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Principles of Instrumental Analysis

Chapter 9

Atomic Absorption and Atomic Fluorescence Spectrometry

[Atomic emission in Chap. 10]

Chapter 9: **Atomic Absorption** (AA) and Atomic Fluorescence (AF) Spectrometry

AAS - **Atomic Absorption Spectrometry**. For half a century, it is the most widely used method for determination of single elements in analytical samples. [Our lab has AAS]

AFS - Atomic **Fluorescence** Spectrometry. It is NOT so well developed as AAS, and thus AFS is not so commonly used. **Only a brief section (two pages) in Chap. 9E, p.249, 250 is discussed.**

AES- Atomic **Emission** Spectrometry → Next chapter, Chap. 10 (for self study). Not covered in classes, owing to time limit.

Ref:

History of development of AAS:

S.R. Koirtyohann, Anal. Chem., 1991, 63, 1024A

W. Slavin, Anal. Chem., 1991. 63, 1033A

[Note: (Chap. 10) - Atomic Emission Spectroscopy [AES] is not covered.], owing to time limit. Our lab does not have AES.

AES - Atomic **Emission** Spectrometry requires higher atomic temperatures.

Atomization is achieved by

1. **Plasma sources**
2. **Electric arc**
3. **Electric spark.**
4. **Other sources**:
   flames; glow discharges, lasers.

The atomizers (listed above) not only convert the samples into atoms, but also **excite them (only a small fractions)** to higher electronic states.

The excited species rapidly relax back to lower states (or ground state), and they emit UV/Vis line spectra that are useful for quantitative/qualitative elemental analyses.

9A SAMPLE ATOMIZATION TECHNIQUES

The two most common methods of sample atomization encountered in AAS and AFS, **flame atomization and electrothermal atomization**, are first described.

We then turn to three specialized **atomization procedures** used in both types of spectrometry.

Note: electrothermal atomization cannot be used in AES.

9A-1 Flame Atomization (see scheme next page)

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.

As shown in **Figure 9-1** **[shown next page]**, a complex set of interconnected processes then occur in the flame.

The first is *desolvation*, in which the solvent evaporates to produce a finely divided solid molecular aerosol.

The aerosol is then *volatilized* to form gaseous molecules. **Dissociation of most of these molecules produces an atomic gas. Some of the atoms in the gas ionize to form cations and electrons.**

Other molecules and atoms are produced in the flame as a result of interactions of the fuel with the oxidant and with the various species in the sample.

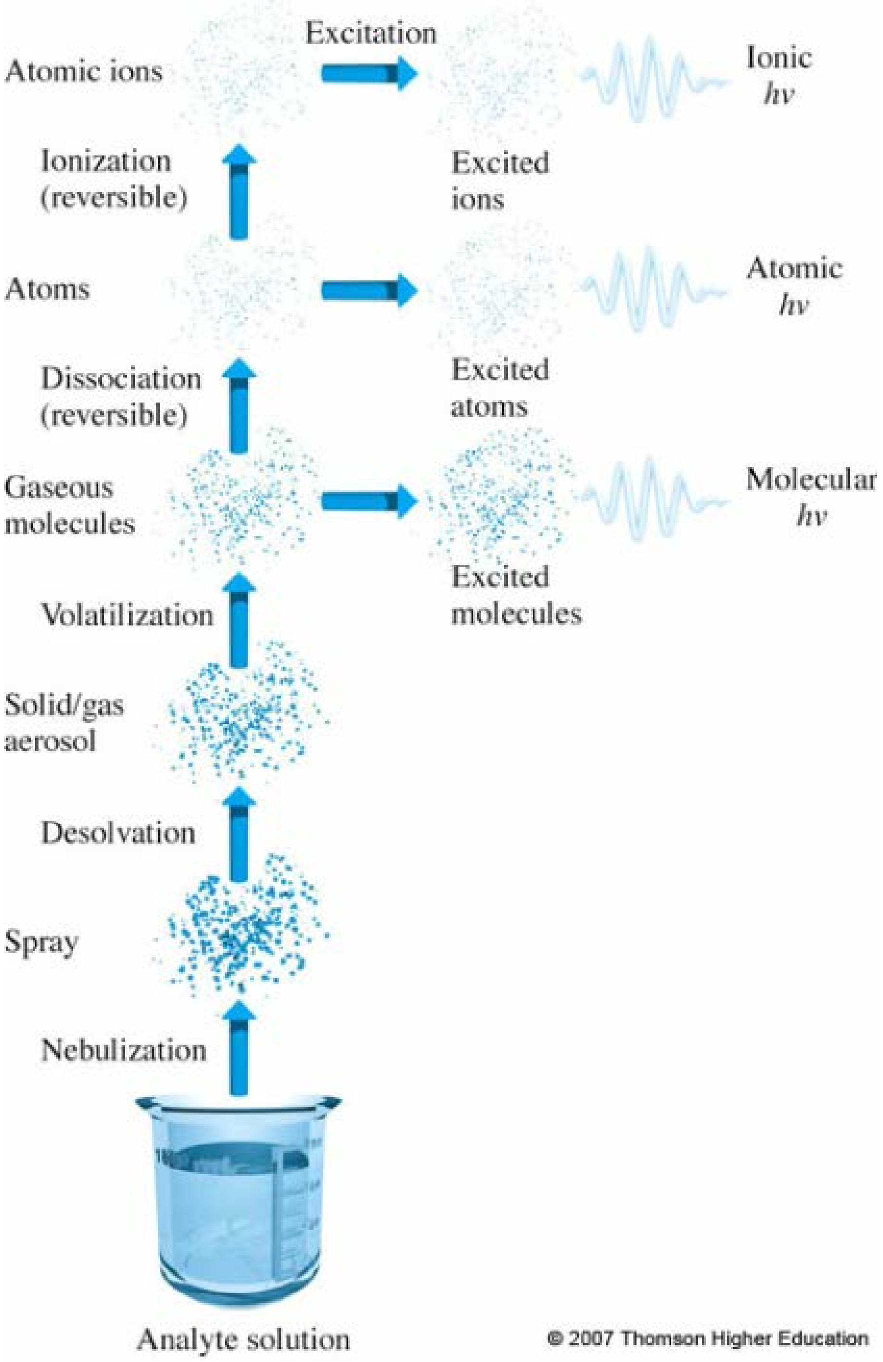


FIGURE 9-1

Processes occurring during atomization.

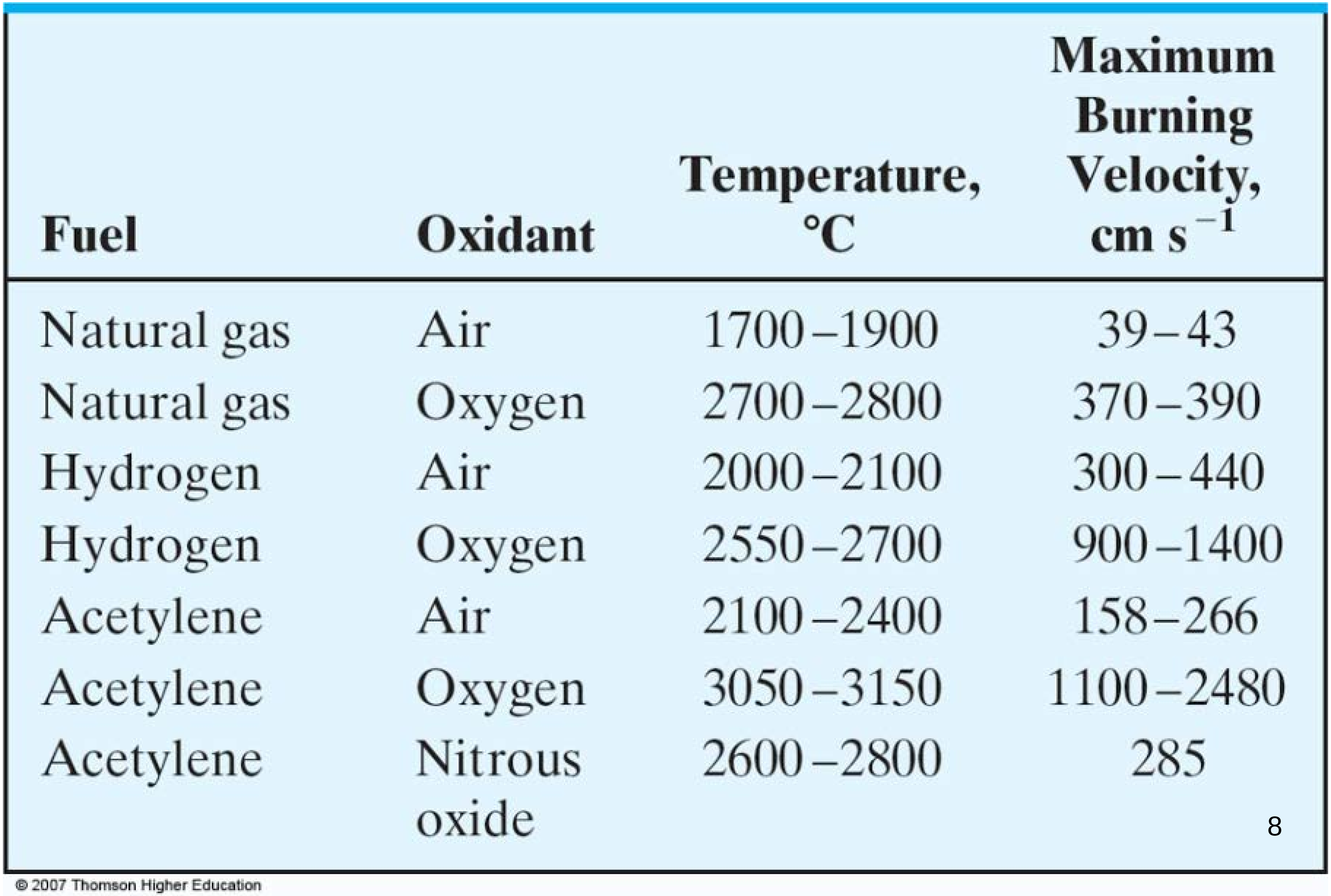
As indicated in **Figure 9-1**, a fraction of the molecules, atoms, ionic, and molecular emission spectra.

With so many complex processes occurring, it is not surprising that atomization is the most critical step in flame spectroscopy and the one that limits the precision of such methods.

Because of the critical nature of the atomization step, it is important to understand the characteristic of flames and the variables that affect these characteristics.

-We will discuss in following sections:

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

Flame Atomizers

Flame atomizers are used for atomic absorption, fluorescence, and emission spectroscopy. [For atomic emission, the flame temperature has be higher.]

Figure 9-5 (next page) is a diagram of a typical commercial laminar-flow burner that uses a concentric-tube nebulizer, such as that shown in **Figure 8-11a**.

The aerosol, formed by the flow of oxidant, is mixed with fuel and passes a series of **baffles** (regulators) 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.

Note: **Atomic emission spectroscopy (AES)** is a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample. The wavelength of the atomic spectral line gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element. [To be discuss later]

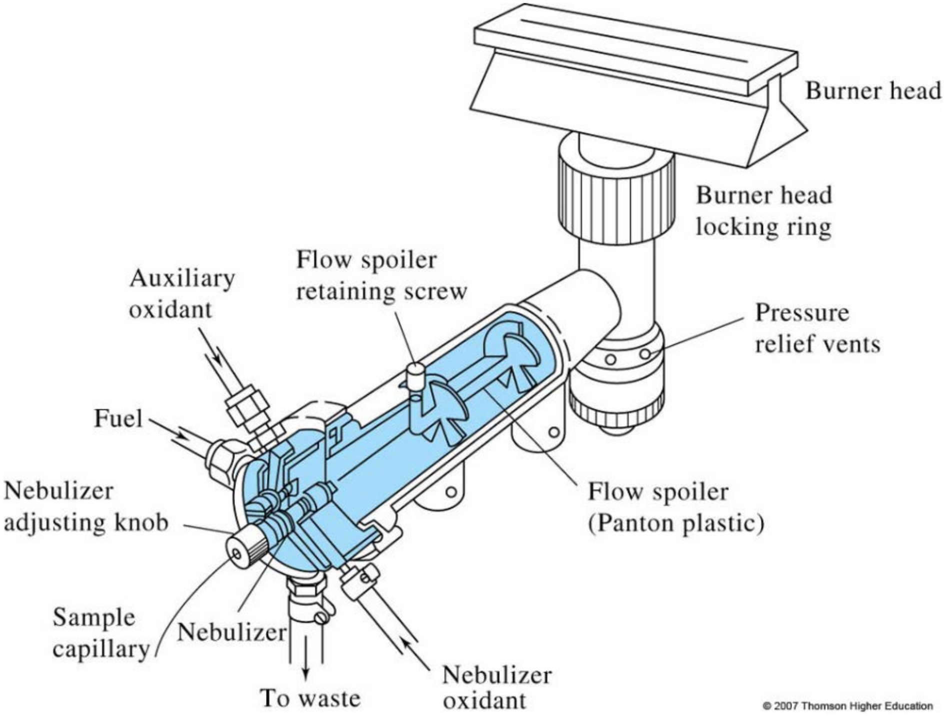
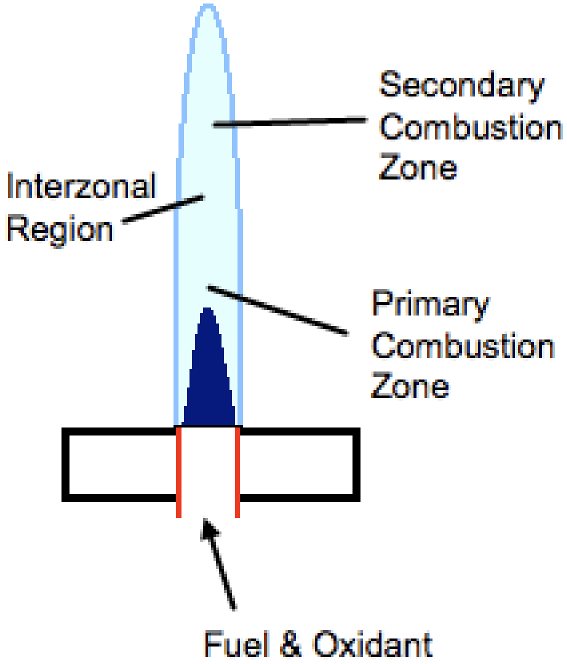
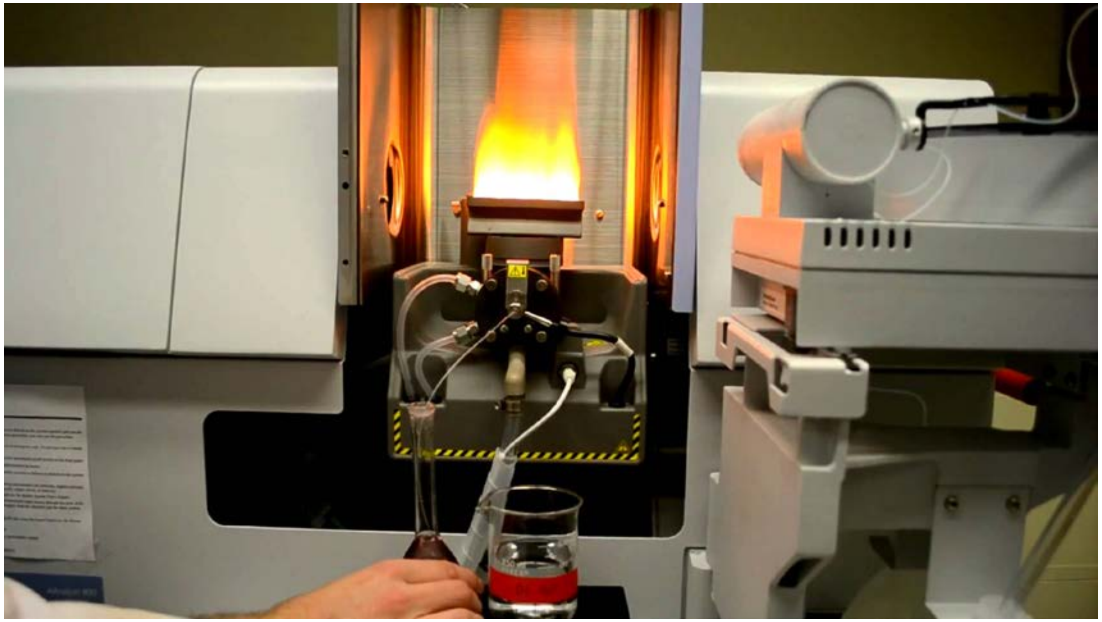


FIGURE 9-5 A laminar-flow burner.

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 (usually acetylene) and air are added mixed with a nebulizer mist. This mixture is then introduced into the flame.

Fuel and Oxidant Regulators.

An important variable that requires close control in flame spectroscopy is the **flow rate of both oxidant and fuel.** It is desirable to be able to vary each over a broad range so that **optimal atomization conditions** can be determined experimentally.

Fuel and oxidant are usually combined in approximately stoichiometric amounts.

- **For the determination of metals that form stable oxides, however, a flame that contains an excess of fuel is often desirable.**

Flow rates are usually controlled by means of double-diaphragm 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 light-weight conical or spherical float is lifted by the gas flow; its vertical position is determined by the flow rate.

Performance Characteristics of Flame Atomizers. P. 233

Flame atomization is the most reproducible of all liquid-sample-introduction methods that have been developed for atomic absorption and fluorescence spectrometry to date.

The **sampling efficiency** of other atomization methods and thus the **sensitivity**, however, are markedly better than in flame atomization.

There are two primary reasons for the lower sampling efficiency of the flame atomizers:

- **First**, a large portion of the sample flows down the drain.
- **Second**, the residence time of individual atoms in the optical path in the flame is brief (~10^{-4} s).

9A-2 **Electrothermal Atomization** p.233

Electrothermal atomizers, which first appeared on the market in the early 1970s, generally provide enhanced sensitivity because the entire sample is atomized in a short period, and the average residence time of the atoms in the optical path is a second or more (this is much longer than that in flame atomizer - 10^{-4} sec).

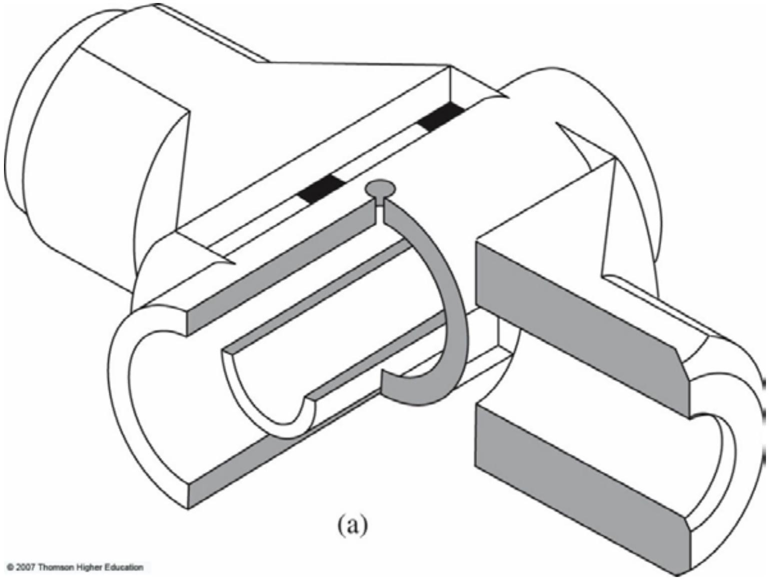
Electrothermal atomizers are used for atomic absorption and atomic fluorescence measurements, but have not been generally applied for direct production of emission spectra.

They are also used for vaporizing samples in inductively coupled plasma emission spectroscopy, however.

In electrothermal atomizers, a few microliters of sample is first evaporated at a low temperature and then ashed at a somewhat higher temperature in an electrically heated graphite tube similar to the one in **Figure 9-6 or in a graphite cup**.

After ashing, the current is rapidly increased to several hundred amperes, which causes the temperature to rise to 2000°C to 3000°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.

Electrothermal Atomization



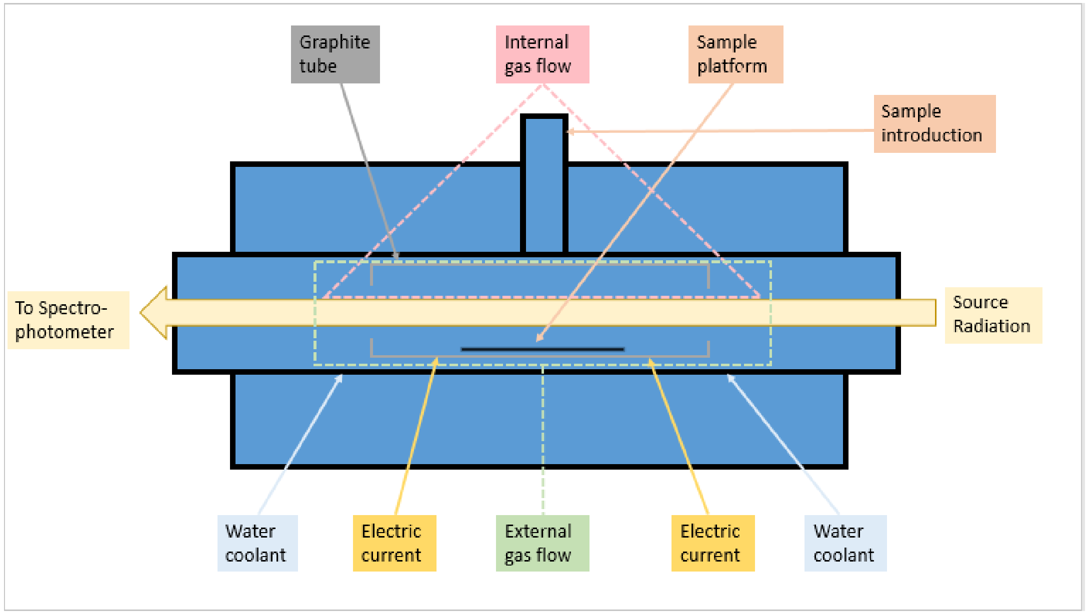


FIGURE 9-6(a) Cross-sectional view of a graphite furnace with integrated L'vov platform.

[Note: our lab AA uses flame atomizer, not this electrothermal atomizer.]

Electrothermal Atomizers

p. 234

Figure 9-6a [next page] is a cross-sectional view of a commercial **electrothermal atomizer**. In this device, atomization occurs in a cylindrical graphite tube that is open at both ends and that has a central hole for introduction of sample by means of a **micropipette**. **The tube is about 5 cm long and has an internal diameter of somewhat less than 1 cm.**

The interchangeable graphite tube fits snugly into a pair of cylindrical graphite electrical contacts located at the two ends of the tube. These contacts are held in a water-cooled metal housing.

Two inert gas streams are provided:

The external stream prevents outside air from entering and incinerating the tube**.**

The internal stream flows into the two ends of the tube and out the central sample port. This stream not only excludes air but also serves to carry away vapors generated from the sample matrix during the first two heating stages.

graphite furnace Fig. 9-6 p. 234

- **Figure 9-6a** illustrates the so-called **L'vov platform**, which is often used in **graphite furnaces** such as that shown in the figure. The platform is also made of graphite and is located beneath the sample entrance port. The sample is evaporated and ashed on this platform. When the tube temperature is increased rapidly, however, atomization is delayed because the sample is no longer directly on the furnace wall. As a result, atomization occurs in an environment in which the temperature is not changing so rapidly, which improves the reproducibility of analytical signals.

- **Figure 9-6b and c** (next page) shows the two ways of heating the graphite furnace while it is held in the optical path. Traditionally, the furnace was heated in the longitudinal mode illustrated in **Figure 9-6b**, which provides a continuously varying temperature profile as shown in the figure.

- The transverse mode, shown in **Figure 9-6c**, gives a uniform temperature profile along the entire length of the tube. This arrangement provides optimum conditions for the formation of free atoms throughout the tube. Recombination of atoms to molecules, atom loss and condensation on the cooler tube ends exhibited in the longitudinal mode are thus minimized in the transverse heating mode.

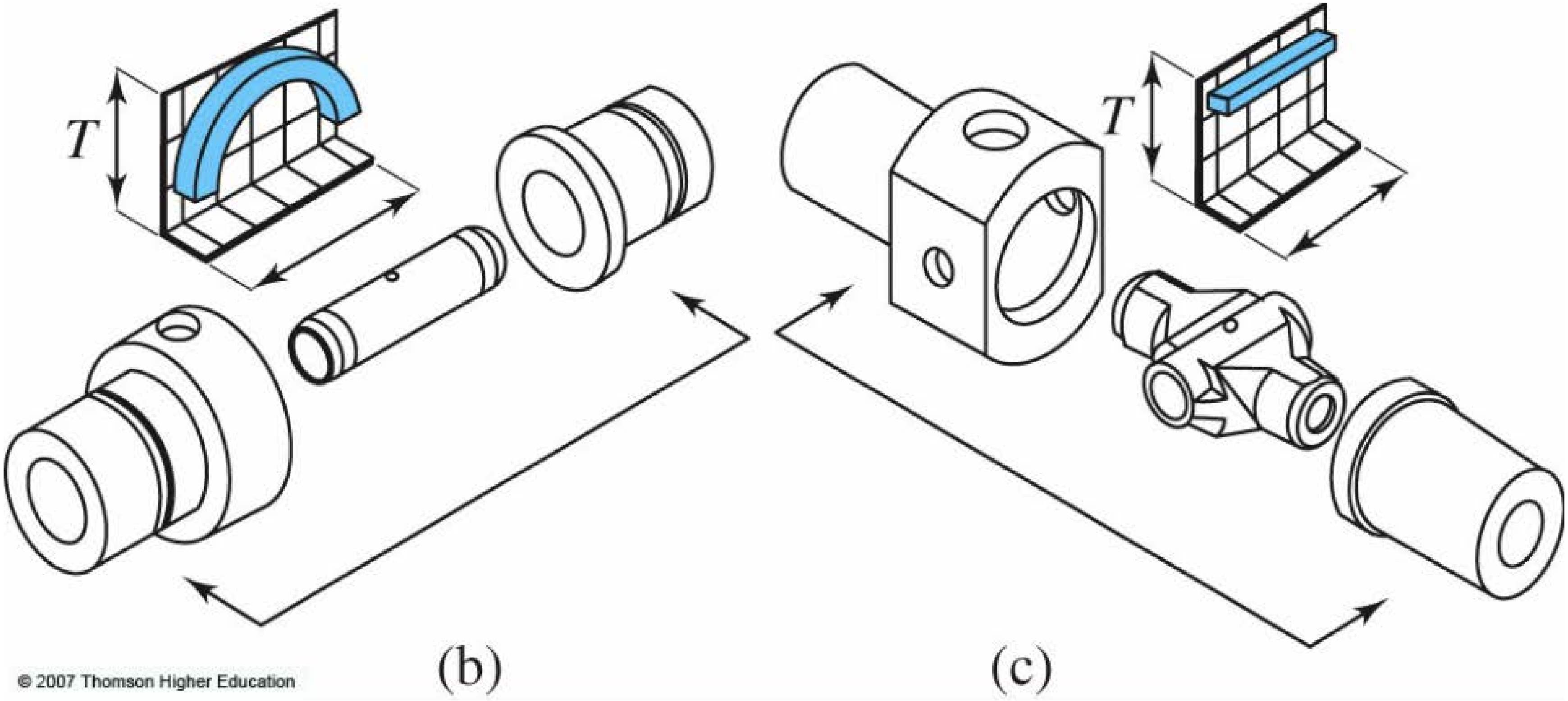


FIGURE 9-6(b)(c) (b) **Longitudinal** configuration of the graphite furnace. Note the temperature profile shown in blue along the path of the furnace. In the longitudinal configuration, the temperature varies continuously along the path, reaching a maximum at the center.

(c) **Transverse** configuration of the furnace. The temperature profile is relatively constant along the path.

Electrothermal atomizer (in contrast to flame atomizer) - Repeat again

Advantages - 優點:

Sensitivity – better **detection limit, which** can be down to 10^{-10} g of analyte or smaller.

Disadvantages-缺點:

1. **precision** is lower (only 5~10%)
2. **slow** measurement (several minutes per elements), due to heating-cooling cycle time.
3. **analytical range is narrower.**

Performance Characteristics of **Electrothermal Atomizers** **p. 235**

→ **Electrothermal atomizers** offer the advantage of **unusually high sensitivity for small volumes of sample**. Typically, sample volumes between 0.5 and 10 mL are used; under these circumstances, absolute **detection limits** typically 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 range of 1% or better that can be expected for flame or plasma atomization.

Furthermore, 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 relatively narrow**, usually less than two orders of magnitude.

As a result, electrothermal atomization is the method of choice when flame or plasma atomization provides inadequate detection limits.

Analysis of **Solids** with Electrothermal Atomizers p. 235

In most methods based on electrothermal atomizers, samples are introduced as **solutions**.

Several reports, however, have described the use of this type of atomizer for the direct analysis of **solid samples**.

One way of performing such measurements is to weigh the finely ground sample into a graphite boat and insert the boat into the furnace manually.

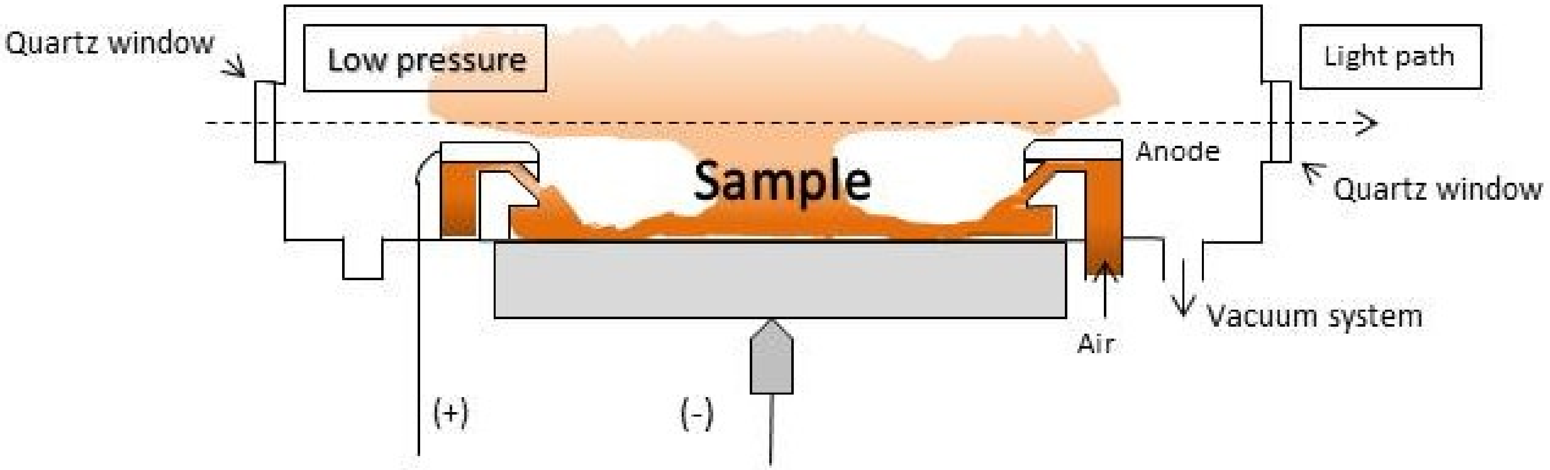
A second way is to prepare a slurry of the powdered sample by ultrasonic agitation in an aqueous medium. The slurry is then **pipetted** into the furnace for atomization.

Flame atomization
Electrothermal atomization
glow-discharge atomization,
hydride atomization

glow-discharge atomization

From “Maryville Univ. Learning”

the sample is placed on a cathode



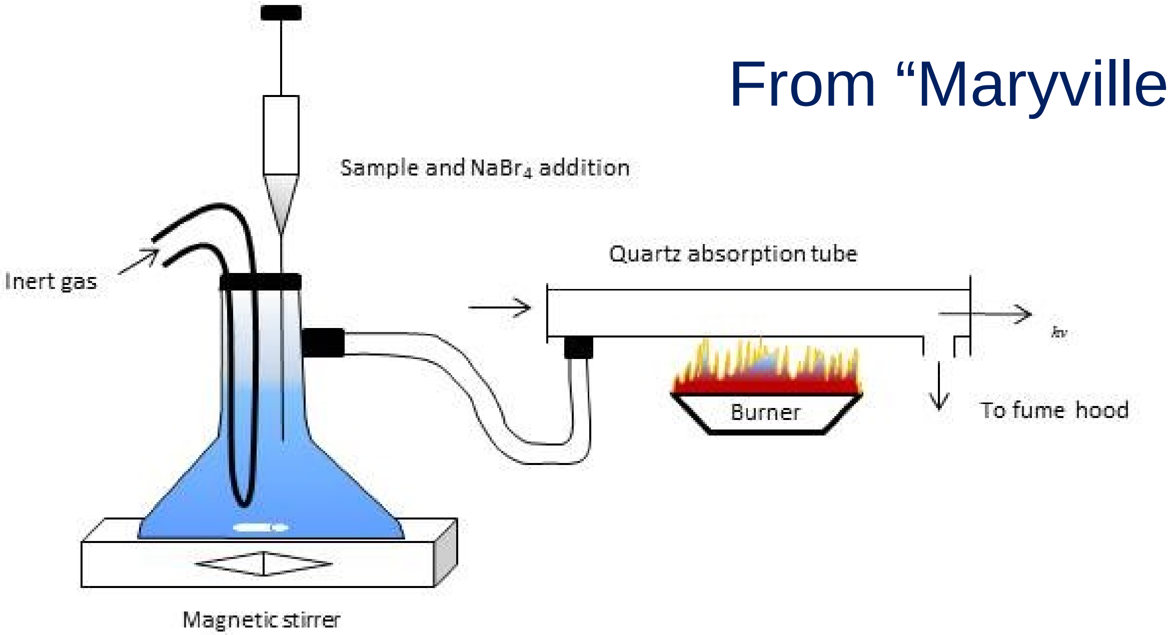
Argon gas is ionized by an applied voltage on the cell, causing the argon ions to accelerate to the cathode where they interact with the sample and eject atoms. This process is called sputtering, the ejection of atoms from a sample as a result of bombardment by energetic species.

In a **hydride generating atomizer**, samples are typically diluted and acidified before being mixed with a hydride source such as **sodium borohydride**.
A volatile **hydride-containing the sample** is generated and carried to the atomization chamber by an inert gas.
<u>During the atomization process, the sample is freed into atoms by heat, releasing the sample from the hydride compound.</u>

Hydride generators are generally used for determination of **heavy metals and other elements, including lead, arsenic, tin, selenium, and bismuth**.

This method is useful for these elements because of its increased detection limit.

A hydride generation and atomization system for AAS



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Output Signal (AA) – ***example of lead*** p. 235

At a wavelength at which absorbance or fluorescence occurs, the transducer output rises to a maximum after a few seconds of ignition followed by a rapid decay back to zero as the atomization products escape into the surroundings. The change is rapid enough (often <1 s) to require a moderately fast data-acquisition system.

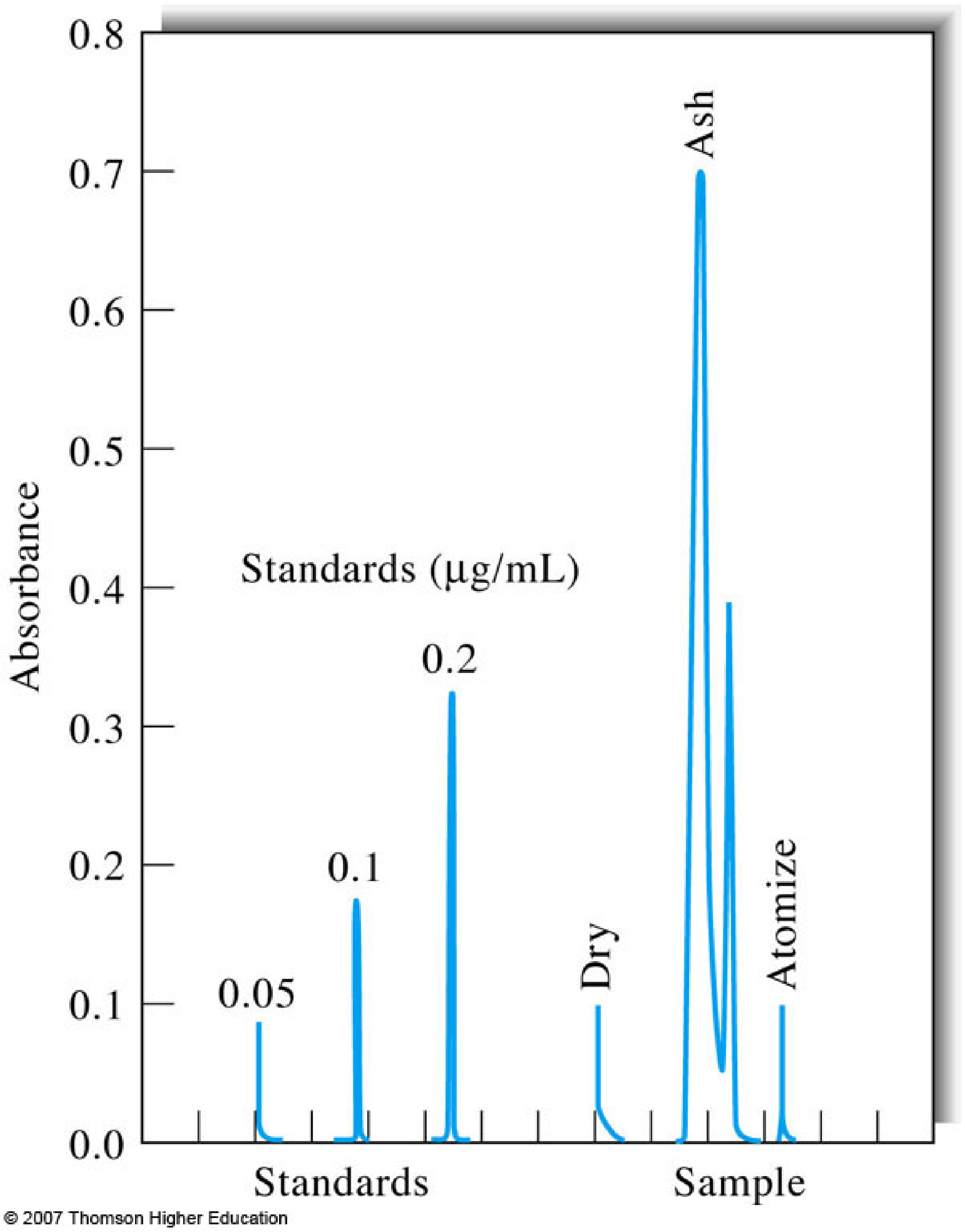
Quantitative determinations are usually based on peak height, although peak area is also used.

Figure 9-7 (next page) shows typical output signals from an atomic absorption spectrophotometer equipped with an **electrothermal atomizer**. **The series of four peaks on the right show the absorbance at the wavelength of a lead peak as a function of time when a 2-μL sample of canned orange juice was atomized.**

During drying and ashing, three peaks appear that are probably due to molecular evaporation products and particulate ignition products.

The three peaks on the left are for lead standards used for calibration.

The sample peak on the far right indicates a lead concentration of about 0.05 μg/mL of juice.



AAS equipped with an **electrothermal atomizer**.

FIGURE 9-7 Typical output for the determination of **lead** 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.

PPT materials taken from web of faculty.virginia.edu

Atomic Absorption Spectroscopy [AAS] & Lead Contamination of Drinking Water

Determination of Lead in Drinking Water using AAS

- Lead exposure causes damage to the brain, kidneys, nervous system, and red blood cells
    - Young children and pregnant women are at the greatest risk
- Drinking water, paint, dust are common lead sources
- Lead pipes, corroded brass fixtures, and lead solder can introduce lead into drinking water

Testing

- EPA advises a level no higher than 15 ppb, especially if there are young children in the household

- Several types of atomic absorption spectroscopy (including graphite furnace) are EPA approved methods

Lead in Drinking Water

- Lead exposure causes damage to the brain, kidneys, nervous system, and red blood cells
  - Young children and pregnant women are at the greatest risk
  - Drinking water, paint, dust common lead sources
- Lead pipes, corroded brass fixtures, and lead solder can introduce lead into drinking water

Limiting Exposure

- Flush pipes every 6 hours for up to 2 minutes
- Use cold water for consumption

Testing

- EPA advises a level no higher than 15 ppb, especially if there are young children in the household
- Individuals use independent labs for testing of home samples
- Several types of atomic absorption spectroscopy (including graphite furnace) are EPA approved methods.

Atomic Absorption Spectroscopy

- Gas phase sample absorbs UV or visible light causing transitions to higher electronic energy levels
- Absorption of light is correlated to concentration using the **Beer Lambert Law**:

$$\mathbf{A = -\log(I / I_o) = \varepsilon bc}$$

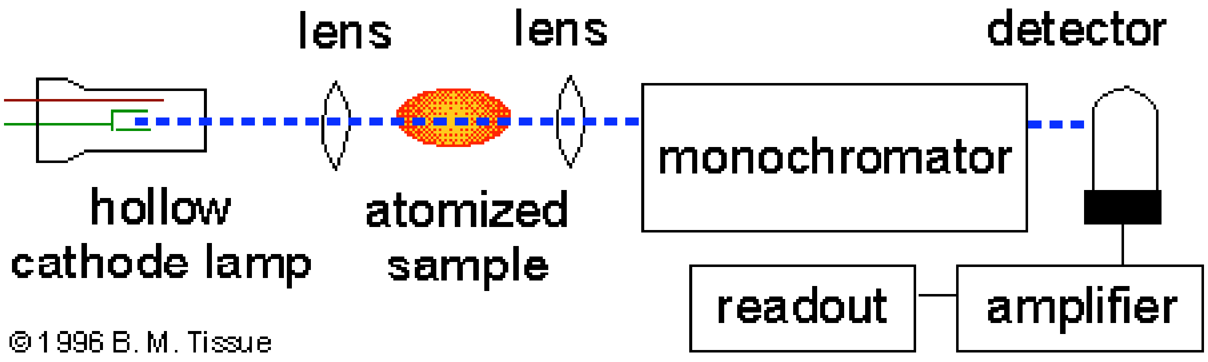
ε= molar absorptivity (L/mol*cm)

b=pathlength of sample cell (cm)

c=concentration of compound (mol/L)

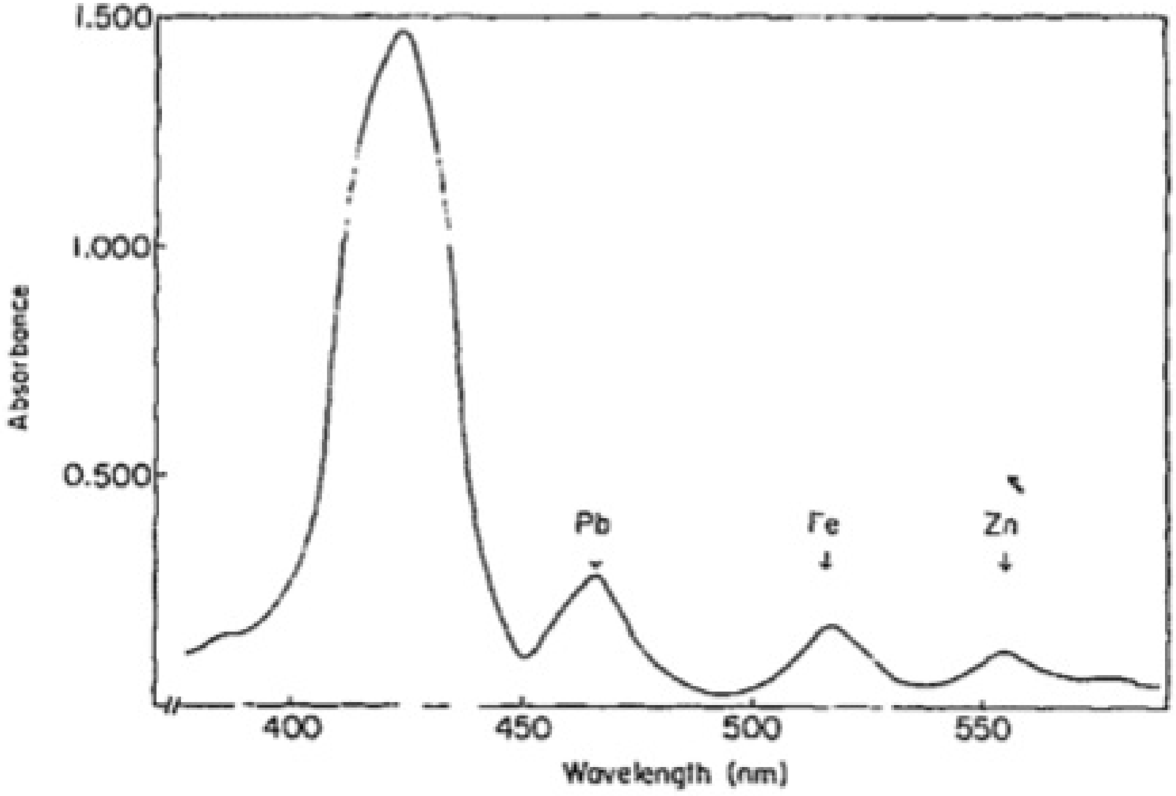
I_o= initial intensity   I=final intensity

Atomic Absorption Spectroscopy



- Light Source: Excitation of Sample
- Atomizer: Flame or gas furnace is used to vaporize sample
- Monochromator: allows for isolation of absorption line
- Light is detected, converted to electrical signal, and amplified

Experimental Results



Atomic Absorption Spectra of a dried blood sample showing peaks for **lead, iron, and zinc** found in the sample (Karai et. al. 1981)

Research

Improvements

- **Pre-concentration** [濃縮] of water samples has been used in order to detect lead easier in samples less than 50 ug/L.

Future Uses

- Similar methods can be used for analysis of lead in **blood samples**. 血鉛 分析

9B **Atomic Absorption** (AAS) **Instrumentation** p. 237

Instruments for AAS (or AA) are similar in general design to that shown in **Figure 7-1a** (previous chapter, shown again in next page for ref.) and consist of a radiation source, a **sample holder**, a wavelength selector, a detector, and a signal processor and readout.

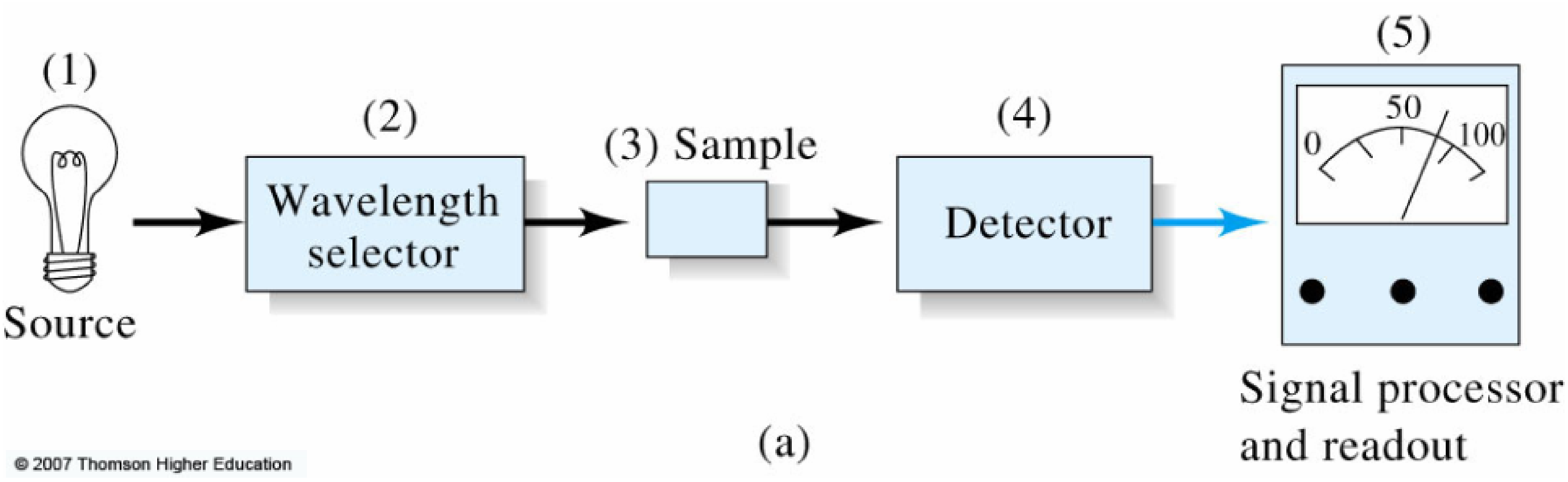
Sample holder for AAS: The **sample holder** in atomic absorption instruments is the atomizer cell that contains the gaseous atomized sample.

Radiation Source

Sample holder (atomizer cell)

Wavelength selector

- **Detector (transducer)**
- **Signal processor**
- **Readout**



- Graph Taken from earlier chapter 7 (not covered)

Flow diagram for AAS

FIGURE 7-1(a) In (a), the arrangement for **absorption** measurements is shown. Note that source radiation of the selected wavelength is sent through the sample, and the transmitted radiation is measured by the detector-signal processing-readout unit. With some instruments, the position of the sample and wavelength selector is reversed.

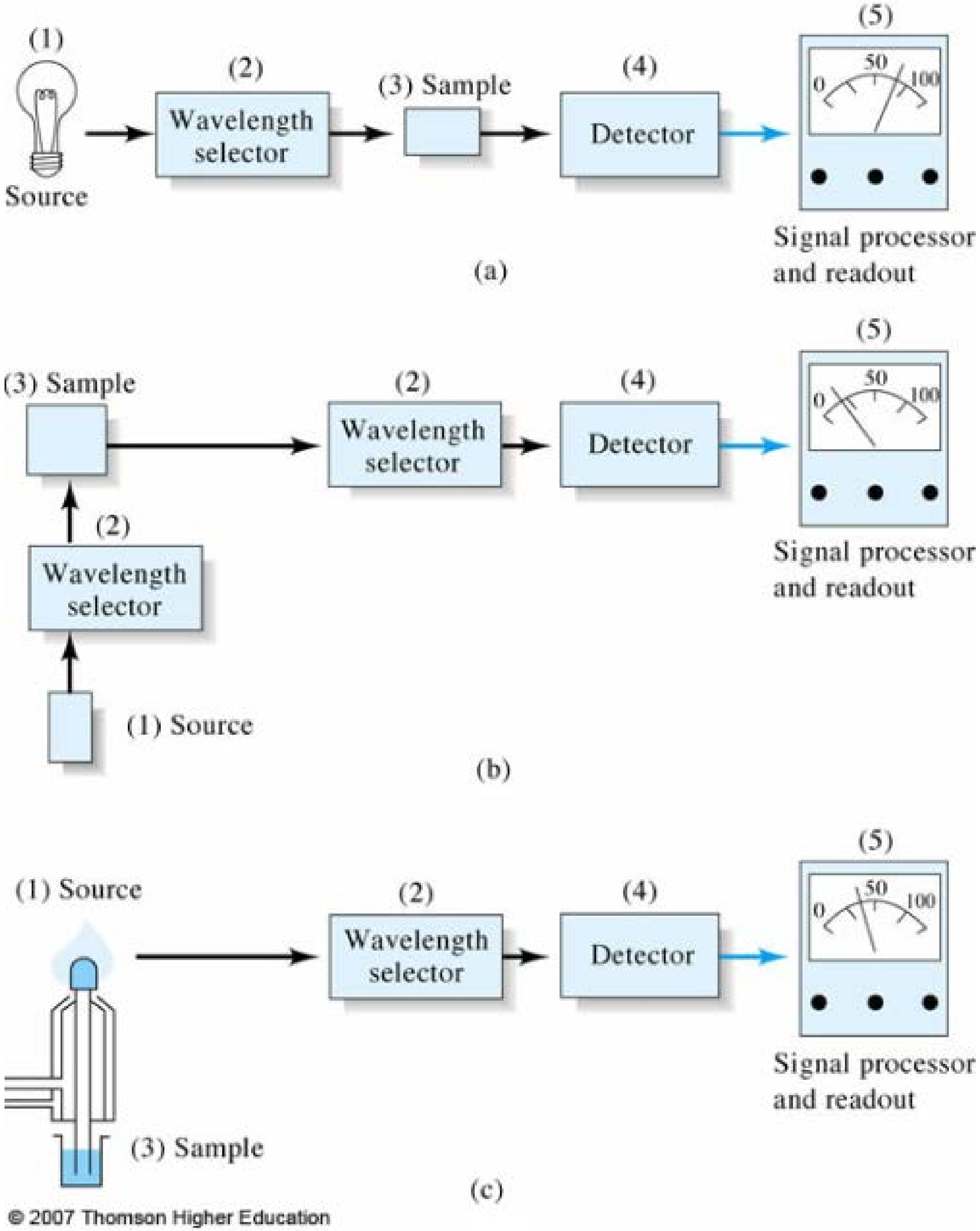


FIGURE 7-1 [taken From previous chapter 7]

Components of various types of instruments for optical spectroscopy.

Scheme flow charts for three types of atomic spectroscopy:

Top:

Middle:

Bottom:

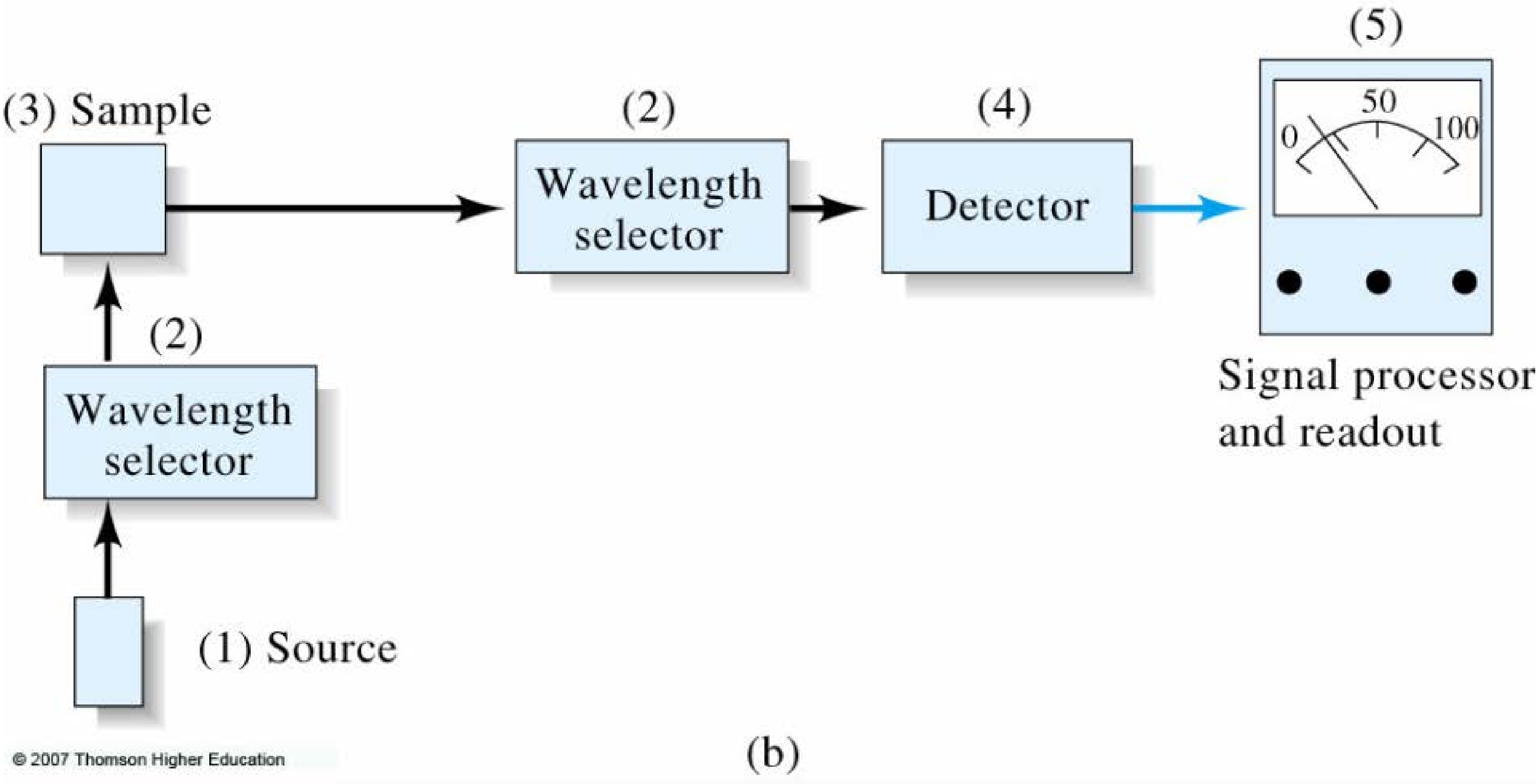


FIGURE 7-1(b) In (b), the configuration for **fluorescence measurements** is shown. Here, **two wavelength selectors are needed to select the excitation and emission wavelengths**.

The selected source radiation is incident on the sample and the radiation emitted is measured, **usually at right angles to avoid scattering.**

9B-1 Radiation source in AA

Atomic absorption methods are potentially highly specific because atomic absorption lines are remarkably narrow (0.002 to 0.005 nm) and because electronic transition energies are unique for each element. On the other hand, narrow line widths create a problem that does not normally occur in molecular absorption spectroscopy.

In Section 13B-2, we show that a linear relationship between the analytical signal (absorbance) and concentration - **that is, for Beer's law as given by Equation 6-34 to be obeyed - requires a narrow source bandwidth relative to the width of an absorption line or band. Even good-quality monochromators, however, have effective bandwidths significantly greater than the width of atomic absorption lines.**

As a result, **nonlinear calibration curves** are inevitable when atomic absorbance measurements are made with an ordinary spectrophotometer equipped with a **continuum radiation source**. Furthermore, the slopes of calibration curves obtained in these experiments are small because only a small fraction of the radiation from the monochromator slit is absorbed by the sample; the result is poor sensitivity.

Cont’d - Radiation source in AA

The problem created by the limited width of atomic absorption lines has been solved by the use of **line sources** with bandwidths even narrower than the absorption line width.

For example, to use the 589.6 nm line of **sodium** as the basis for determining the element, a sodium emission line at this same wavelength is isolated to serve as the source.

In this instance, a sodium vapor lamp in which sodium atoms are excited by an electrical discharge may be used to produce the line.

The other sodium lines emitted from the source are removed with filters or with a relatively inexpensive monochromator.

Hollow-Cathode Lamps ***– radiation source for AA***

The most common source for atomic absorption measurements is the **hollow-cathode lamp**, such as the one shown in **Figure 9-11 (next page)**.

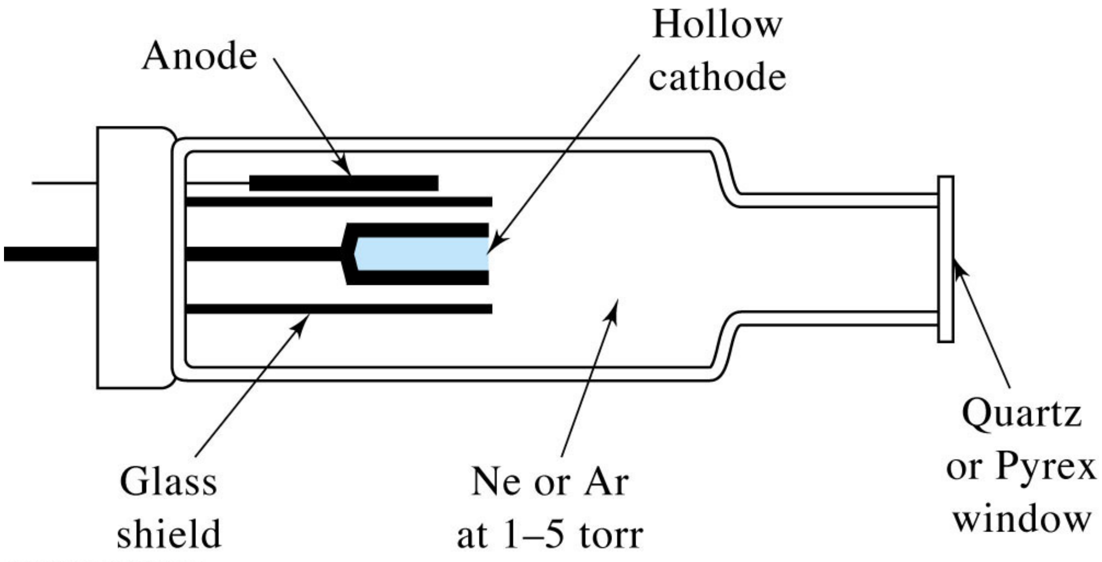
This type of lamp consists of **a tungsten (W) anode (positive-charged)** and a **cylindrical cathode (negative-charged)** sealed in a glass tube filled with neon or argon (Ar) at a pressure of 1 to 5 torr. The cathode is constructed of the metal (Li, Cu, Ni, Pb, etc) whose spectrum is desired or serves to support a layer of that metal.

Ionization of the inert gas (Ar) occurs when a potential difference on the order of 300 V is applied across electrodes, which generates a current of about 5 to 15 mA as ions and electrons migrate to the electrodes.

If the voltage is sufficiently large, the **gaseous cations** acquire enough kinetic energy to dislodge some of metal atoms from the **cathode surface** and produce an atomic cloud in a process called *sputtering*.

A **portion** of the **sputtered (vaporized) metal atoms** 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 the tube and are re-deposited.

The **cylindrical configuration** of the cathode tends to **concentrate** the radiation in a limited region of the metal tube; this design also enhances the probability that **re-deposition will occur at the cathode** rather than on the glass walls.



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- Disadvantage of hollow cathode lamps:

- A **separate lamp source** is needed for each element.

  e.g.: Sodium vapor lamp for Na element.

  Lithium vapor lamp for Li element.

  Copper vapor lamp for Cu element.

In some other designs, the cathodes of some lamps consist of **a mixture of several metals**. Such lamps permit the determination of more than a single element.

[-However, radiation quality of such mixed lamps is not as good as individual-metal lamps]

Electrodeless Discharge Lamps (EDL) p.239

- **Intensities are two-orders of magnitude greater than hollow cathode lamp.**
- A sealed quartz containing a few torrs of argon and a small quantity of the metal whose spectrum is of interest.
- **No electrode** – argon is **energized by microwaves**.
- Ionized argon is accelerated to excite the atoms.
- Available for 15 or more elements.

- Ref. to Fig. 9-12 (p. 239, next page). **Figure 9-12** is a schematic of a commercial EDL, which is powered by a **27-MHz radio-frequency source**.

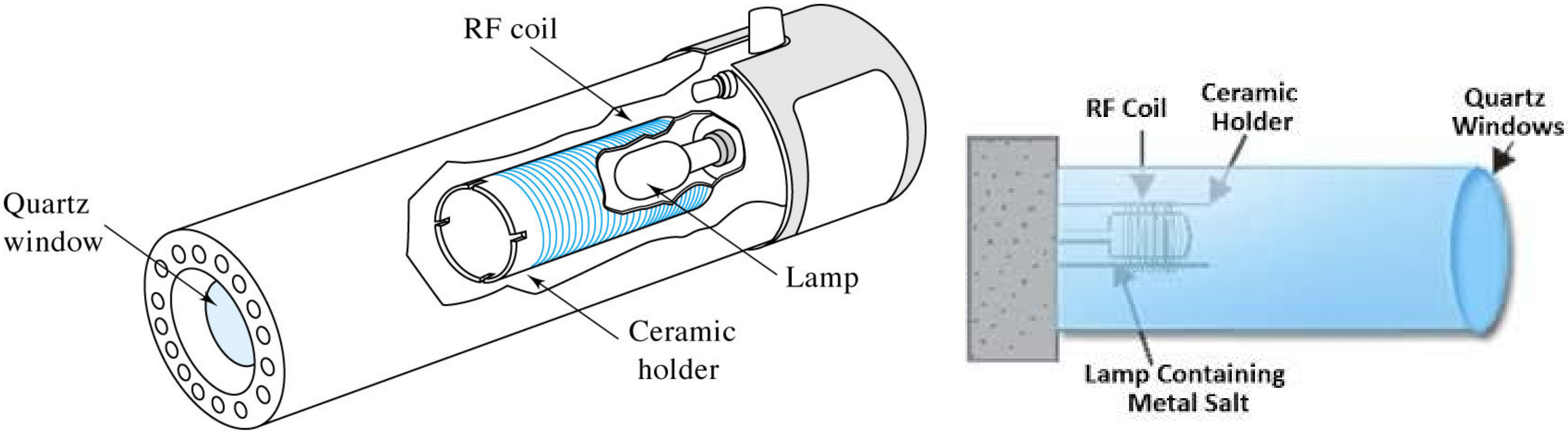

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FIGURE 9-12 Cutaway of an EDL- **Electrodeless Discharge Lamps.**

The internal **electrodeless lamp** or **induction light** is a gas discharge lamp in which the power required to generate light is transferred from outside the lamp envelope to the gas inside via an **electric or magnetic field**, in contrast with a typical gas discharge lamp that uses internal electrodes connected to the power supply by conductors that pass through the lamp envelope.

There are three advantages to elimination of the internal electrodes:

Extended lamp life

higher efficiency

9B-2 Spectrophotometers

P240-242

Instruments for atomic absorption measurements are offered by numerous manufacturers; **both single- and double-beam designs are available**. The range of sophistication and cost (upward of a few thousand US dollars) is substantial.

In general, the instrument must be capable of providing a sufficiently **narrow bandwidth** to isolate the line chosen for the measurement from other lines that may interfere with or diminish the sensitivity of the determination.

A glass filter suffices for some of the alkali metals, which have only a few widely spaced resonance lines in the visible region. An instrument equipped with easily interchangeable interference filters is available commercially.

A separate filter and light source are used for each element. Satisfactory results for the determination of twenty-two metals are claimed.

Most instruments, however, incorporate good-quality ultraviolet-visible monochromators, many of which are capable of achieving a bandwidth on the order of 1 Å.

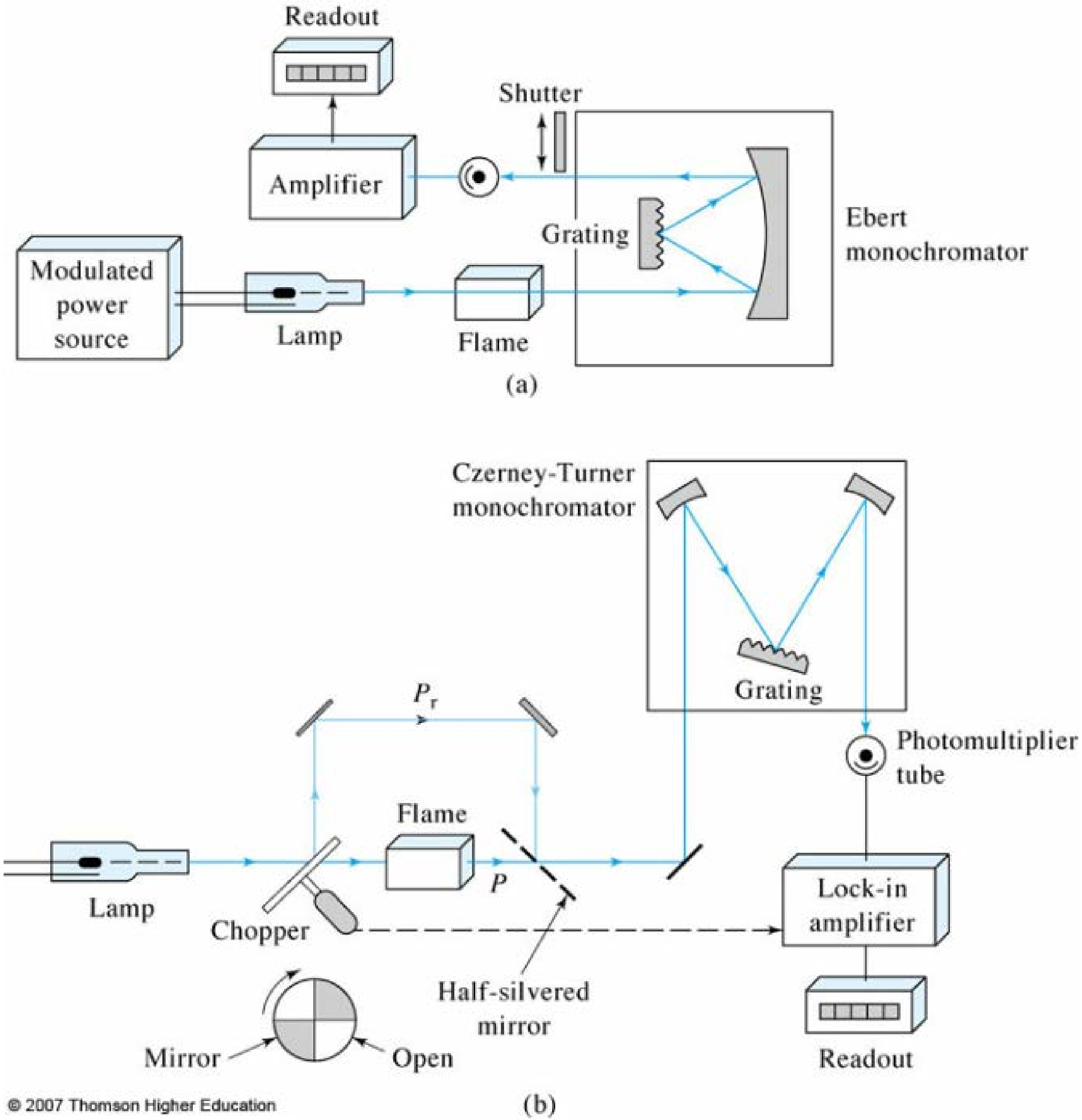


FIGURE 9-13

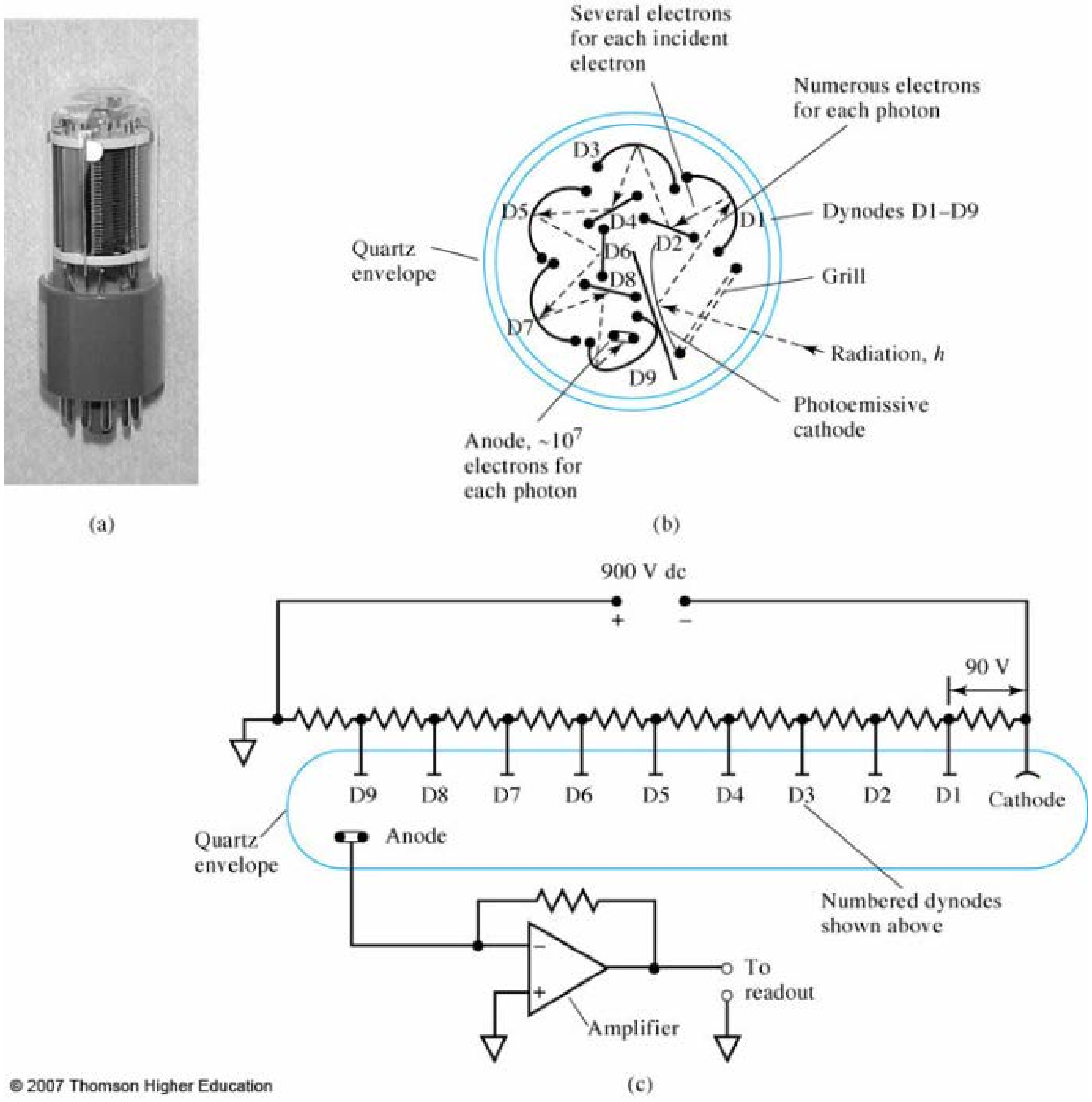
Typical **flame** spectrophotometers.

Photomultiplier tubes as **transducers (detector-偵測器)**

Most atomic absorption instruments use **photomultiplier tubes**, which were described in **Section 7E-2,** as transducers. (shown next page).

As pointed out earlier, electronic systems that are capable of discriminating between the modulated signal from the source and the continuous signal from the sample are required.

Most instruments currently on the market are equipped with **computer systems** that are used to control instrument parameters and to control and manipulate data.



(a) (b) (c)

FIGURE 7-31 Photomultiplier tube. [taken from previous chapter]

Single-Beam Instruments

p. 240

A typical **single-beam instrument**, such as that shown in **Figure 9-13a (next page)**, consists of several hollow-cathode sources (only one of which is shown), a chopper or a pulsed power supply, an atomizer, and a simple grating spectrophotometer with a photomultiplier transducer. It is used in the manner described on page 159. The dark current is nulled with a shutter in front of the transducer.

The 100% transmittance adjustment is then made while a **blank** is aspirated (i.e., released) into the flame or ignited in a non-flame atomizer.

Finally, the transmittance is obtained with the **sample** replacing the blank.

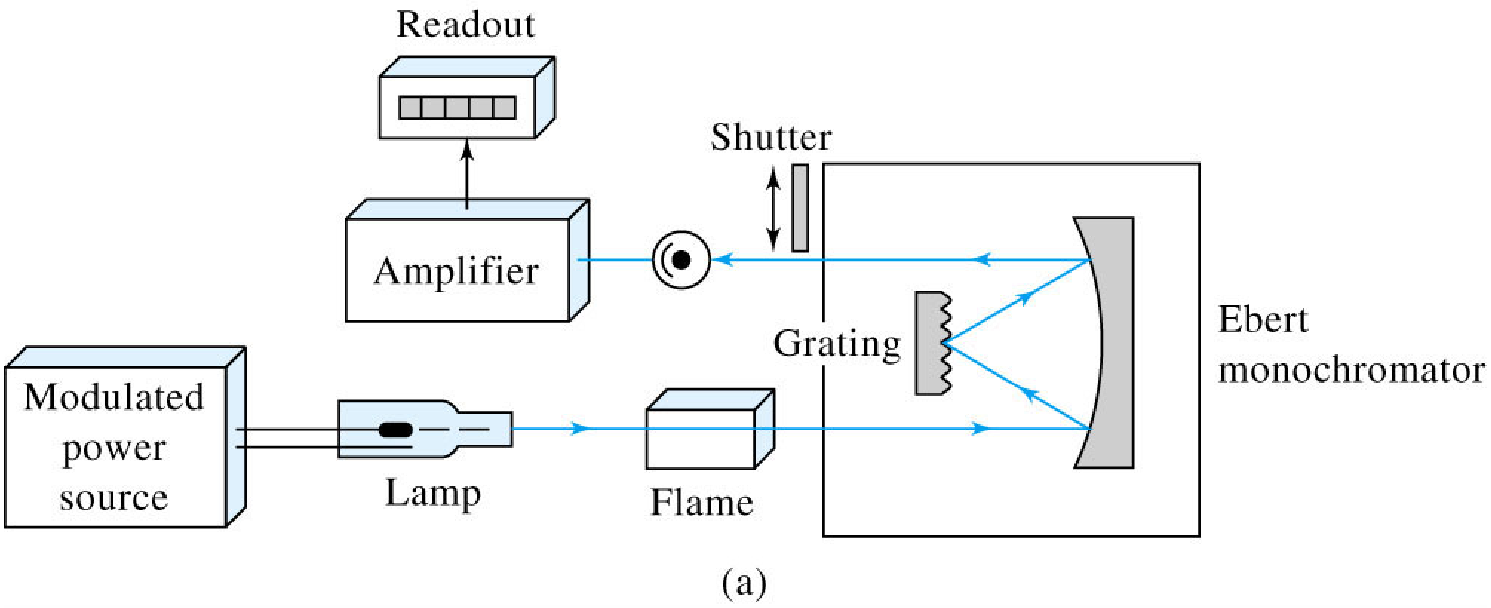
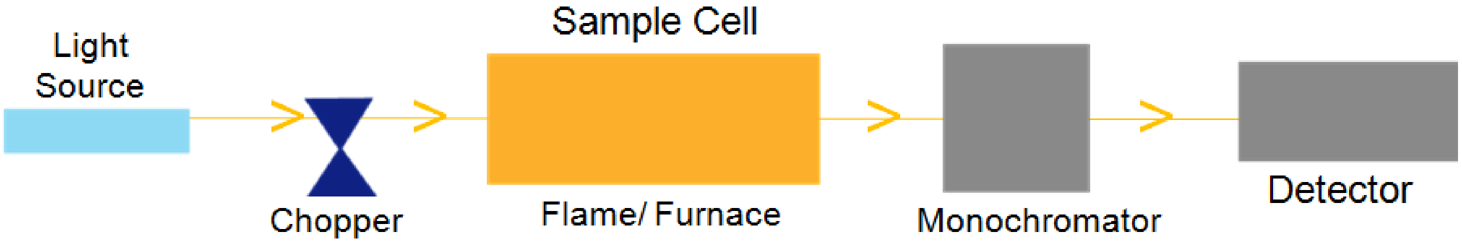


FIGURE 9-13(a) Single-beam design.



Chopper: modulation (light source switched on and off)

NOTE: Modulation serves to differentiate the light coming from the source lamp from the emission from the flame.

Double-Beam *Instruments*

p. 241

Figure 9-13b is a schematic of a typical **double-beam-**in-time 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 **Czerny-Turner grating monochromator**; a **photomultiplier tube** serves as the **transducer**. The output from the latter is the input to a lock-in amplifier that is synchronized with the chopper drive.

The ratio between the reference and sample signal is then amplified and fed to the **readout**, which may be a digital meter or a computer.

It should be noted that the **reference beam** in atomic **double-beam** instruments **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. Methods of correcting for these losses are discussed in the next section.

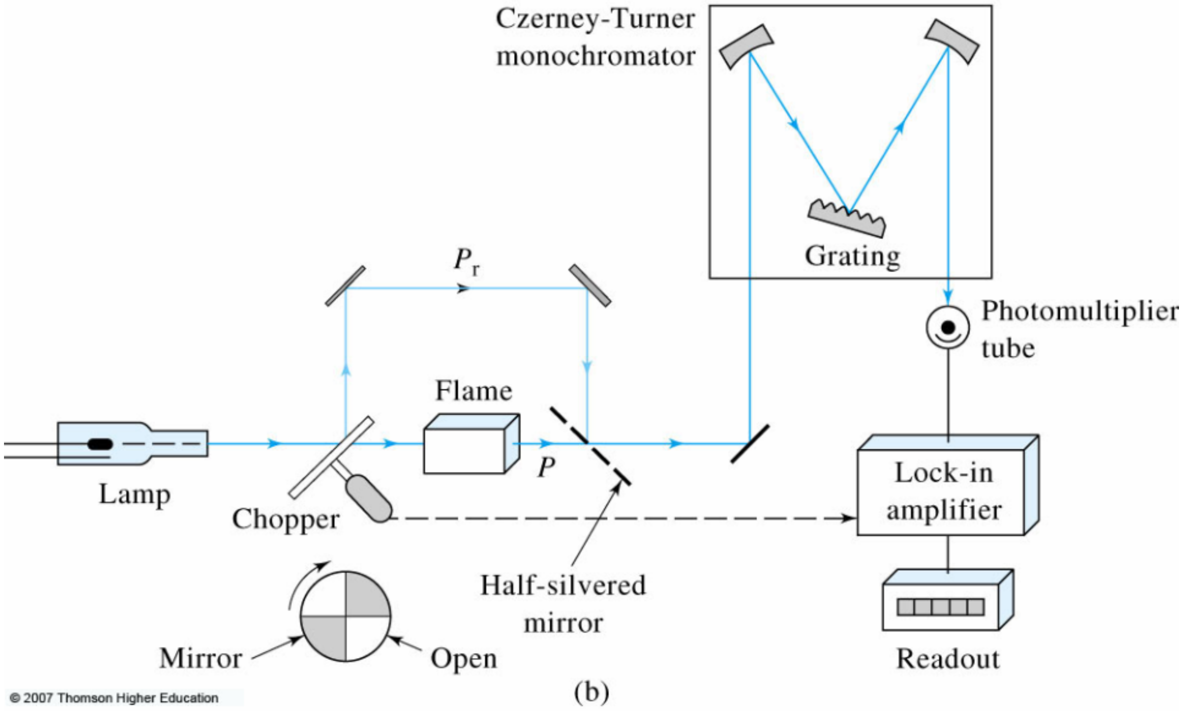


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FIGURE 9-13(b) Double-beam design.

Single vs. double:

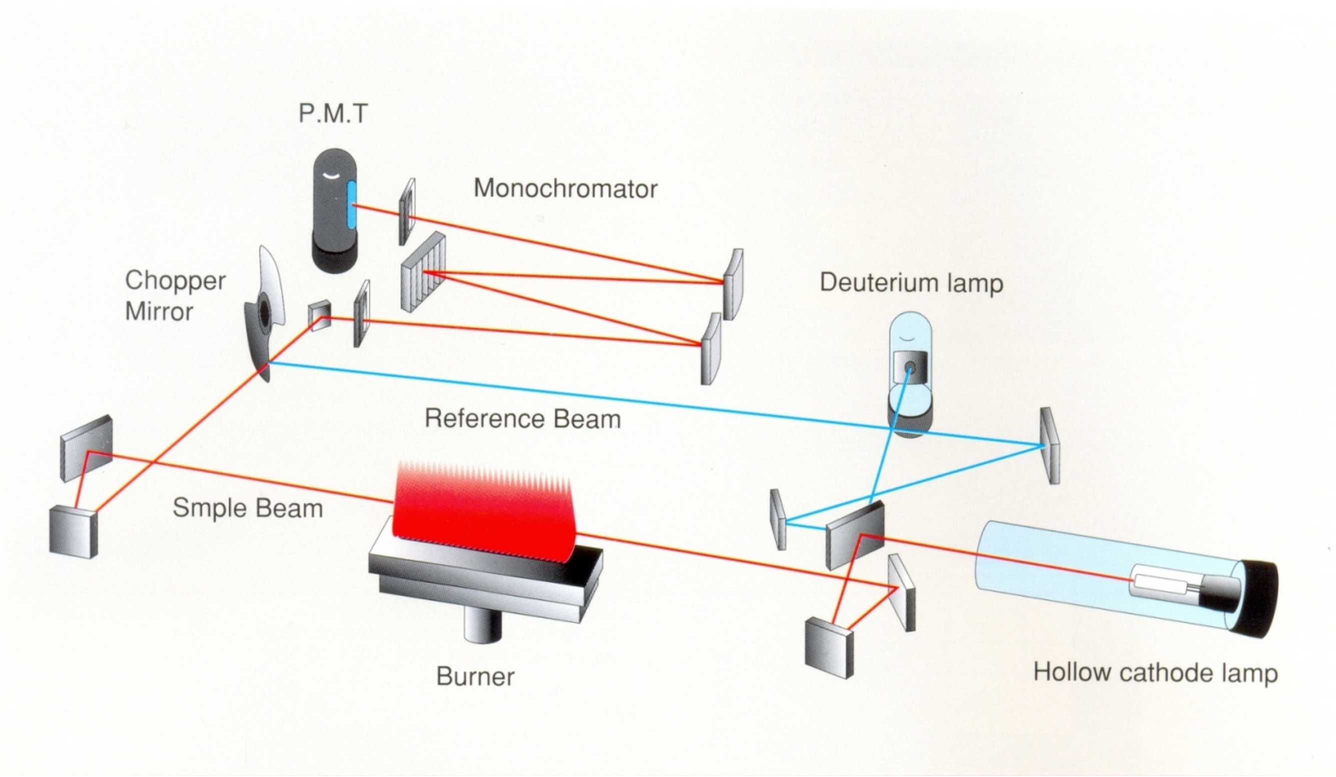
-A **double beam** spectrophotometer is utilized by the scientific community to help simplify spectrophotometry. This is one of the key benefits of two beams of light versus a single beam spectrophotometer.

-Many applications that require characteristics such as **high speed, stability, and flexibility are better suited for the dual beam configuration**.

-The measurements taken with a **double beam** spectrophotometer tend to be **more reproducible**, making them a much appreciated boon to a number of industries.

實驗室 AA儀器 - 2007

Double Beam - High Performance Optical System -



9C. **Interference** in AA Spectroscopy p.241

Interferences of two types are encountered in atomic absorption methods.

1.**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 monochromator becomes impossible.

2.**Chemical interferences** result from various chemical processes occurring during atomization that alter the absorption characteristics of the analyte.

9C.1 **Spectral** Interferences - band overlap or lines too close.

Because the emission lines of hollow-cathode sources are so very narrow, interference because of overlapping lines is rare.

For such an interference to occur, the separation between the two lines would have to be less than about 0.1 Å.

For example, a vanadium (Va) line at 3082.11Å interferes in the determination of aluminum based on its absorption line at 3082.15Å. → **The interference is easily avoided, however, by observing the aluminum line at 3092.7Å instead**.

Two-line Correction Method.
The continuum-source Correction Method.
Background Corrections

9C.2 Chemical Interferences: p.244

1. **Formation of compounds of low volatility**

Perhaps the most common type of interference is **formation of compounds of low volatility with the analyte**, thus reduce the fractions of analyte that is atomized. → Low results are the outcome.

An example is the decrease in **calcium** absorbance observed with increasing concentrations of **sulfate or phosphate**. These anions form compounds with calcium (CaSO4, etc…) that are difficult to volatilize.

For example, at a fixed calcium concentration, the absorbance falls off nearly linearly with **increasing sulfate or phosphate [SO_2-, PO_4-) concentrations** until the anion-to-calcium ratio is about 0.5; the absorbance then levels off at about 30% to 50% of its original value and becomes independent of anion concentration.

2. **Dissociation Equilibria**

3. **Ionization Equilibria**

3. **Ionization** Equilibria [chemical interference] p. 245

- **Ionization** of atoms and molecules is small in combustion mixture that involves **air** as oxidant, and can often be neglected. (-low flame temperatures)

- In **higher-temperature flames** where oxygen or nitrous oxide serves as the oxidant; however, **ionization** becomes important, and **there is a significant concentration of free electrons produced by the equilibrium** [Eq. 9-1].

$$M \leftrightarrow M^+ + e^- \qquad (9\text{-}1)$$

Ionization Equilibria

p.245

- Small at low temp (air as oxidant), but becomes important at higher temp's (oxygen or nitrous oxide as oxidants).

$$\underset{\text{(atom)}}{M} \leftrightarrow \underset{\text{(ion)}}{M^+} + \underset{\text{(free electrons)}}{e^-} \qquad (9\text{-}1)$$

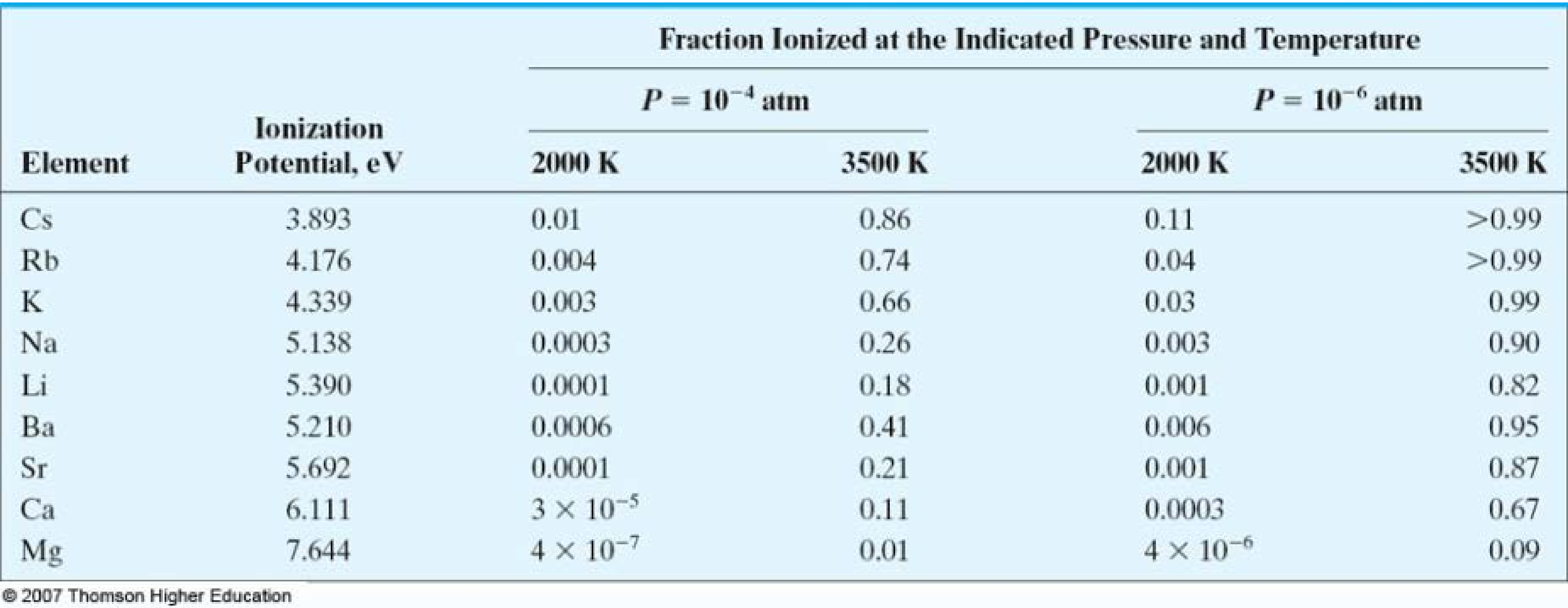
$$K = \frac{[M^+][e^-]}{[M]} \qquad (9\text{-}2)$$

- If **no other source of electrons** is present, Eq.(9-2) may be written as:
- $K=[\alpha^2/(1-\alpha)]P$
- where α **is the fraction of M ionized**, P= partial pressure of metal in gaseous mixture before ionization.

- Ref. to **Table 9-2** (calc. fractions ionized for several common metals under conditions of flame spectroscopy - 2000~3500K)

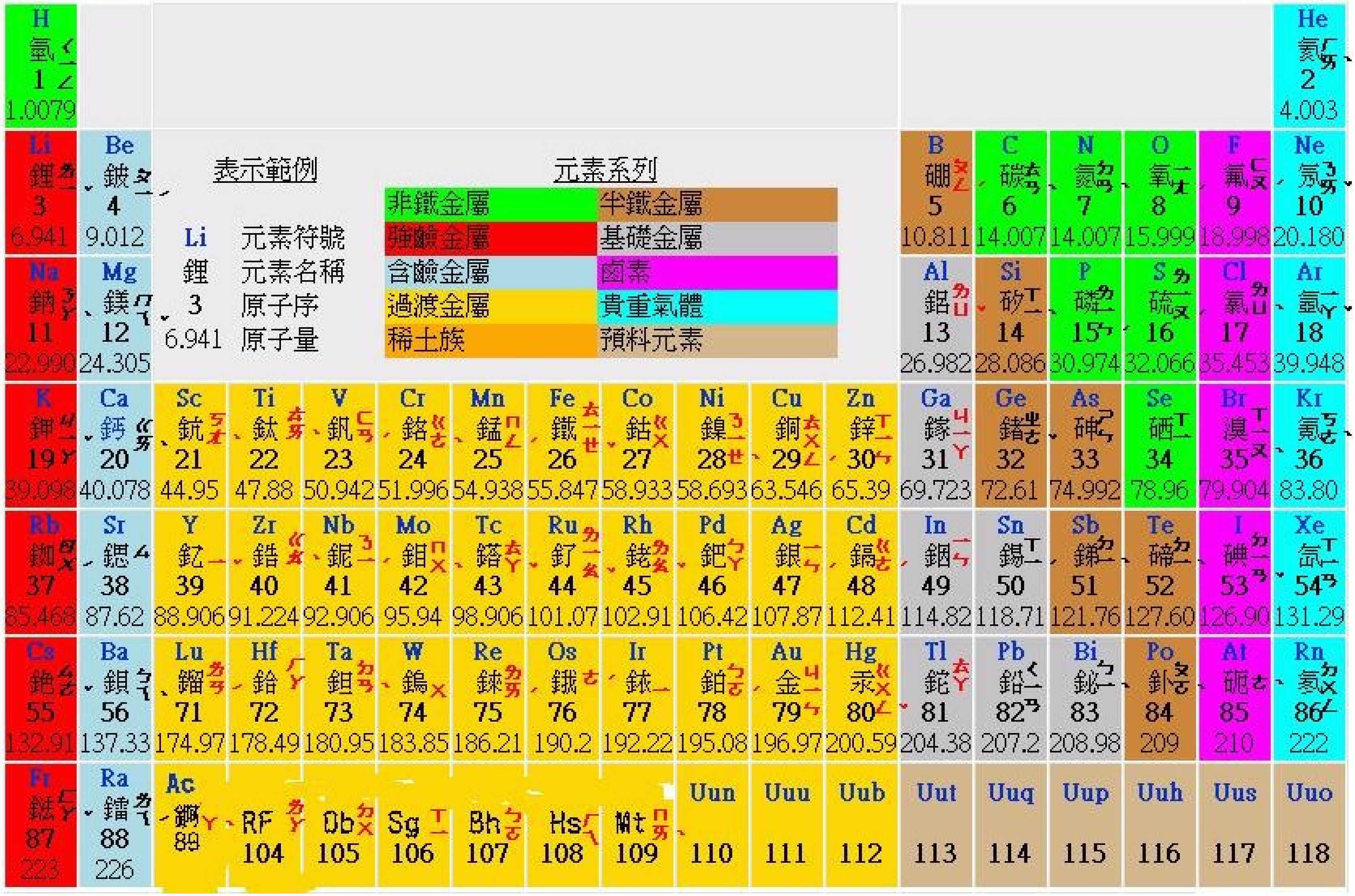
TABLE 9-2

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

Alkali metals (Li, Na, K, Rb, Cs, Fr, etc), under H, in periodic table



H 氫 1 1.0079																	He 氦 2 4.003
Li 鋰 3 6.941	Be 鈹 4 9.012											B 硼 5 10.811	C 碳 6 14.007	N 氮 7 14.007	O 氧 8 15.999	F 氟 9 18.998	Ne 氖 10 20.180
Na 鈉 11 22.990	Mg 鎂 12 24.305											Al 鋁 13 26.982	Si 矽 14 28.086	P 磷 15 30.974	S 硫 16 32.066	Cl 氯 17 35.453	Ar 氬 18 39.948
K 鉀 19 39.098	Ca 鈣 20 40.078	Sc 鈧 21 44.95	Ti 鈦 22 47.88	V 釩 23 50.942	Cr 鉻 24 51.996	Mn 錳 25 54.938	Fe 鐵 26 55.847	Co 鈷 27 58.933	Ni 鎳 28 58.693	Cu 銅 29 63.546	Zn 鋅 30 65.39	Ga 鎵 31 69.723	Ge 鍺 32 72.61	As 砷 33 74.992	Se 硒 34 78.96	Br 溴 35 79.904	Kr 氪 36 83.80
Rb 銣 37 85.468	Sr 鍶 38 87.62	Y 釔 39 88.906	Zr 鋯 40 91.224	Nb 鈮 41 92.906	Mo 鉬 42 95.94	Tc 鎝 43 98.906	Ru 釕 44 101.07	Rh 銠 45 102.91	Pd 鈀 46 106.42	Ag 銀 47 107.87	Cd 鎘 48 112.41	In 銦 49 114.82	Sn 錫 50 118.71	Sb 銻 51 121.76	Te 碲 52 127.60	I 碘 53 126.90	Xe 氙 54 131.29
Cs 銫 55 132.91	Ba 鋇 56 137.33	Lu 鎦 71 174.97	Hf 鉿 72 178.49	Ta 鉭 73 180.95	W 鎢 74 183.85	Re 錸 75 186.21	Os 鋨 76 190.2	Ir 銥 77 192.22	Pt 鉑 78 195.08	Au 金 79 196.97	Hg 汞 80 200.59	Tl 鉈 81 204.38	Pb 鉛 82 207.2	Bi 鉍 83 208.98	Po 釙 84 209	At 砈 85 210	Rn 氡 86 222
Fr 鍅 87 223	Ra 鐳 88 226	Ac 錒 89	RF 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Uun 110	Uuu 111	Uub 112	Uut 113	Uuq 114	Uup 115	Uuh 116	Uus 117	Uuo 118

表示範例

Li	元素符號
鋰	元素名稱
3	原子序
6.941	原子量

元素系列

非鐵金屬	半鐵金屬
強鹼金屬	基礎金屬
含鹼金屬	鹵素
過渡金屬	貴重氣體
稀土族	預料元素

p.246 - ionization equilibria

If alkali metals (Li, Na, K, etc – see table next page) are also present, ionization occurs in much greater extents:

$$B \leftrightarrow B^+ + e^- \qquad \text{(B = alkali metal atom)}$$

As a result, ionization of [$M \leftrightarrow M^+ + e^-$] (in Eq. 9-1) will be "suppressed".

That is, atomic atom [M] is increased.

→ And as a result, intensity of atomic emission or absorption of M increases.

Ref. to →Fig 9.17 (Effect of K on Sr-38)

Cont'd - Ionization Equilibria p. 246

- It is important to appreciate the treatment of ionization process as an **equilibrium** - with free electrons as one of the products.
- The degree of ionization of M will be decreased by the mass-action effect of electrons formed from B.

- This implies that degree of ionization of a metal will be strongly influenced by the presence of other ionizable metals in the flame.

- Thus, if the medium contains **not only M**, but also **species B** as well, and if B ionizes according to

$$B \rightarrow B^{+} + e^{-}$$

$$[e^{-}] = \mathbf{[B^{+}]} + [M^{+}]$$

Cont'd

p. 246

- Atom-ion equilibria in flames create a number of important consequences in flame spectroscopy.

- For examples, intensities of atom emission or absorption lines for **alkali metals**, potassium, rubidium, and cesium, *are affected by **temperatures** in a complex way, **as following**:*

- -Increased temp. causes an increase in population of excited atoms (according to **Boltzmann relationship** - [Eq. 8-1]).
- -However, it also causes a decrease in concentration of atoms resulting from **ionization equilibria**.

→ Temperature of atomization (especially in emission) must be balanced.

Cont’d: Ionization concern - for alkali metals - Li, Na, K, etc

- Owing to the concern:
- Increased temp. → causes an **increase** in population of excited atoms – (**Boltzmann** relationship.)
- Counter-acting effect: increased temp. → leads to a **decrease** in conc. of atoms as a result of ionization [$M \rightarrow M^+ + e^-$].
- Thus, under some circumstances, **a decrease** (and not an increase) in emission or absorption may be observed in **hotter flames** – owing to ionization.
- For this reason, **lower temp’s are usually used for analysis of alkali metals. [Reasons as stated above]**

Cont’d - ionization equilibria

The effects of shifts in ionization equilibria can usually be eliminated by addition of an ionization suppressor, which provides a relatively high conc. of electrons to the flame.

→ This results in suppression of ionization of the analyte. [Fig. 9-17, this page]

Note the significant increase in slope of these curves as strontium (Sr, 38) ionization is repressed by the increasing concentration of K ions and electrons.

Note also the enhanced sensitivities produced by using nitrous oxide instead of air as the oxidant.

The higher temp. achieved with nitrous oxide enhances the degree of decomposition and volatilization of the Sr compounds in the plasma.

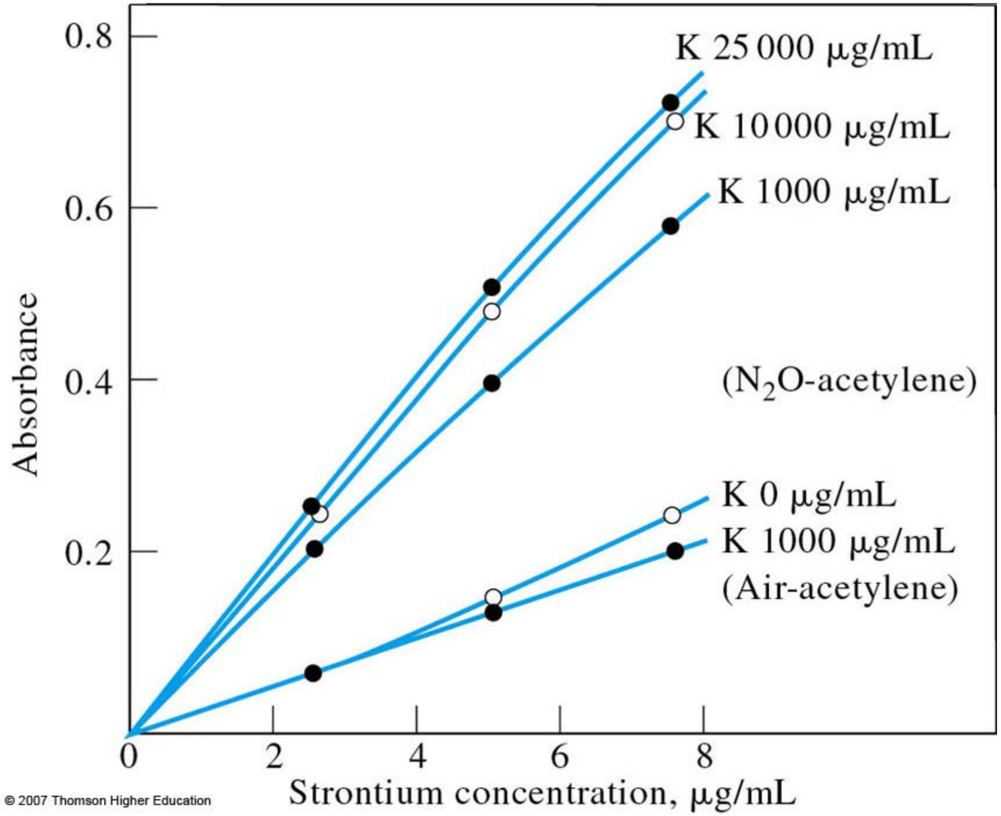


FIGURE 9-17 Effect of potassium concentration on the calibration curve for strontium (Sr).

9D AA ANALYTICAL TECHNIQUES P247-249

This section deals with some of the **practical details** that must be considered in **flame or electrothermal** atomic absorption analysis.

9D-1. 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.

Cont’d **Sample preparation**

Decomposition of materials such as those just cited usually requires rigorous treatment of the sample at high temperatures accompanied by a risk of losing the analyte by volatilization or as particulates in smoke.

Furthermore, the reagents used in decomposing a sample often introduce the kinds of chemical and **spectral interferences** that were discussed earlier.

Additionally, the analyte may be present in these reagents as an impurity. **In fact, unless considerable care is taken, it is not uncommon in trace analyses to find that reagents are a larger source of the analyte than the samples - a situation that can lead to serious error even with blank corrections.**

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 (wet ashing);** combustion in an oxygen bomb or other closed container to avoid loss of analyte; ashing at a high temperature; and high-temperature fusion with reagents such as boric oxide, sodium carbonate, sodium peroxide, or potassium pyrosulfate. [Similar to chem. Analy.]

Cont’d - Sample preparation

One of the advantages of **electrothermal atomization** is that some materials can be atomized directly, thus avoiding the solution step.

For example, **liquid samples** such as blood, petroleum products, and organic solvents can be pipetted directly into the furnace for ashing and atomization.

Solid samples, such as plant leaves, animal tissues, and some inorganic substances, can be weighed directly into cup-type atomizers or into tantalum boats for introduction into tube-type furnaces.

- **Calibration (for solid samples) is, however, usually difficult and requires standards that approximate the sample in composition.**

9D-3 Effect of **Organic Solvents**

- Early in the development of atomic absorption spectroscopy, it was recognized that **enhanced absorbances** could be obtained if the solutions contained low-molecular-weight **alcohols, esters, or ketones.**

- 1.The **effect of organic solvents** is largely attributable to **increased nebulizer efficiency**; the **lower surface tension** of such solutions results in **smaller drop sizes** and a resulting increase in the amount of sample that reaches the flame.

- 2.In addition, **more rapid solvent evaporation** may also contribute to the effect.

9D-4 Calibration Curves

- In theory, atomic absorption should follow **Beer's law (Equation 6-34)** with absorbance being directly proportional to concentration.
- Unfortunately, calibration curves are often **nonlinear**, so it is counterproductive to perform an atomic absorption analysis without experimentally confirming the linearity of the instrument response.

- Thus, a calibration curve that covers the range of concentrations found in the sample should be prepared periodically. In addition, the number of uncontrolled variables in atomization and absorbance measurements is sufficiently large to warrant measurement of one standard solution each time an analysis is performed.

- It is even better to use **two standards** that bracket the analyte concentration. Any deviation of the standard from the original calibration curve can then be used to correct the analytical result.

9D-6 Application of AAS – to metals or metalloids

- AAS is a sensitive means for the **quantitative determination of more than sixty metals or metalloid elements.** [**Metalloid: nonmetal element, like arsenic (As), but has chemical properties of a metal.**]

Reason of AA not suitable for nonmetallic atoms:

→The AA resonance lines for the **non-metallic elements** are generally located at **wavelengths shorter than 200 nm (0.2 μm),** thus preventing their determination by non-vacuum spectrophotometers.

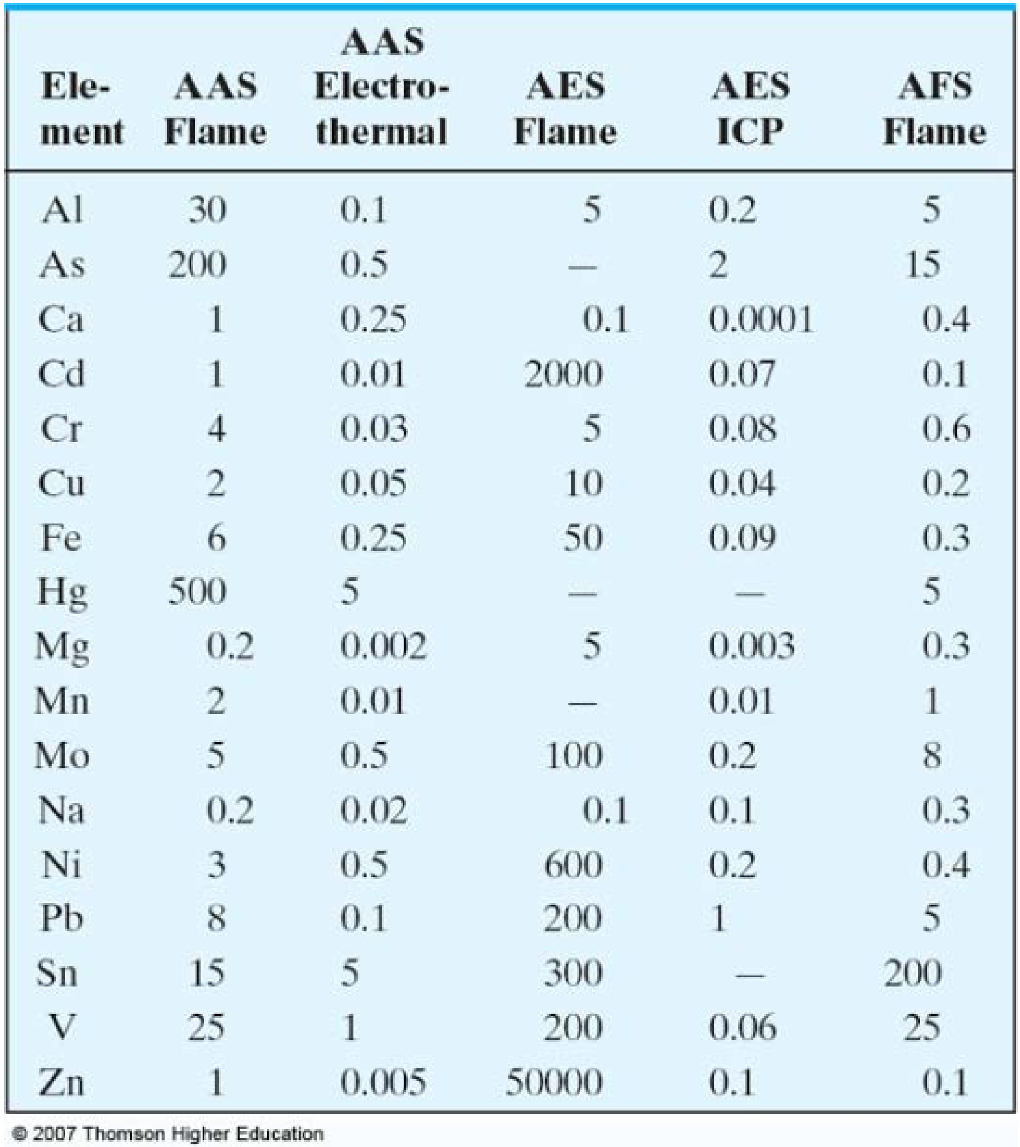
Detection Limits - AA

- Columns two and three of **Table 9-3** present detection limits for a number of common elements by flame and electrothermal atomic absorption.

- For comparison, detection limits for some of the other atomic procedures are also included. Small differences among the quoted values are not significant.
- Thus, an order of magnitude is probably meaningful, but a factor of 2 or 3 certainly is not.

- For many elements, detection limits for atomic absorption spectroscopy with **flame atomization lie in the range of 1 to 20 ng/mL, or 0.001 to 0.020 ppm**;
- **for electrothermal atomization, the corresponding figures are 0.002 to 0.01 ng/mL, or 2×10^{-6} to 1×10^{-5} ppm.**

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

Accuracy - AA

- Under the usual conditions, the **relative error** associated with a flame atomic absorption analysis is of the order of 1 % to 2%. With special precautions, this **figure** can be lowered to a few tenths of a percent. (-higher precision)

- **Errors** encountered with electrothermal atomization usually exceed those for flame atomization by a factor of 5 to 10 – (5-10% error). (-lower precision)

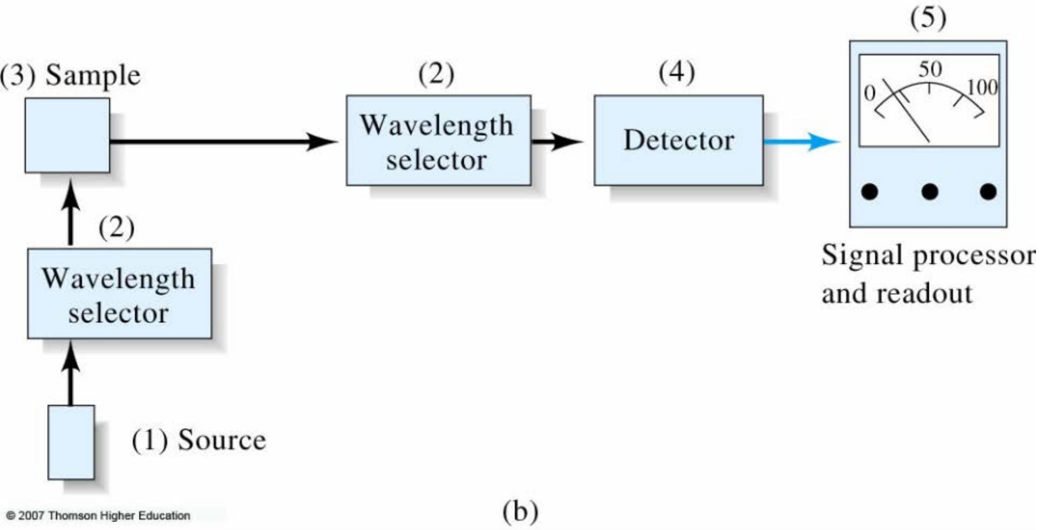
9E ATOMIC **FLUORESCENCE** SPECTROSCOPY (AFS)

- AFS is *not as popular as absorption or emission spectroscopy.*

- Over the years, significant research effort has been devoted to the development of analytical methods based on **atomic fluorescence.**
- To date, however, the procedure has not found widespread use because of **the overwhelming successes of atomic emission, and especially atomic absorption methods,** which were developed prior to atomic fluorescence by more than a decade.

- As mentioned earlier, these successes have led to the availability of **absorption and emission** instruments from numerous commercial sources.

- In recent years, a number of manufacturers have introduced atomic **fluorescence spectrometers useful for determining elements that form vapors and hydrides, such as Pb, Hg, Cd, Zn, As, Sb, Bi, Ge, and Se. (– thus no high-T atomization is required) [Note: this is possible only for atomic fluorescence method.]**



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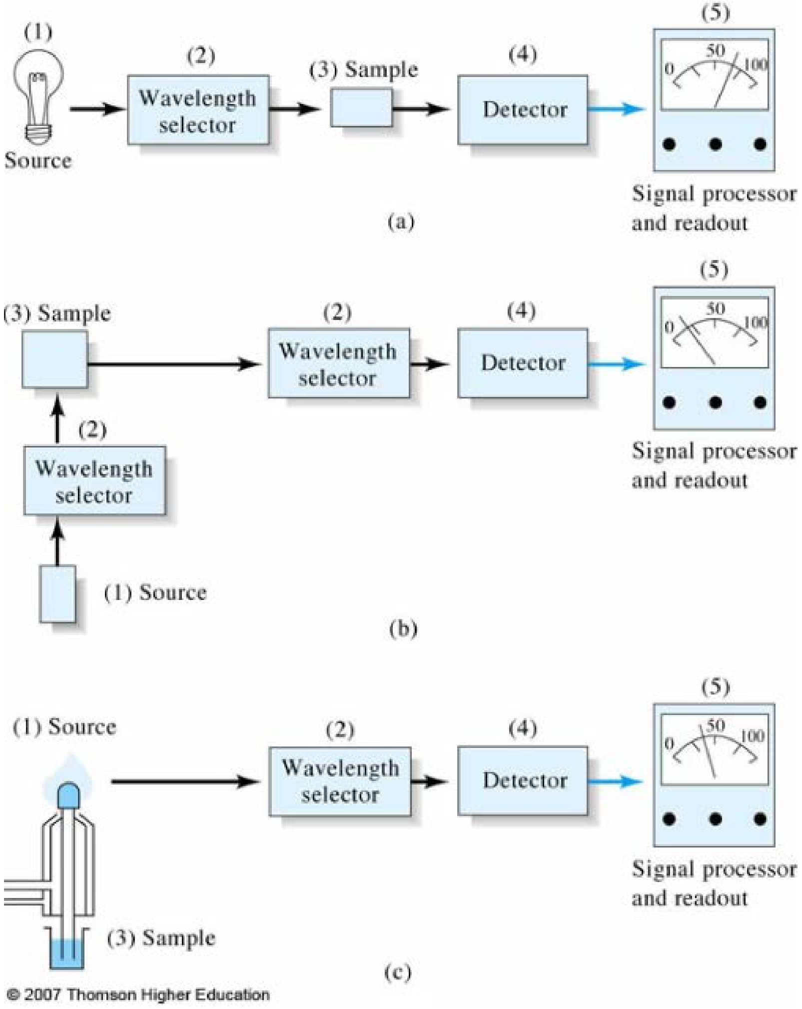
ATOMIC **FLUORESCENCE** SPECTROSCOPY (top).

Note the differences among (a) AAS, (b) AFS, and (c) AES → Right diagrams.



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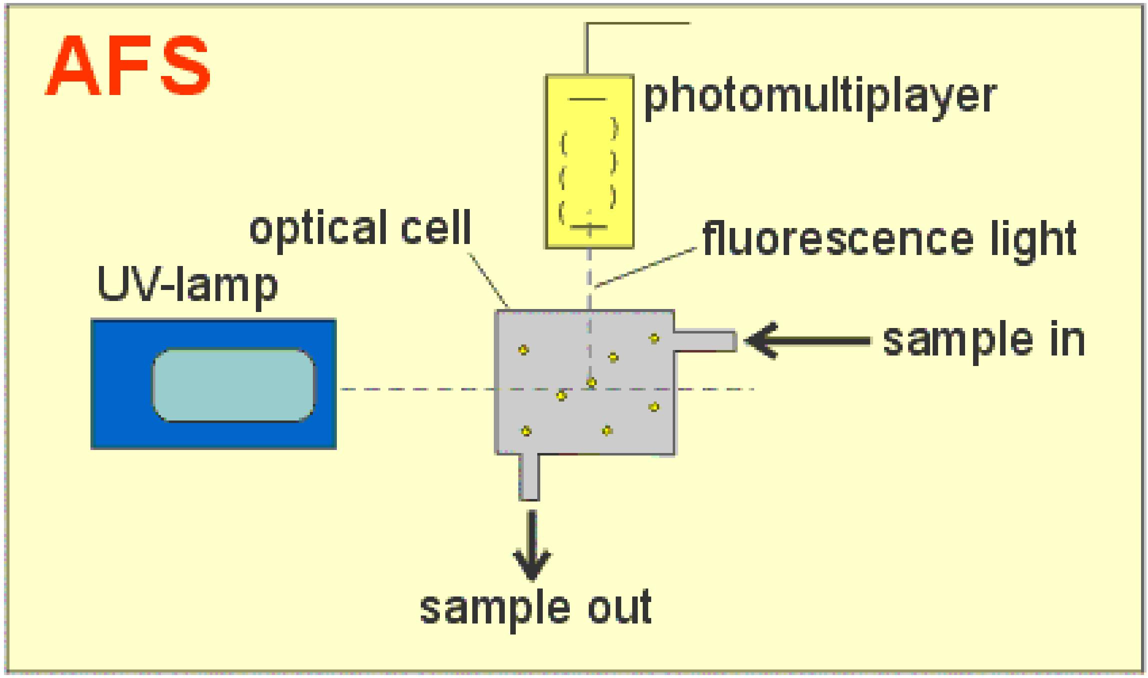
ATOMIC **FLUORESCENCE** SPECTROSCOPY [AFS] – Not as widely used as AAS



atomic fluorescence Instrument

Flame is used as atomizer and excitation of atoms

Cont’d

- The limited use of atomic florescence has not arisen so much from any inherent weakness of the procedure**, but rather because the advantages of atomic fluorescence have been small relative to the well-established absorption and emission methods.**

- Thus, although **fluorescence methods**, particularly those based on electrothermal atomization, are somewhat **more sensitive for several elements**, the procedure is also less sensitive and appears to have a smaller useful concentration range for several others.

- Furthermore, dispersive **fluorescence instruments** are somewhat **more complex and more expensive** to purchase and maintain.

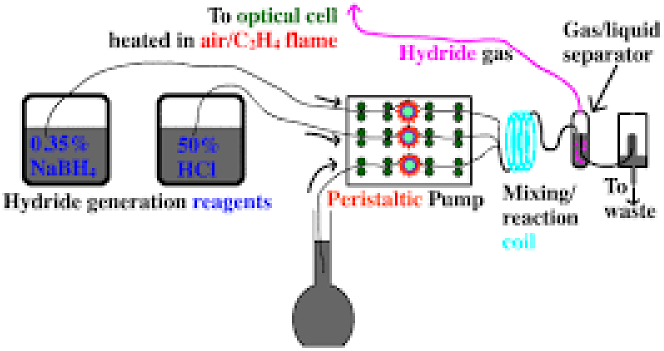
Applications of Atomic Fluorescence Spectrometry (AFS) - is an ideal detection technique for special studies concerning **hydride forming elements** (mainly **As, Se and Sb) and Hg**. [H_2Se, H_3AS, SbH_3, etc]

The analytical features of AFS, such as detection limits below the µg L^{-1} and the wide linear calibration range, up to the mg L^{-1}, allow its application to a great variety of **environmental, biological and food samples**.

AFS - a suitable detection technique in special studies for arsenic, selenium, antimony and mercury, etc.

Compared **to ICP-MS**, AFS has very similar sensitivity and linear range, **but is a relatively simple set-up and has lower investment and maintenance costs.**

The volatile species of As, Se and Sb, obtained from liquid samples after **hydride generation (see diagram below)**, are carried with an argon (Ar) flow to a gas–liquid separator, followed by **atomization and excitation in an argon–hydrogen diffusion flame**.



Hydride Generator

End of Chap. 9 – AAS, AFS

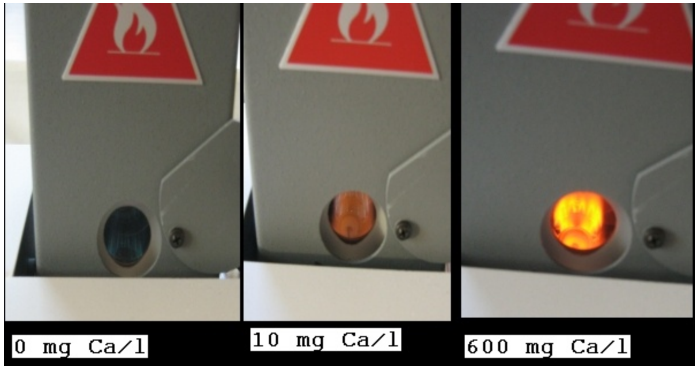
Next: Chap 10 - AES

Chap. 10 – AES

"Atomic emission spec" [AES] . (Chap. 10) is not covered in full. But outlines are discussed as following:

Atomic emission spectroscopy (**AES**) is a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample.

The wavelength of the atomic spectral line gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element. [Following is example of Ca in flame – orange color]



AES:

In this method, a sample of the material to be analyzed is brought into flame in the form of a sprayed solution or gas.

→Free atoms of the material are produced when the flame heat evaporates the solvent and breaks the chemical bonds of the analyte (atomization).
→The heat also changes the atoms into electronically charged particles (i.e., excited state) which emits light when they get back to the ground electronic state.

Light is emitted (emission) at a wavelength **characteristic to each element** which is then dispersed by a prism or grating and detected in spectrometer.

Flame emission spectroscopy is frequently used while studying alkali metals for pharmaceutical research and analysis.
[Note: Alkali metals are different from "Alkaline Earth Metals"]
Alkali metals: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr). [鹼金屬]

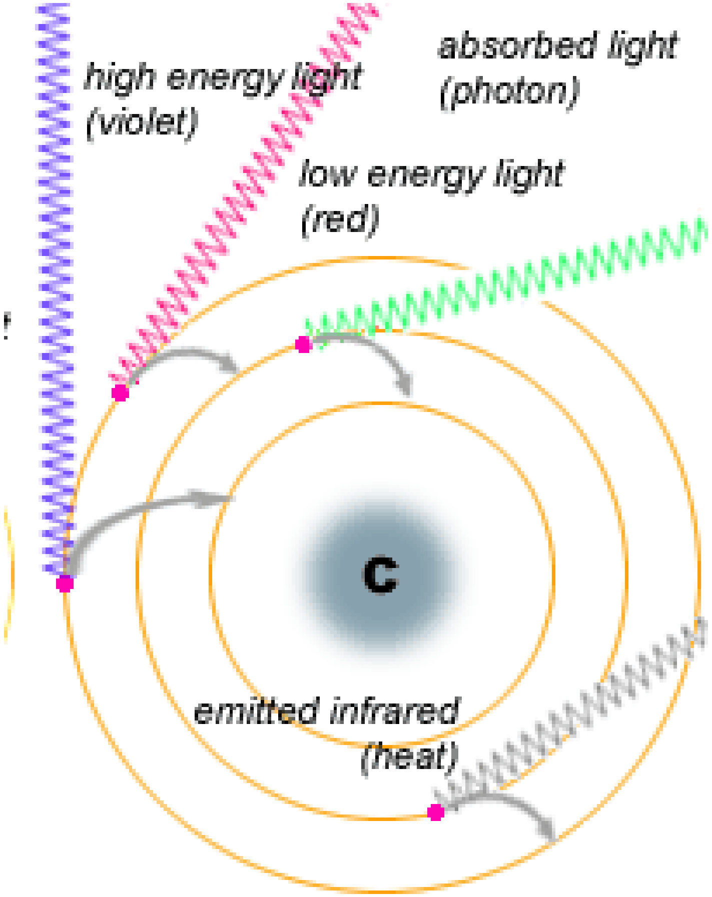
Question:

Does an element emits only one colour?

Yes and no.....

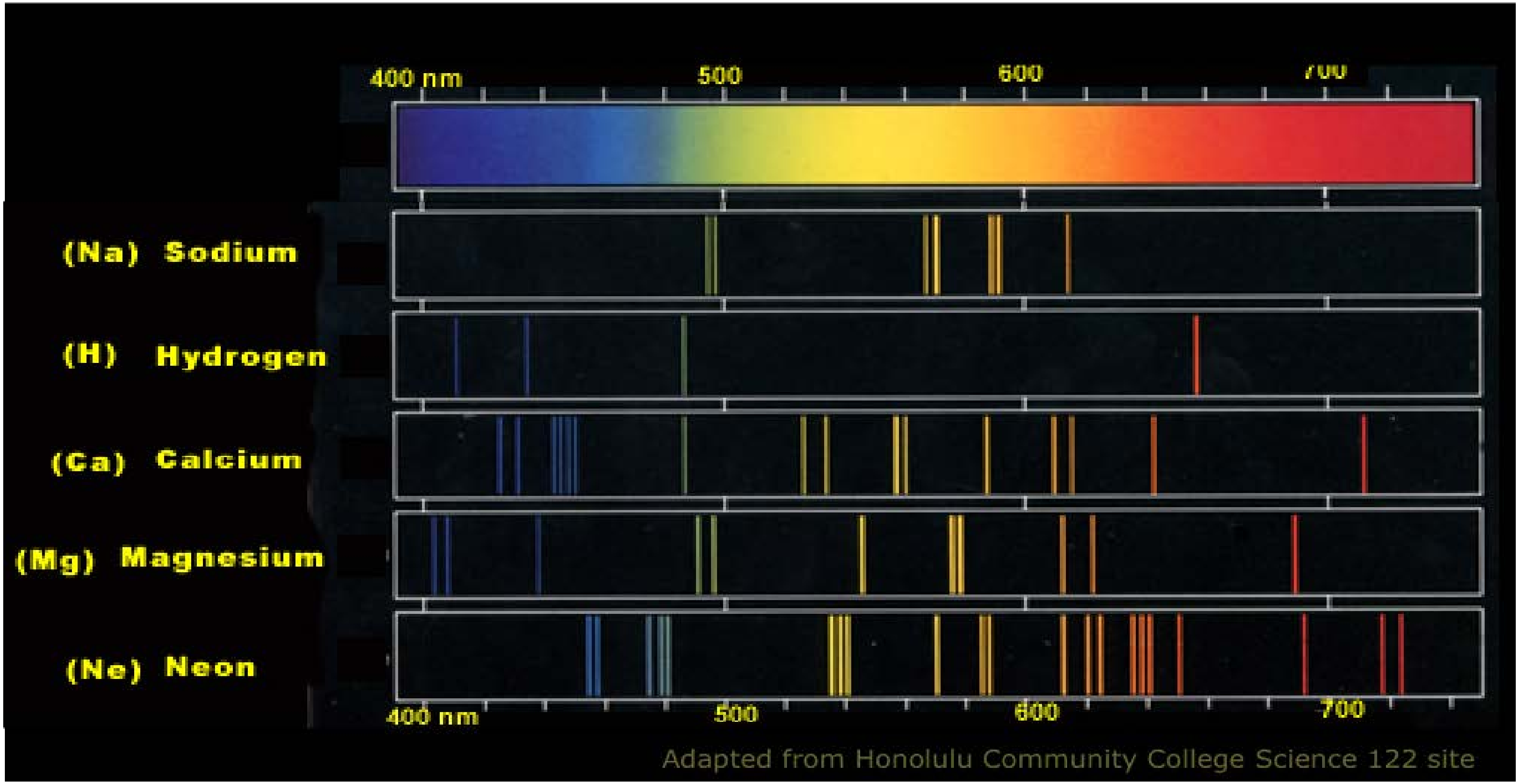
→We see only one colour **but, as** electrons travel between different energy levels, they release different photons and wavelengths.

→ We just see the most dominant wavelength.



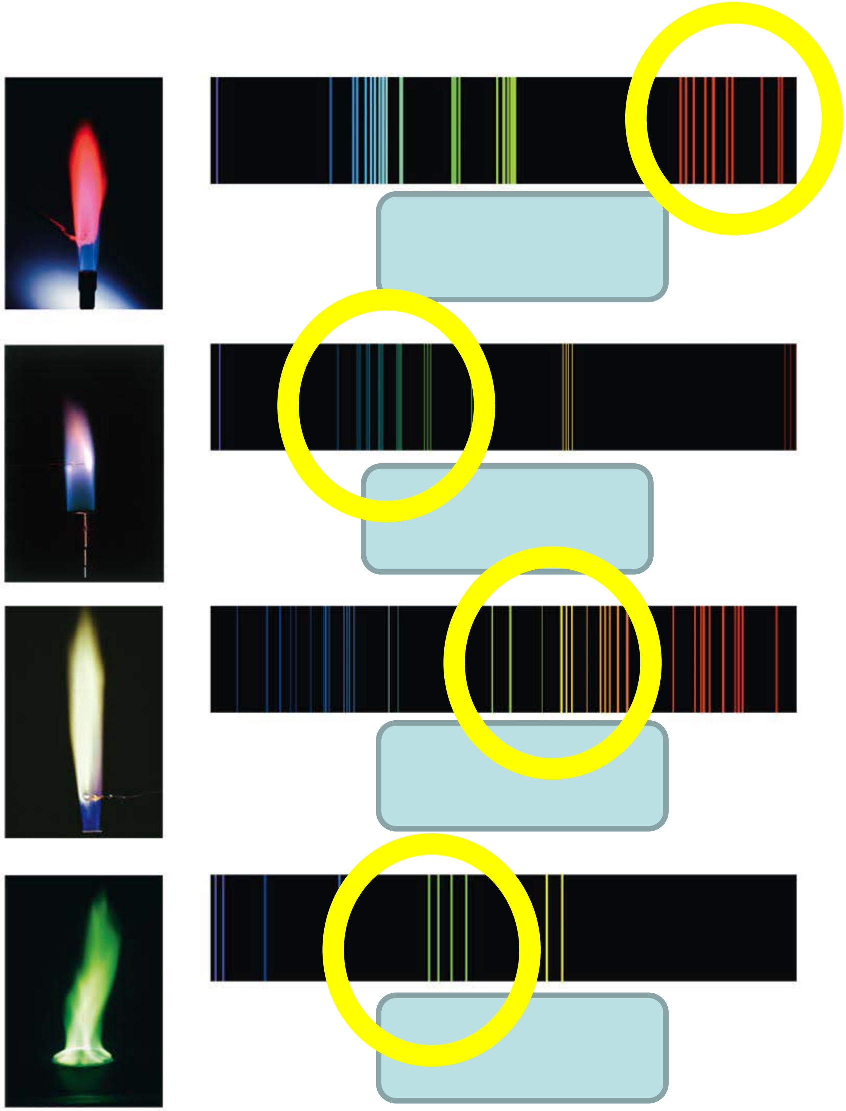
For example, Na+ light is broken up into bands within the spectrum

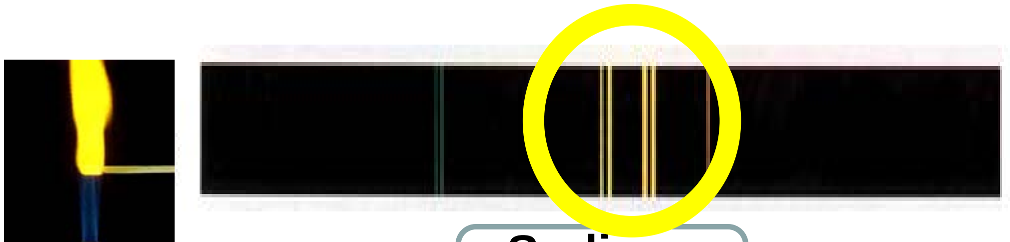
- Notice **each element has a unique spectrum** that is emitted, referred to as its ‘Fingerprint’ and allows us to determine which element is becoming excited



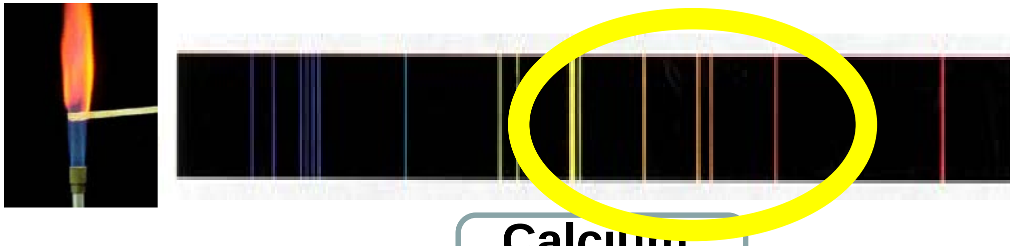
Adapted from Honolulu Community College Science 122 site

Flame test colours





Sodium, Na



Calcium, Ca

Chap. 10 → Self-Study

Atomic Emission Spectrometry (AES)

– Self study

- Outlines of AE briefly discussed as following:

- AES - Relaxation of excited species produces UV and visible line spectra that are useful for qualitative and quantitative analysis.

- **Historically, AES was based on flame, or electric arc/spark atomization.**

- **→ By now, plasma sources (Table 8-1, ICP) have become the most important sources for AES.**

- 10A.
- **Note:** Plasma: is an electrical conducting gaseous mixture containing a significant conc. of cations and electrons (net charge approaching zero).

Flame emission spectroscopy

A sample of a material (analyte) is brought into **the flame** as either a gas, sprayed solution, or directly inserted into the flame by use of a small loop of wire, usually platinum. The heat from the flame evaporates the solvent and breaks chemical bonds to create free atoms.

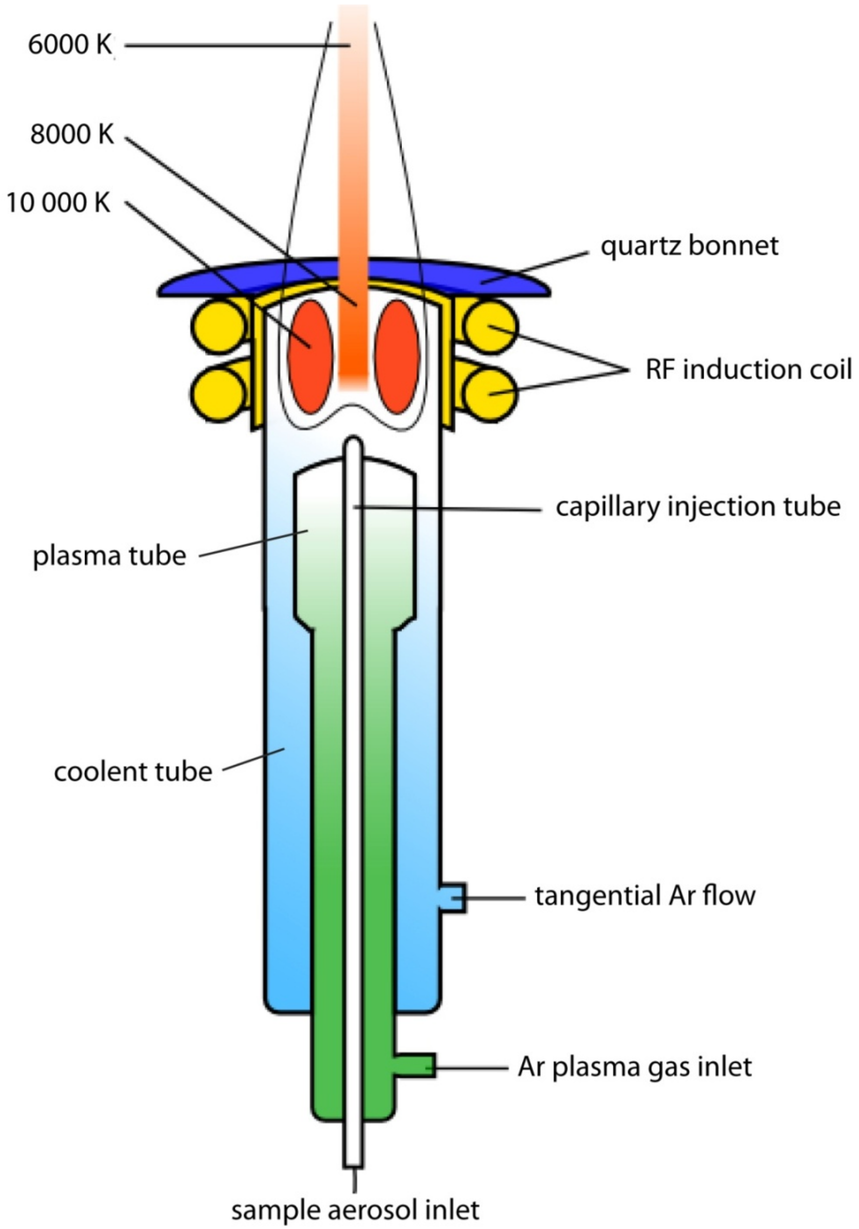
The thermal energy also **excites the atoms into excited electronic states** that subsequently emit light when they return to the ground electronic state. Each element emits light at a characteristic wavelength, which is dispersed by a grating or prism and detected in the spectrometer.

Inductively coupled plasma (ICP) atomic emission spectroscopy

(ICP-AES) uses an inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element

Spark and arc atomic emission spectroscopy

Spark or arc atomic emission spectroscopy is used for the analysis of metallic elements in solid samples. For non-conductive materials, the sample is ground with graphite powder to make it conductive.



ICP - **A schematic diagram of the inductively coupled plasma source (ICP) is shown in Figure 10.58. [left]**

The ICP torch consists of three concentric quartz tubes, surrounded at the top by a **radio-frequency induction coil.**

The sample is mixed with a stream of Ar using a nebulizer, and is carried to the plasma through the torch's central capillary tube.
Plasma formation is initiated by a spark from a Tesla coil.

NOTE: A **Tesla coil** is an electrical resonant transformer circuit invented by Nikola Tesla around 1891.[1]
It is used to produce high-voltage, low-current, high frequency alternating-current electricity

10A,10B - Plasma vs. Arc/spark sources for AES

- 10A – Emission spectroscopy based on Plasma sources
- Instrumentation

- Three types of <u>high-T plasma </u>are available:
  - Inductively coupled plasma (ICP).
  - Direct current plasma (DCP).
  - Microwave-induced plasma (MIP). [Not widely for analysis, not available from manufacturer]

self study, p. 235-251

- 10B - Emission spectroscopy based on Arc/spark sources

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Advantages of **plasma, arc, and spark emission** spectrometry in comparison with flame and electrothermal absorption methods (Chap.9) p.230

1. High T → lower inter-element interference.

2. Good emission spectra are obtained for most elements under a single set of excitation. **Spectra for dozens of elements can be recorded simultaneously. Important for multi-element analysis of very small samples.** By comparison, flame sources are less satisfactory because optimum excitation conditions vary widely from element to element.

3. The more energetic plasma sources permit determination of low conc. of elements that tend to form oxides (i.e., refractory compounds).

4. Plasma sources permit the determination of **nonmetals, such as chlorine, bromine, iodine, sulfur, etc**.

End of Chap. 9 – AAS, AFS
Chap. 10 - Atomic Emission spectroscopy (AES)

Next class:

Chap. 12: Atomic X-ray Spectroscopy.

Including:

X-ray emission,
absorption,
fluorescence, and
diffraction.]