Module 3

Flame Emission and Atomic Absorption spectroscopy

Reference text book : Instrumental Methods of Analysis, 7th edition. H.H. Willard, L.L. Merritt, J.A. Dean, F.A. Settle, CBS Publishing & Distribution

Syllabus

- Introduction
- Instrumentation for flame spectrometric methods
- Flame emission spectrometry
- Atomic absorption spectrometry
- Atomic fluorescence spectrometry
- Interferences associated with Flames & furnaces,
- Applications
- Comparison of FES and AAS.

Link for animation video
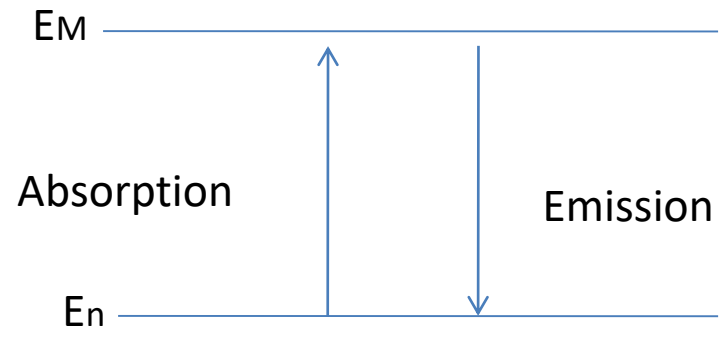
- Flame emission spectroscopy:

https://www.youtube.com/watch?v=9DYV25Ki-kc

https://www.youtube.com/watch?v=2LeUkiI1ow0

- Atomic absorption spectroscopy

https://www.youtube.com/watch?v=I5dO8AYa3eU

Introduction

- The absorption and emission of radiant energy by atoms in the sample provide powerful analytical tools for both qualitative and quantitative analysis.

- Analyte : a substance whose chemical constituents are being identified and measured.

- Principle: combustion flame converts analyte in the solution to atoms . These free atoms absorb the thermal energy and jump to electronic excited state.

Principle in Flame Emission Spectroscopy

- In flame emission spectroscopy, the combustion flame does not only frees the atom it also supplies the energy necessary to move the electrons of the free atoms from ground state to excited state. The energy which is emitted by the excited atoms when returning to the ground state provides the basis for analytical determination in FES.

Principle in Atomic absorption spectroscopy

- External source (like hallow cathode lamp)is used to excite the atoms from its ground state.

- The flame that contains the free atom becomes the sample cell. The free atoms absorb radiation focused on the cell from external source .

- Incident radiation absorbed by the atoms moving from ground state to the excited state provides analytical data.
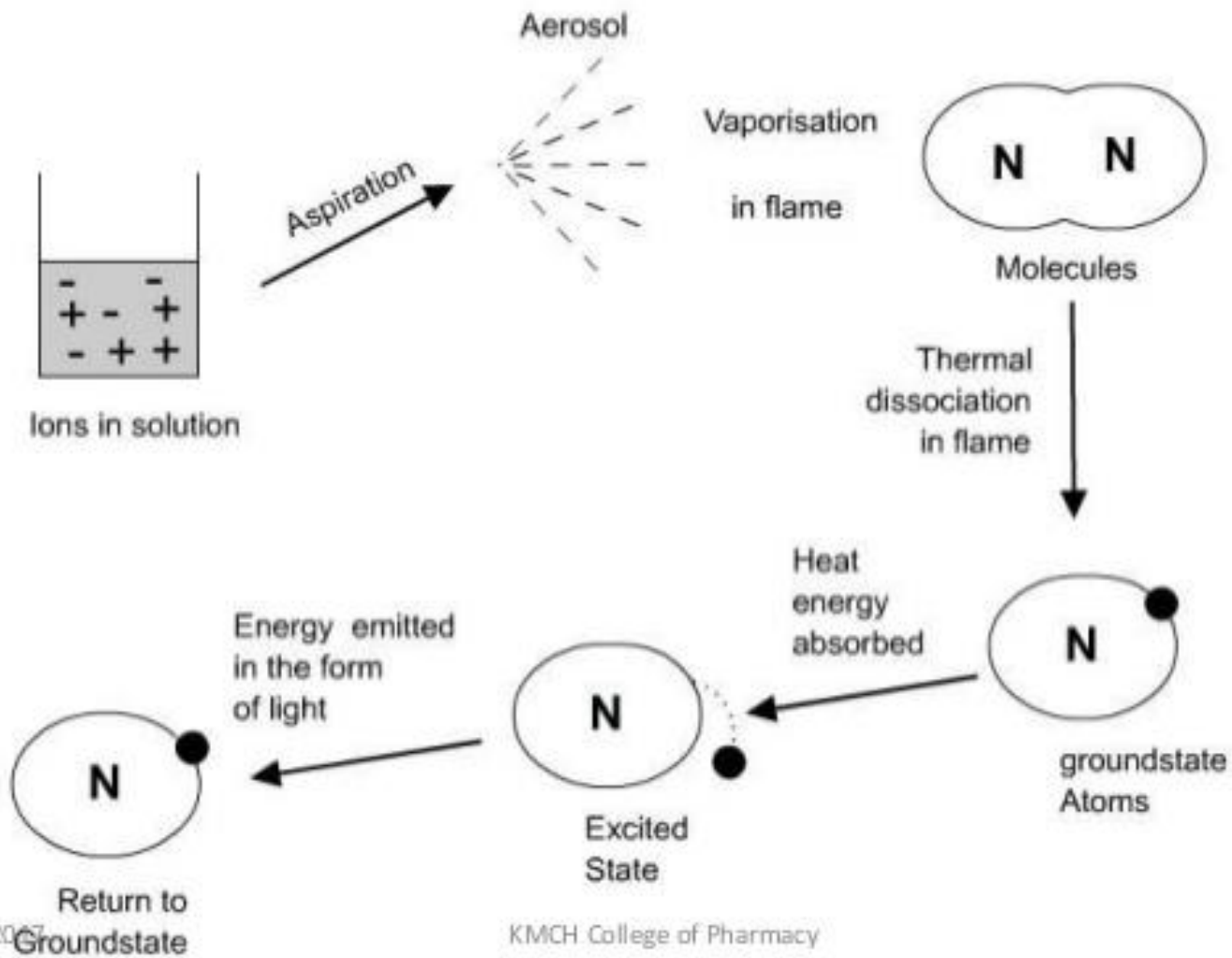
Applications of Atomic Absorption Spectroscopy

- water analysis (*e.g. Ca, Mg, Fe, Si, Al, Ba content)*
- food analysis
- analysis of animal feedstuffs (*e.g. Mn, Fe, Cu, Cr, Se,* Zn)
- analysis of additives in lubricating oils and greases (Ba, Ca, Na, Li, Zn, Mg)
- analysis of soils
- clinical analysis (blood samples: whole blood, plasma, serum; Ca, Mg, Li, Na, K, Fe)

APPLICATIONS

❖ FES has found wide application in agricultural and environmental analysis, industrial analyses of ferrous metals and alloys as well as glasses and ceramic materials, and clinical analyses of body fluids.

❖ FES can be easily automated to handle a large number of samples. Array detectors interfaced to a microcomputer system permit simultaneous analyses of several elements in a single sample

❖ They are also used to determine the metals present in Chemicals, Soil, Cements, Plant materials, Water, Air pollutants and Oceanography

- Burner: A component of AAS system made of solid metal body having slit on the flat top surface to provide the flame required for atomisation of the sample

- Detector: A component of the system that records the intensity of the transmitted or absorbed light. Photomultiplier tube is the commonly used detector in AAS

- Aerosol : suspension of fine solid or liquid particles

- Nebuliser: A device for producing an aerosol of sample inside spray chamber

- Impact bead: A device inside spray chamber for removal of large sized droplets from sample stream

- Monochromator: A device used for dispersion of incident light using prism or grating, reflecting mirrors and a combination of entrance and exit slits for isolation of required wavelength and collimation of the light beam

- Atom : The smallest particle of an element or compound
- Absorbance: The amount or fraction of incident light absorbed by the ground state atoms.
- Orifice: Small bore tube opening
- Atomisation: Process of reduction of sample to ground state atoms by application of heat by means of a flame or a graphite furnace.
- Excitation: Excitation of a ground state atom to higher energy states by means of electromagnetic radiation
- Interference: Effects resulting in variation of results due to spectral or non-spectral interferences

Aerosol

Aspiration

Vaporisation
in flame

N   N

Molecules

Ions in solution

Thermal
dissociation
in flame

Energy emitted
in the form
of light

Heat
energy
absorbed

N

Excited
State

N

groundstate
Atoms

N

Return to
Groundstate

INSTRUMENTATION FOR FLAME SPECTROMETRIC METHODS

- components provide the following functions required in each method

  (1) deliver the analyte to the flame

  (2) induce the spectral transitions (absorption or emission) necessary for the determination of the analyte

  (3) isolate the spectral lines required for the analysis

  (4) detect the increase or decrease in intensity of radiation at the isolated lines(s)

  (5) record these intensity data.

1.Pretreatment of Sample

- Flame FES requires that the analyte be dissolved in a solution in order to undergo nebulization

- The analyst must be aware of substances that interfere with the emission measurement

- When these substances are in the sample, they must be removed or masked (complexed)

- Reagents used to dissolve samples must not contain substances that lead to interference problems.

2. Sample Delivery

- The device that introduces the sample into the flame or plasma plays a major role in determining the accuracy of the analysis.

- most popular sampling method is nebulisation

- An introduction system for liquid samples consists of three components:

  (1) A nebulizer that breaks up the liquid into small' droplets

  (2) An aerosol modifier that removes large droplets from the stream, allowing only droplets smaller than a certain size to pass

  (3) The flame or atomizer that converts the analyte into free atoms.
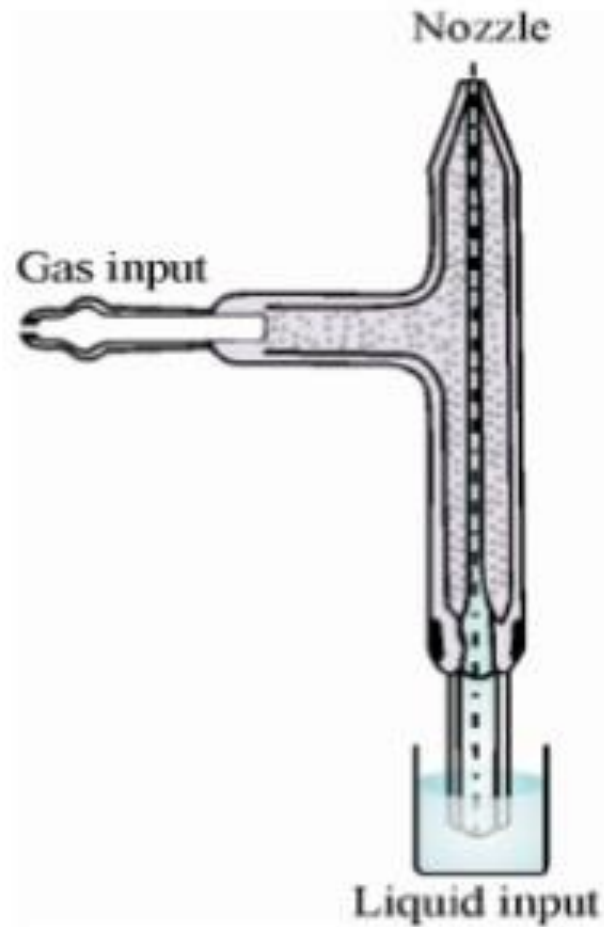
3. Nebulization

Fig. 7.9: Concentric type pneumatic nebuliser

- Pneumatic nebulization is the technique used in most atomic spectroscopy determinations
- The sample solution is introduced through an orifice into a high- velocity gas jet, usually the oxidant
- The sample stream may intersect the gas stream in either a parallel or perpendicular manner
- The liquid stream begins to oscillate, producing filaments. Finally, these filaments collapse to form a cloud of droplets in the aerosol modifier or spray chamber.

- In the spray chamber the larger droplets are removed from the sample stream by mixer paddles or broken up into smaller droplets by impact beads or wall surfaces
- The final aerosol, now a fine mist, is combined with the oxidizer/fuel mixture and carried into the burner
- Droplets larger than about 20 μm are trapped in the spray chamber and flow to waste
- In AAS only a small percentage (usually 2% or 3%) of the nebulized analyte solution reaches the burner

4. Atomization

- The atomization step must convert the analyte within the aerosol into free analyte atoms in the ground state for FES analysis.

- The sequence of events involved in converting a metallic element, M, from a dissolved salt, MX, in the sample solution to free M atoms in the flame is depicted in Figure below

FIGURE 9.4

Flame atomization processes for the salt MX. Asterisk (*) indicates excited state.
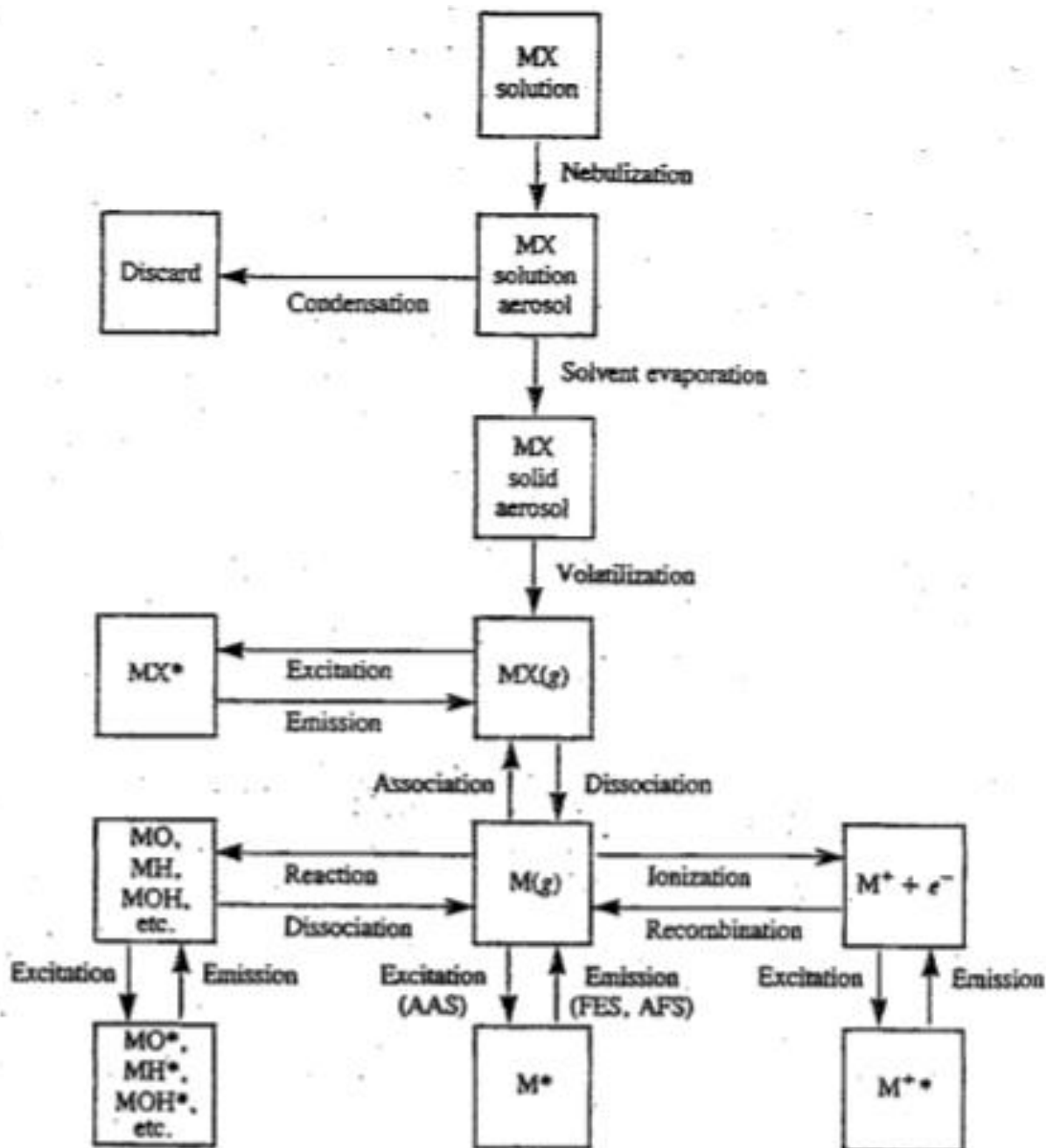
Flame Atomizers

- Metallic element M is dissolved in the salt solution MX.

- After nebulisation the aersol droplets enter the flame , the solvent is evaporated .

- Small dry solid particles are left out in the flame which is converted to NIX vapor .

- Finally a portion of MX molecules are dissociated to give neutral free atoms

- Process which interfere with the production of free analyte atoms.

- These processes include: (1) excitation and emission of radiation by MX(g) molecules, (2) reaction of M(g) atoms with flame components at high temperatures to produce molecules and ions that also absorb and emit radiation, and (3) formation of M+x ions, which in addition to reducing the efficiency of free-atom production

- The flame remains the most generally useful atomizer for atomic spectroscopy despite the developments in electrothermal atomization

Laminar flow flame

- Flames are not uniform in composition, length or cross section.

LAMINAR FLOW BURNER

Fuel in →
Oxidant in →
Sample
Aspirator air
Drain
Flame
Burner
Mixing baffles
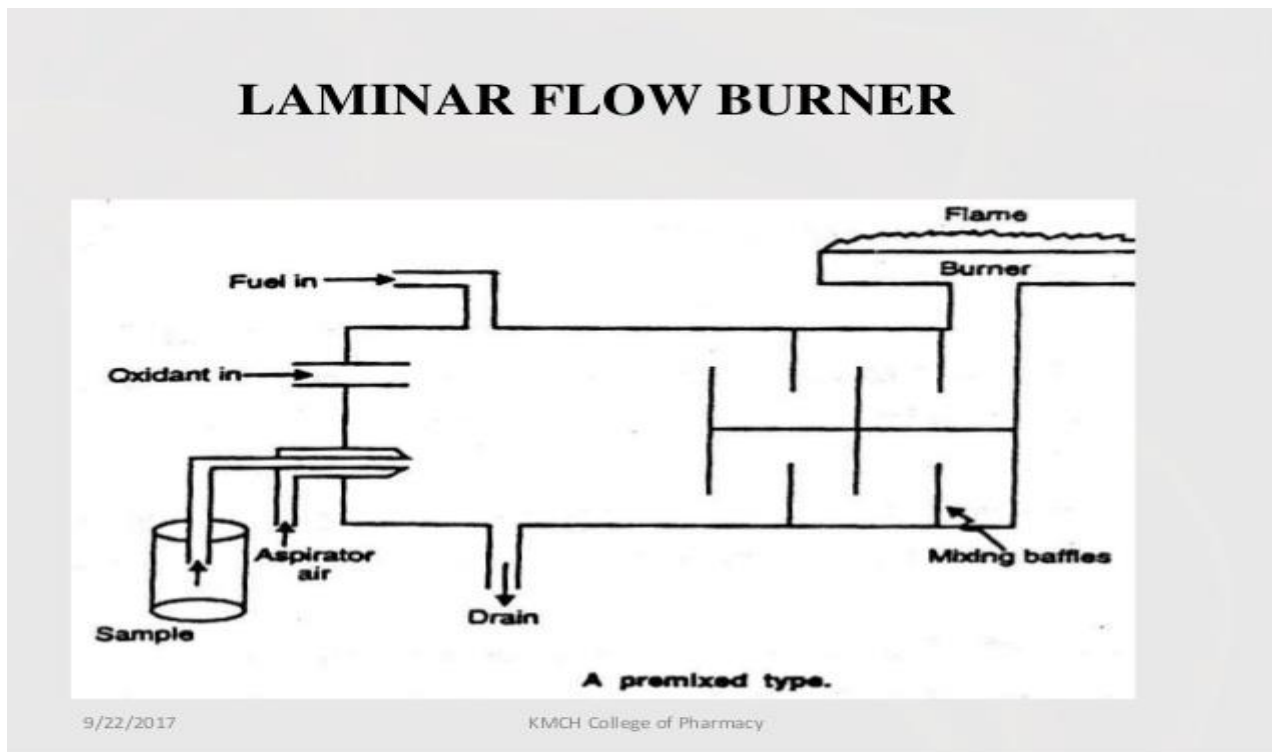
A premixed type.

LAMINAR FLOW (PREMIX) BURNER.

❖ In this type of the burner, aspirated sample, fuel and oxidant are thoroughly mixed before reaching the burner opening and then entering the flame.

❖ Important feature of this is that only a small portion (about 5%) of the sample reaches the flame in the form of small droplets and is easily decompose.

ADVANTAGES:

❖ Premix burner is non-turbulent ,noiseless and stable.

❖ Easy decomposition which leads to high atomization.

❖ Can handle solution up to several % without clogging.

DEMERITS

❖ When it contains 2 solvents, the more vol. will evaporate and lesser will remain undissociated.
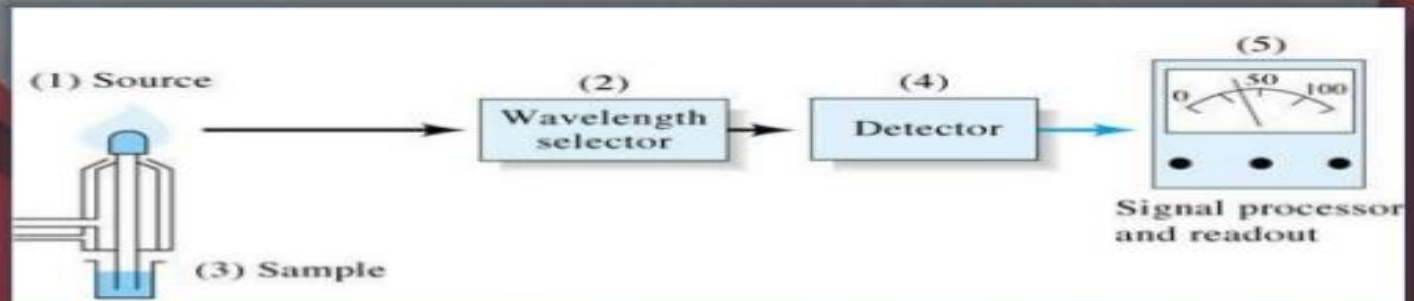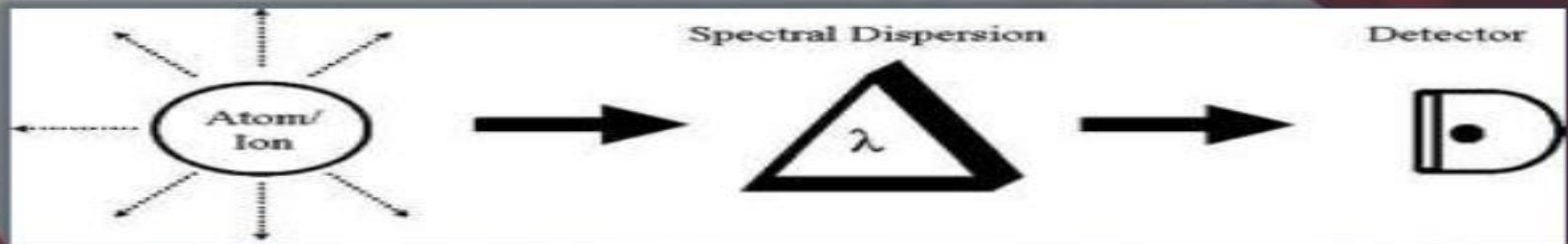
- Region A: The unburned hydrocarbon gas mixture passes into a region of free heating about 1mm thickness i.e in region B

- Region B: the mixture is heated by energy from the region C. diffusion of radicals into region B initiates combustion. Flame gases travel upward from the reaction zone with velocities of 1-10 m/s.

- Region C gases that emerge from region c consists of mainly of co2,co, h2o, and n2, traces of h2,h ,o can be seen. In region C thermal equilibrium cannot be achieved.

- Region D: most suitable for AAS measurements, gases reach thermal equilibrium at this region. This region is more cooler and more oxidizing than the primary oxidizing region C.
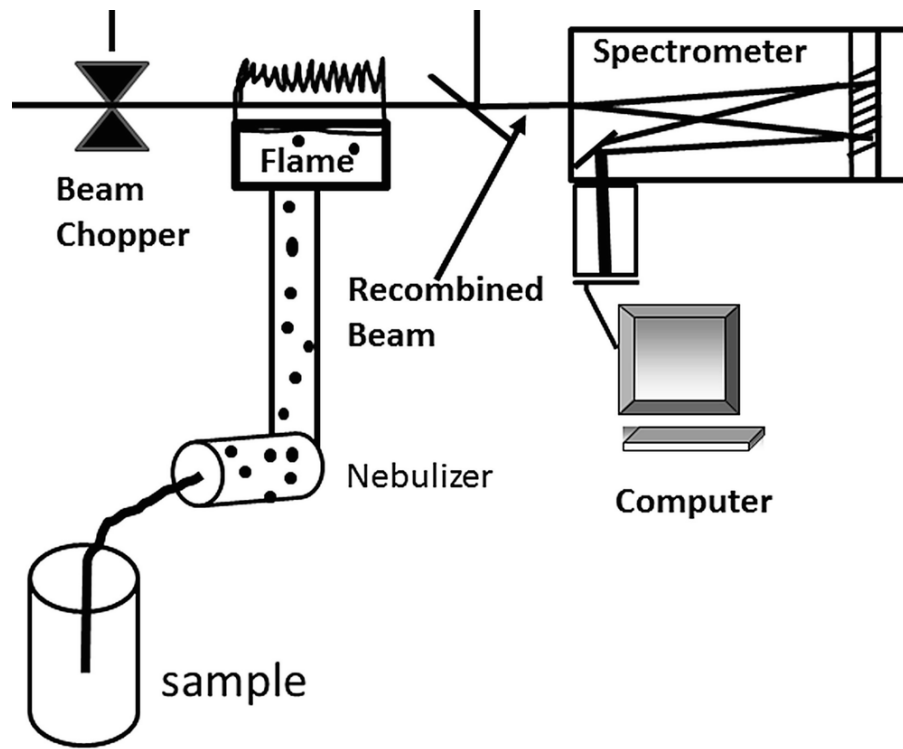
Flame Emission Spectroscopy

- In flame emission spectrometry, the sample solution is nebulized (converted into a fine aerosol) and introduced into the flame where it is desolvated, vaporized, and atomized, all in rapid succession.

- Atoms are raised to excited states via thermal collisions

- Upon their return to a lower or ground electronic state, the excited atoms and molecules emit radiation

- The emitted radiation passes through a monochromator that isolates the specific wavelength for the desired analysis.

- A photodetector measures the radiant power of the selected radiation, which is then amplified and sent to a readout device, meter, recorder, or microcomputer system.

Schematic Diagram Of Instrumentation

Spectral Dispersion

Detector

Atom/ Ion

λ

(1) Source

(2) Wavelength selector

(4) Detector

(5)

50

0   100

Signal processor and readout

(3) Sample

Beam Chopper

Flame

Recombined Beam

Spectrometer

Nebulizer

Computer

sample

- A grating spectrometer, equipped with a laminar flow burner and good detection read out system , serves equally well for FES and AAS because both require the measurement of the intensity of selected wavelengths.

- FES requires a monochromator capable of providing a bandpass of 0.05nm or less

- Slits should be adjustable for greater flow of radiation

- The instrument should have sufficient resolution to minimize the flame background emission.
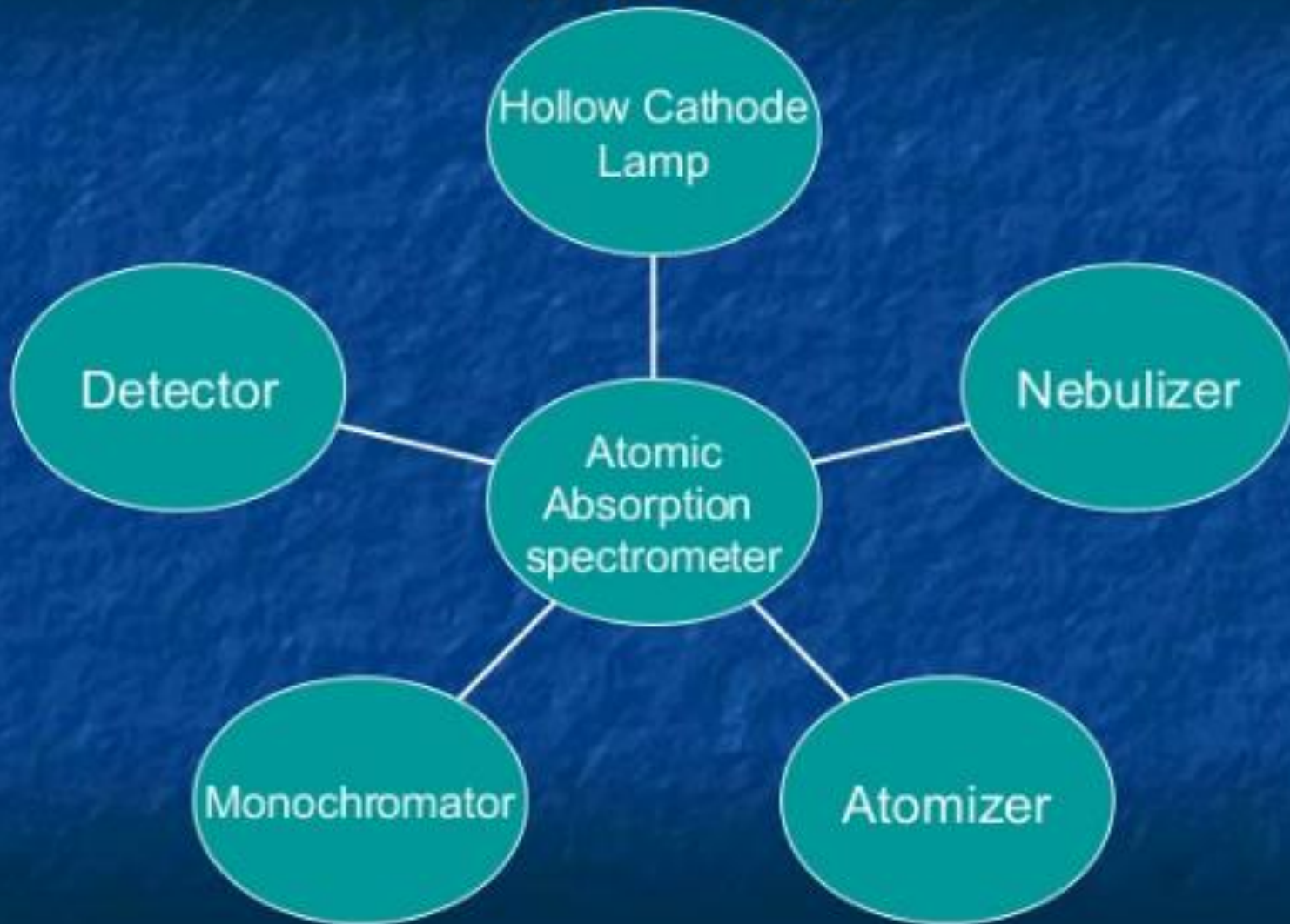
Atomic absorption spectroscopy

- Atomic absorption spectroscopy is one of the most widely used methods in analytical chemistry.

- AAS phenomenon can be divided into two major process:

1. The production of free atoms from the sample

2. Absorption of radiation from an external sources by these atoms.

- https://www.shsu.edu/~chm_tgc/primers/AAS.html
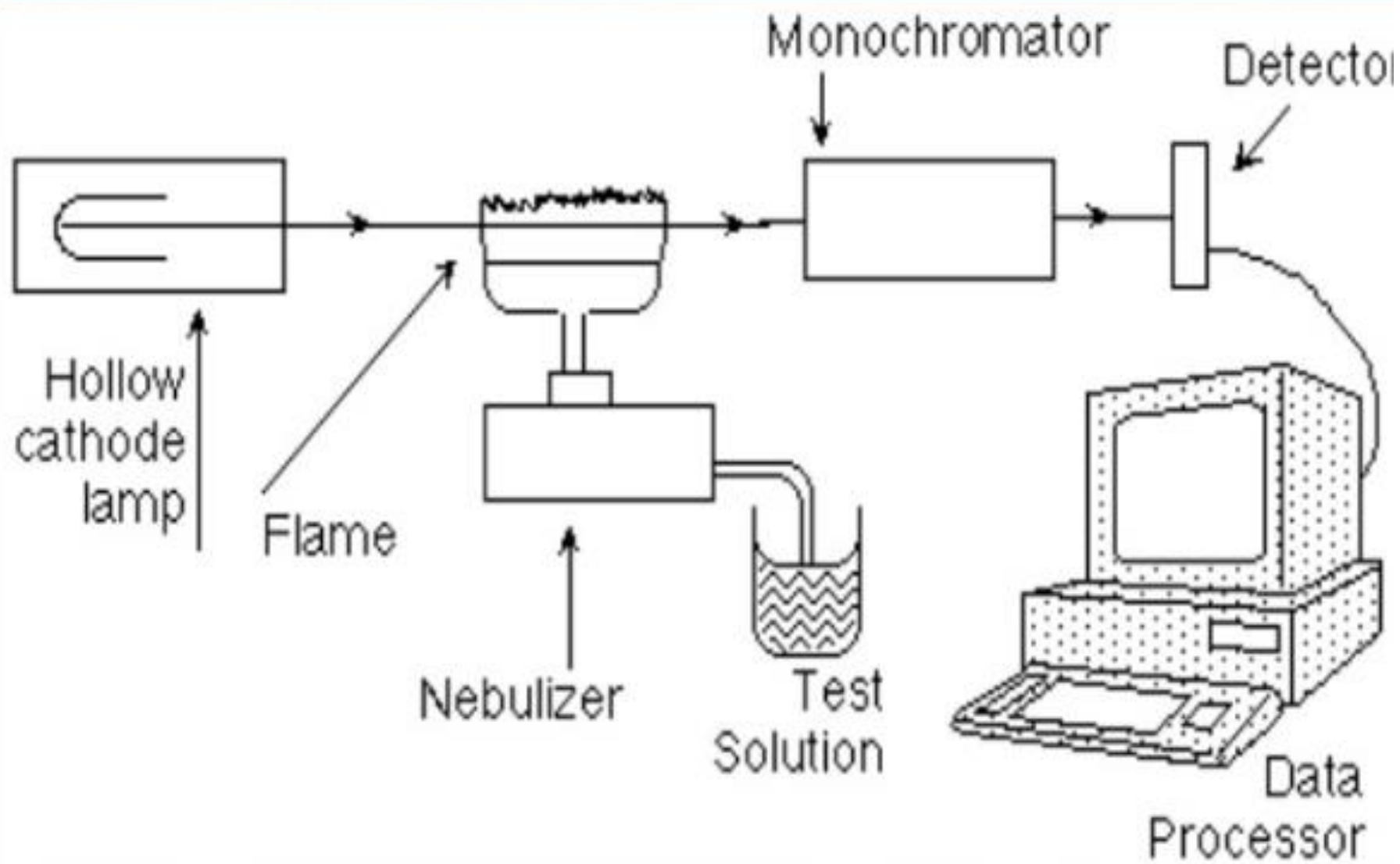
- Atomic Absorption Spectroscopy is a very common technique for detecting metals and metalloids in samples.

- It is very reliable and simple to use.

- It can analyze over 62 elements.

- It also measures the concentration of metals in the sample.

THEORY:

Monochromator

Detector

Hollow cathode lamp

Flame

Nebulizer

Test Solution

Data Processor

- The absorption of radiation by free atoms in the flame involves the transition of these atoms from highly populated ground state to an excited electronic state.

- The transition between the ground state and the first excited state known as the first resonance line is the line with the strongest absorptivity.

- Analysis requires high sensitivity, the first resonance line of the analyte is used.

- The wavelength of the first resonance line for all metals and many metalloids is longer than 200nm

- The first resonance line for most non metals falls into the vacuum ultraviolet region below 185nm and therefore, cannot be measured with conventional spectrometers.

- Thus AAS instrumentation finds wide application for analysis of metals and metalloids.

- For AAS to function as a quantitative method the width of the line emitted by the narrow line source must be smaller than the width of the absorption line of the analyte in the flame

- The shape of the spectral line emitted by the source is critical parameter in AAS.
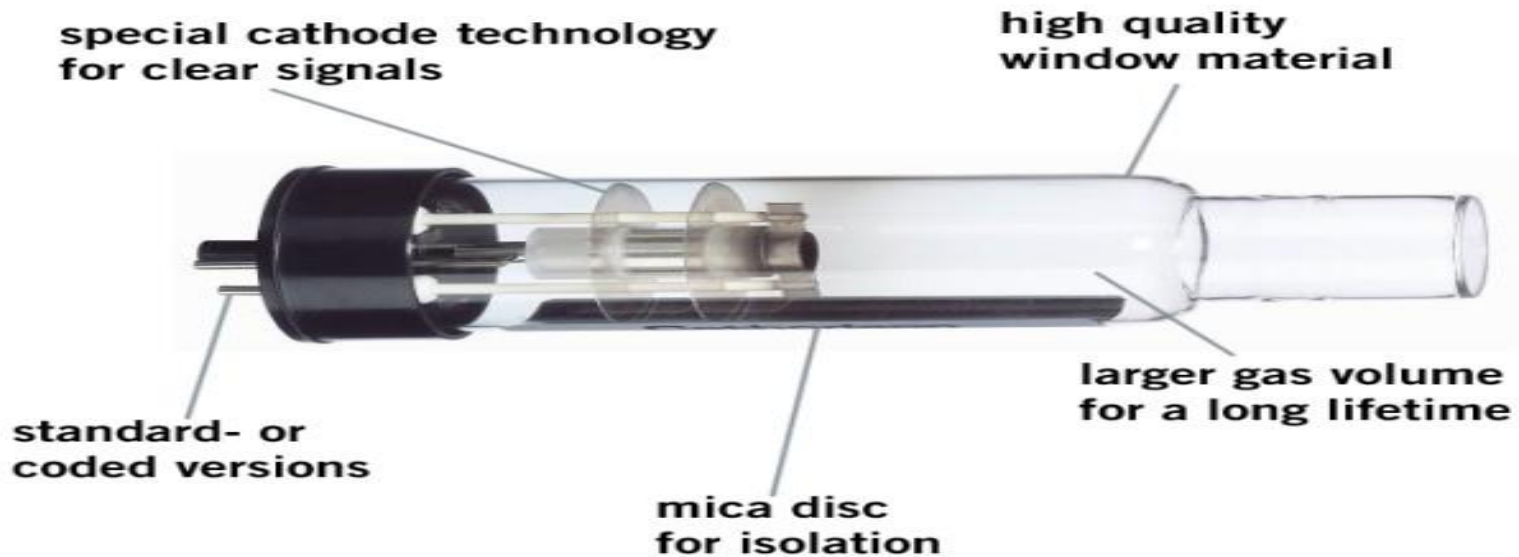- Working of atomic absorption spectroscopy:

  The flame gases are considered as a sample cell that contains free, unexcited analyte atoms capable of absorbing radiation at the wavelength of the resonance line emitted by the external source.

  unabsorbed radiation passes through a monochromator that isolates the resonance line and then into a photo detector that measures the power of transmitted radiation.

- Absorption is determined by the difference in the radiant power of the resonance line in the presence and absence of the analyte atoms in the flame.

- Specifications for typical atomic absorption spectrophotometer:

- 0.33-0.5m focal length czerny Turner Monochromator with a 64x64mm grating ruled with 2880 grooves/mm and blazed at 210 nm to cover a range of wavelengths of 190-440nm

- A second grating, ruled with 1440 grooves/mm and blazed at 580nm . The two gratings are mounted back to back on a turntable
- The geometry of the beam of radiation must be designed to provide optimum performance with both flame and electrothermal atomizers
- Optical elements are needed to focus the source of lamp
- Microcomputer enables the instrument to calculate the best analytical curves, computer ratios, apply appropriate statistical techniques and present ressult in graphical or tabular form.

Hollow cathode lamps

special cathode technology for clear signals

high quality window material

standard- or coded versions

mica disc for isolation

larger gas volume for a long lifetime

- Hollow cathode lamps (HCL) are discharge lamps designed for use in Atomic Absorption (AA) instruments. They consist of a cathode made from the element of interest.

- Hollow cathode lamp has pyrex body with and end window of quartz

- The lamp is evacuated and filled with an inert gas usually argon or neon

- Lamps operate at currents below 30mA and voltages up to 400 V

- The cathode is bombarded by positively charged , inert gas ions. The ions are accelerated towards the cathode surface by the electrical potential.

- Positively charged ions collide with the negatively charged cathode surface, the metal atoms of cathode of the cathode are ejected

- The metal atoms absorb energy and move to excited electronic state. And finally emit the radiation

Atomic Fluorescence Spectrometry

- Atomic fluorescence spectroscopy (also known as atomic spectrofluorometry or atomic fluorimetry) is a technique used in biochemical, medical, and chemical applications that require very high sensitivity as well as precision and accuracy.

- The technique behind atomic fluorescence spectroscopy is similar to atomic absorption spectrometry in that a sample absorbs light at a particular wavelength to promote its electrons from its ground electronic state into an excited state.

- From this excited electronic state, the electron drops down to a lower electronic state emitting a photon with a specific wavelength in the process. By measuring the intensity of the emitted light at particular frequencies, it is possible to determine the concentration of the element
- In AFS the exciting source is placed at right angles to the flame
- Some of the incident radiation is absorbed by the free atoms of the test element
- After this , energy is released as atomic fluorescence
- Then it is passed through monochromator, lens and amplified and passed to detector.

- The best burner system for AFS is probably a combination of acetylene/ nitrous oxide and hydrogen/argon/ oxygen using rectangular flame with premixed laminar flow burner .

- The intensity of the fluorescence is linearly proportional to the exciting radiation flux.

- When there is no analyte, only background radiation from the flame is detected.

- AFS exhibits its greatest sensitivity for elements that have high excitation energies

Interferences associated with Flames and Furnaces

- Interferences can be separated into four general categories:

1. Back Ground Absorption

2. Spectral line interferences

3. Vaporization Interferences

4. Ionization effects

Background Absorption

- It is caused by the large number of species present in the flame that are capable of broad band absorption of radiation.

- Few elements which are responsible for background absorption are metal oxides, hydrogen molecules, OH radicals, and some part of solvent molecules.

- This background absorption results in direct interferences and corresponding error in analytical results.

- There are number of techniques used correction of background absorption techniques.

- A solution that contains none analyte can be prepared and its absorbance at the resonance line of the analyte determined. The absorbance of this blank solution is then used to correct the measurements obtained from the sample.

- A more precise technique involves measuring the absorbance at a wavelength close to the resonance lines used in determination

- The use of broadband, continuous source of radiation in conjunction with the hollow cathode line source is popular technique for background correction.

Spectral line interferences

- Spectral interference is caused by radiation overlap of absorption line due to emissions from another element or compound.

  If an absorbing wavelength of an element , not being determined but present in the sample falls within the measuring line of the element of interest, the absorbance of the element will be measured together with the analyte of interest and give a higher absorbance value.

- Interference of this type is closely associated with the resolving power of the monochromator.

- In flame AAS and AFS this interference can be minimized by amplitude modulation of the radiation source. No such possibility exists in FES.

- Manganese triplet, gallium line, potassium doublet , lead etc are the few instances which cause interference

Vaporization Interference

- Some component of the sample alters the rate of vaporization of salt particles that contain the analyte which lead to the vaporization interferences.

- It is due to the chemical reaction of particles that change the vaporization behavior of particles.

- Hotter flames reduce vaporization interferences

- Use of the acetylene/nitrous oxide flame is often justified due to its better decomposing efficiency.

- Use of proper reagents also reduce vaporization interference.

- In Calcium AAS determinations, a few hundred parts per million of lanthanum or strontium are often added to solutions to minimize interferences due to phosphate.

Ionization interferences

- In high temperature flames atoms with low ionization potential become ionized

- Ionization of atoms reduce the free atoms , which in turn lowers the sensitivity of the determination.

- This problem is readily over come by adding an excess of more easily ionized elements such as K, Cs, or Sr to suppress ionization .

- These elements suppress the ionization of analyte atoms.

Comparison of AAS and FES

Comparison between FES and AAS

Flame Emission spectroscopy	Atomic Absorption spectroscopy
1. Amount of light emitted by excited atom is measured.	1. Amount of light absorbed by ground state atom is measured.
2. Absorption intensity and signal response greatly influenced by temperature variation.	2. Absorption intensity and signal response does not depend upon temperature.
3. Beer's law is not obeyed.	3. Beers law is obeyed.
4. Intensity of emitted radiation is directly proportional to the number of atoms in excited state.	4. Intensity of absorbed radiation is directly proportional to the number of atoms in ground state.
5. Relation between emission intensity vs. concentration is not much linear.	5. Absorption intensity vs concentration of analyte is much linear.
6. Atomization and excitation flame used.	6. Atomization flame used.
7. Intensity vs concentration data is obtained.	7. Absorbance vs concentration data is obtained
8. Limited to alkali and alkali earth metals.	8. Useful for more than 70 metals.

- FES is better for determinations that involve alkali, alkaline earth and rare earth elements as well as Ga, In and Tl.

- Flame AAS permits Ag, Al, AU, Cd, CU, Hg etc to be detected with high sensitivity.

- FES provides multi element analysis.

- Alkemade showed that AAS can be more sensitive for a given element only if the brightness of the lamp exceeds that of balckbody at the temperature of flame.

Question bank and assignments

- Explain the components of flame spectrometric method and its functions.
- Give the applications of FES and AAS.
- With a neat block diagram, explain the flame atomization processes for the salt MX.
- Explain atomic absorption spectrometry with a neat diagram
- Explain the sequence of events involved in flame atomization process, with a neat block diagram.
- Discuss the laminar flow flame, with a neat schematic.
- List the interferences associated with flames and furnaces
- With a neat schematic arrangement, explain the flame emission spectrophotometer (FES)
- Explain the atomic fluorescence spectrometer with a neat diagram.
- List the applications of flame emission spectroscopy.
- Give the applications of atomic absorption spectroscopy.
- What is nebulization? With neat sketches explain how nebulisation is done

Topics to be discussed in detail in the regular class

- Electro thermal vaporization
- Chemical vaporization
- Background absorption

9 FLAME EMISSION AND ATOMIC ABSORPTION SPECTROSCOPY

9.1 INTRODUCTION

The absorption and emission of radiant energy by atoms provide powerful analytical tools for both quantitative and qualitative analysis (see Chapter 5). Flame emission spectroscopy (FES) has been used since the early 1900s. In the 1960s, atomic absorption spectroscopy (AAS) was developed as an analytical method. Most recently, new sources for plasma emission spectroscopy offer capabilities that complement FES and AAS for many analyses.

Table 9.1 summarizes atomic spectroscopic methods. This chapter will discuss methods that use combustion flames and a single nonflame method, electrothermal AAS. Chapter 10 will present emission spectroscopic methods that use nonflame excitation sources. Two major limitations apply to all atomic spectroscopic methods: (1) their limited ability to distinguish among oxidation states and chemical environments of the analyte elements and (2) their insensitivity to nonmetallic

TABLE 9.1   PRIMARY METHODS FOR ATOMIC SPECTROSCOPY

Method (abbreviation)	Energy source	Measured quantity
Emission	*Source of excitation*	
Flame emission spectroscopy (FES)	Flame (1700–3200 °C)	Intensity of radiation
Atomic fluorescence spectroscopy (AFS)	Flame (1700–3200 °C)	Intensity of scattered radiation
Electric arc	Plasma from dc arc (4000–6500 °C)	Intensity of radiation
Electric spark	Plasma from ac spark (4500 °C)	Intensity of radiation
Inductively coupled plasma (ICP)	Argon plasma produced by induction from high-frequency magnetic field (6000–8500 °C)	Intensity of radiation
ICP-AFS	Same as ICP	Intensity of scattered radiation
Direct-current argon plasma	Argon plasma produced by a dc arc (6000–10,500 °C)	Intensity of radiation
Absorption	*Source of atomization*	
Flame atomic absorption spectroscopy (FAAS)	Flame (1700–3200 °C)	Absorption of radiation
Electrothermal absorption spectroscopy	Electric furnace (1200–3000 °C)	Absorption of radiation

224

elements. The latter limitation has been overcome for selected nonmetals by modifying the optical components to extend the range of usable wavelengths farther into the ultraviolet region.

The relationship between analyte concentration and the measured signal is different for the methods discussed in this chapter. Flame emission spectroscopy and atomic fluorescence spectroscopy (AFS) are emission methods and therefore the intensity of the emitted radiation is directly proportional to the concentration. In AAS determinations, the absorbance is measured and the concentration of the analyte is related to the signal by the Lambert-Beer law, usually called Beer's law.

The Role of Combustion Flames in FES and AAS

Combustion flames provide a means of converting analytes in solution to atoms in the vapor phase freed of their chemical surroundings. These free atoms are then transformed into excited electronic states by one of two methods: absorption of additional thermal energy from the flame or absorption of radiant energy from an external source of radiation.

In the first method, known as flame emission spectroscopy (FES), the energy from the flame also supplies the energy necessary to move the electrons of the free atoms from the ground state to excited states. The intensity of radiation emitted by these excited atoms returning to the ground state provides the basis for analytical determinations in FES.

In the second method, atomic absorption spectroscopy (AAS), the flame that contains the free atoms becomes a sample cell. The free atoms absorb radiation focused on the cell from a source external to the flame. As in all absorption spectroscopic methods, the incident radiation absorbed by the free atoms in moving from the ground state to an excited state provides the analytical data. A major modification of AAS was the replacement of the flame by an electrothermal furnace (electrothermal atomic absorption spectroscopy, EAAS), resulting in improved detection limits for many elements.

In both FES and flame AAS, the sample solution is introduced as an aerosol into the flame, where the analyte ions are converted into free atoms. Once formed, the free atoms are detected and determined quantitatively by FES or AAS. If the source of exciting radiation is placed at right angles to both the flame and the optical axis of the spectrometer, a method known as atomic fluorescence spectroscopy (AFS) results. This technique has dramatically improved detection limits for certain elements. At this time only one atomic fluorescence instrument is available commercially, an inductively coupled plasma (ICP-AFS) unit from Baird Corporation.

Although inductively coupled plasma and dc plasma are finding increased use (see Chapter 10), FES and AAS remain the workhorses for many analyses (Table 9.2). FES still offers the lowest detection limits for the alkali metals and good limits for many other elements. Flame AAS, the method of choice for many elements in the 1960s and 1970s, now provides the lowest detection limits for only a few elements. It is, however, widely used for many routine determinations. Electrothermal AAS provides the best known detection limits for a large number of elements (see Appendix G).

TABLE 9.2

"BEST" DETECTION LIMITS FOR ATOMIC SPECTROSCOPIES (NANOGRAMS PER MILLILITER)

Li 0.001 A.G	Be 0.003 D.E											B 0.1 E	C 44 E	N *	O * E	F *
Na 0.004 A.D	Mg 0.0002 D											Al 0.01 D	Si 0.005 D	P 0.3 D	S 10 D.E	Cl E
K 0.004 A.D	Ca 0.0001 E	Sc 0.4 E	Ti 0.03 E	V 0.06 D.E	Cr 0.004 D	Mn 0.0005 D	Fe 0.01 D	Co 0.008 D	Ni 0.05 D.E	Cu 0.005 D	Zn 0.0003 C.D	Ga 0.01 D	Ge 0.1 D	As 0.02 B.D	Se 0.02 B.C.D	Br E
Rb 0.02 A	Sr 0.002 E	Y 0.04 E	Zr 0.06 E	Nb 0.2 E	Mo 0.02 D		Ru 30 B.E.F	Rh 0.1 D	Pd 0.05 D	Ag 0.001 D	Cd 0.0002 D	In 0.006 D.G	Sn 0.03 D	Sb 0.08 B.C.D	Te 0.002 B	I 3 D.E
Cs 0.02 A.D	Ba 0.01 D.E		Hf 10 E	Ta 5 E	W 0.8 E	Rs 6 D.E.F	Os 0.4 E	Ir 0.5 D	Pt 0.2 D	Au 0.01 D	Hg 0.001 B.C	Ti 0.01 D	Pb 0.007 D	Bi 0.01 B.D		

La 0.1 E	Ce 0.4 E	Pr 10 E	Nd 0.3 E		Sm 1 E	Eu 0.06 A.E	Gd 0.4 E	Tb 0.1 E	Dy 4 E.F	Ho 0.7 D	Er 0.3 D.E	Tm 0.2 E	Yb 0.01 D.E
	Th 3 E		U 1.5 E										

A. Flame emission spectrometry
B. Flame atomic absorption
C. Atomic fluorescence spectrometry
D. Electrothermal atomic absorption
E. ICP
F. DCP
G. Laser-assisted ionization

* Spectra from these elements have been observed in the but detection limits are not available in a comparable

SOURCE: After M. Parsons and S. Major, *Appl. Spectrosc.*, 37 (5), 411 (1983). With permission.
NOTE: See Appendix G for a more complete listing.

Flame Spectrometric Methods

Even though the characteristics of free-atom formation in the flame and problems associated with interferences are common to the three flame spectrometric methods (FES, AAS, and AFS), each method has its own instrumentation, unique advantages, and definite limitations.

INSTRUMENTATION FOR FLAME SPECTROMETRIC METHODS[1,2]

The basic components of flame spectrometric instruments are discussed in this section. These components provide the following functions required in each method: (1) deliver the analyte to the flame, (2) induce the spectral transitions (absorption or emission) necessary for the determination of the analyte, (3) isolate the spectral lines required for the analysis, (4) detect the increase or decrease in intensity of radiation at the isolated lines(s), and (5) record these intensity data.

Pretreatment of Sample[3]

Flame AAS and FES require that the analyte be dissolved in a solution in order to undergo nebulization (see the next section). The wet chemistry necessary to dissolve the sample in a matrix suitable for either flame method is often an important component of the analytical process. The analyst must be aware of substances that interfere with the absorption or emission measurement (Section 9.4). When these substances are in the sample, they must be removed or masked (complexed). Reagents used to dissolve samples must not contain substances that lead to interference problems.

Sample Delivery

The device that introduces the sample into the flame or plasma plays a major role in determining the accuracy of the analysis. The most popular sampling method is nebulization of a liquid sample to provide a steady flow of aerosol into a flame. An introduction system for liquid samples consists of three components: (1) a nebulizer that breaks up the liquid into small droplets, (2) an aerosol modifier that removes large droplets from the stream, allowing only droplets smaller than a certain size to pass, and (3) the flame or atomizer that converts the analyte into free atoms.

Nebulization

Pneumatic nebulization is the technique used in most atomic spectroscopy determinations. The sample solution is introduced through an orifice into a high-velocity gas jet, usually the oxidant. The sample stream may intersect the gas stream in either a parallel or perpendicular manner (Figure 9.1a). Liquid is drawn through the sample capillary by the pressure differential generated by the high-velocity gas stream passing over the sample orifice. The liquid stream begins to oscillate, producing filaments. Finally, these filaments collapse to form a cloud of droplets in the aerosol modifier or spray chamber. In the spray chamber the larger droplets are removed from the sample stream by mixer paddles or broken up into smaller

droplets by impact beads (Figure 9.1b) or wall surfaces. The final aerosol, now a fine mist, is combined with the oxidizer/fuel mixture and carried into the burner (Figure 9.2).

A typical distribution range of droplet diameters is shown in Figure 9.3. Droplets larger than about 20 μm are trapped in the spray chamber and flow to waste. The distribution of drop sizes is a function of the solvent as well as the

FIGURE 9.1

(a) Construction of pneumatic nebulizer and (b) breakdown of liquid filament into droplets.
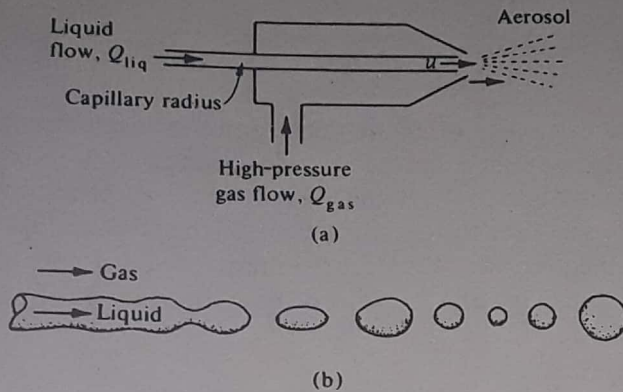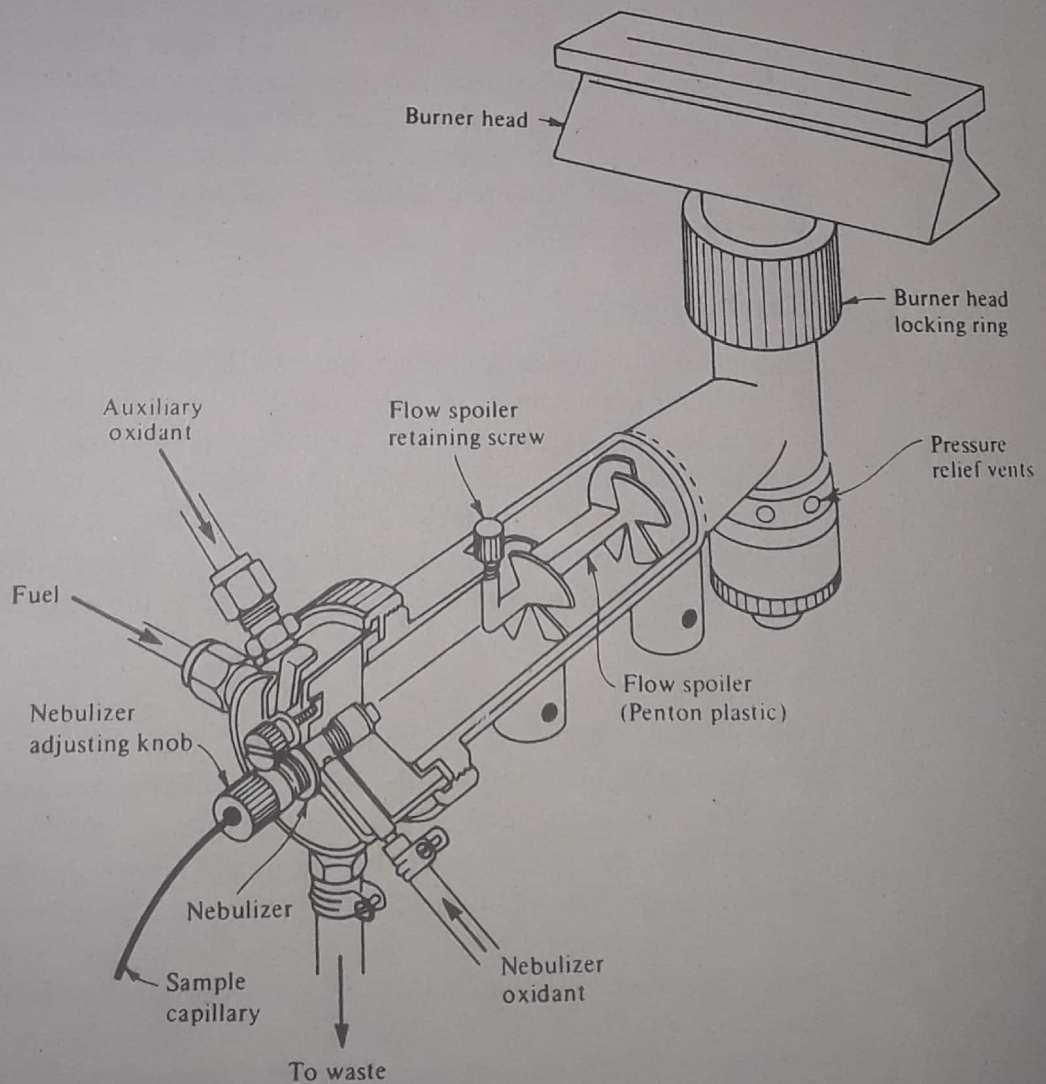

FIGURE 9.2

Slot burner and expansion chamber. (Courtesy of Perkin-Elmer Corp.)

components of the sampling system. In AAS only a small percentage (usually 2% or 3%) of the nebulized analyte solution reaches the burner.

The diameter of the aerosol droplets produced by the nebulizer is determined by the physical properties of the sample solution as described in the following equation.[4]

$$d_s = \frac{585}{v}\left(\frac{\gamma}{\rho}\right)^{0.5} + 597\left[\frac{\eta}{(\gamma\rho)^{0.5}}\right]^{0.45} \cdot 1000\left[\frac{Q_l}{Q_g}\right]^{1.5} \tag{9.3}$$

where d_s is the Sauter mean diameter of the aerosol droplets (the diameter of the drop with a volume-to-surface-area ratio the mean of the distribution), v is the velocity difference between gas and liquid flows (m/sec), γ is the surface tension of the liquid (dyne/cm), ρ is the liquid density (g/mL), η is the liquid viscosity (poise), and Q_l and Q_g are the volume flow rates of the liquid and gas respectively (mL/sec). The equation has proved valuable in predicting trends for aerosol generation. Unanticipated changes in viscosity and surface tension are avoided by keeping the sample and standard matrices identical and by avoiding total acid or salt concentrations greater than about 0.5%.

Atomization

The atomization step must convert the analyte within the aerosol into free analyte atoms in the ground state for AAS, FES, and AFS analysis. Very small sample volumes (5–100 µL) or solid samples can be handled by flameless electrothermal methods.

Flame Atomizers. The sequence of events involved in converting a metallic element, M, from a dissolved salt, MX, in the sample solution to free M atoms in the flame is depicted in Figure 9.4. (After the aerosol droplets containing MX enter the flame, the solvent is evaporated, leaving small particles of dry, solid MX. Next, solid MX is converted to MX vapor. Finally, a portion of the MX molecules are dissociated to give neutral free atoms. These M atoms are the species that absorb
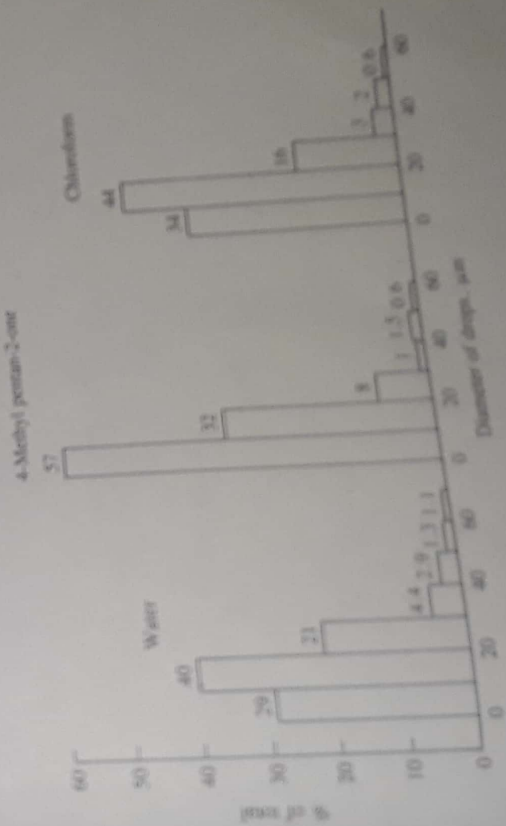

4-Methyl pentan-2-one

Chloroform

Water

% of total

Diameter of drops, µm

radiation in AAS and AFS, and they are the potential emitting species in FES. The efficiency with which the flame produces neutral analyte atoms is of equal importance in all the flame techniques.

If the events proceed vertically from the top down in Figure 9.4, the efficiency of free-atom production is high. Processes that branch horizontally interfere with the production of free analyte atoms. These processes include: (1) excitation and emission of radiation by MX(g) molecules, (2) reaction of M(g) atoms with flame components at high temperatures to produce molecules and ions that also absorb and emit radiation, and (3) formation of M^{+x} ions, which, in addition to reducing the efficiency of free-atom production, complicate the analysis by adding lines to the spectrum.

The flame remains the most generally useful atomizer for atomic spectroscopy despite the developments in electrothermal atomization. A satisfactory flame source must provide the temperature and fuel/oxidant ratio required for a given analysis. The maximum operating temperature of the flame is determined by the identities of the fuel and oxidant (Table 9.3), whereas the exact flame temperature is fixed by the fuel/oxidant ratio. In addition, the spectrum of the flame itself should not interfere

FIGURE 9.4

Flame atomization processes for the salt MX. Asterisk (*) indicates excited state.
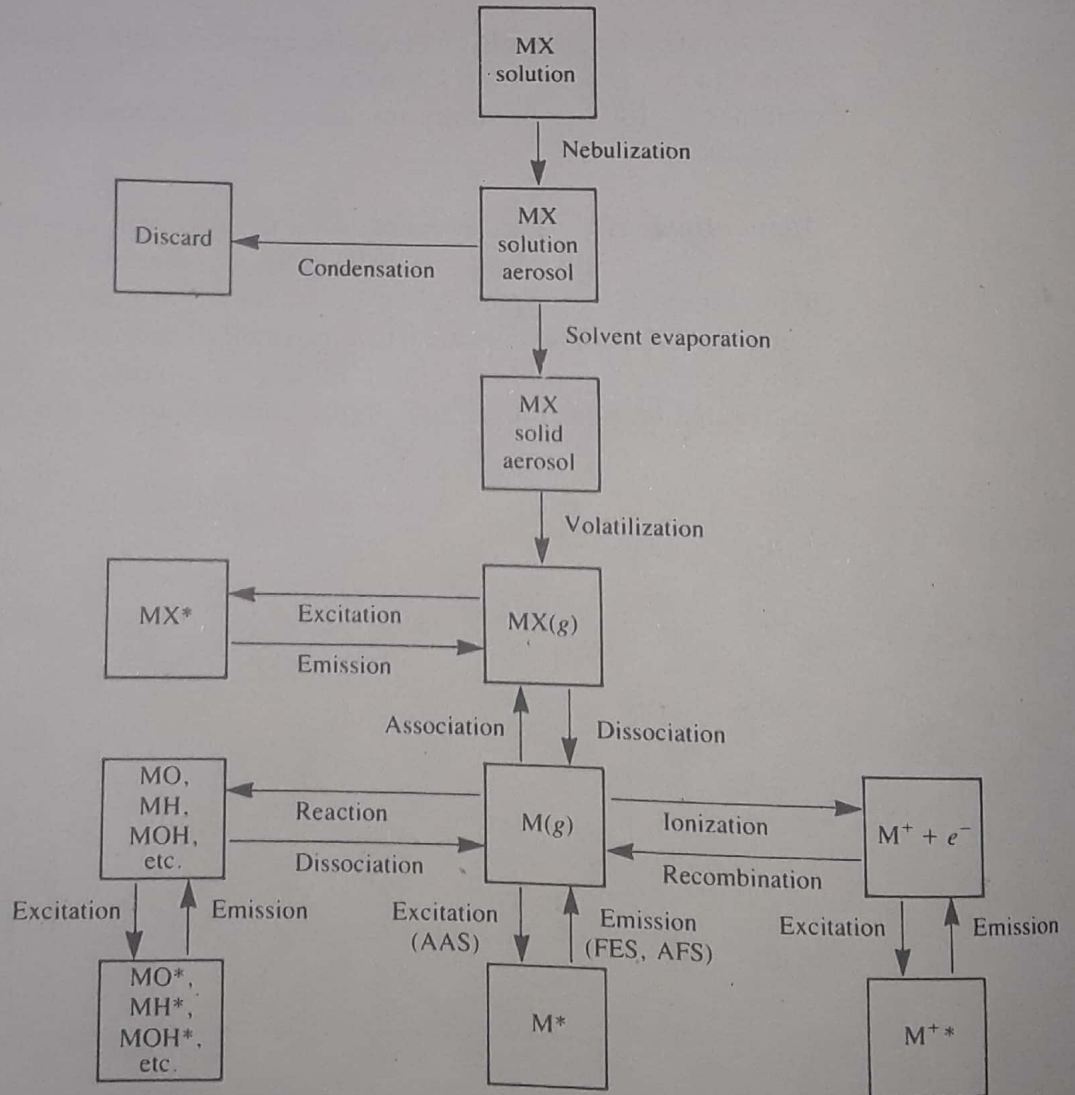
with the emission or absorption lines of the analytes. Components of the flame gases limit the usable range to wavelengths longer than 210 nm.

Flames are not uniform in composition, length, or cross section. The structure of a premixed flame, supported on a laminar flow burner, is shown in Figure 9.5. (Laminar flow is defined as a mode of gas flow in which the lines of flow are approximately parallel and change smoothly, if at all, in time and space.) Emerging from region A, the unburned hydrocarbon gas mixture passes into a region of free heating about 1 mm thickness (region B). In this region, the mixture is heated by energy (conduction and radiation) from region C. Diffusion of radicals into region B initiates combustion. Flame gases travel upward from the reaction zone with velocities of 1–10 m/sec. Gases that emerge from region C consist mainly of CO_2,

CHARACTERISTICS OF COMMON PREMIXED FLAMES

Fuel	Oxidant	Temperature* (°C)	Burning velocity† (cm sec⁻¹)
Acetylene	Air	2400	160–266 (160)
Acetylene	Nitrous oxide	2800	260
Acetylene	Oxygen	3140	800–2480 (1100)
Hydrogen	Air	2045	324–440
Hydrogen	Nitrous oxide	2690	390
Hydrogen	Oxygen	2660	900–3680 (2000)
Propane	Air	1925	43

* Stoichiometric mixture.
† Values in parentheses are probably the ones most applicable to laboratory burners.

URE 9.5
ematic structure of a
inar flow flame.

- Outer cone Secondary reaction (combustion) zone
- Interconal layer (faint) Region D
- Blue cone Primary reaction zone Region C
- Preheating Region B
- Premixed $C_2H_2 + O_2$ Fine droplets of solution Region A

Light path

Air to be entrained (shown on left side only)
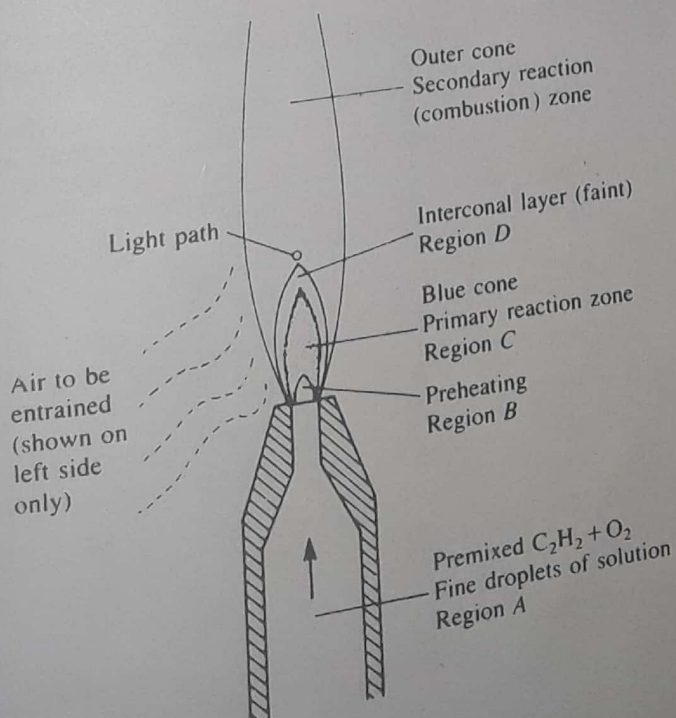
CO, H_2O, and N_2 if air is used as an oxidant. Lesser amounts of H_2, H, O, OH, and NO are also found at this point. The specific composition of the gases is dependent on the composition of the initial mixture. In region C, the concentration of radicals (C_2, CH, H_3O^+, HCO^+) is too high for the gases to achieve thermal equilibrium. The conditions in this region are reducing and the intense emission of radiation from flame components can create noise problems at the detector. As a result, this region is rarely used for AAS unless refractory oxides must be reduced (e.g., BO_2) to obtain the atomic emission.

As the gases reach region D (Figure 9.5), the interconal zone, they approach thermal equilibrium. This region is cooler and more oxidizing than the primary reaction zone (region C). Oxidation is completed in the outer cone with the assistance of surrounding air. The conditions in region D are optimum for most AAS measurements.

The temperature of the flame (Table 9.3) determines its utility in both AAS and FES. The exact temperature depends on the fuel/oxidant ratio and is generally highest for a stoichiometric mixture. Fuel-rich flames are usually cooler. Optimum temperatures vary for AAS and FES but in both cases depend on the excitation and ionization potentials of the analyte (Table 9.4). Temperatures high enough to cause ionization of the analyte atoms are usually undesirable in both methods unless an ionization buffer (an easily ionizable element added to the matrix to suppress ionization of the analyte) is added to the sample.

The concentration of unexcited and excited atoms in a flame is determined by the fuel/oxidant ratio. It varies in different parts of the flame. Studies of atomic or molecular distributions within the flame envelope have been made by measuring absorption, emission, or fluorescence as the flame is moved vertically (or horizontally) relative to the light path of the optical system. Figure 9.6 shows the distribution of free atoms obtained by absorption measurements in a 10-cm long acetylene/air

TABLE 9.4

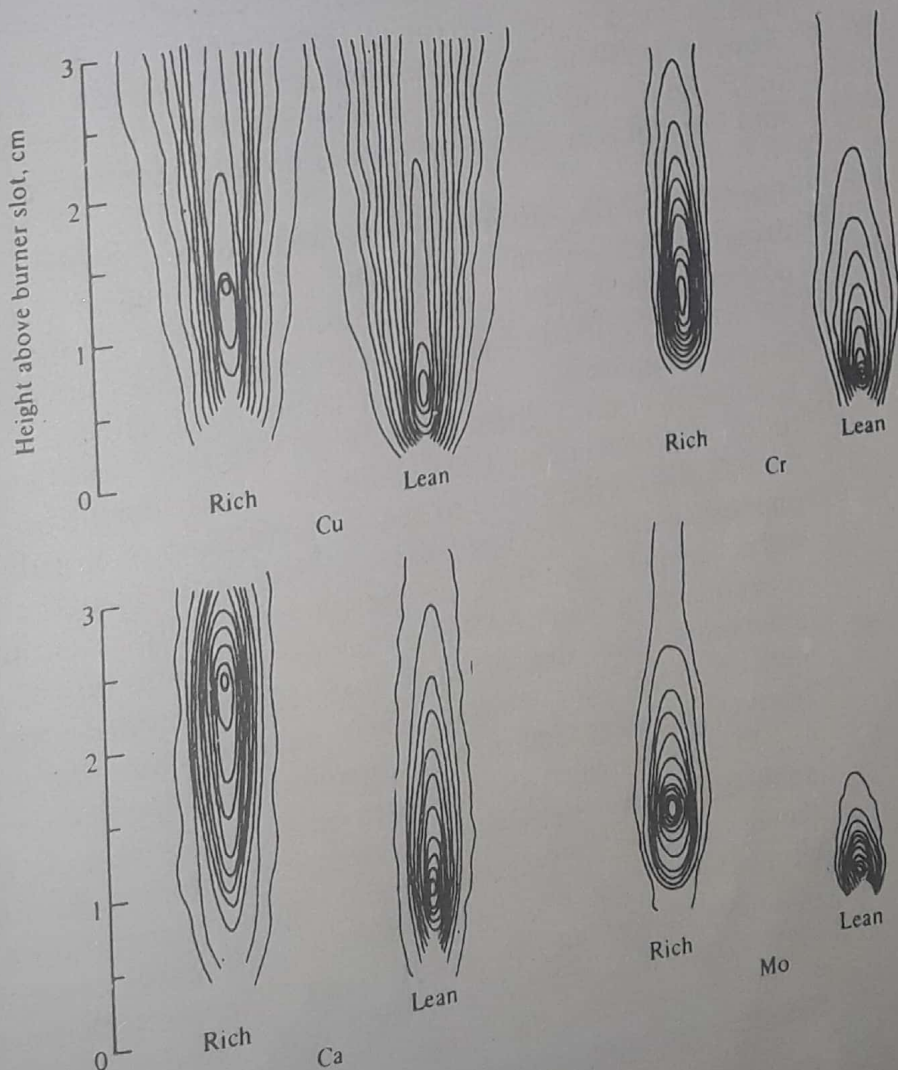PERCENT IONIZATION OF SELECTED ELEMENTS IN FLAMES*

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

* Partial pressure of metal atoms in the flame is assumed to be 1×10^{-6} atm for acetylene/air and acetylene/oxygen flames, and approximately 10^{-8} atm for the acetylene/nitrous oxide flame.

flame. Contours are drawn at intervals of 0.1 absorption unit with maximum absorbance at the center. Different elements exhibit different free-atom flame profiles. Neither the area of observation nor the fuel/oxidant ratio is critical for copper, whereas for molybdenum, the region of maximum free-atom concentration is sharply localized. The height of the maximum free-atom concentration is the point at which the increased atomization with flame height is just balanced by the rate of decrease in the concentration of free atoms through dilution by the flame gases and the formation of oxides and hydroxides.

The distribution pattern obtained by measuring atomic emission often differs dramatically from that obtained from absorption measurements for a given element. For example, the emission lines of boron (249.7 nm) and antimony (259.8 nm) are either absent or very weak in the outer mantle of a stoichiometric flame, but they appear in high concentrations in the reaction zone of a fuel-rich flame. A fuel-rich acetylene flame (ratio of fuel to oxidant exceeds that needed for stoichiometric combustion) provides the reducing atmosphere necessary for the production of a large free-atom population of those elements that have a tendency to form refractory oxides. Incandescent carbon particles present in fuel-rich flames cause luminosity that produces a high background. Thus the position of observation and the fuel/oxidant ratio must be optimized for each element in both FES and flame AAS methods.

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CHAPTER 9
Flame Emission and
Atomic Absorption
Spectroscopy

9.2 In
Flame
Method

In FES, the acetylene/air flame is used for practically all determinations involving alkali metal elements. The higher flame temperature of the acetylene/ nitrous oxide flame is required for analysis of the alkaline earth metals as well as Ga, In, Tl, Cu, Co, Cr, Ni, and Mn. The hotter flame allows the sensitive analysis of additional elements whose refractory oxides are not reduced to the atomic state in acetylene/air flames. The acetylene/nitrous oxide flame is unique in combining high temperature with a propagation rate and analyte residence time not much greater than those of the cooler acetylene/air flame. Special burner heads (5 cm slot length, 0.5 mm width) and control units for igniting and extinguishing the flame are required to eliminate the risk of flashback into the spray chamber and consequent explosion. Proper safety precautions should be taken in operating all flame instruments, both FES and AAS units.

Shielding a flame with a sheath of inert gas, blown around the outside of the flame, causes an elongation of the interconal zone. This elongation reduces noise and provides a wider range of excitation conditions over a small flame volume. Shielding is particularly useful for multielement FES determinations if there is a means for adjusting the burner height (relative to the observation light path). Shielded flames are also used in AFS but usually not required in AAS.

In flame AAS, the fuel/oxidant ratio and observation height are chosen to provide the maximum number of free atoms while minimizing interferences from emission, ionization, or compound formation. For elements where stable (refractory) oxide, carbide, or nitride formation reduces the concentration of free atoms in the flame, two approaches can increase the number of free atoms: (1) use a cooler, reducing acetylene/air flame to minimize the formation of the thermal stable species or (2) use a hotter acetylene/nitrous oxide flame to dissociate these stable species into free atoms (in spite of the risk of decreasing free atoms through ionization).

Electrothermal Atomization.[5,6] As we have seen, the nebulizing system used with flames wastes the sample, and the residence time of free analyte atoms in the portion of the flame where they absorb radiation from the external source is short. Electrically heated devices, such as graphite furnaces and carbon rod analyzers, are common flameless atomizers that complement flame AAS. The most attractive features of electrothermal AAS are (1) high sensitivity (analyte amounts of 10^{-8} to 10^{-11} g absolute), (2) the ability to handle small sample volumes of liquids (5–100 μL), (3) the ability to analyze solid samples directly without pretreatment (in most cases), and (4) low noise from the furnace. Matrix effects from components in the sample other than the analyte are usually much more severe than those encountered in flame AAS and thus the precision, typically 5%–10%, compares unfavorably with that of flame AAS. Electrothermal atomizers are much more difficult to use than flame atomizers, although computer control of the electrical heating cycles has reduced many operational difficulties.

Electrothermal AAS has increased sensitivity because the production of free analyte atoms by an electrically heated carbon atomizer is more efficient than with a flame atomizer. If samples of equal analyte concentration are atomized by an electrothermal and by a flame device, a much higher concentration of analyte per unit time appears in the optical path of the electrothermal atomizer. However, electrothermal atomizers can maintain the relatively high concentration of free atoms for only a brief time, whereas flame atomizers can produce a signal as long as the sample solution is being atomized. Any variation in the rate of atomization

during the comparatively short time available for measurement of radiation absorption in the furnace can lead to serious analytical errors. It is therefore much easier to reproduce results using a flame atomizer because of the longer measurement times for minimizing signal variations by averaging.

An apparatus for electrothermal atomization consists of three components: the workhead, the power unit, and the controls for the inert gas supply. The workhead replaces the burner-nebulizer assembly in the AAS spectrometer. The power unit supplies the operating current at the proper voltage to the workhead. Computer control at the workhead provides the reproducible heating conditions necessary for analysis. The gas control unit provides for metering and control of the flow of inert gas around the exterior and through the workhead during the analysis. This inert environment prevents destruction of the graphite at high temperatures by air oxidation. Sometimes hydrogen gas is introduced into the tube if the unit uses a hydrogen diffusion flame during the reductive ashing cycle.

The heated graphite analyzer, shown in Figure 9.7, consists of a hollow graphite cylinder 28 mm long and 8 mm in diameter, positioned in such manner that the radiation from the external source (hollow-cathode tube) passes through the center of the cylinder. The interior of the cylinder is coated with pyrolytic graphite. Electrodes at the end of the cylinder are connected to a low-voltage, high-current power supply capable of delivering up to 3.6 kW to the cylinder walls. Liquid samples are introduced with a microsyringe through the small opening in the top of the cylinder. Solid samples can be introduced through the end of the tube with a special sampling spoon or on a microdish made of tungsten.

A metal housing surrounding the furnace is water-cooled to allow the entire atomizer unit to be rapidly restored to ambient temperature after each sample has been atomized. Inert gas, usually argon, enters the graphite cylinder at both ends and exits through the sample introduction port at the center of the tube. This gas flow ensures that matrix components vaporized during the ashing step are quickly removed and that nothing is deposited on the inner wall of the tube where subsequent vaporization during the atomizing step could produce a large background absorption signal. Removable quartz windows at each end of the tube prevent ambient air from entering. The inert gas that flows around the exterior of the tube is controlled by a separate valve.

FIGURE 9.7

Cross section of a heated graphite atomizer. (Courtesy of Perkin-Elmer Corp.)
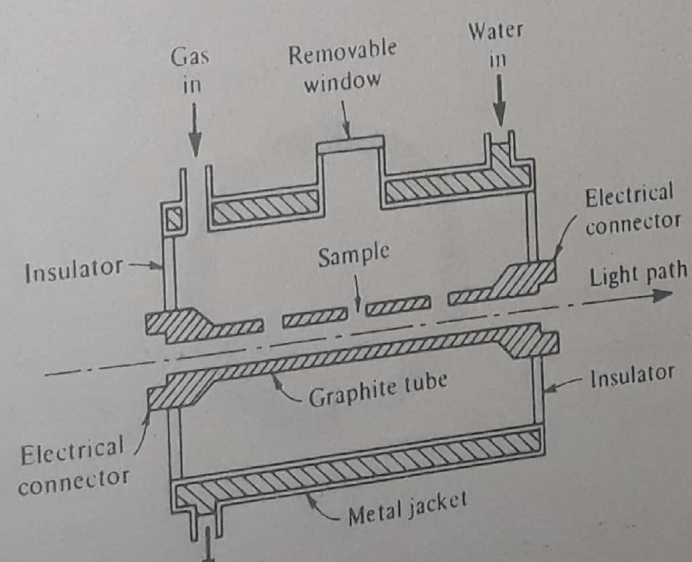
A miniature version of the furnace is the carbon rod atomizer (Figure 9.8). It consists of a three-piece tube or cup unit. The workhead that contains the small furnace is supported between two graphite electrodes inserted in water-cooled terminal blocks. The furnace itself is 9 mm long and 3 mm in diameter with a maximum sample capacity of 10 μL for smooth tubes and 25 μL for tubes with grooves (or threads). The central unit can be replaced with a vertical cup held between the two electrodes. This version is useful for solid samples or samples that require preliminary chemical treatment performed directly in the cup. All units are coated with pyrolytic graphite. In normal use the carbon rod atomizer is protected from oxidation by a sheath of inert gas directed onto the rod from a chimney beneath. When hydrogen gas is added to generate a reducing environment, the gas ignites spontaneously when the cup or tube reaches incandescence.

A thin graphite plate, known as the L'vov platform, added to the bottom of the graphite tube allows for better control of atomization (Figure 9.9). The sample is placed on the plate and is heated by radiation from the walls so that the temperature increase of the plate is delayed relative to that of the tube walls and the gaseous vapor inside the tube. With this device, the walls and vapor can reach a steady-state

FIGURE 9.8

Carbon rod atomizer:
(a) horizontal rod version and (b) vertical cup version. (Courtesy of Varian Associates, Inc.)
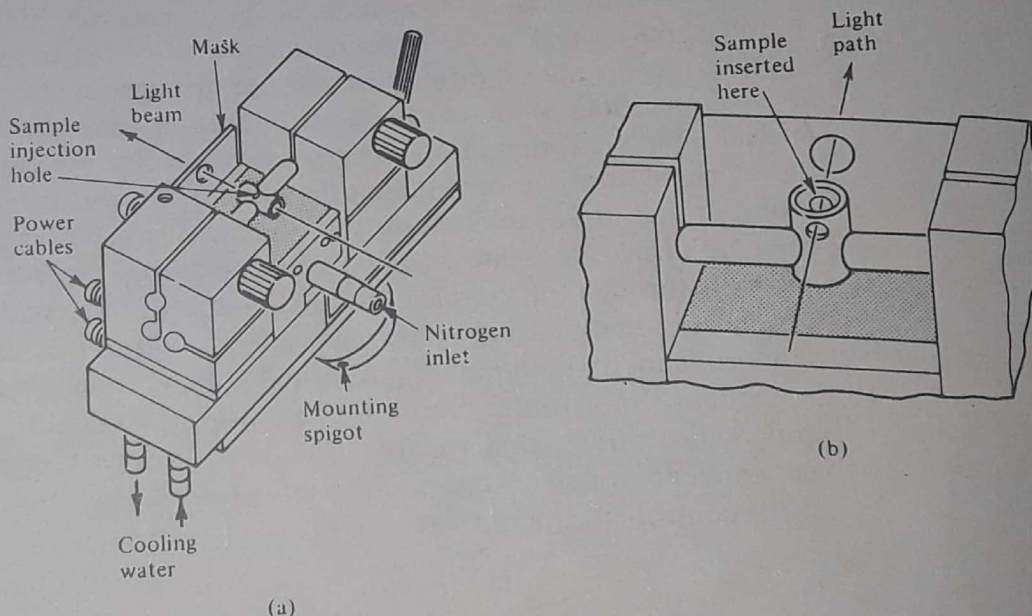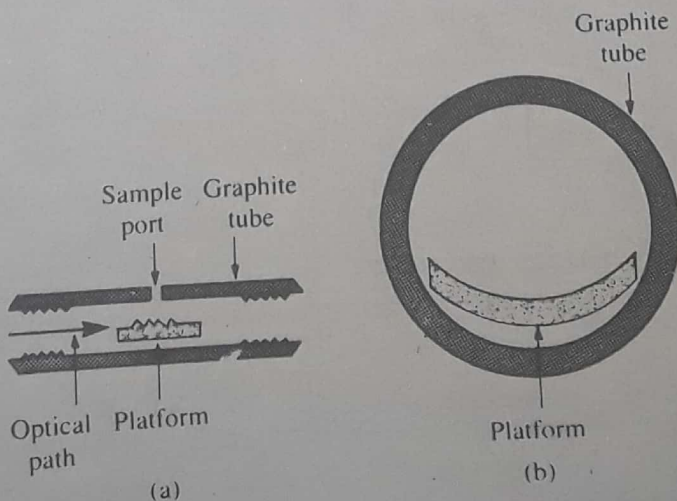

(a)

(b)

FIGURE 9.9

(a) The modified L'vov platform. Side view of the platform position within the graphite tube. Tube dimensions, 28 × 6 (i.d.) mm. Platform dimensions, 7 × 5 mm. (b) The modified L'vov platform, end view. [After S. R. Koirtyohann and M. A. Kaiser, *Anal. Chem.*, 54(14), 1518A (1982), by permission.]

(a)

(b)

temperature before the sample is atomized. This technique requires fast recording of the absorbance signal, since the peaks appear and disappear rapidly.

After insertion or injection of the sample into the electrothermal atomizer, a heating sequence is initiated to take the sample through three steps: dry, ash or char, and atomize (Figure 9.10). The control of heating is independently programmable, with a temperature ramp and isothermal hold time available for each step. In the drying cycle, the sample is heated for 20–30 sec at 110–125 °C to evaporate any solvent or extremely volatile matrix components. The sample that remains after this step appears as a slight stain or crust on the interior of the graphite tube or rod. The ash or char cycle is performed at an intermediate temperature selected to carry out the necessary processes, volatilization of higher-boiling matrix components and pyrolysis of matrix materials such as fats and oils that will crack and carbonize. This step often converts the analyte to a different chemical state. The obvious problem at this stage is loss of analyte if the ashing temperature is too high or is maintained for too long.

In the final stage, the optimum maximum power is applied to raise the furnace unit to the selected atomization temperature. In this step the analyte residue is dissociated and volatilized into free atoms responsible for the observed absorption. The transient signal produced by the brief period of absorption provides the output to the recorder or microcomputer data processing system. Both peak height and peak area have been used to determine the concentration of analyte.

The proper temperature and timing parameters must be carefully selected for each step in the electrothermal process. The identity of the analyte and the composition of the sample matrix are the most important factors in choosing these parameters. The evaporation of solvent in the drying cycle must be smooth and gentle to avoid mechanical losses by foaming or splattering. The progress of the drying step can be observed by monitoring the absorption signal without background correction. The escaping vapors should produce a smooth curve without the appearance of humps or spikes, which indicate that the heating rate is too rapid. The ashing cycle is followed in the same way; usually no analyte is lost

FIGURE 9.10

Temperature profile with ramp heating. (Courtesy of Pye Unicam.)
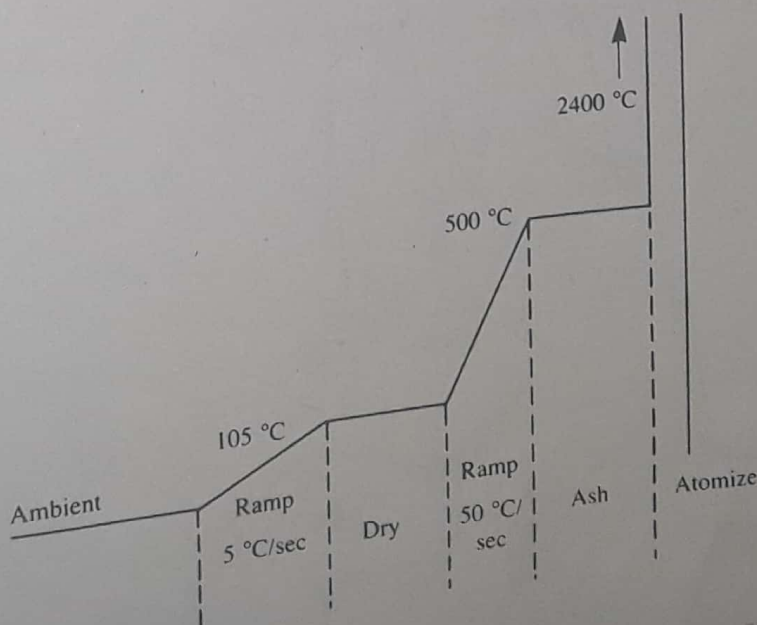
until a specific temperature is reached, and then the analyte signal appears in the form of a sharp peak (Figure 9.11). Most organic materials pyrolyze at around 350 °C, leaving a residue of amorphous carbon. At this temperature, a stream of air or oxygen may be introduced into the furnace to convert this carbon residue into carbon dioxide.

A wide variety of samples can be handled directly with little or no pretreatment required. These include organic solvents, viscous liquids, liquids that contain a high concentration of dissolved solids, and pulverized solids. The ashing step destroys organic components, thus eliminating the need for pretreatment of these samples. In contrast to flame AAS, the lifetime of the free atoms in the optical path is short, approximately $\frac{1}{100}$ sec or less. The absorption signal must be measured rapidly, requiring fast response from both the detector and recording system. Care should be exercised in replacing a flame atomizer with an electrothermal atomizer. In many cases the response time of an instrument adequate to measure the relatively stable signal from analyte absorption in the flame is not fast enough to measure the transient signal from an electrothermal atomizer.

The deterioration of the atomizer surface with use creates two major problems that directly affect analytical results. First, the peak height for a given concentration of analyte decreases with use, and second, the electrical resistance of the atomizer changes. These effects are minimized by preheating the graphite to form a hard pyrolytic layer on the surface. This coating prevents the sample from soaking into the graphite and thus gives more reproducible atomization for carbide-forming elements. The operational lifetime of the tube or furnace surface is also prolonged.

Accurate temperature sensors are required for control of the power source. Recently, silicon photodiodes have been used for sensing and controlling temperatures of 600–3000 °C. These diodes have the rapid response times needed for the precise reproduction of heating conditions. The response times of thermocouples are usually too slow for tight control of heating.

FIGURE 9.11

Appearance of analyte peak after matrix smoke. (Courtesy of Pye Unicam.)

Start of
atomization
sequence

Matrix
smoke

Analyte
peak
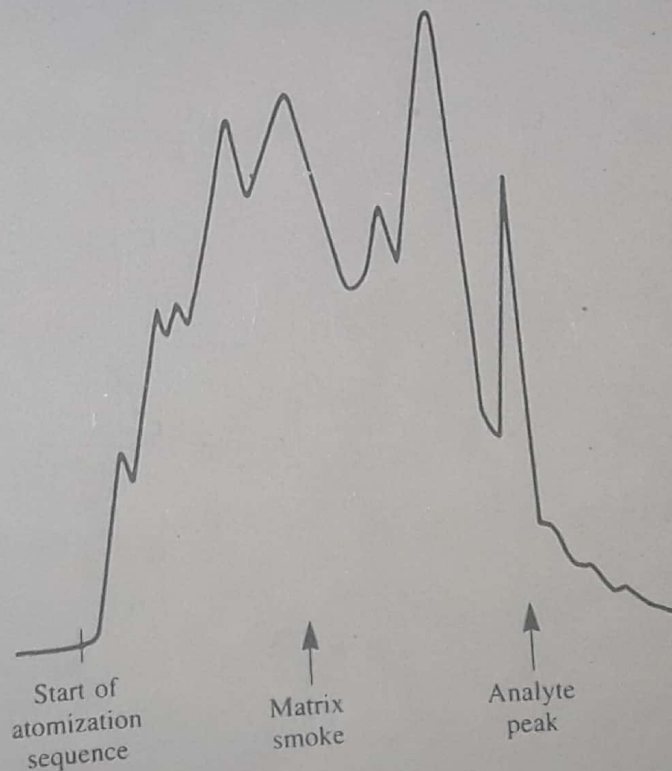
Electrothermal atomizers lead to background absorption due to incomplete combustion or decomposition of molecules during the final atomization step. In addition, residual ash and solvent materials may be present and contribute to the background through partial decomposition. This background absorption can be large and is often variable, depending on the analyte matrix. Thus it is necessary to provide a means for background correction. Recently, very rapid heating systems have been shown to reduce matrix effects.

Substitution of the graphite furnace by a tungsten ribbon creates a less expensive atomizer with a reduction in electrical power consumption and elimination of water cooling (Figure 9.12).[7] The tungsten atomizer has the following advantages over conventional graphite furnaces: (1) reduction in matrix interferences due to the faster heating rates of tungsten (6000 °C/sec), (2) elimination of memory effects and interference because tungsten is less porous than any form of graphite, and (3) increased sensitivity and lower detection limits. In most applications the sample is injected directly into the cell that contains the heated tungsten filament. Arsenic, selenium, and mercury are analyzed by using nickel, silver, and selenium, respectively, as matrix modifiers, and then injecting the analyte solutions directly. This technique eliminates the need for hydride-generation and cold-vapor attachments for the analyses of As, Se, and Hg.

Chemical Vaporization.[8]   For elements (As, Bi, Ge, Sb, Se, Sn, and Te) that form volatile, covalent hydrides, the technique of hydride formation and subsequent analysis improves the atomization efficiency by quantitatively transferring the analyte as a hydride into the vapor phase. Electrodeless discharge lamps are often used as sources for this technique to provide the higher intensity required for elements such as As and Se. Chemical vaporization offers improved detection limits for the elements listed above as well as for the direct determination of elemental mercury.

Most AAS instrument manufacturers offer apparatus for the chemical pretreatment of samples to generate a volatile product that is then subjected to AAS measurement. The apparatus consists of a vapor-generation unit in which a metallic hydride or mercury vapor is produced. The vapors are then injected into the atomizer in a stream of insert gas. Commonly used atomizers for hydrides are either

FIGURE 9.12
Use of a tungsten ribbon instead of a carbon furnace avoids the need for high electrical current. The standard filament reaches 2400 °C at 6000 °C/sec.
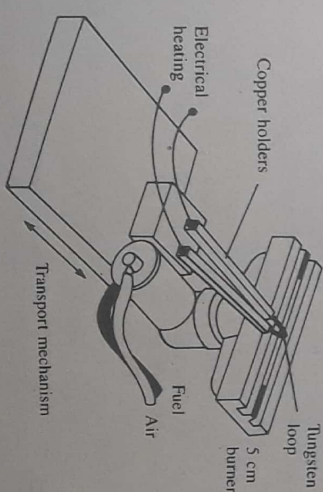
an air/hydrogen flame or a relatively low-temperature, tube-type quartz furnace. Gaseous hydrides may be generated with sodium borohydride, dispensed in pellet form, as the reducing agent added to an acidic solution. The atoms in mercury vapor generated by heating or chemical reaction may be analyzed directly without further atomization.
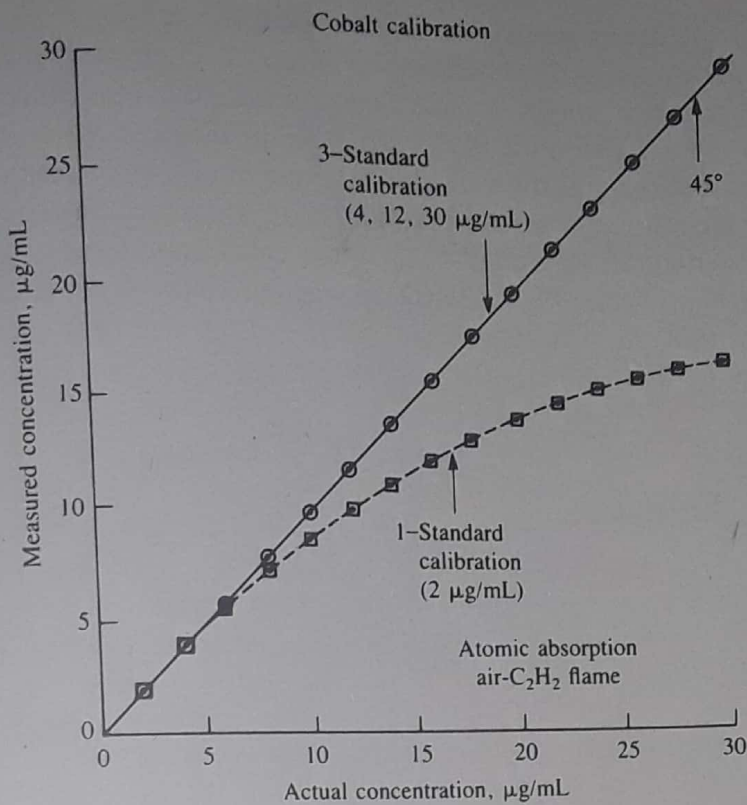
Spectrometers

The spectrometers used to isolate the wavelengths of interest for a specific determination are described in Sections 9.4 and 9.5. These components are similar to those used in visible and ultraviolet instruments discussed in Chapter 6.

Detector-Readout Unit

Since the wavelengths of the analytical resonance lines fall in the ultraviolet-visible portions of the spectrum, the most common detectors for AAS, AFS, and FES are photomultiplier (PM) tubes (see Chapter 6). Care must be taken never to exceed the saturation limit of the PM tube by flooding it with light, too much radiation from the flame, or a high concentration of sample components, even though these signals are eliminated by modulation in the final signal readout. When the electronic noise in the detector-amplifier system can be reduced to a negligible level, scale expansion can be used profitably. With this technique, the zero point is displaced off-scale by applying a potential opposite to the signal arriving from the detector. Thus, the full scale of the readout device can be used as the upper end of a greatly expanded scale. In AAS, the reading for small decreases in transmitted radiation may be increased manyfold.

In a single-beam instrument, noise originating in the flame can be minimized by a chopper that modulates radiation from the sample, P, and reference P_0, so that the alternating beams strike the detector at a frequency determined by the speed of the beam chopper (see Section 2.5). Current from the PM tube is converted to a voltage using a high resistance in the feedback loop of an operational amplifier. After P and P_0 have been demodulated, the absorbance is calculated by taking the difference, $\log_{10} P_0 - \log_{10} P = \log_{10}(P_0/P)$. Sample absorbance may be measured and averaged for different periods of time. These integration times typically range from 0.1 to 90 sec. Long integration times are desirable for optimizing the S/N ratio. Integrating dc signals for precisely limited time periods is a powerful method of reducing noise (see Sections 2.5 and 2.6).

Although many instruments have the computational capability to correct for nonlinear calibration curves in regions of high analyte concentrations, this function is most easily performed by microcomputer-controlled instruments. In the linear region, data from one standard and a blank are sufficient to define the relationship between concentration and absorbance. In nonlinear regions, three standards and a blank are usually sufficient to permit a software curve-corrector algorithm to function accurately (Figure 9.13). It is important that these algorithms have a threshold control to allow the analyst to adjust the calibration curve in only the region of nonlinearity. Even though the software is capable of fitting curves in the nonlinear regions, it is unwise to run samples with absorbances that fall in the upper portion of the curved segment of the calibration curve. In this region the absorbance

Cobalt calibration

change per unit concentration (sensitivity) becomes small and therefore the uncertainty of the measurement becomes large.

FLAME EMISSION SPECTROMETRY[9]

In flame emission spectrometry, the sample solution is nebulized (converted into a fine aerosol) and introduced into the flame where it is desolvated, vaporized, and atomized, all in rapid succession. Subsequently, atoms and molecules are raised to excited states via thermal collisions with the constituents of the partially burned flame gases. Upon their return to a lower or ground electronic state, the excited atoms and molecules emit radiation characteristic of the sample components. The emitted radiation passes through a monochromator that isolates the specific wavelength for the desired analysis. A photodetector measures the radiant power of the selected radiation, which is then amplified and sent to a readout device, meter, recorder, or microcomputer system. A typical FES instrument is shown in Figure 9.14.

The radiant power of the spectral emission line that appears at frequency v, I_v, is determined by the number of atoms that simultaneously undergo the spectral transition associated with the emission line. It is given by the expression

$$P_v = \frac{V \cdot A_t \cdot h \cdot v \cdot N_0 \cdot g_u \cdot e^{-E/kT}}{B(T)} \tag{9.2}$$

where V is the flame volume (aperture ratio) viewed by the detector, A_t is the number of transitions each excited atom undergoes per second, N_0 is the number of free

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analyte atoms present in the electronic ground state per unit volume (which is proportional to the concentration of analyte in the sample solution nebulized), g_u is the statistical weight of the excited atomic state, k is the Boltzmann constant, T is the absolute temperature, $B(T)$ is the partition function of the atom over all states, and E is the energy of the excited state. Equation 9.2 indicates that the higher the flame temperature, the greater the number of atoms in the excited state. The ratio of excited atoms to ground-state atoms under conditions of thermal equilibrium is given in Table 9.5 for selected emission lines of some commonly determined elements.

FIGURE 9.14

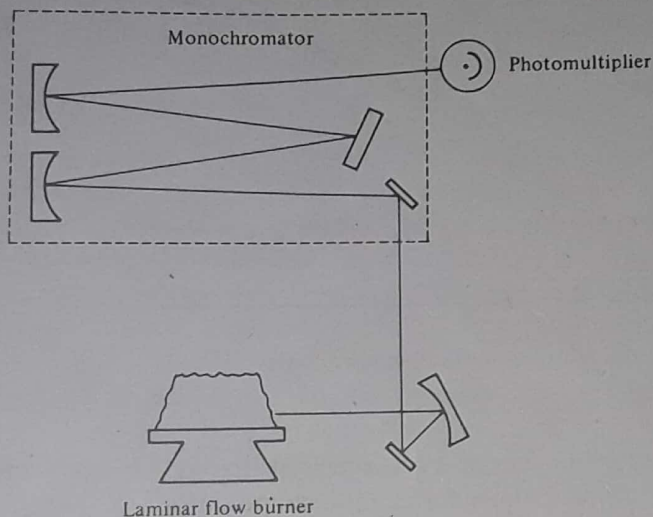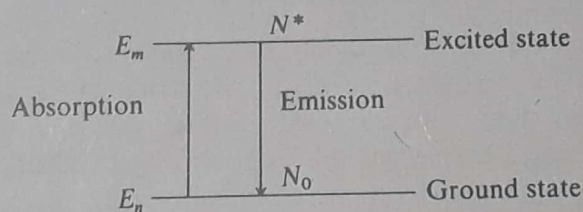Schematic arrangement of a flame emission spectrophotometer.

TABLE 9.5

VALUES OF N^*/N_0 FOR VARIOUS RESONANCE LINES

$$N^*/N_0 = (g_m/g_n)e^{-\Delta E_u/kT}$$

Resonance line		g_m/g_n	ΔE (in eV)	N^*/N_o 2000 K	3000 K
Cs	8521	2	1.45	4.44×10^{-4}	7.24×10^{-3}
Na	5890	2	2.10	9.86×10^{-6}	5.88×10^{-4}
Ca	4227	3	2.93	1.21×10^{-7}	3.69×10^{-5}
Fe	3720		3.33	2.29×10^{-9}	1.31×10^{-6}
Cu	3248	2	3.82	4.82×10^{-10}	6.65×10^{-7}
Mg	2852	3	4.35	3.35×10^{-11}	1.50×10^{-7}
Zn	2139	3	5.80	7.45×10^{-15}	5.50×10^{-10}

[A grating spectrometer, equipped with a laminar flow burner and a good detection-readout system, serves equally well for FES and flame AAS because both require the measurement of the intensity of selected wavelengths of radiation that emerge from the flame. The wavelengths usually fall into the visible or ultraviolet region] and the resulting photons are detected by photomultiplier tubes (see Chapter 6). [FES requires a monochromator capable of providing a bandpass of 0.05 nm or less in the first order.] Slits should be adjustable to allow for greater radiant power for situations where high resolution is not required. Spectrometers of 0.33–0.5 m focal length with adjustable slits meet these requirements. [The instrument should have sufficient resolution to minimize the flame background emission] and to separate atomic emission lines from nearby lines and molecular fine structure. In contrast, emission band spectra from molecular species show up more clearly with instruments of low dispersion. The ability to scan a portion of a spectrum is often a desirable instrumental feature. Proper positioning of the flame to ensure sampling of the optimum flame zone is important. The best entrance optics design just fills the monochromator optics with a solid angle of radiation. At a high aperture ratio, the limit of detection is restricted, not by the shot noise of the photodetector, but by the instability of the flame and the flicker noise of emission from the matrix.

Background correction in FES can be accomplished with a dual-channel instrument (see Section 9.6). One channel is tuned to the emission line of the analyte and the other is set to a nearby wavelength where analyte emission is not observed, but where background emission from the flame or continuum is measured. The analytical signal is the difference in the intensities from the two wavelengths. The Zeeman method of correction (Section 9.6) can also be applied to FES measurements.

ATOMIC ABSORPTION SPECTROMETRY[10,11]

The absorption of radiation by atoms in the sun's atmosphere was first observed in 1814. However, it was only in 1953 that an Australian physicist, Alan Walsh, demonstrated that atomic absorption could be used as a quantitative analytical tool in the chemical laboratory. Today AAS is one of the most widely used methods in analytical chemistry.

The AAS phenomenon can be divided into two major processes: (1) the production of free atoms from the sample and (2) the absorption of radiation from an external source by these atoms. The conversion of analytes in solution to free atoms in the flame was discussed earlier in this chapter.

The absorption of radiation by free atoms (those analyte atoms removed from their chemical environment but not ionized) in the flame involves a transition of these atoms from the highly populated ground state to an excited electronic state (see Section 5.3). Although other electronic transitions are possible, the 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. Usually the transition between the ground state and the first excited state, known as the first resonance line, is the line with the strongest absorptivity. The

absorptivity for a given element decreases as the energy difference between the ground state and the excited states increases. All other factors being equal, if an analysis requires high sensitivity, the first resonance line of the analyte is used.

The wavelength of the first resonance line for all metals and many metalloids is longer than 200 nm, the short wavelength limit for operation in the conventional ultraviolet region. The first resonance line for most nonmetals falls into the vacuum ultraviolet region below 185 nm and, therefore, cannot be measured with conventional spectrometers) Thus AAS instrumentation finds wide application for the analysis of metals and metalloids. The optical systems of AAS instruments can be modified to detect resonance lines of nonmetals (<200 nm), but these modifica-tions add a significant expense to the instrument and are not commonly used.

For AAS to function as a quantitative method, the width of the line emitted by the narrow-line source (see Section 9.3) must be smaller than the width of the absorption line of the analyte in the flame (Figure 9.15). The shape of the spectral line emitted by the source is a critical parameter in AAS. The flame gases are considered as a sample cell that contains free, unexcited analyte atoms capable of absorbing radiation at the wavelength of the resonance line emitted by the external source. Unabsorbed radiation passes through a monochromator that isolates the resonance line and then into a photodetector that measures the power of the trans-mitted radiation. Absorption is determined by the difference in radiant power of

FIGURE 9.15

Atomic absorption mea-surements and results.

$$A = \log\left(\frac{P_0}{P}\right) = \epsilon bc$$
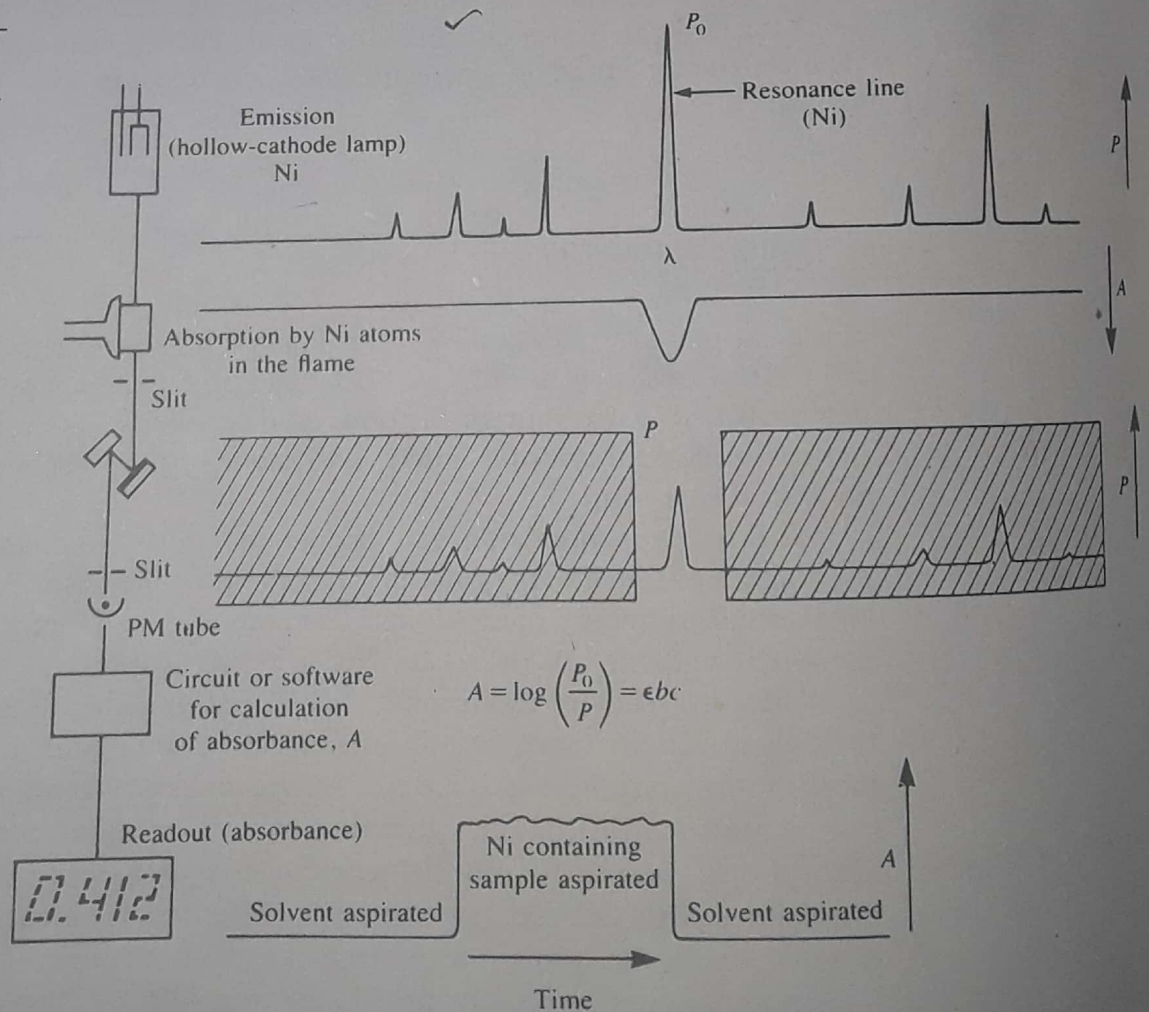
the resonance line in the presence and absence of analyte atoms in the flame. Instrumentation for AAS is shown in Figure 9.16.

Transitions from the ground state to the first excited state occur when the frequency of incident radiation from the source is exactly equal to the frequency of the first resonance line of the free analyte atoms. Part of the energy of the incident radiation, P_0, is absorbed. The transmitted power, P, may be written

$$P = P_0 e^{-(k_v \cdot b)} \tag{9.3}$$

where k_v is the absorption coefficient of the analyte element and b is the average thickness of the absorbing medium—that is, the horizontal path length of the radiation through the flame. Around the center of the resonance line there is a finite band of wavelengths caused by absorption line broadening within the flame and also broadening associated with the emission source. The two principal causes of line broadening are Doppler (see p. 248) and Lorentz, or pressure broadening. Lorentz broadening is caused by collisions of the absorbing atoms with other molecules or atoms present in all flames. These collisions cause the analyte atoms to have a small range of energies centered on the resonance frequency, resulting in a broadening of the resonance line.

For Equation 9.3 to be valid, the bandwidth of the incident radiation from the source absorbed by the analyte atoms must be narrower than the absorption line of the analyte. This means that the line width of the primary radiation source must be less than 0.001 nm, the usual width of resonance lines found in the absorption spectra of free atoms (Figure 9.15). This requirement on the width of resonance lines emitted from the source arises because all but the most expensive monochromators have bandpasses greater than 0.01 nm. Walsh demonstrated that a hollow cathode made of the same element as the analyte emits lines that are narrower than the corresponding atomic absorption line width of the analyte atoms in the flame. This is the basis for current commercial AAS instrumentation.

Specifications for a typical atomic absorption spectrophotometer might include a 0.33–0.5-m focal length Czerny-Turner monochromator with a 64 × 64-mm grating ruled with 2880 grooves/mm and blazed at 210 nm to cover a range of

Optical diagrams of (a) a single-beam and (b) a double-beam atomic absorption spectrometer. (Courtesy of Instrumentation Laboratories, Inc.)
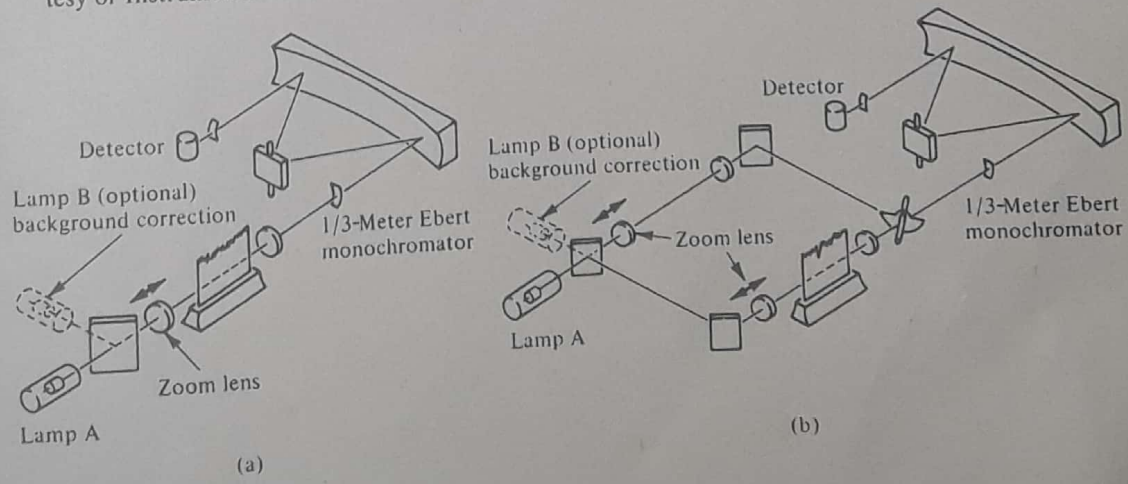
wavelengths of 190–440 nm. A second grating, ruled with 1440 grooves/mm and blazed at 580 nm, covers the range of 400–900 nm. The two gratings are often mounted back-to-back on a turntable. Spectral bandwidths should be 0.03–7 nm in the ultraviolet and 0.06–14 nm in the visible region. They should be keyboard- or switch-selectable. The geometry of the beam of radiation must be designed to provide optimum performance with both flame and electrothermal atomizers. Optical elements are needed to focus an image of the source lamp on the flame (or furnace), collect a small solid angle of radiation from the flame (or furnace), and provide sufficient radiant flux at the photodetector. Such a system minimizes the effect of radiation produced by thermal emission of analyte atoms in the flame. One design has a zoom lens system to produce optimum transmission of radiation for any resonance line.

The more sophisticated AAS system shown in Figure 9.17 is a two-channel, double-beam, microcomputer-controlled spectrophotometer capable of background correction in either one or two channels (see Section 9.6). The instrument can determine two elements simultaneously, thereby doubling the speed of single-element instruments. Alternatively, analytical accuracy can be improved by using the element in one channel as an internal standard (see Section 2.8). In another operating mode, the instrument can extend the analytical range of a given element; the same element is determined in both channels but with resonance lines of different sensitivity. It is also possible to determine the ratios between the concentrations of two elements, an internal standard and the unknown. This operating mode minimizes errors that result from fluctuations in flame conditions, aspiration rate, sample viscosity, and temperature of the sample solution.

The microcomputer contained in an AAS system (see Section 4.6) enables the instrument to calculate the best analytical curves in one or both channels using up to five standards, compute ratios, apply appropriate statistical techniques, and present

FIGURE 9.17

Optical schematic of a two-channel, double-beam atomic absorption spectrometer. (Courtesy of Instrumentation Laboratories, Inc.)
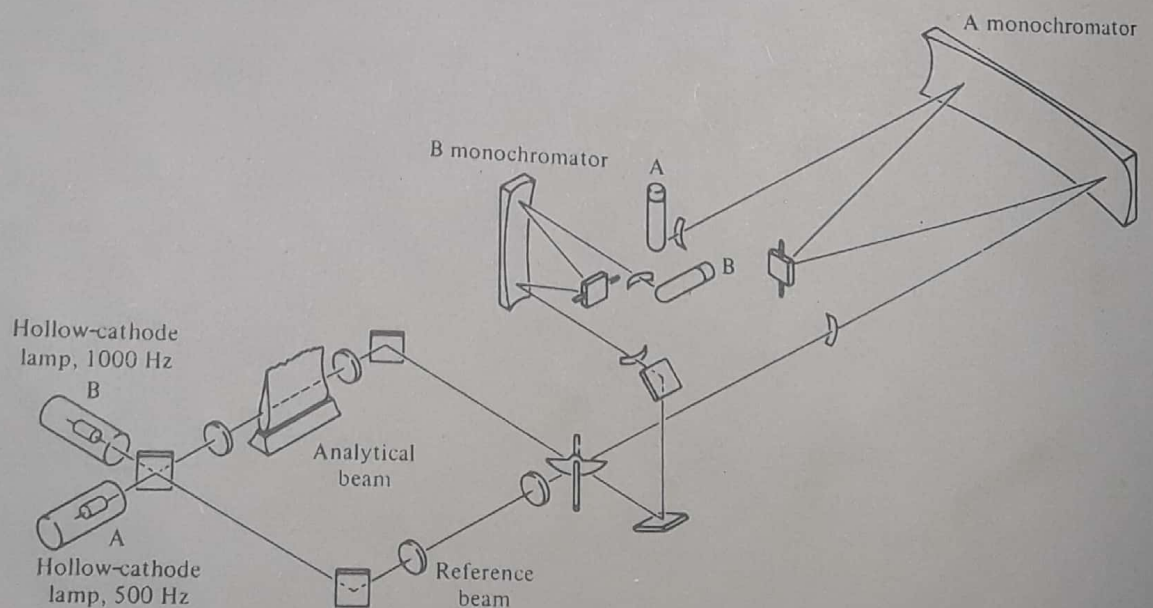
results in graphical or tabular form. In addition the microcomputer can be programmed to handle routine tasks associated with any determination: selection of the resonance wavelength, slit width, fuel and oxidant flows, burner height, lamp current, and electrothermal furnace operating parameters.[12] A deuterium lamp, used for background correction, can be applied independently to either or both channels (see Section 9.6).

The hollow-cathode lamp has become the source most often used in AAS. The electrodeless discharge lamp provides a more intense and stable source for certain elements in AAS; it is also the source of choice for atomic fluorescence measurements.

A hollow-cathode lamp has a Pyrex body with an end window of quartz. Within, an anode wire is positioned along the outside of the cylindrical cathode, as shown in Figure 9.18. The cathode is made of (or lined on the interior with) the element to be determined. The lamp is evacuated and filled with an inert gas, usually argon or neon, at a pressure of 4–10 torr. Lamps operate at currents below 30 mA and voltages up to 400 V. Discharge occurs between the two electrodes, ionizing some of the inert fill gas atoms. The cathode (40 mm i.d.) is bombarded by these energetic, positively charged, inert gas ions. The ions are accelerated toward the cathode surface by the electrical potential that exists between the two electrodes. When the positively charged ions collide with the negatively charged cathode surface, the metal atoms of the cathode are ejected (sputtered) into the gaseous atmosphere inside the lamp. Here, the metal atoms absorb energy by colliding with fast-moving filler gas ions, are elevated to excited electronic states, and finally return to the ground state by emitting radiation characteristic of the metallic cathode.

With lamps that contain elements with high ionization potentials, neon is used as the fill gas. Neon improves the intensity of the emitted resonance lines, since its ionization potential is greater than that of argon. Argon is usually used only when there is a neon line in close proximity to a resonance line of the cathode element. When the cathode is formed into a cylinder or cup, the discharge tends to concentrate in the cup. In this configuration more efficient sputtering and excitation occur. The addition of a protective shield (nonconductive) of mica around the outside of the cathode just behind the lip of the cup causes the lamp to radiate more intensely by preventing spurious discharges around the outside of the cathode.
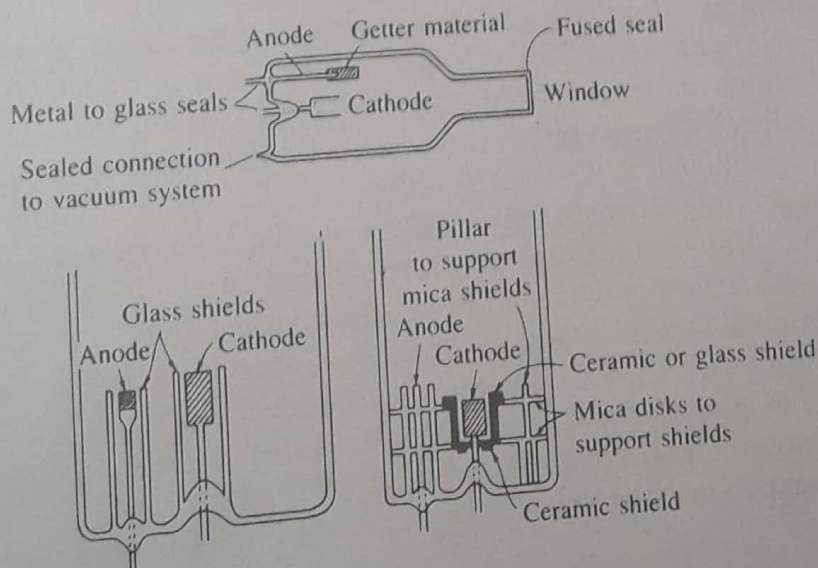

FIGURE 9.18

Schematic diagram of shielded-type hollow-cathode lamp.

Cathode construction differs for various metals. If the metal is easily worked, the entire cathode may be made from it. If an expensive metal is involved, a thin liner of the metal is inserted into a copper cathode. (Consequently, copper resonance lines appear in the spectrum of many lamps.) When the metal's melting point is low, a cuplike carrier electrode is used. For hard or brittle metals, an alloy or sinter of pressed metal powder is used. Multielement lamps are also constructed in this fashion using metal powders.

As mentioned, the shape of the spectral line emitted by the source is an important parameter in AAS determinations. Although increasing the lamp current beyond a certain optimum value increases its output intensity, the sensitivity for many elements is reduced through line broadening or self-reversal. Doppler broadening is caused by the motions of the radiating atoms as a result of thermal activity at the hot cathode. For a given emission line, the line broadening is proportional to the square root of the temperature. Thus, to produce the required narrow emission lines, the temperature of the radiating plasma near the cathode must be kept as low as possible. This is done by keeping the lamp current small. Self-reversal or self-absorption is caused by the absorption of radiation by unexcited atoms in the source lamp. These unexcited atoms of the cathode material exist in the cooler portions of the lamp. Reduction of line intensity due to self-reversal is proportional to the length of the path traveled by emitted radiation in the lamp and the lamp current. Good lamp design can minimize this type of absorption by reducing the path length and reducing lamp current.

A liability of AAS is the need (usually) for a different hollow-cathode lamp for each element to be analyzed. On the positive side, these light sources with their narrow emission line widths provide virtual specificity for each element. Multiele-ment lamps are available for a few combinations of elements. The cathode is made from sections or rings of the different elements or from an alloy or pressed powder that contains the elements blended so as to obtain emission lines of equal intensity from each element. During the lifetime of the lamp, the more volatile metal sputters at a faster rate and slowly covers the other elements. This leads to an increase in intensity of the volatile element and a steady decrease in the intensities of the other elements. In general, multielement lamps sacrifice some sensitivity when compared with single-element lamps.

Another approach in overcoming the single-element, single-lamp problem is the lamp turret accessory. Up to six individual lamps are located in the turret and are kept at the correct operating currents for the elements involved, thus eliminating delays caused by warming up the lamps. Computer-controlled rotation of the turret brings the lamp for the element selected into the source position and no further adjustment is required. This accessory is invaluable when several elements are to be determined in the same solution. All types of hollow-cathode lamps have finite operating lifetimes; they are often warranted for 5000 mA-hr.

For volatile elements, where reduced intensity and short lamp life are problems with hollow-cathode lamps, an electrodeless discharge lamp offers an alternative source. This lamp has also found application in AFS where its high-intensity output improves the determinations. Electrodeless discharge lamps are fabricated by sealing small amounts of the metal, iodine (or the more volatile metal iodide salt), and argon at a low pressure in a small quartz tube. This tube is placed inside a ceramic cylinder on which an antenna from a microwave generator (2450 MHz,

RF coil

Quartz window

Lamp

Ceramic holder
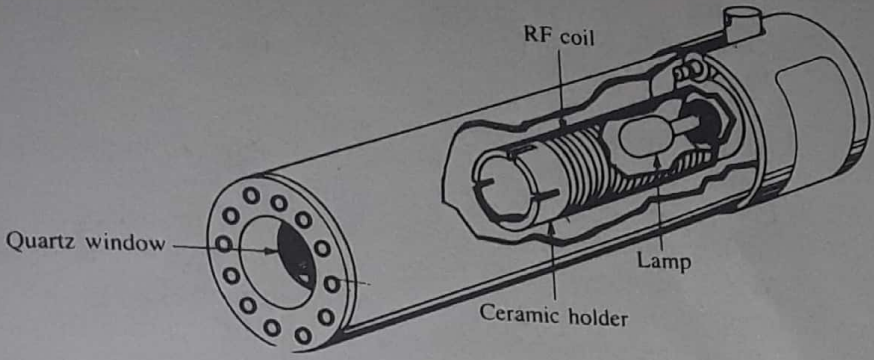
200 W) is coiled (Figure 9.19). When an alternating field of sufficient power is applied, the coupled energy vaporizes and excites the atoms inside the tube, thus producing their characteristic emission spectrum. Lamp temperature is an important operating parameter; an increase in temperature of 130 °C can effect a 1000-fold increase in line intensity. Optimum temperature varies with different elements.
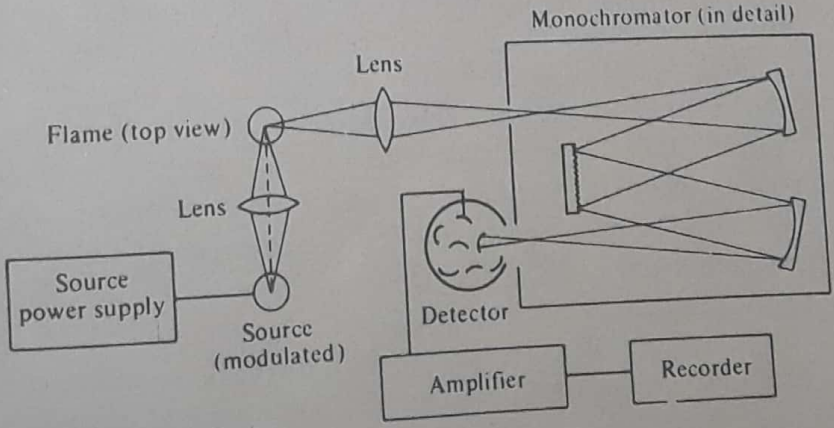
Electrodeless discharge lamps cannot be powered with hollow-cathode tube power supplies; a separate power supply must be provided. Warm-up periods of 30 min are required to stabilize the lamp output.

ATOMIC FLUORESCENCE SPECTROMETRY[13,14]

The basic principle of atomic fluorescence spectroscopy (AFS) is the same as that of molecular fluorescence described in Chapters 5 and 8. Free analyte atoms formed in a flame absorb radiation from an external source, rise to excited electronic states, and then return to the ground state by fluorescence. AFS offers the same advantages over AAS for trace analysis that molecular fluorescence has over ordinary absorption spectroscopy; the radiation from fluorescence is measured (in principle) against a zero background, whereas ordinary absorption measurements involve the ratio of two signals.

In AFS the exciting source is placed at right angles to the flame and the optical axis of the spectrometer (Figure 9.20). Some of the incident radiation from the

IGURE 9.20
chematic diagram of
quipment for atomic
uorescence spectro-
etry.

Monochromator (in detail)

Lens

Flame (top view)

Lens

Source power supply

Source (modulated)

Detector

Amplifier

Recorder

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source is absorbed by the free atoms of the test element. Immediately after this absorption, energy is released as atomic fluorescence at a characteristic wavelength upon the return of the excited atoms to the ground state.

The best burner system for AFS is probably a combination of acetylene/nitrous oxide and hydrogen/oxygen/argon using a rectangular flame with a premixed laminar flow burner (see Section 9.2). The flame should have a low background and a low quenching cross section, in addition to being efficient in producing a large free-atom population. Although the influence of flame background on detection limits in AFS is most severe with an unmodulated source and dc detection, the presence of intense flame background is a problem even in systems that use modulation. Even though the unmodulated flame background is not amplified directly with ac modulation, its presence results in noise at the output of the amplifier. A commercial instrument for AFS, the Baird atomic inductively coupled plasma system, is discussed in Section 10.4.

The intensity of the fluorescence is linearly proportional to the exciting radiation flux. When there is no analyte, only background radiation from the flame is detected. This difference between AFS and AAS is significant near the analyte detection limit and makes AFS the method of choice for trace analysis for selected metals. AFS exhibits its greatest sensitivity for elements that have high excitation energies.

9.6 INTERFERENCES ASSOCIATED WITH FLAMES AND FURNACES

Essentially the same interferences occur in FES and flame AAS but to different extents. The literature contains many contradictory statements and hasty generalizations based on inadequate measurements and misunderstandings. Interferences can be separated into four general classes: (1) background absorption, (2) spectral line interference, (3) vaporization interference, and (4) ionization effects.

Background Absorption

The background associated with flames is caused by the large number of species present in the flame that are capable of broad band absorption of radiation. The species include metal oxides, hydrogen molecules, OH radicals, and portions of fragmented solvent molecules. Radiation emitted from the hollow-cathode source is absorbed by these species as well as by the analyte atoms. This background absorption results in a direct interference and a corresponding error in analytical results.

In some respects, background absorption in AAS is a more serious problem than in FES because it is likely to go unnoticed. The monochromatic nature of the source negates the need for scanning. Even with automatic background correction, care must be exercised in obtaining measurements. In areas of high background absorption (50%–80%), the signal may be displaced into the high-absorption region (>90%) where measurement error is at a maximum.

A number of techniques correct for background absorption. A solution that contains none of the analyte can be prepared and its absorbance at the resonance

line of the analyte determined. The absorbance of this "blank" solution is then used to correct the measurements obtained from sample solutions. This procedure requires that the matrix of the blank and sample solutions be similar and that the absorption of the blank is indeed a measure of the background absorption. In practice, it is difficult to prepare the solutions required to make accurate background corrections with this procedure.

A more precise technique involves measuring the absorbance at a wavelength close to the resonance line used in the determination. This absorbance measurement is used to correct the absorbance signal at the resonance line. This technique assumes that the variation due to the background absorption is insignificant over the small wavelength difference involved. It allows the correction to be made using only the sample solution. The problem with this technique is locating an appropriate resonance line close to the line used for the determination.

The use of a broad-band, continuous source of radiation in conjunction with the hollow-cathode line source is a popular technique for background correction. The resonance line of the hollow cathode is absorbed by both free analyte atoms and molecular species in the flame. The radiation from the continuous source, usually a deuterium lamp, is absorbed over the entire bandwidth of wavelengths passed by the monochromator, usually 0.1–0.2 nm, while the free analyte atoms absorb in a narrow range (0.005–0.001 nm). Thus, the decrease in the intensity of radiation from the continuous source is due almost entirely to absorption by the components of the background, whereas absorption by the free analyte atoms is negligible. In this situation, absorption of radiation from the deuterium lamp is a measure of the background and the background correction is made at the same nominal wavelength as the resonance line used for the AAS determination.

The use of a broad-band continuous source for background correction can be incorporated into either single-beam or double-beam optical configurations. The modulation frequency used to chop the beams from the radiation sources must provide for fast correction, up to three corrections per 10 msec. This rate of signal correction is required because both the sample and background may change rapidly, especially in the case of electrothermal atomization. At wavelengths in the visible region, additional problems arise because the deuterium source intensity is weaker than the output of many hollow-cathode sources that operate at optimum current levels. Substitution of the deuterium lamp with a 150-W xenon-mercury lamp provides adequate intensity from 200 to 600 nm.

The Zeeman effect on radiation emitted from hollow-cathode tubes has been used to correct for background.[15] If an intense, alternating magnetic field is applied to a hollow cathode, the lamp emits a single line at the resonance frequency and a doublet centered about the resonance frequency but shifted slightly in wavelength from the resonance line by Zeeman splitting (Figure 9.21). The signal from the resonance line is affected by both atomic and background absorption, whereas the signal from the nonresonance doublet is affected only by background absorption. The difference between these signals provides a measurement of the corrected atomic absorption. This technique offers the advantage of using a single radiation source and only one optical path through the atomizer. When separate sources are used, it is sometimes difficult to match exactly the optical paths. A difficulty associated with the technique is that the magnetic field can cause instability in the lamp, resulting in an irregular emission signal.

The pulsed hollow-cathode lamp background correction also uses a single radiation source.[16] Two absorption measurements are made, one with the lamp run at a normal low current value and a second with the lamp pulsed to a large current value. The first measurement indicates the absorbance due to both analyte atoms and background, whereas the second measurement indicates primarily background. (The large current eliminates the resonance line due to self-reversal and thus provides a measurement of the background absorption.) Substraction of these two absorption measurements yields a corrected value for atomic absorption. The lamp must not be pulsed to too high a current or else the tube-life will be shortened. This technique appears to be easier to implement and operate than the Zeeman method.

Spectral Line Interference

Spectral line interferences occur when a line of interest cannot be readily resolved from a line of another element or from a molecular band. Interference of this type is closely associated with the resolving power of the monochromator. Atomic line interferences are more serious in FES, even in those instruments that contain the best monochromators. Their bandpass is still an order of magnitude broader than the line profiles of cathode lamps (typically 0.005 nm) and absorbing atoms in AAS. Molecular spectral interference is also more severe in FES. Chemilumines-cence (see Section 5.4) of molecular fragments formed in the flame gas is a major source of molecular interference. In flame AAS and AFS this interference can be minimized by amplitude modulation of the radiation source. No such possibility exists in FES.

Instances of serious spectral interference in FES involve the manganese triplet (403.1, 403.3, 403.5 nm), the gallium line (403.3 nm), the potassium doublet (404.4,

FIGURE 9.21
Zeeman splitting.
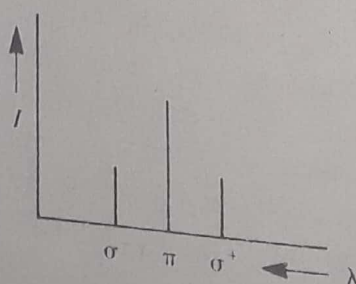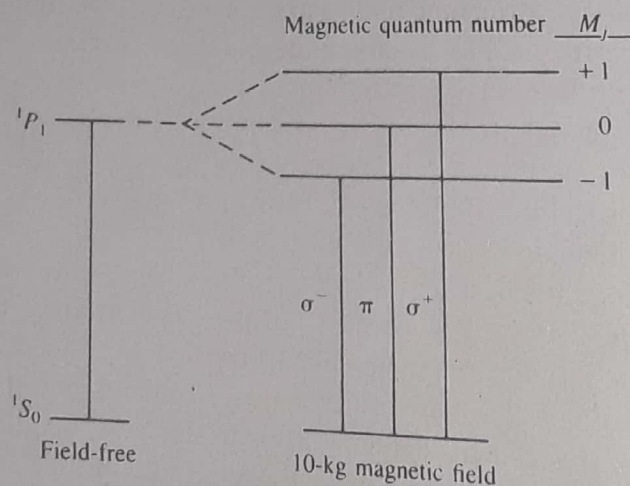
404.7 nm), and the lead line (405.8 nm). The band systems of CaOH extending from 543 to 622 nm interfere with the sodium doublet (589.0, 589.6 nm) and the barium line (553.6 nm).

Vaporization Interference

(Interferences of this type arise when some component of the sample alters the rate of vaporization of salt particles that contain the analyte.)(They arise from a chemical reaction that changes the vaporization behavior of the solid,)or as the result of a physical process in which the vaporization of the matrix controls the release of the analyte atoms.

(Hotter flames tend to minimize vaporization interferences)(Use of the acetylene/ nitrous oxide flame is often justified because it is better for decomposing refractory phosphates, sulfates, silicates, and aluminates)than the cooler acetylene/air flame. The shifting of equilibrium of reactions involving these thermally stable molecules, due to small uncontrolled changes in flame temperatures, influences AAS and FES to similar degrees. Thus, in situations involving thermally stable analyte molecules, AAS results are apparently as dependent on flame temperature as those obtained from FES.

(Metal compounds in the flame are usually simple di- or triatomic molecules such as CaO or CaOH. Elements such as Na, Cu, Tl, Ag, and Zn are almost completely atomized in the flame; they do not form compounds with flame components in noticeable proportions) All(aline-earth elements form monoxides) unless very fuel-rich flames are used. Some metals such as Al and Ti form refractory oxides, which are extremely stable. As a result, the free-atom concentrations of these metals are negligible in flames of stoichiometric composition and moderate temperature. However, these metals may be analyzed in the reducing environment of a fuel-rich acetylene/nitrous oxide flame.

Releasing agents provide a chemical means for overcoming some vaporization interferences by pretreatment of sample solutions. In calcium AAS determinations, a few hundred parts per million of lanthanum or strontium are often added to solutions to minimize interference due to phosphates. At these concentrations, lanthanum or strontium preferentially binds phosphate, thus releasing the calcium for atomic absorption. Calcium is also released from phosphate by complexing the calcium with EDTA. Once in the flame the EDTA is destroyed. The calcium does not reform with the phosphorus entities in the flame gases. Thus, a releasing agent may either combine with the interfering substance or deny the analyte to the interfering substance by mass action. In either situation the analyte is left free to vaporize in the flame.

When the physical characteristics (viscosity and surface tension) of the sample and calibration solutions are different, an interference occurs that affects the rate of nebulization of analyte atoms into the flame (see Equation 9.1) and therefore the rate of vaporization of analyte. Errors caused by this type of interference are minimized by the method of standard additions (see Section 2.8).

Ionization Interference

At elevated flame and furnace temperatures, atoms with low ionization potentials become ionized (Table 9.5). Any ionization reduces the population of both the

ground state and the excited state of neutral free atoms, thus lowering the sensitivity of the determination. This problem is readily overcome by adding an excess (ca. 100-fold) of a more easily ionized element such as K, Cs, or Sr to suppress ionization in both sample and calibration solutions. The more easily ionized atoms produce a large concentration of electrons in the vapor. These electrons, by mass action, suppress the ionization of analyte atoms. Thus, suppressant should be added to samples that contain variable amounts of alkali metals analyzed by acetylene/air flames to stabilize free-electron concentrations. The addition of suppressants is even more important in analyses that require the hotter acetylene/nitrous oxide flames.

9.7

APPLICATIONS

Flame Emission Spectroscopy

Most applications of both FES and flame AAS have been the determination of trace metals, especially in liquid samples. It should be remembered that FES offers a simple, inexpensive, and sensitive method for detecting common metals, including the alkali and alkaline earths, as well as several transition metals such as Fe, Mn, Cu, and Mn. FES has been extended to include a number of nonmetals: H, B, C, N, P, As, O, S, Se, Te, halogens, and noble gases. FES detectors for P and S are commercially available for use in gas chromatography (see Chapter 18).

FES has found wide application in agricultural and environmental analysis, industrial analyses of ferrous metals and alloys as well as glasses and ceramic materials, and clinical analyses of body fluids. FES can be easily automated to handle a large number of samples. Array detectors interfaced to a microcomputer system permit simultaneous analyses of several elements in a single sample.

Atomic Absorption Spectroscopy

AAS has been used for trace metal analyses of geological, biological, metallurgical, glass, cement, engine oil, marine sediment, pharmaceutical, and atmospheric samples. As in FES, liquid samples usually present few problems in pretreatment. Thus, most solid samples are first dissolved and converted to solutions to facilitate analysis. Gas samples are generally pretreated by scrubbing out the analyte and analyzing the scrubbing solution or adsorbing the analytes on a solid surface and then leaching them into solution with appropriate reagents. Direct sampling of solids may be accomplished using an electrothermal furnace.

The chemistry involved in the pretreatment of samples is a vital component of both FES and AAS determinations. In trace analysis, the analyst must be alert to possible sources of sample contamination such as storage containers, impurities in pretreatment reagents and solvents, and incomplete removal of prior samples from the nebulizer system. Careful attention must be given to minimizing contamination from room dust and contact with an analyst's skin or clothing and laboratory glassware.

The detection limits and sensitivities provide a means of comparing the quantitative characteristics of atomic spectroscopic methods for a given element

9.8

(see Section 2.3).[17] Table 9.2 summarizes the detection limits for FES, flame AAS, electrothermal AAS, and AFS. ICP and DCP methods are discussed in Chapter 10.

COMPARISON OF FES AND AAS[18,19]

A comparison of the analytical performances of AAS and FES reveals that the two methods complement each other in many respects. FES is better for determinations that involve alkali, alkaline-earth, and rare earth elements as well as Ga, In, and Tl. Flame AAS permits Ag, Al, Au, Cd, Cu, Hg, Pb, Te, Sb, Se, and Sn to be detected with high sensitivity. The performance of both methods for other elements is similar. The choice of the method depends on the matrix to be analyzed and the sensitivity and the selectivity desired. In routine analyses it is reasonable to combine both methods. FES, however, has one important advantage in that it permits simultaneous quantitative, multielement analyses. AFS exhibits its greatest sensitivity for elements with analytical lines at shorter wavelengths and thus competes more strongly with AAS.

Alkemade has compared FES and flame AAS on a theoretical basis.[20] He showed that AAS can be more sensitive for a given element only if the brightness of the lamp exceeds that of a blackbody at the temperature of the flame, with both measured at the wavelength of the analytical line. For nonthermal sources (electrical discharges), such as hollow-cathode lamps, the spectral radiance of the lamp may be much greater than that of the flame, permitting better performance of AAS at shorter wavelengths. The reader should consult Alkemade's paper for details of commonly accepted fallacies concerning AAS. The higher temperatures of inductively coupled and dc plasmas provide the necessary excitation energies at all wavelengths.

For most elements, the flame is a primary source of noise in FES or flame AAS signals. Since background intensity is considerably greater in FES than in AAS, the flame noise may influence detection limits more strongly in FES. In AAS, the lamp used as a primary radiation source is an additional source of noise. There is no consistent difference in the reproducibility of results between the two methods. Relative standard deviations of 0.5%–1.0% are obtained in favorable cases. Except for work near the detection limit, the instability of the nebulizer and flame is the major contribution to the scattering of results in both methods.

For many elements electrothermal AAS provides lower detection limits than either FES or flame AAS. The analytical trade-offs for these lower limits of detection are a decrease in precision and an increase in the time required for analysis.

PROBLEMS

1. For the analysis of cement samples, a series of standards was prepared and the emission intensity for sodium and potassium was measured at 590 and 768 nm, respectively. Each standard solution contained 6300 μg/mL of calcium as CaO to compensate for the influence of calcium on the alkali readings. The results are shown