# Atomic Spectrometric Methods

Flame Emission Spectrometry (FES)

Atomic Absorption Spectrophotometry (AAS)

Introduction:

• absorption and emission of radiation energy by atoms is a powerful analytical tool for both quantitative and qualitative analysis

• passage of UV or Vis radiation through a medium consisting of monoatomic particles (ex gaseous mercury or sodium), result in the absorption of few well defined wavelength
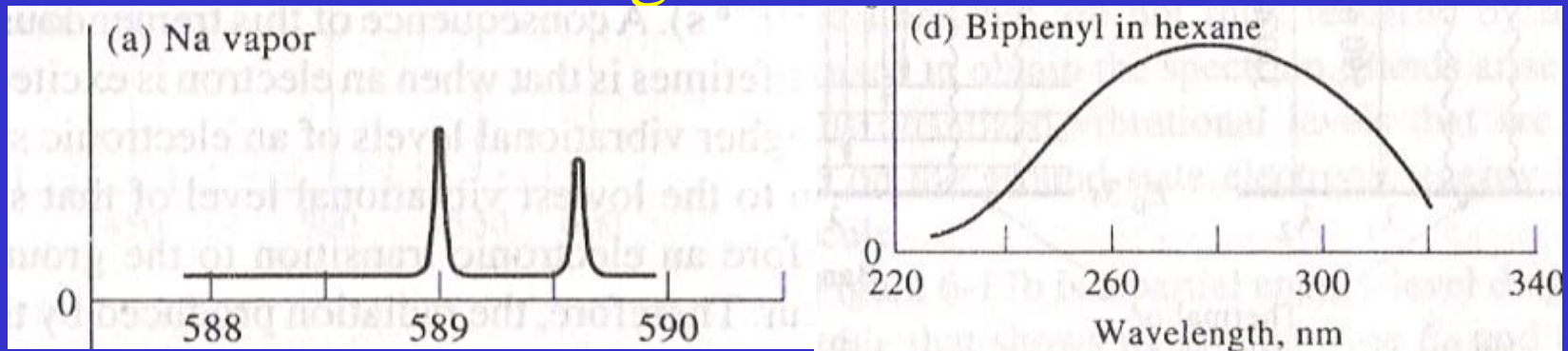
Atomic absorption (a) and Molecular absorption (b) spectra

• relative simplicity of atomic spectra is due to the small number of possible energy states for the absorbing species.

• excitation can occur only by an **electronic process** in which one or more of the electrons of the atom are raised to a higher energy level.

• ex. sodium vapor exhibits two sharp absorption peaks at 589.0 and 589.6 nm due to excitation of $3s$ electron to two $3p$ states

Atomic spectrometry is widely used in many laboratories, particularly whenever trace element analyses are required. Environmental samples are analyzed for heavy-metal contamination, and pharmaceutical samples may be analyzed for metal impurities. The steel industry needs to determine minor components, as well as major ones. The particular technique used will depend on the sensitivity required, the number of samples to be analyzed, and whether single-element or multielement measurements are needed. The following discussion gives the capabilities of the techniques.

Flame emission spectroscopy (FES):

a) the sample solution is converted into a fine aerosol (nebulized) and sprayed into the flame to desolvated, vaporized and atomized (the source of excitation energy is a flame).

b) species are raised to excited states via **thermal collision** with the constituents of the partially burned flame gases.

c) their return to a lower electronic state results in radiation emission characteristic of the species

d) monochromator isolates the specific wavelength of emitted radiation and photodetector measures the radiant power of the selected radiation.
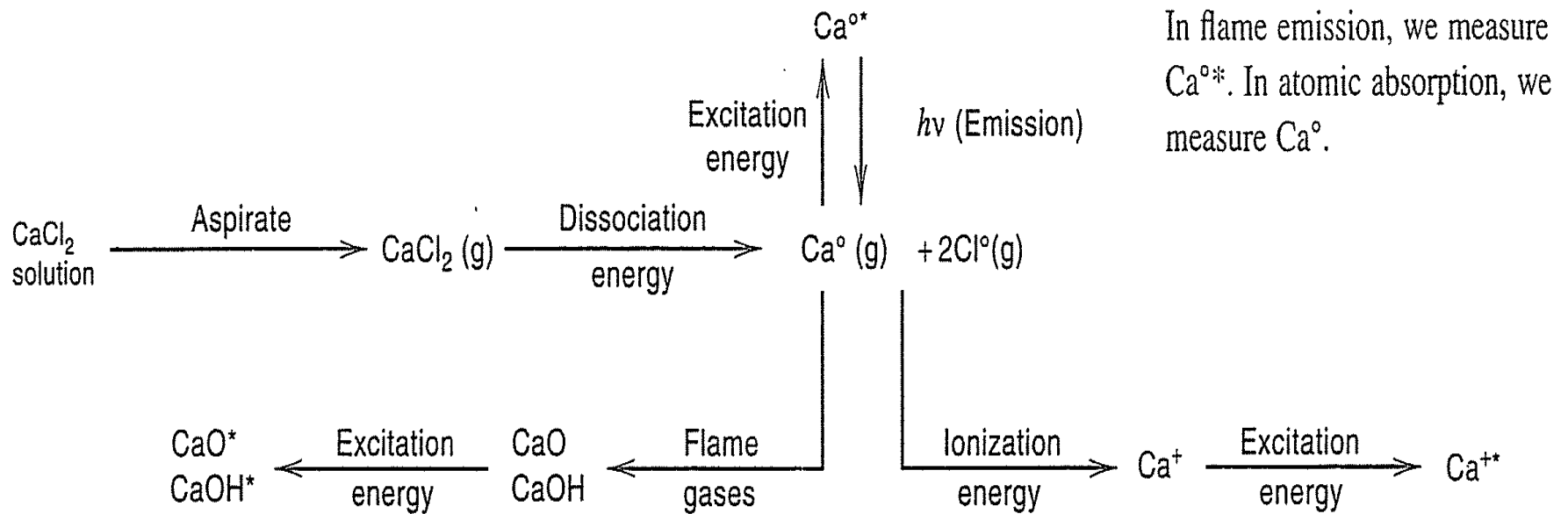
Fig. 17.1. Processes occurring in flame.

Atomization

- It is the conversion of molecules to their component atoms in gaseous state ; and it is carried out by introduction of the molecules solution in the flame in very fine droplets.

In Flame Emission

 - Atoms in gaseous state in the flame absorb thermal energy from the flame itself, some of the atoms get excited & as they return back to the ground state they emit radiation having energy equal to that absorbed.

- The emission is proportional to the number of excited atoms, which is proportional to the total number of atoms in the flame i.e. the sample concentration.

Flame Spectra

The spectra of gaseous, atomic particles consist of well defined narrow discrete lines arising from electronic transition of outermost electrons.

Since there is no bonds, atoms undergo electronic transition only, no vibrational or rotational transitions.

The energy to which the atoms are subjected must be less than the ionization potential.

The resonance wave - length (at which the most intense absorption and emission occur) is: 671 nm for lithium,   589 nm for sodium and   767 nm for potassium.

The number of atoms of an element excited by the flame depends on:

1- Flame temperature

2- The energy difference between the excited and ground states.

Accordingly

- The number of excited atoms in the flame is considerably small, even in the case of alkaline metals which are easily excited.

  Sodium at 2500 k^0, 0.017% of the atoms are excited.

- Other metals the number of excited atoms is extremely small e.g. in case of zinc only 10^{-9} are excited.

- Any increase of the flame temperature is accompanied by great increase in the number of excited atoms.

Distribution between Ground and Excited States
## Most Atoms Are in the Ground State

The relative populations of ground-state (N_0) and excited-state (N_e) populations at a given flame temperature can be estimated from the **Maxwell–Boltzmann expression**:

$$\frac{N_e}{N_0} = \frac{g_e}{g_0} \, e^{-(E_e - E_0)/kT} \tag{17.1}$$

where g_e and g_0 are the *statistical weights* of the excited and ground states, respectively; E_e and E_0 are the energies of the two states ($= h\nu$; E_0 is usually zero); k is the Boltzmann constant (1.3805×10^{-16} erg K^{-1}); and T is the absolute tem-

In flame emission methods, we measure the excited-state population; and in atomic absorption methods (below), we measure the ground-state population. Because of chemical reactions that occur in the flame, differences in flame emission and atomic absorption sensitivities above 300 nm are, in practice, not as great as one would predict from the Boltzmann distribution. For example, many elements react partially with flame gases to form metal oxide or hydroxide species, and this reaction detracts from the atomic population equally in either method and is equally temperature dependent in either.

Schematic arrangement of a typical flame emission spectrophotometer:
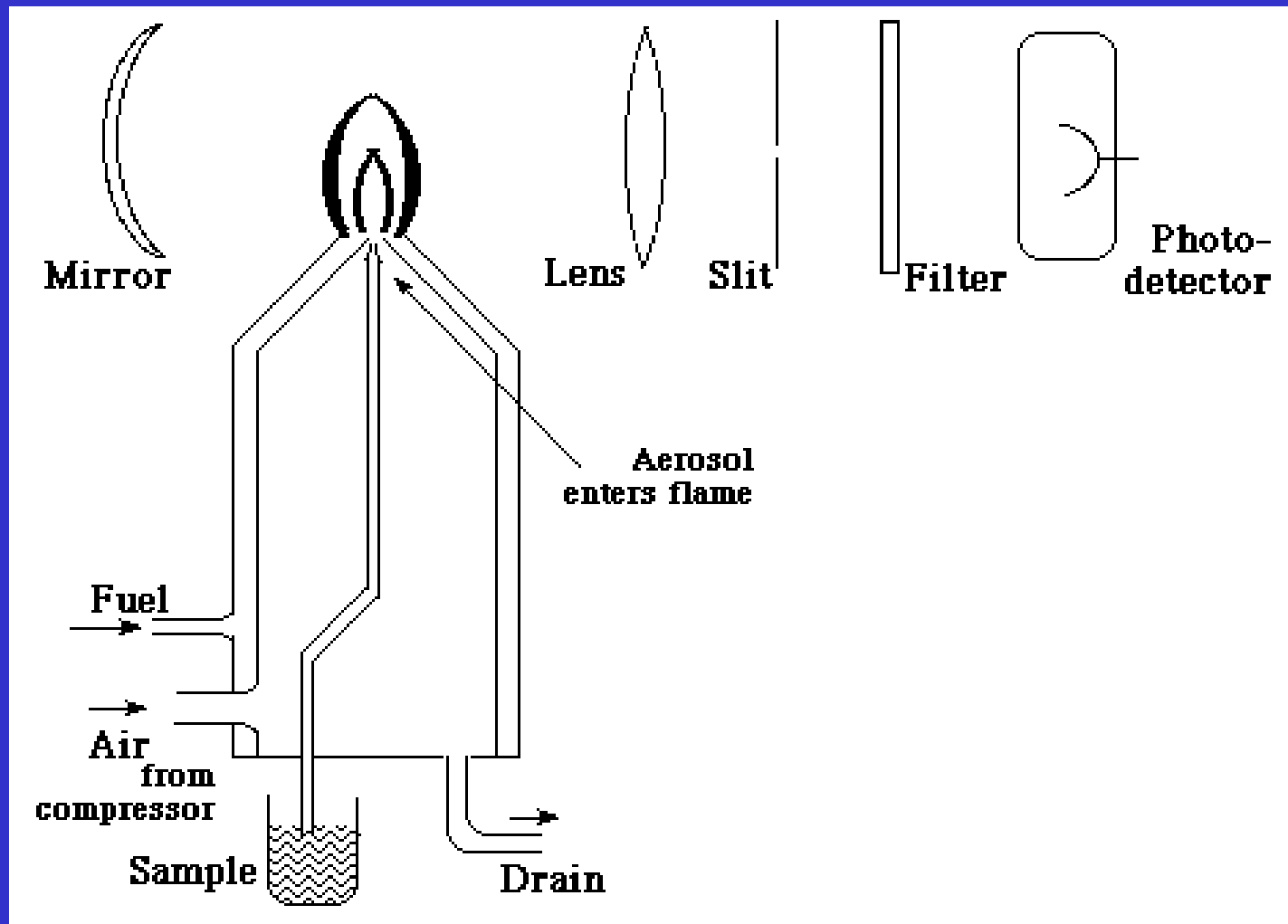
Atomic Absorption Spectrophotometry

PRINCIPLES

The sample solution is aspirated into a flame as in flame emission spectrometry, and the sample element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state, as shown dramatically in Table 17.1. These ground-state atoms can absorb radiation of a particular wavelength that is produced by a special source made from that element (see Sources). The wavelengths of radiation given off by the source are the same as those absorbed by the atoms in the flame.

Atomic absorption spectrophotometry is identical in principle to absorption spectrophotometry described in the previous chapter. The absorption follows Beer's law. That is, the *absorbance* is directly proportional to the pathlength in the flame and to the concentration of atomic vapor in the flame. Both of these variables are difficult to determine, but the pathlength can be held constant and the concentration of atomic vapor is directly proportional to the concentration of the analyte in the solution being aspirated. The procedure used is to prepare a calibration curve of concentration in the solution versus absorbance.

The major disadvantage of making measurements by atomic absorption, as we shall see below, is that a different source is required for each element.

**Atomic Absorption Spectroscopy**: involve two processes:

a) production of free atoms from the sample, i.e. analyte atoms removed form their chemical environment but not ionized (as in FES).

b) absorption of radiation from an external source by these atoms.

Absorption of radiation by free atoms in the flame involves a transition of these atoms from the ground state to an excited electronic state.

• atomic absorption spectrum of an element consists of a series of resonance lines, all originating with the ground electronic state and terminating in various excited states.

• transition between the **ground state** and the **first excited state** is the line with the strongest absorptivity (k/a **first resonance line**) and this is used in AAS analysis.

(a) Na vapor

0   588   589   590
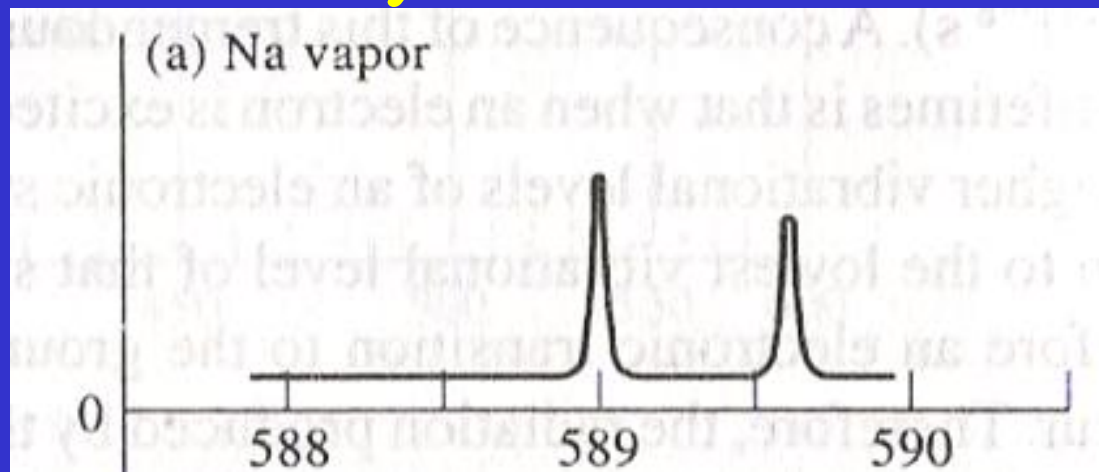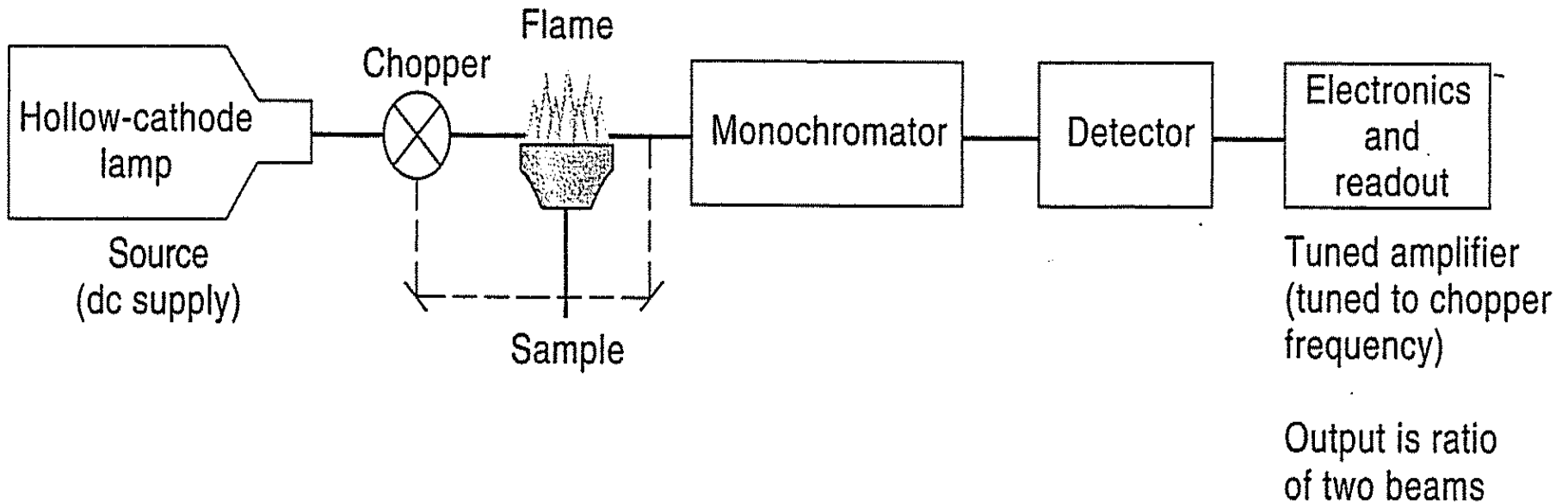
INSTRUMENTATION

Atomic Absorption Instrumentation: consist of a radiation source, sample holder, a wavelength selector, a detector, and a signal processor and readout unit. OR sources, burners and flames.

a) Radiation source:

• in order for Beer's law, to be followed, band-width of the source must be narrow relative to the width of an absorption peak (0.002-0.005nm)

• as a result nonlinear calibration curves are inevitable when continuous radiation source are used

• problem is solved by using the **line sources** with bandwidths narrower than absorption peaks

Hollow Cathode lamps:

• consist of a **tungsten anode** and a **cylindrical cathode** (of metal to be analyzed)sealed in a glass tube filled with inert gas

Figure 9-11 Schematic cross section of a hollow cathode lamp.
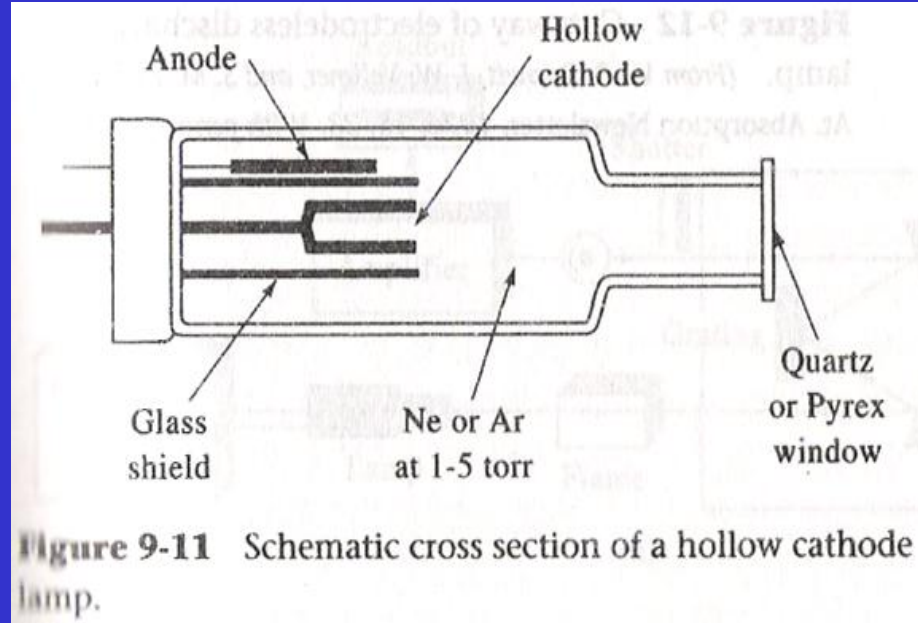
• when potential is applied, ionization of inert gas occurs and gaseous cation dislodge some of the metal atoms from the cathode surface

• portion of metal atoms are in excited states and emit their characteristic radiation as they return to the ground state

• variety of hollow cathode lamps are available commercially.

• some cathodes are made up of a mixture of several metals permitting analysis of many elements.

b) Sample holder: It is the atomizer cell that contains the gaseous atomized sample.

c) Monochromator: to select a desirable wavelength.

d) Detector: most common detectors for AAS and FAS are photomultiplier tube.

2. Burners. The burner used in most commercial instruments is the **premix chamber burner**, sometimes called the **laminar-flow burner**. This is illustrated in Figure 17.4. The fuel and support gases are mixed in a chamber before they enter the burner head (through a slot) where they combust. The sample solution is aspirated through a capillary by the **Venturi effect** using the support gas, usually air, for the aspiration. The air creates a partial vacuum at the end of the capillary, drawing the sample through the capillary. It is broken into a fine spray at the tip. This is the usual process of **nebulization**.[4] The larger droplets of the resulting aerosol condense and drain out of the chamber. The remaining fine droplets mix with the combustion gases and enter the flame. As much as 90% of the droplets condense out, leaving only 10% to enter the flame.

Premix burners are generally limited to relatively low-burning velocity flames. Although a large portion of the aspirated sample is lost in the chamber, the "atomization efficiency" (efficiency of producing atomic vapor) of that portion of the sample that enters the flame is high because the droplets are finer. Also, the pathlength is long. Combustion with premix burners is very quiet. A popular version of the premix burner is the **Boling** burner. This is a three-slot burner head that results in a broader flame and less distortion of the radiation passing through at the edges of the flame (see Figure 17.4). This burner warps more easily than others, though, and care must be taken not to overheat it.

3. Flames. The chief flames that are used for atomic absorption and emission spectrometry are listed in Table 17.2 together with their maximum burning temperatures. The most widely used flames for atomic absorption are the air–acetylene flame and the nitrous oxide–acetylene flame with premix burners. The latter high-temperature flame is not required and may even be detrimental for many cases in atomic absorption because it will cause ionization of the gaseous atoms (see below). However, it is very useful for those elements that tend to form heat-stable oxides in the air–acetylene flame (the "refractory elements"). The air–acetylene and other hydrocarbon flames absorb a large fraction of the radiation at wavelengths below 200 nm, and an argon–hydrogen-entrained air flame is preferred for this region of the spectrum for maximum detectability. This is a colorless flame, and entrained air is the actual oxidant gas. It is used for elements such as arsenic (193.5 nm) and selenium (197.0 nm), when they are separated from the sample solution by volatilization as their hydrides (AsH_3, H_2Se) and passage of these gases into the flame. This is necessary because this cool flame is more subject to chemical interferences than other flames (see the following paragraphs). A nitrous oxide–acetylene flame offers an advantage in this region of the spectrum when danger of molecular interference exists; the flame absorption is relatively small at short wavelengths.

In flame emission spectrometry, a hot flame is required for the analysis of a large number of elements, and the nitrous oxide–acetylene flame is used. The oxy-acetylene flame has a high burning velocity and cannot be used with a conventional premix burner. The nitrous oxide–acetylene flame can, however, be used with a premix burner. Because of its high temperatures, a special, thick, stainless steel burner head must be used to prevent it from melting. A "cool" air–propane or similar flame is preferred for the flame emission spectrometry of the easily excited elements sodium and potassium because of decreased ionization of these elements.

Types of Flames:

- the spectrum of the flame itself should not interfere with the emission or absorption line of the analyte.

- **maximum operating temperature** and **exact flame temperature** is determined by the **type** and **ratio** of fuel and oxidant, respectively.

Fuel	Oxidant	Temperatures, °C	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

Role of combustion Flames in FES and AAS:

- flames convert species in solution to atoms in the vapor phase freed of their chemical surrounding.

- free atoms are then transformed into excited electronic state by one of two methods:

a) **absorption of additional thermal energy from the flame**: flame energy is utilized to move the electrons of the free atoms from the ground to excited state.

When these excited atoms return to the ground state, radiation is emitted (FES).

b) absorption of radiation energy from an external source:free atoms absorb incident radiation and becomes excited.

the flame containing free atoms becomes a **sample cell**.

In both FES and flame AAS, the sample solution is introduced as an aerosol into the flame.

A major modification of AAS is the replacement of the flame by an **electrothermal furnace** (electrothermal atomic absorption spectroscopy: EAAS) improving detection limits for many elements.

Pretreatment of sample

- for flame AAS and FES the sample should be dissolved in a solution (matrix) in order to undergo nebulization.

- chemistry necessary to dissolve the sample in a suitable matrix is very important component of the analytical process.

- reagents used to dissolve samples must not contain substances that interfere with absorption or emission measurement.

Delivery of sample

Nebulization of a liquid to provide a steady flow of aerosol into a flame, is the most popular method.

Liquid sample delivery system consists of 3 components:

a) **a nebulizer** - breaks up the liquid into small droplets (aerosol),

b) **an aerosol modifier**- removes large droplets from the stream, and

c) **the flame or atomizer** - converts the analyte into free atoms

Nebulization: sample solution is introduced through an orifice into a high velocity gas jet, usually the oxidant, in either parallel or perpendicular manner

Liquid flow, Q_{liq}

Capillary radius

High-pressure gas flow, Q_{gas}

(a)

Aerosol

Gas

Liquid

(b)
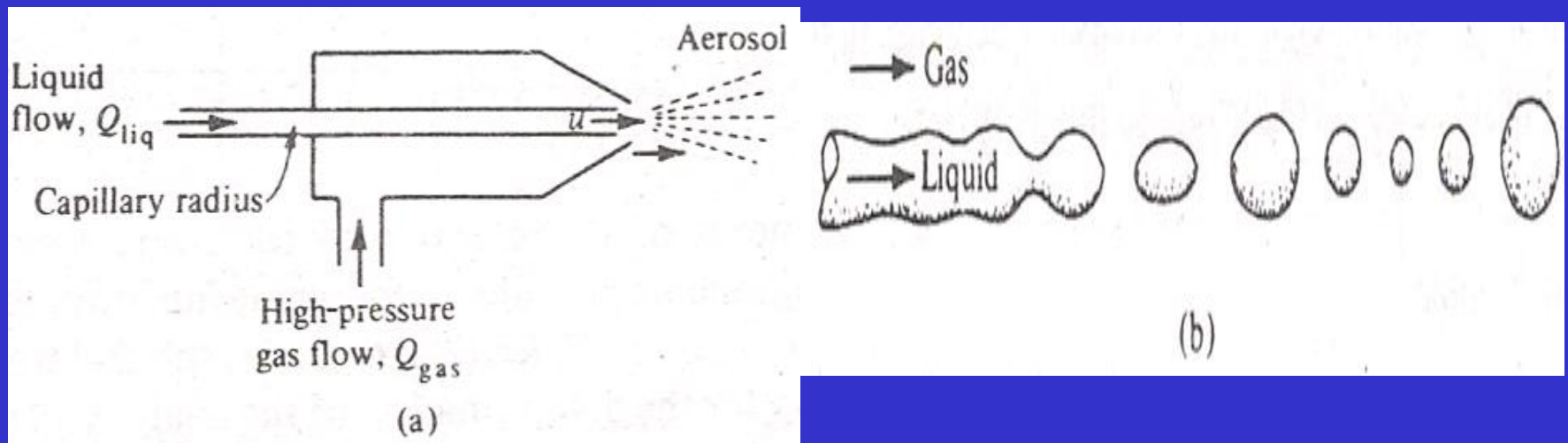
• sample stream is converted into a cloud of droplet in the **aerosol modifier or spray chamber**, combined with the oxidizer/fuel and carried to the burner

Atomization: step converts the analyte within the aerosol into free analyte atoms in the **ground state** for AAS and FES analysis.

Two common methods are: Flame atomization and electrothermal atomization

Flame atomization: nebulized sample (+ gaseous oxidant/fuel) is carried into a flame where complex set of events occurs.

Ex. conversion of a **metallic element** M from a dissolved salt, MX in the sample to free **M atoms.**

1)When aerosol containing MX enter the flame, the solvent is evaporated, leaving particles of dry, solid MX (**desolvation**)

2) solid MX is converted to MX vapor (**volatilization**)

3) portion of MX molecules are dissociated to give free M atoms (**Dissociation**)

• these atoms are the species that absorb radiation in AAS and emit radiation in FES

Other processes also occurs during atomization which interfere with the production of free analyte atoms:

a) excitation and emission of radiation by **MX(g)** molecules.

b) reaction of **M(g) atoms** with flame components to produce species that also absorb and emit radiation.

c) formation of **M^{+*} ions** which not only reduces efficiency of free-atom production but also complicate the analysis by adding lines to spectrum.

- Flow rate : it is very important to control the flow rate of fuel/oxidant mixture which depend on the <u>kind of fuel and oxidant</u> used.

- if the gas flow rate does not exceed the burning velocity, the flame propagate itself back into the burner (**<u>flashback</u>**).

- as the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and burning velocity are equal (stable).

- at higher flow rates, the flame rises and eventually blows off of the burner.

- optimum flame temperature varies for AAS and FES and depend on the excitation and ionization potential of the analyte.
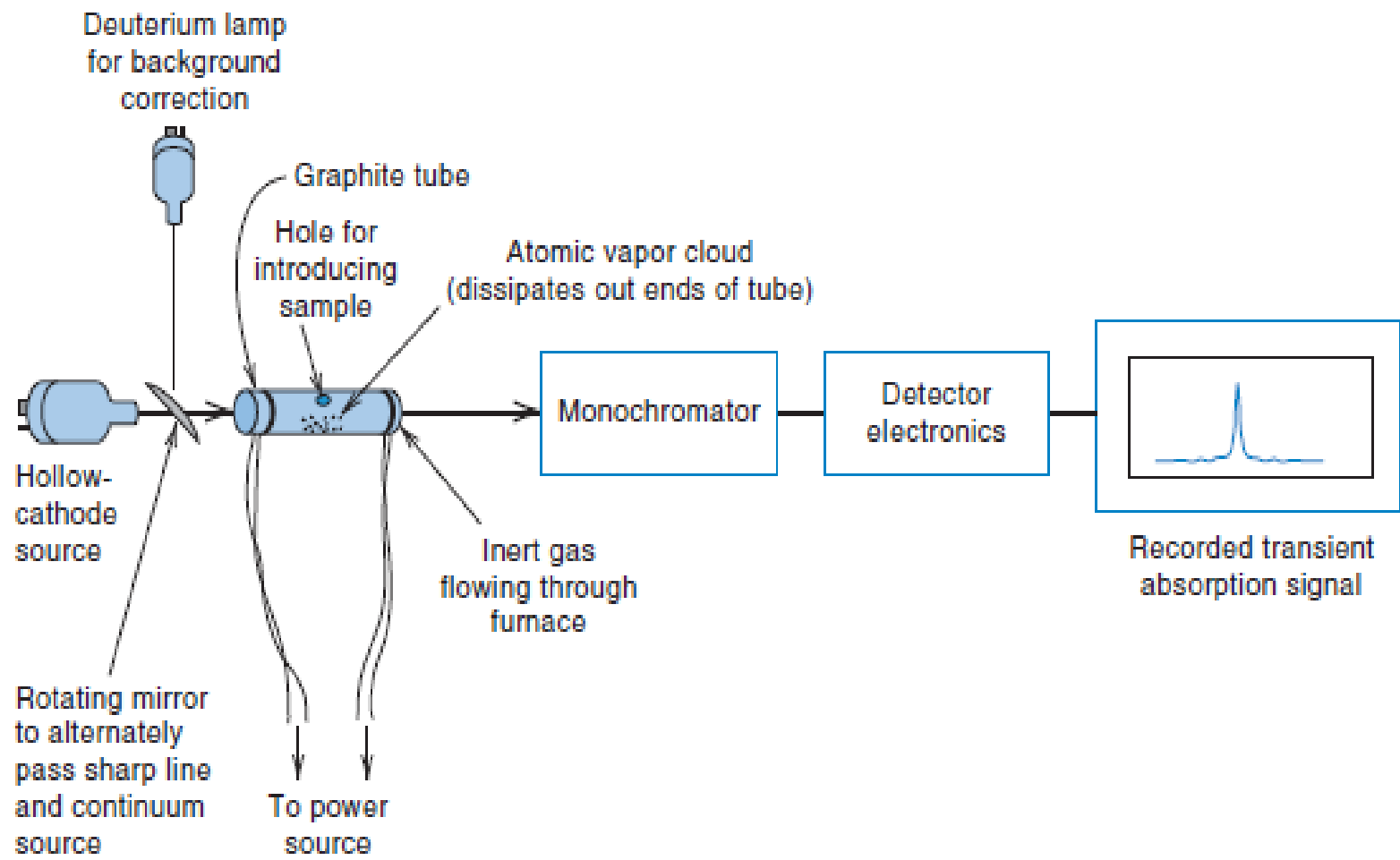
PERCENT IONIZATION OF SELECTED ELEMENTS IN FLAMES*

Element	Ionization potential (eV)	Acetylene/ air, 2400 °C	Acetylene/ oxygen, 3140 °C	Acetylene/ nitrous oxide, 2800 °C
Lithium	5.391	0.01	16.1	
Sodium	5.139	1.1	26.4	
Potassium	4.340	9.3	82.1	
Rubidium	4.177	13.8	88.8	
Cesium	3.894	28.6	96.4	
Magnesium	7.646		0.01	6
Calcium	6.113	0.01	7.3	43
Strontium	5.694	0.01	17.2	84
Barium	5.211	1.9	42.3	88
Manganese	7.43			5

- high temperature causing ionization of the analyte atom is undesirable in both methods.

Electrothermal Atomizers - Ultrasensitive

- electrically heated devices viz. **graphite furnaces** and **carbon rod analyzer**, are common electrothermal, flameless, atomizers.

- In electrothermal atomizer, few μl of sample are first evaporated, then ashed in electrically heated graphite and atomized.

- used for atomic absorption but has not been generally used for emission spectroscopy.

Deuterium lamp for background correction

Graphite tube

Hole for introducing sample

Atomic vapor cloud (dissipates out ends of tube)

Monochromator

Detector electronics

Recorded transient absorption signal

Hollow-cathode source

Inert gas flowing through furnace

Rotating mirror to alternately pass sharp line and continuum source

To power source

Electrothermal methods are complementary to flame methods. The latter are better suited when the analyte element is at a sufficiently high concentration to measure and adequate solution volume is available. They provide excellent reproducibility, and interferences are usually easier to deal with. On the other hand, electrothermal atomization excels when either the concentrations or available sample amounts are very small. Additionally, in many cases it is possible to analyze solid samples directly by electrothermal AAS. Method development and calibration of electrothermal methods require more care, however.

Some of the advantages of electrothermal are:

a) High sensitivity, because production of free analyte atoms is more efficient than flame atomizer.

b) Ability to handle small volume of sample (5-100 μl).

c) Ability to analyze **solid samples** directly without pretreatment (in most cases).

d) Low noise from the furnace.

e) Can maintain relatively high conc. of free atoms, albeit for only a brief time.

Disadvantage:

- much more difficult to use than flame atomizer.

- precision is less because **matrix effect** from component in sample are much more severe than encountered in flame AAS.

- reproducibility of the results is less.

In electrothermal atomizer, sample is processed in 3 steps

a) **drying cycle**: sample is heated to evaporate any solvent or volatile matrix component

b) **ash cycle** is then convert the analyte to a different chemical state
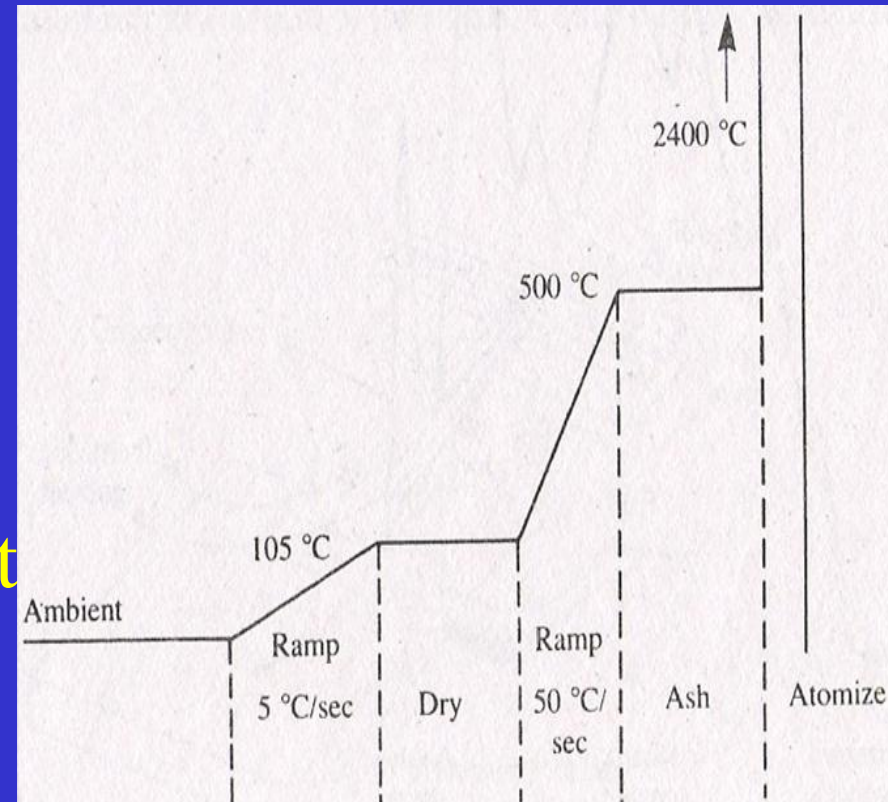
c) in **atomize cycle** the analyte residue is **dissociated** and **volatilized** into free atoms by raising the furnace temp to the selected atomization temperature

Interferences

- Interference is any effect that changes the signal when analyte concentrations remain unchanged.

- While atomic absorption spectroscopy is relatively free from interferences, there are a number of interferences which must be dealt with.

1) Spectral Interferences:

• arise when the absorption or emission of an interfering species either overlaps or lies so close to the analyte band that resolution by the monochromator become impossible

• Example:

Al   308.216 nm

V   308.211 nm

•Solution:

Separate elements or use a different line (which may be less sensitive).

Two types

1) Background Radiation
- Broad band emission by excited molecules and radicals in flame

2) Overlapping emission lines
  - Emission by different elements of the same wavelength as the analyte element

2) Chemical Interferences:
(Formation of Stable or Refractory Compounds)

• Elements that form very stable compounds are said to be <u>refractory</u> because they are not completely atomised at the temperature of the flame or furnace.

• Solution

• Use a higher flame temperature (nitrous oxide/acetylene)

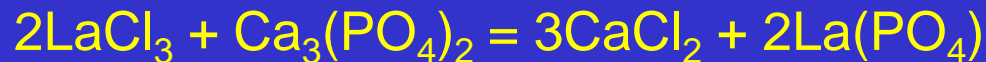• Use a release agent

• Use protective chelation

Examples

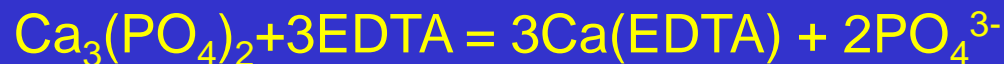- Determination of calcium in the presence of sulfate or phosphate (e.g. in natural waters)

$$3Ca^{2+} + 2PO_4^{3-} = Ca_3(PO_4)_2$$

(stable compound)

- **Release agent**

Add 1000 ppm of $LaCl_3$

$$2LaCl_3 + Ca_3(PO_4)_2 = 3CaCl_2 + 2La(PO_4)$$

$CaCl_2$ readily dissociates

- **Protective chelation**

$$Ca_3(PO_4)_2 + 3EDTA = 3Ca(EDTA) + 2PO_4^{3-}$$

Ca(EDTA) dissociates readily.

3) Ionization Interferences:

• atoms with low ionization potential become ionized reducing the population of both the ground state and excited state free atoms

• by adding an excess of easily ionized element (viz. K, Cs or Sr), ionization in the sample and calibration solution can be suppressed

• more easily ionized atoms produces a large concentration of electrons in the vapor and, by mass action, **suppresses the ionization of analyte atoms**

$$M(g) \rightarrow M^+(g) + e^-$$

- A problem in the analysis of alkali metal ions at low flame temperatures and other elements at higher temperatures.

- Because alkali metals have the lowest ionisation potentials, they are most extensively ionised in flames.

- At 2450 K and a pressure of 0.1 Pa, sodium is 5% ionised.

- Potassium is 33% ionised under the same conditions.

- Ionised atoms have energy levels which are different to the parent atoms

  – therefore the analytical signal is reduced.

Solution:

- Add an ionization suppressor

- Add an easily ionized element such as Cs.

- Add 1000 ppm of CsCl when analysing Na or K.

- Cs is more readily ionised than either Na or K.

- This produces a high concentration of electrons in the flame.

4) Physical Interferences

- The amount of sample reaching the flame is dependent on the physical properties of the solution:
  - viscosity
  - surface tension
  - density
  - solvent vapour pressure.
- To avoid differences in the amount of sample and standard reaching the flame, it is necessary that the physical properties of both be matched as closely as possible.
- Example:
  - Analysis of blood

Non-Atomic Absorption

- Non-atomic absorption is caused by **molecular absorption** or **light scattering** by solid particles in the flame.

- The absorption measurement obtained with a hollow cathode lamp is the sum of the atomic absorption and the non-atomic absorption.

- The interference is corrected for by making a simultaneous measurement of the non-atomic absorption using a continuum source (usually deuterium)

- this is called **background correction**

Internal Standard and Standard Addition Calibration

- In atomic spectrometric methods, signals can frequently vary with time due to factors like fluctuations in gas flow rates and aspiration rates. Precision can be improved by the technique of internal standards. As an example, a multichannel flame photometer can be used for the measurement of sodium

  and potassium in serum.

- An internal standard undergoes similar interferences as the

  analyte. Measurement of the ratio of the analyte to internal standard signals cancels the interferences.

- The **internal standard** element should be chemically similar to the analyte element, and their wavelengths should not be too different.

- Another difficulty often encountered in atomic-spectrometric methods (and in many other analytical methods) is suppression or enhancement of the signal by the sample matrix. This can be due to physical or chemical reasons that arise from a mismatch of the sample matrix and the standards used for calibration. For example, if the sample has higher viscosity than the standards, the aspiration rate will not be the same; if the sample contains a combustible organic solvent, the effective temperature in the flame will be different compared to a purely aqueous standard.

- The technique of **standard addition** can be utilized to minimize matrix induced errors. A linear dependence generally simplifies the interpretation of the data.

- In **standard addition calibration**, the standard is added to the sample, and so it experiences the same matrix effects as the analyte.