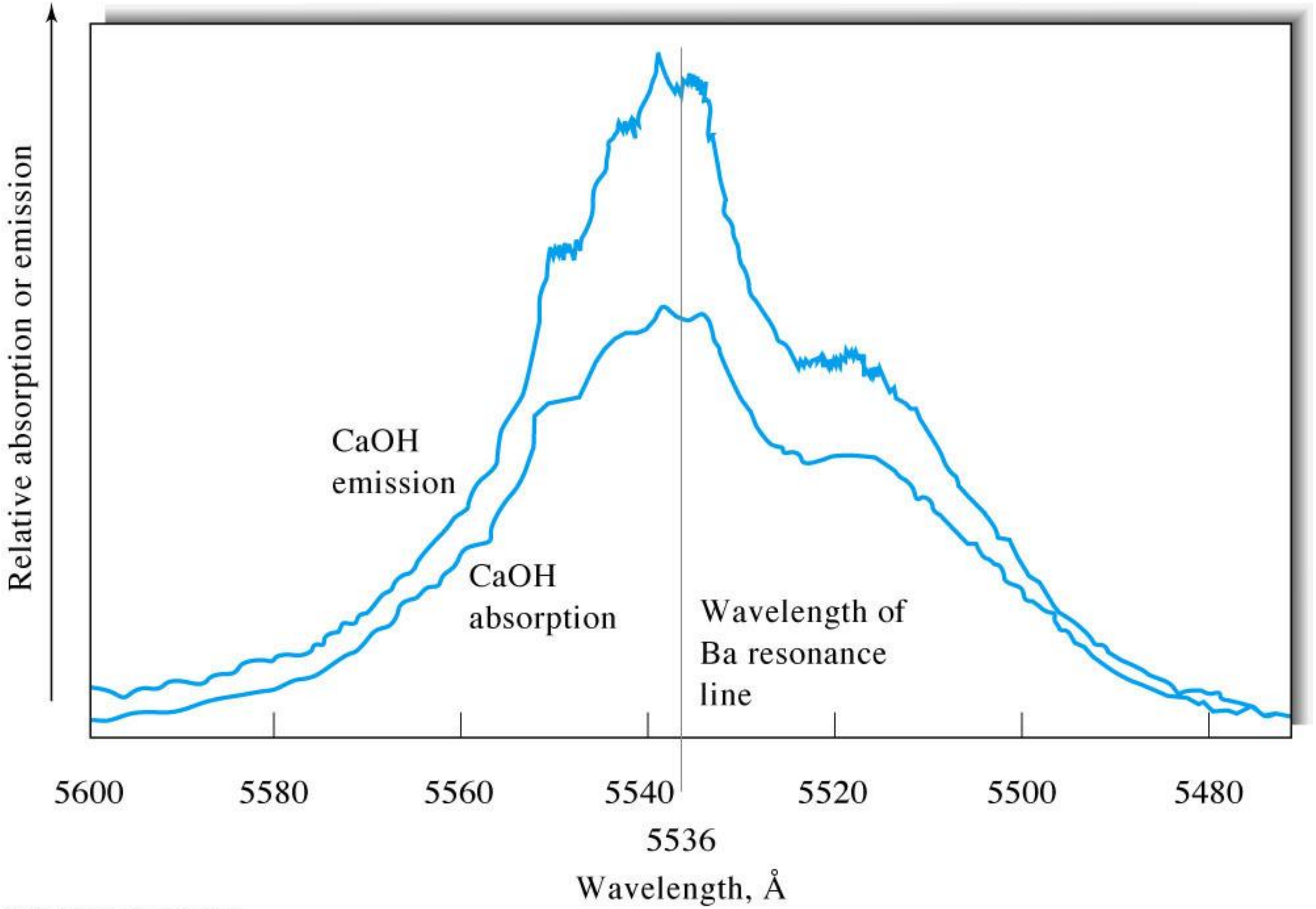
Spectral interference can occur due to overlapping lines. e.g. a vanadium line at 308.211 nm interferes in an analysis based upon the aluminum absorption line at 308.215 nm. This type of interference can be avoid by employing the aluminum line at 309.27 nm instead.

(II) Interference due to Scattering:

Spectral interferences result from the presence of combustion products that exhibit *broadband absorption* or particulate products that *scatter radiation*. Both diminish the power of the transmitted beam. A blank can be aspirated into the flame to make the correction.

(III) Interference from the Sample matrix.

An example of a potential matrix interference due to absorption occurs in the *determination of barium in alkaline earth mixture*. The wavelength of Ba line used for atomic absorption analysis appears in the center of a broad absorption band for CaOH. The effect can be eliminated by substituting *nitrous oxide for air* as the *oxidant* which yields a higher temperature that decomposed the CaOH and eliminates the absorption band.


Relative absorption or emission
CaOH emission
CaOH absorption
Wavelength of Ba resonance line
5600
5580
5560
5540
5536
5520
5500
5480
Wavelength, Å

…Spectral Interferences continued…

(IV) Large particle size refractory oxides.

Concentrated solution of elements such as Ti, Zr and W which form refractory oxides can cause spectral interference due to scattering.

(V) Scattering due to organic solvent or organic impurities;

in the sample can cause scattering interference from carbonaceous particle because of incomplete combustion of the organic matrix.

✓Fortunately, with flame atomization, spectral interferences by matrix products are not widely encountered and often can be avoided by variations in the analytical variables, such as *flame temperature and fuel-to-oxidant ratio*.

✓Alternatively, if the source of interference is known, an excess of the interfering substance can be added to both sample and standards. Provided the excess added to the standard sample is large with respect to the concentration from the sample matrix, the contribution from the sample matrix will become insignificant. The added substance is sometimes called a *radiation buffer. The method of* standard additions can also be used advantageously in some cases.

Several methods have been developed for correcting for spectral interferences caused by matrix products.

Methods for correcting spectral interferences

1. The Two-Line Correction Method:

- The two-line correction procedure uses a line from the source as a *reference*, This line should *lie as close as possible to the analyte line* but *must not be absorbed by the analyte*.
- If these conditions are met, it is assumed that any decrease in power of the reference line from that observed during calibration arises from absorption or scattering by the matrix products of the sample.
- This decrease in power is then used to correct the absorbance of the analyte line,
- the reference line may be from an impurity in the hollow cathode, a neon or argon line from the gas contained in the lamp, or a nonresonant emission line of the element that is being determined,
- Unfortunatelv, a suitable reference line is often not available,

2. Continuum-Source Correction Method:

✓ In this technique, a deuterium lamp provides a source of continuum radiation throughout the ultraviolet region.

✓ Radiation from the continuum source and the hollow-cathode lamp are passed alternately through the electrothermal atomizer.

✓ The absorbance of the deuterium radiation is then subtracted from that of the analyte beam.

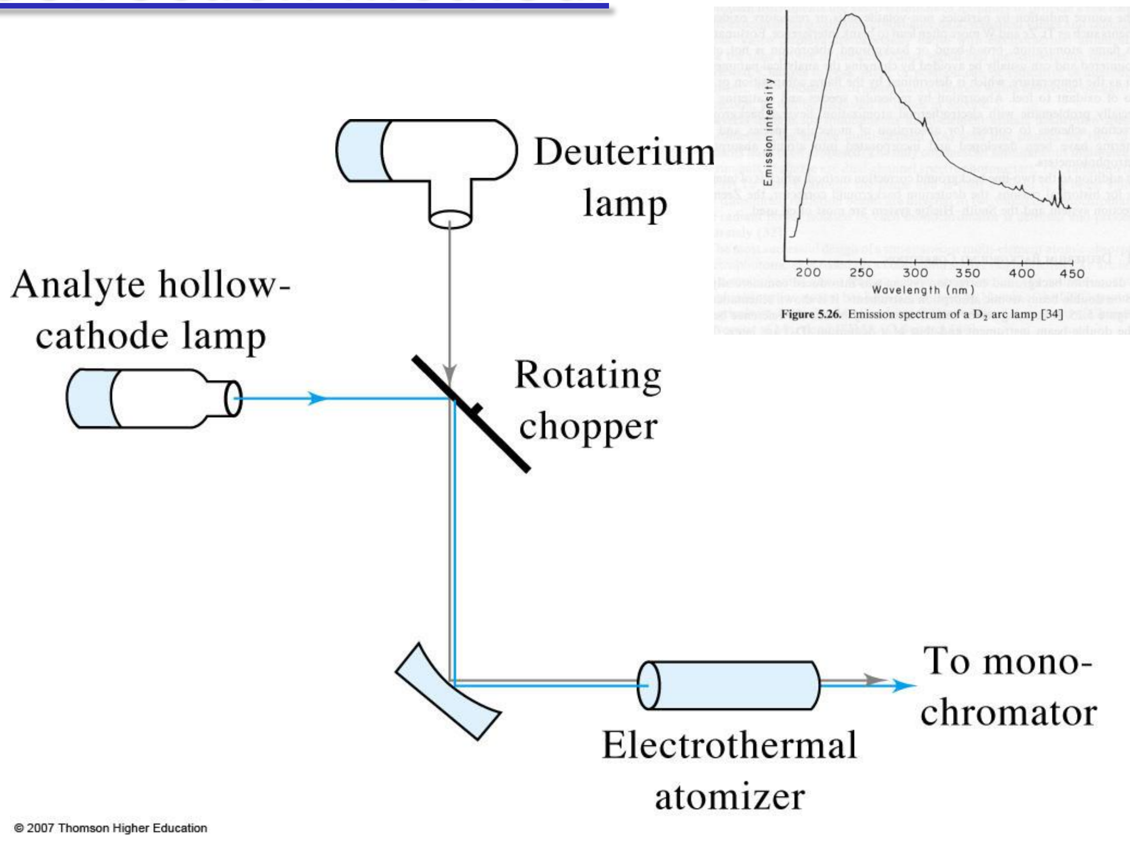


Figure 5.26. Emission spectrum of a D_2 arc lamp [34]

© 2007 Thomson Higher Education

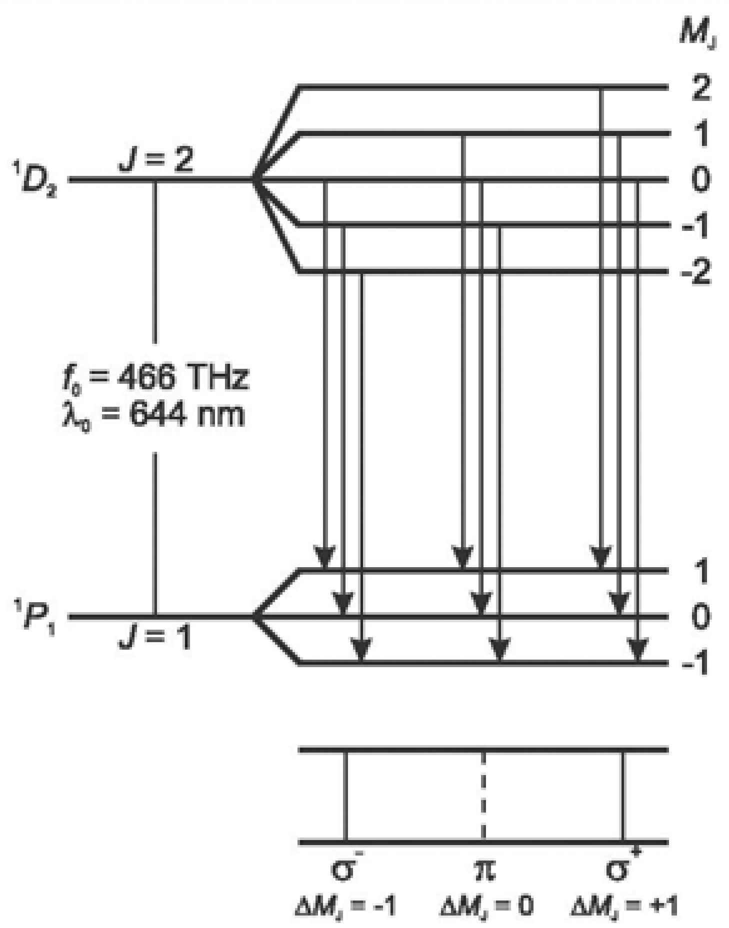
Unfortunately, the performance of this method is often less than ideal, which leads to undercorrection in some systems and overcorrection in others.

✓ if the two lamps are not in perfect alignment,

✓ the radiant output of the deuterium lamp in the visible region is low enough to preclude the use of this correction procedure for wavelengths longer than 350 nm,

3. Zeeman Effect Background Correction:

- When an atomic vapor is exposed to a strong magnetic field (10 kG), a splitting of electronic energy levels of the atoms takes place that leads to formation of several absorption lines for each electronic transition.
- These lines are separated from one another by about 0,01 nm, with the sum of the absorbances for the lines being exactly equal to that of the original line from which they were formed.
- Several splitting patterns arise depending on the type of electronic transition that is involved in the absorption process. The simplest splitting pattern, which is observed with singlet transitions, leads to a central, π line and two equally spaced satellite σ *lines, The central* π *line, which is at the original wavelength,* has an absorbance that is twice that of each σ *line,*



Level splitting and transitions of the normal Zeeman effect in Cadmium

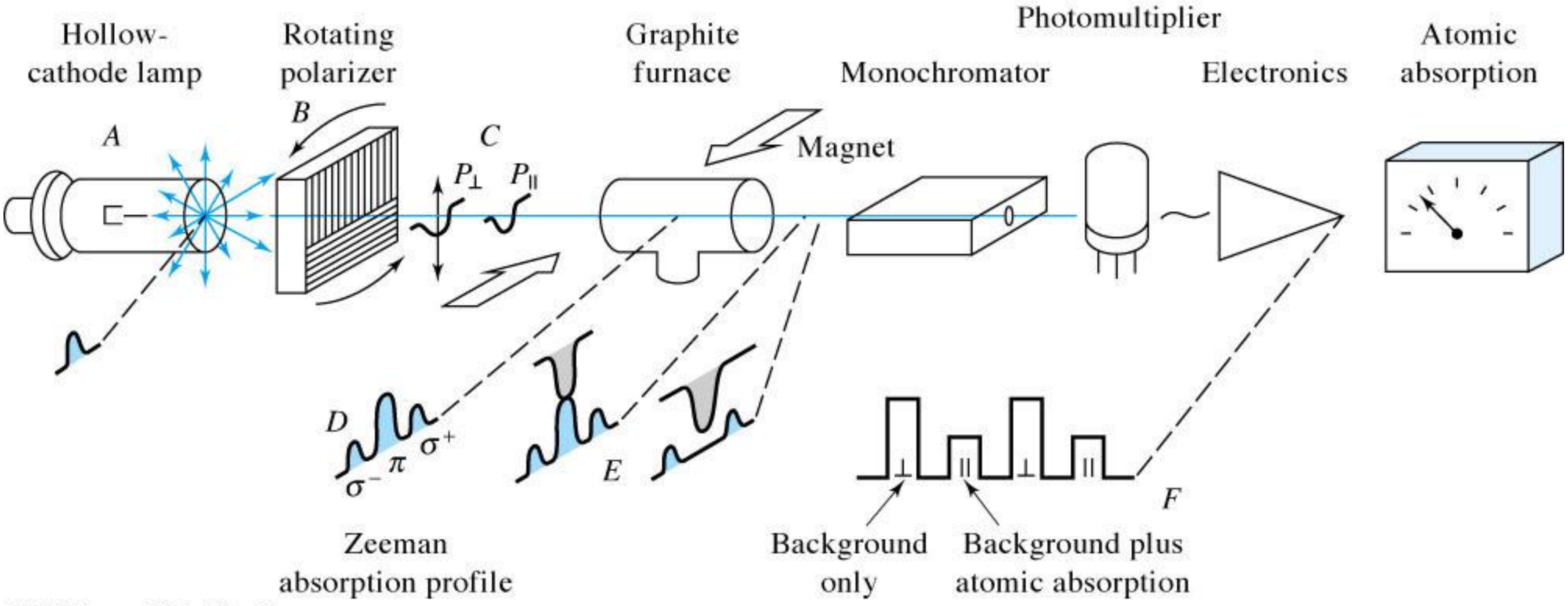
3. Zeeman Effect Background Correction:

- Application of the Zeeman effect to atomic absorption instruments is based on the differing response of the two types of absorption lines to polarized radiation,
- Unpolarized radiation from an ordinary hollow-cathode source *A* is passed through a rotating polarizer *B, which separates the* beam into two components that are plane-polarized at 90° to one another C.

•These beams pass into a graphite furnace. A permanent 11-kG magnet surrounds the furnace and splits the energy levels into the three absorption peaks shown in *D.*

-The π *line absorbs* only that radiation that is *polarized in a direction parallel to the external magnetic field;*

- The σ *lines, in contrast, absorb only radiation polarized at 90° to the field*.



© 2007 Thomson Higher Education

3. Zeeman Effect Background Correction:

- A second type of Zeeman effect instrument has been designed in which a magnet surrounds the hollow-cathode source. Here, it is the emission spectrum of the source that is split rather than the absorption spectrum of the sample.
- This instrument configuration provides an analogous correction.

✓ Zeeman effect instruments provide a more accurate correction for background than the other methods.

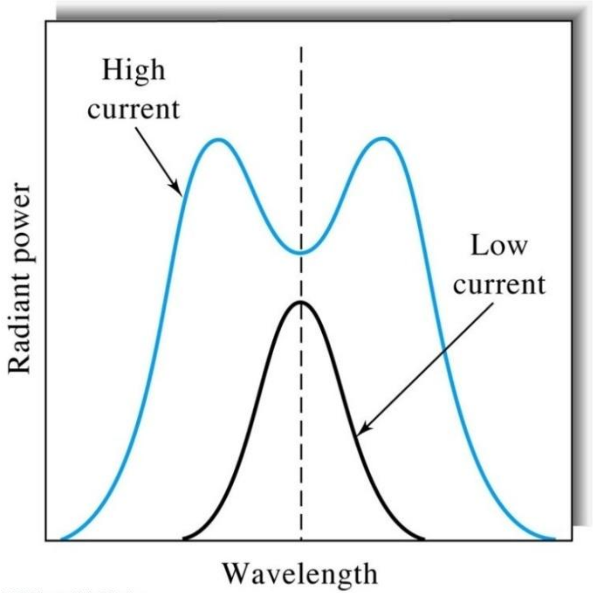
✓ Complex and expensive

✓ These instruments are particularly useful for electrothermal atomizers and permit the direct determination of elements in samples such as urine and blood.

✓The decomposition of organic material in these samples leads to large background corrections and, as a result susceptible to significant error.

4. BG Correction Based on Source Self-Reversal

- also called the Smith-Hieftje BG correction
- is based on *the self-reversal or self-absorption behavior of radiation emitted from HCL* when they are operated *at high currents*.
- High currents produce large concentrations of non-excited atoms, which are capable of absorbing the radiation produced from the excited species.
- An additional effect of high currents is to significantly broaden the emission line of the excited species. The net effect is to produce a line that has a minimum in its center, which corresponds exactly in wavelength to that of the absorption peak



© 2007 Thomson Higher Education

- Alignment is simple,
- One source HCL used⇒ inexpensive
-works at all wavelengths
- be used with any atomizer

- To obtain corrected absorbances, the lamp is programmed to run alternately at low (6-20 mA) and high currents (100-500mA).
- *The total absorbance (analyte+BG)* is obtained during the *low current* operation and the *background absorbance* is provided by measurements during the high current operation ofr the HCL.

2. Chemical Interferences:

(I) Formation of Compounds of Low Volatility:

- The most common type of interference is *by anions* that form compounds of low volatility with the analyte and thus reduce the rate at which the analyte is atomized. The decrease in calcium absorbance that is observed with increasing concentrations of sulfate or phosphate.
- Example of *cation interference* have also been recognized. Aluminum is found to cause low results in the determination of magnesium, apparently as a result of the formation of a heat-stable aluminum/magnesium compound.

Solutions:

- *Higher temperature*
- *Releasing agents: cations that react preferentially with the interferants* and prevent its interaction with the analyte, e.g; addition of an excess of Sr or La minimizes the interference of phosphate in the determination of Ca
- *Protection agents: form stable but volatile species with the analytes (i.e. EDTA,APDC….). e.g;* 8-hydroxyquinoline suppresses the interference of aluminum in the determination of calcium and magnesium.

(II) Dissociation Equilibria:

Gaseous environment of a flame or a furnace, numerous dissociation and association reactions lead to conversion of the metallic constituents to the elemental state. Some of these reactions are reversible

$$MO \rightleftharpoons M + O$$

$$M(OH)_2 \rightleftharpoons M + 2OH$$

Where M is the analyte atom.

$$VO_x \rightleftharpoons V + O_x$$

$$AlO_x \rightleftharpoons Al + O_x$$

$$TiO_x \rightleftharpoons Ti + O_x$$

(III) Ionization Equilibria:

✓ Ionization of atoms and molecules is small in combustion mixtures that involve air as the oxidant, and generally can be neglected.

✓ In higher temperatures of flames where oxygen or nitrous oxide serves as the oxidant, however, ionization becomes important, and a significant concentration of free electrons exists

$$M \rightleftarrows M^{+} + e^{-} \qquad K = [M^{+}][e^{-}] / [M]$$

✓ if the medium contains not only species M but species B as well, and if B ionizes, then the degree of ionization of M will be decreased by the mass-action effect of the electrons formed from B.

$$B \rightleftarrows B+ + e-$$

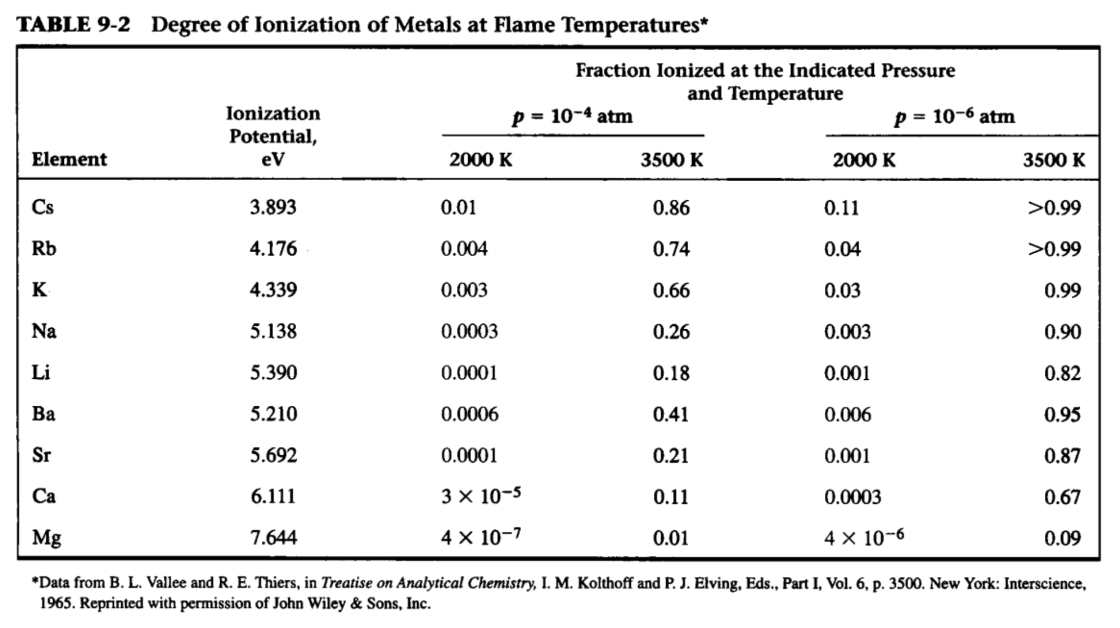


TABLE 9-2 Degree of Ionization of Metals at Flame Temperatures*

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

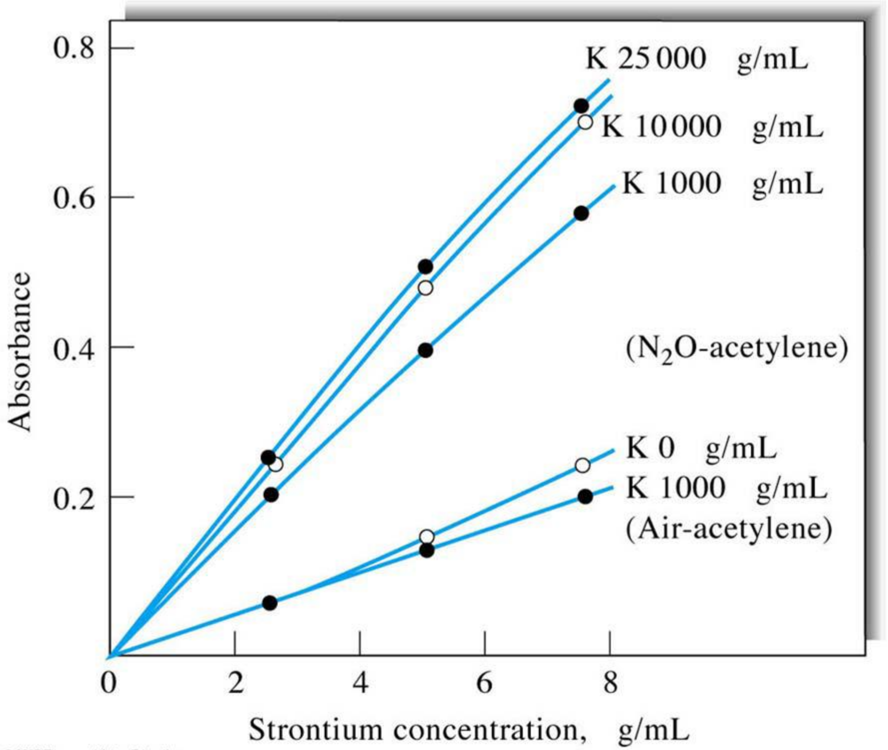
*Data from B. L. Vallee and R. E. Thiers, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 6, p. 3500. New York: Interscience, 1965. Reprinted with permission of John Wiley & Sons, Inc.

B can then act as an *ionization suppressor.*

A decrease in concentration of atoms resulting from ionization occurs. Thus, under some circumstances decrease in emission or absorption may be observed in hotter flames.

Solution: *ionization suppressor* which provides a relatively high concentration of electrons to the flame; suppression of ionization of the analyte results.

Effect of K concentration on calibration curve for Sr



- Note the significant increase in slope of these curves as strontium ionization is repressed by the increasing concentration of potassium ions and electrons.
- Note also the enhanced sensitivity produced by using nitrous oxide instead of air as the oxidant.
- The higher temperature achieved with nitrous oxide undoubtedly enhances the degree of decomposition and volatilization of the strontium compounds **in the flame.**

ATOMIC ABSORPTION ANALYTICAL TECHNIQUES

Sample Preparation:

-A disadvantage of flame spectroscopic methods is the requirement that the sample be introduced into the excitation source in the form of a solution, most commonly an aqueous one.

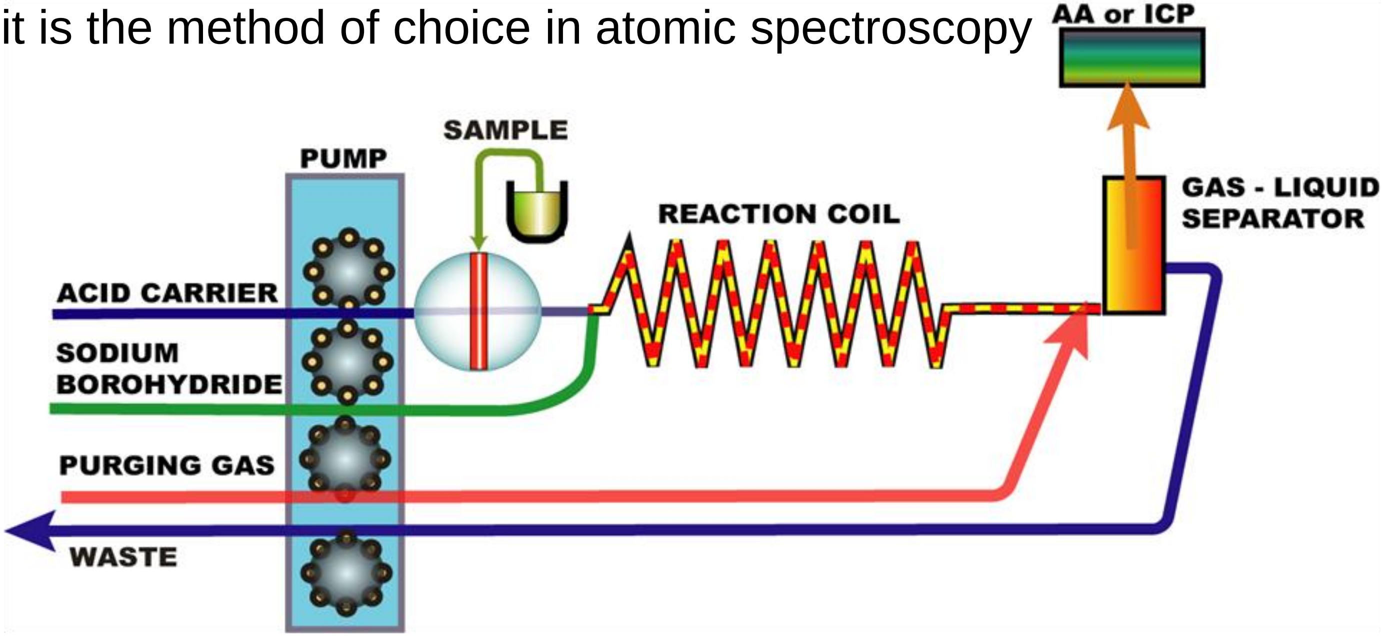
- Unfortunately, many materials of interest, such as soils, animal tissues, plants petroleum products and minerals are not directly soluble in common solvents, and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization.

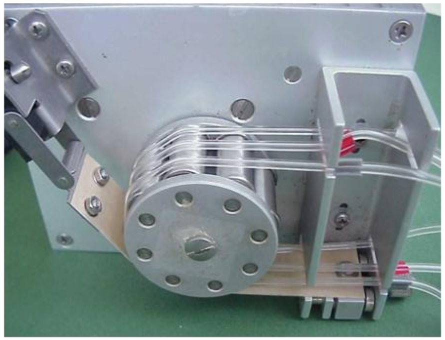
- Indeed, the decomposition and solution steps are often more time consuming and introduce more error than the spectroscopic measurement itself.

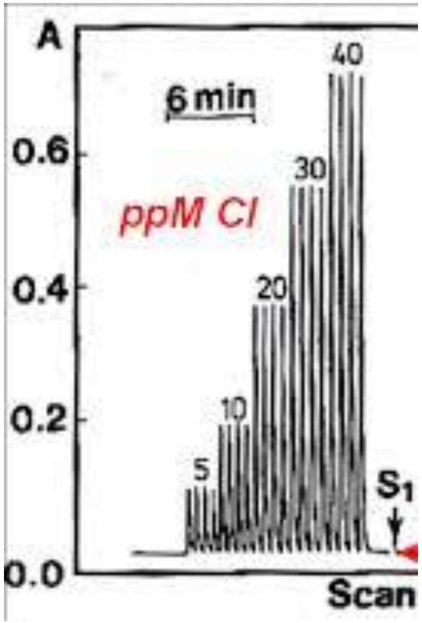
- Some of the common methods used for decomposing and dissolving samples for atomic absorption methods include treatment with hot mineral acids; oxidation with liquid reagents, such as sulfuric, nitric, or perchloric acids; combustion in an oxygen bomb or other closed container to avoid loss of analyte.

Sample Introduction by Flow Injection

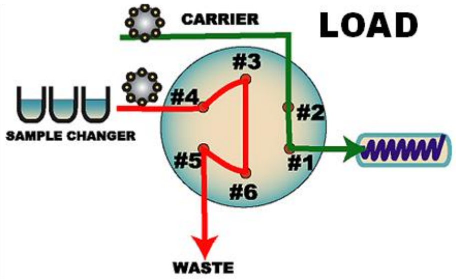
- FIA is an automated method of chemical analysis in which a sample is injected into a flowing carrier solution that mixes with reagents before reaching a detector.
- when the highest level *of repeatability* is required or only *a small amount of sample is available*, it is the method of choice in atomic spectroscopy

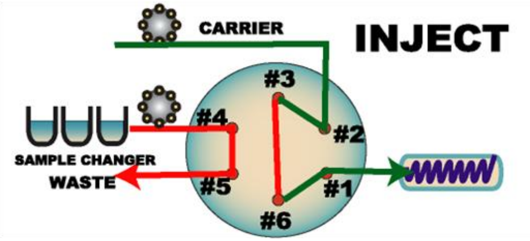


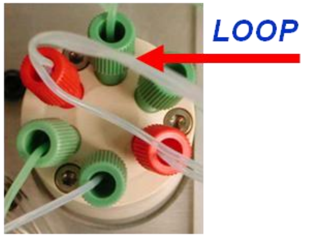




A two position, six port injection valve with a fixed loop for well defined sample volumes

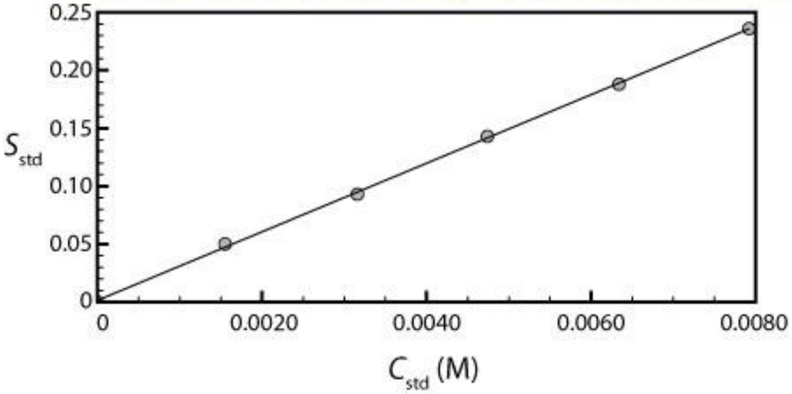


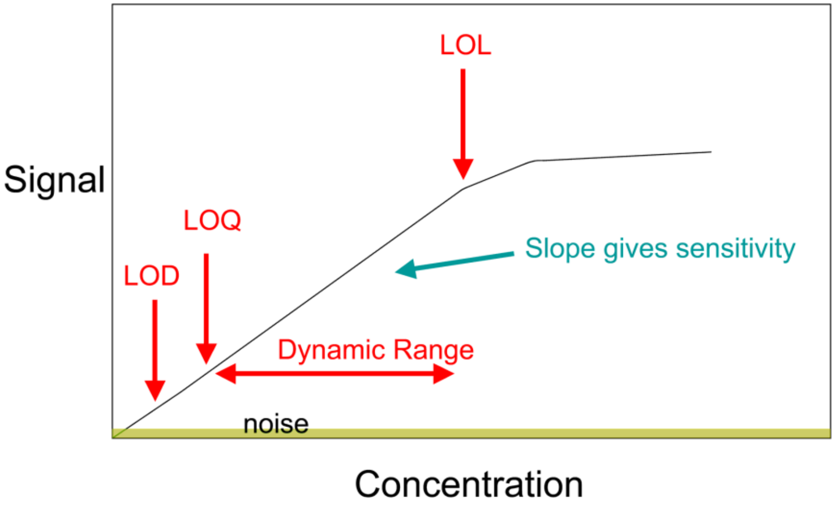




Calibration Curve

- ✓ Atomic absorption should follow Beer’s law, A= e. b. C
- ✓ however, departures from linearity are often encountered,
- ✓ A calibration curve that covers the range of concentrations found in the sample should be prepared.





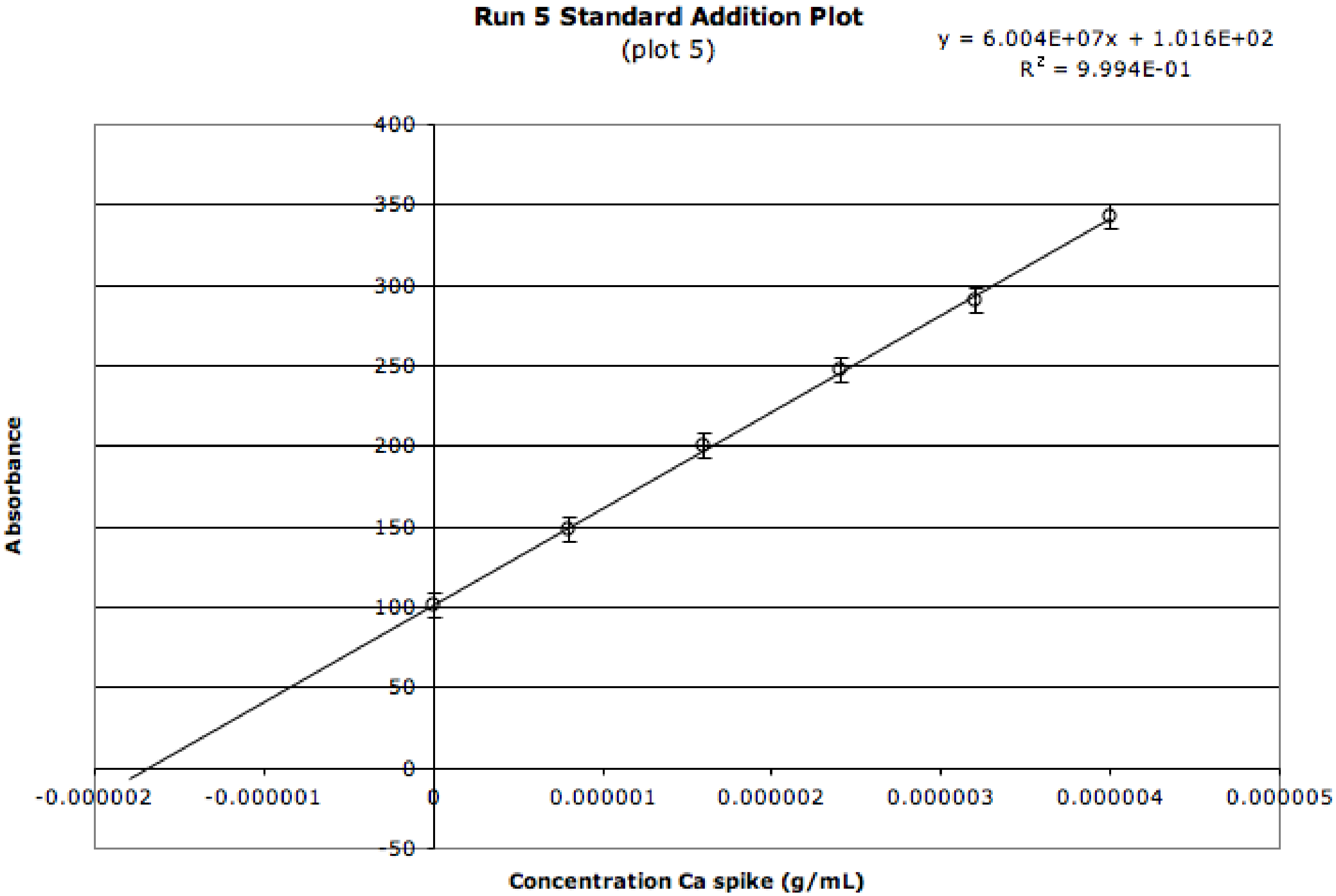
A calibration curve plot showing limit of detection (LOD), limit of quantification (LOQ), dynamic range, and limit of linearity (LOL).

- ➢*LOD is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidance limit*
- ➢ *LOD defined as 3 * standard deviation of the blank, and at the LOQ defined as 10 * standard deviation of the blank*

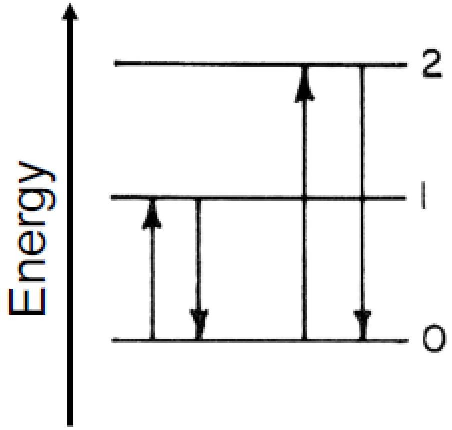
Standard Addition Method:

- It is widely used in atomic absorption spectroscopy in order to partially or completely compansate for the chemical and spectral interferences introduced by the sample *matrix.*
- *differing amounts of* standard is added directly to the same amount of aliquots of analyzed sample, diluted to a volume and analyzed at the wavelength of interest.

This process is also called spiking.



Atomic Fluorescence Spectroscopy (AFS)



- There are five basic types of fluorescence: resonance fluorescence, direct-line fluorescence, stepwise-line fluorescence, sensitized fluorescence and multi-photon fluorescence.
- The figure shows an energetic diagram level for resonance fluorescence.
- In all cases, the basic instrumentation is the same. EDL are the best excitation sources for AFS.
- The advantage of AFS over AAS is that it provides better limits of detection for several elements.

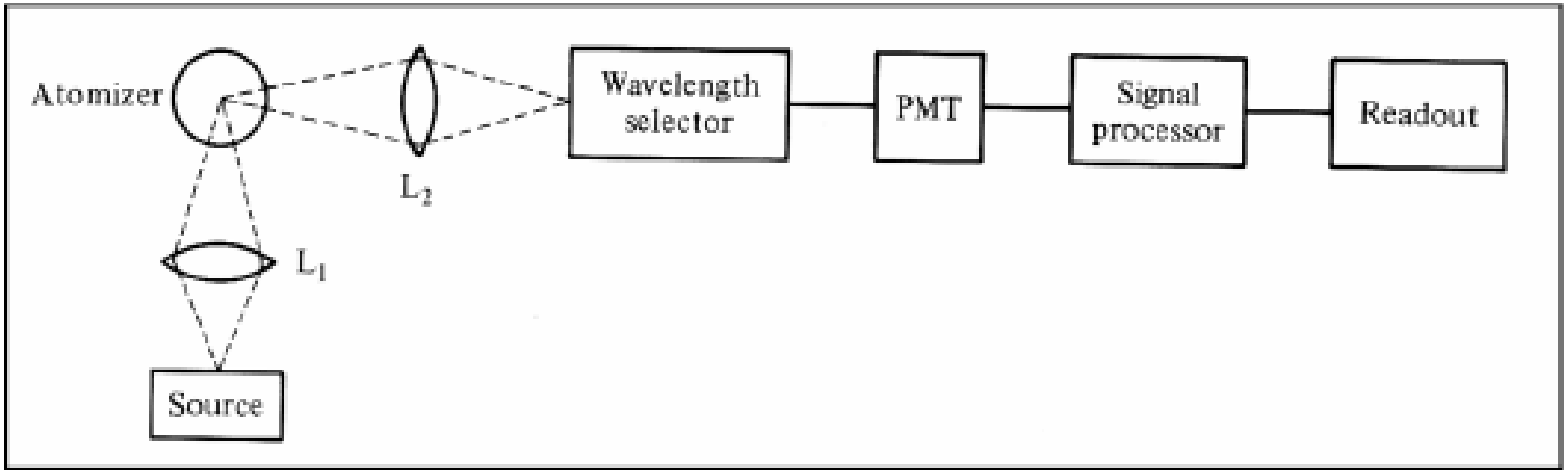


TABLE 9-3 Detection Limits (ng/mL)[a] for Selected Elements

Element	AAS Flame	AAS Electrothermal	AES Flame	AES ICP	AFS Flame
Al	30	0.1	5	0.2	5
As	200	0.5	—	2	15
Ca	1	0.25	0.1	0.0001	0.4
Cd	1	0.01	2000	0.07	0.1
Cr	4	0.03	5	0.08	0.6
Cu	2	0.05	10	0.04	0.2
Fe	6	0.25	50	0.09	0.3
Hg	500	5	—	—	5
Mg	0.2	0.002	5	0.003	0.3
Mn	2	0.01	—	0.01	1
Mo	5	0.5	100	0.2	8
Na	0.2	0.02	0.1	0.1	0.3
Ni	3	0.5	600	0.2	0.4
Pb	8	0.1	200	1	5
Sn	15	5	300	—	200
V	25	1	200	0.06	25
Zn	1	0.005	50000	0.1	0.1