Analytical chemistry

Lecture №26

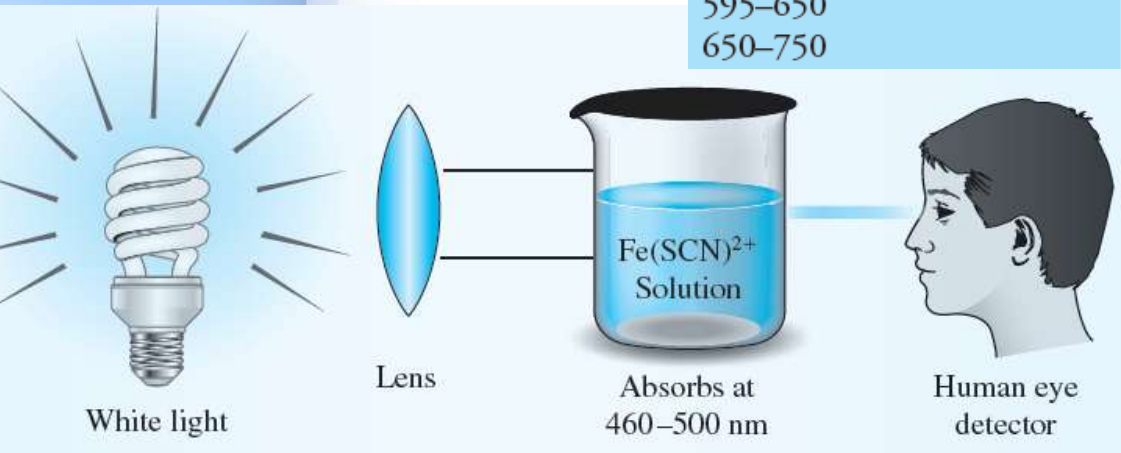
Absorption spectroscopy
Part I

Why is a Red Solution Red?

An aqueous solution of the complex $Fe(SCN)^{2+}$ is not red because the complex adds red radiation to the solvent. Instead, it absorbs green from the incoming white radiation and transmits the red component. Thus, in a colorimetric determination of iron based on its thiocyanate complex, the maximum change in absorbance with concentration occurs with green radiation; the absorbance change with red radiation is negligible. In general, then, the radiation used for a colorimetric analysis should be the complementary color of the analyte solution. The following table shows this relationship for various parts of the visible spectrum.

The Visible Spectrum

Wavelength Region Absorbed, nm	Color of Light Absorbed	Complementary Color Transmitted
400–435	Violet	Yellow-green
435–480	Blue	Yellow
480–490	Blue-green	Orange
490–500	Green-blue	Red
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Blue
595–650	Orange	Blue-green
650–750	Red	Green-blue



White light from a lamp or the sun strikes an aqueous solution of $Fe(SCN)^{2+}$. The fairly broad absorption spectrum shows a maximum absorbance in the 460 to 500 nm range. The complementary red color is transmitted.

ULTRAVIOLET AND ABSORPTION METHODS

The focus of this chapter is photon spectroscopy, using ultraviolet, visible, and infrared radiation. Because these techniques use a common set of optical devices for dispersing and focusing the radiation, they often are identified as optical spectroscopies.

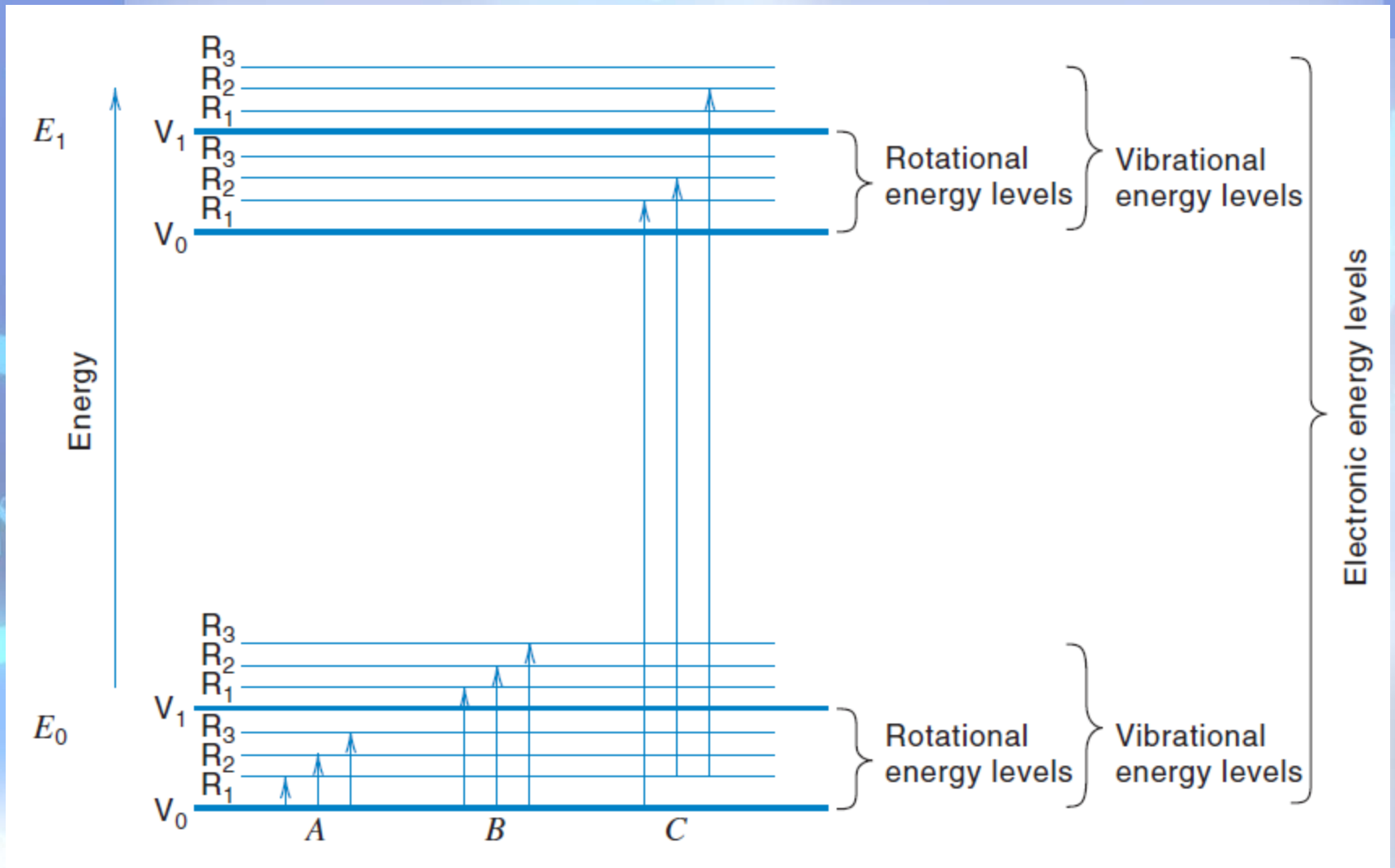
For convenience we will usually use the simpler term "***spectroscopy***" in place of photon spectroscopy or optical spectroscopy; however, it should be understood that we are considering only a limited part of a much broader area of analytical methods.

Type of Energy Transfer	Region of the Electromagnetic Spectrum	Spectroscopic Technique
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis[a]	UV/Vis spectroscopy[b]
		atomic absorption spectroscopy[b]
	infrared	infrared spectroscopy[b]
		raman spectroscopy
	microwave	microwave spectroscopy
		electron spin resonance spectroscopy
	radio waves	nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	atomic emission spectroscopy[b]
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	fluorescence spectroscopy[b]
		phosphorescence spectroscopy[b]
		atomic fluorescence spectroscopy

Molecular Absorption

Usually, a molecule exists in the state of *lowest energy the* ***ground state.*** However, absorption of light of the right frequency (in the UV-region) raises a molecule to an **excited state *i.e., a state of higher energy.***

There are three basic processes by which a molecule can absorb radiation; in all cases, the molecule is raised to a higher internal energy level, the increase in energy being equal to the energy of the absorbed photon *(hv). The three types of* internal energy are **quantized;** that is, they exist at discrete levels**. First,** the molecule ***rotates*** about various axes, the energy of rotation being at definite energy levels, so the molecule may absorb radiation and be raised to a higher rotational energy level, in a **rotational transition. Second,** the atoms or groups of atoms within a molecule ***vibrate*** relative to each other, and the energy of this vibration occurs at definite quantized levels. The molecule may then absorb a discrete amount of energy and be raised to a higher vibrational energy level, in a **vibrational transition. Third,** the outer shell electrons of a molecule, valence ***electrons***, may be raised to a higher electron energy, corresponding to an **electronic transition.** The relative energy levels of the three transition processes are in the order electronic > *vibrational > rotational, each being about an order of magnitude different in its energy level.* Rotational transitions thus can take place at very low energies (long wavelengths, that is, the microwave or far-infrared region), but vibrational transitions require higher energies in the infrared to near-infrared region, while electronic transitions require still higher energies (in the visible and ultraviolet regions). olecule absorbs a photon by undergoing an energy transition exactly equal to the energy of the photon. The photon must have the right energy for this quantitized transition.



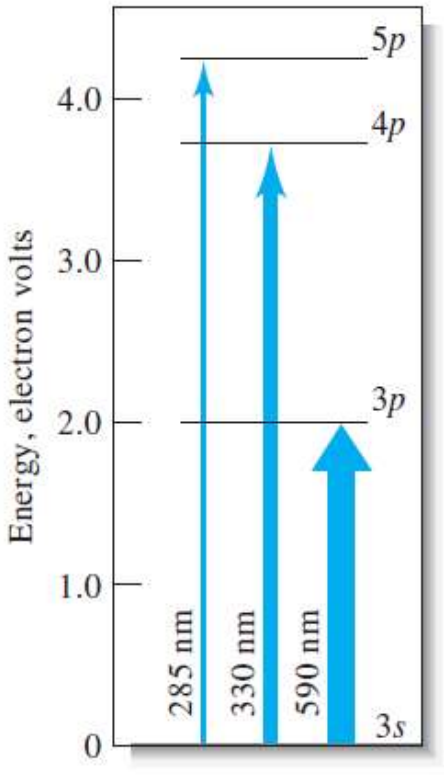
Energy level diagram illustrating energy changes associated with absorption of electromagnetic radiation: ***A***, *pure* rotational changes (far infrared); ***B***, *rotational–vibrational changes* (infrared and near infrared); ***C***, *rotational–vibrational–electronic* transitions (visible and ultraviolet). E_0 *is electronic ground state and* E_1 is first electronic excited state.

A molecule absorbs a photon by undergoing an energy transition exactly equal to the energy of the photon. The photon must have the right energy for this quantitized transition.

The total energy *E associated with a* molecule is then given by

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

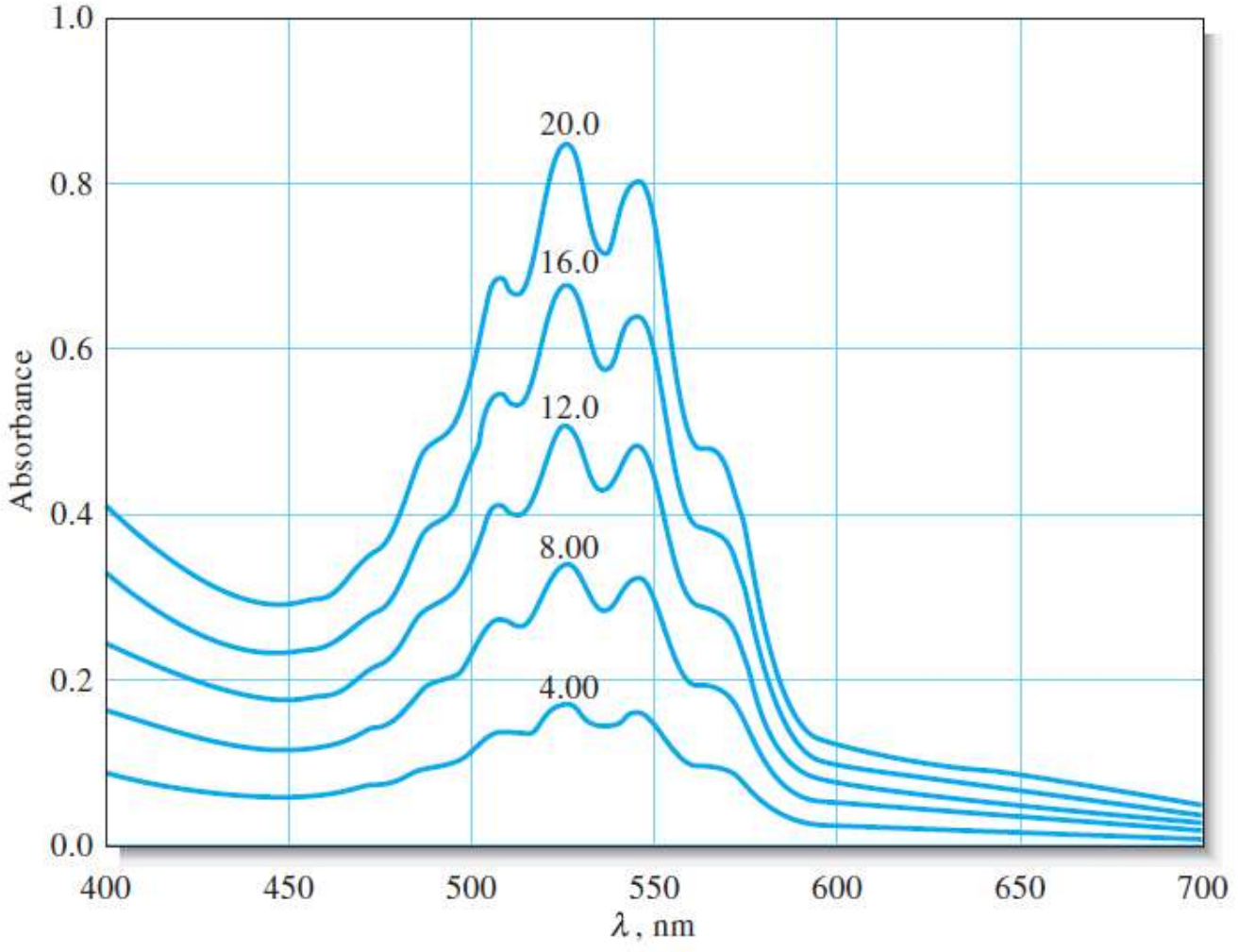
where *Eelectronic is the energy associated with the electrons in the various outer orbitals* of the molecule, *Evibrational is the energy of the molecule as a whole due to interatomic* vibrations, and *Erotational accounts for the energy associated with rotation of the molecule* about its center of gravity.



At still higher energies (visible and ultraviolet wavelengths), different levels of electronic transition take place, and rotational and vibrational transitions are superimposed on these. *This results in an even larger number of possible transitions.* Although all the transitions occur in quantized steps corresponding to discrete wavelengths, these individual wavelengths are too numerous and too close to resolve into the individual lines or vibrational peaks, and the net result is a spectrum of broad *bands of absorbed wavelengths.* Due to lack of fine structure, UV-Visible spectra are not particularly useful for structure determinations.

Discrete electronic transitions (visible and ultraviolet regions) are superimposed on vibrational and rotational transitions. The spectra are even more “smeared.”

An absorption spectrum is a plot of absorbance versus wavelength, as illustrated. Absorbance could also be plotted against wavenumber or frequency. Modern scanning spectrophotometers produce such an absorption spectrum directly. Older instruments sometimes displayed transmittance and produced plots of *T or %T versus wavelength.*



Typical absorption spectra of potassium permanganate at five different concentrations.

Electronic Spectra and Molecular Structure

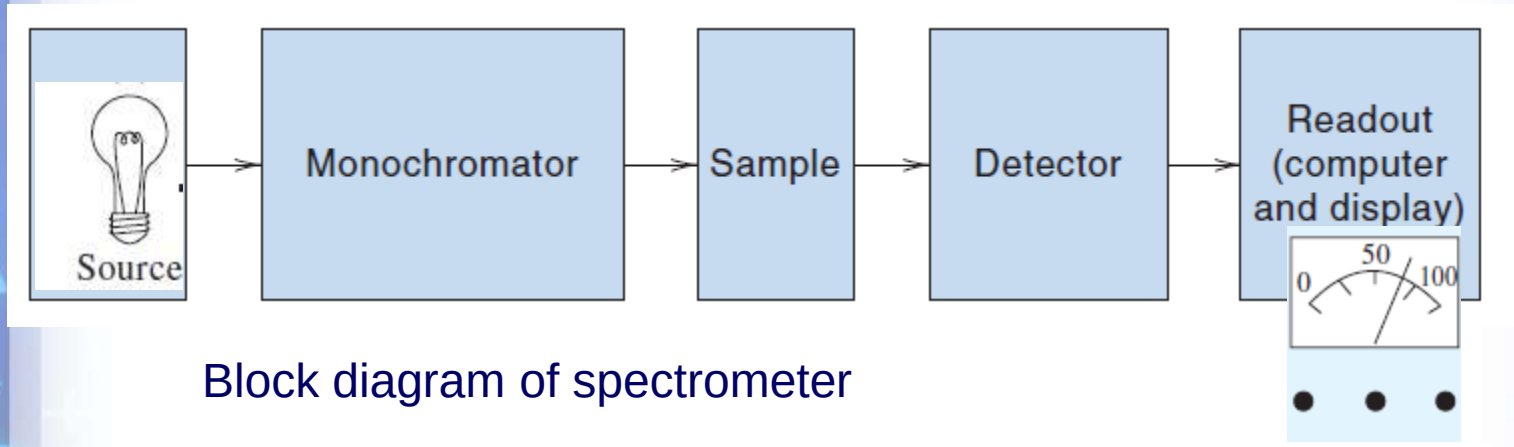
The electronic transitions that take place in the visible and ultraviolet regions of the spectrum are due to the absorption of radiation by specific types of bonds, and functional groups within the molecule. The wavelength and extent of absorption depend on the precise molecular structure. The wavelength of absorption is a measure of the energy required for the transition. The intensity of absorption is dependent on the probability of the transition occurring when the electronic system and the radiation interact and on the polarity (dipole moment) of the excited state of the ***chromophore***, which is different from that in the ground state.

The absorbing groups in amolecule are called **chromophores.** A molecule containing a chromophore is called a **chromogen.** An **auxochrome** does not itself absorb radiation**,** but, if present in a molecule, it can enhance the absorption by a chromophore and/or shift the wavelength of absorption when attached to the chromophore. Examples are hydroxyl groups, amino groups, and halogens.

Spectral changes can be classed as follows: 1) ***bathochromic shift***—absorption maximum shifted to longer wavelength, 2) **hypsochromic shift**—absorption maximum shifted to shorter wavelength, 3) hyperchromism—an increase in molar absorptivity, 4) **hypochromism**—a decrease in molar absorptivity.

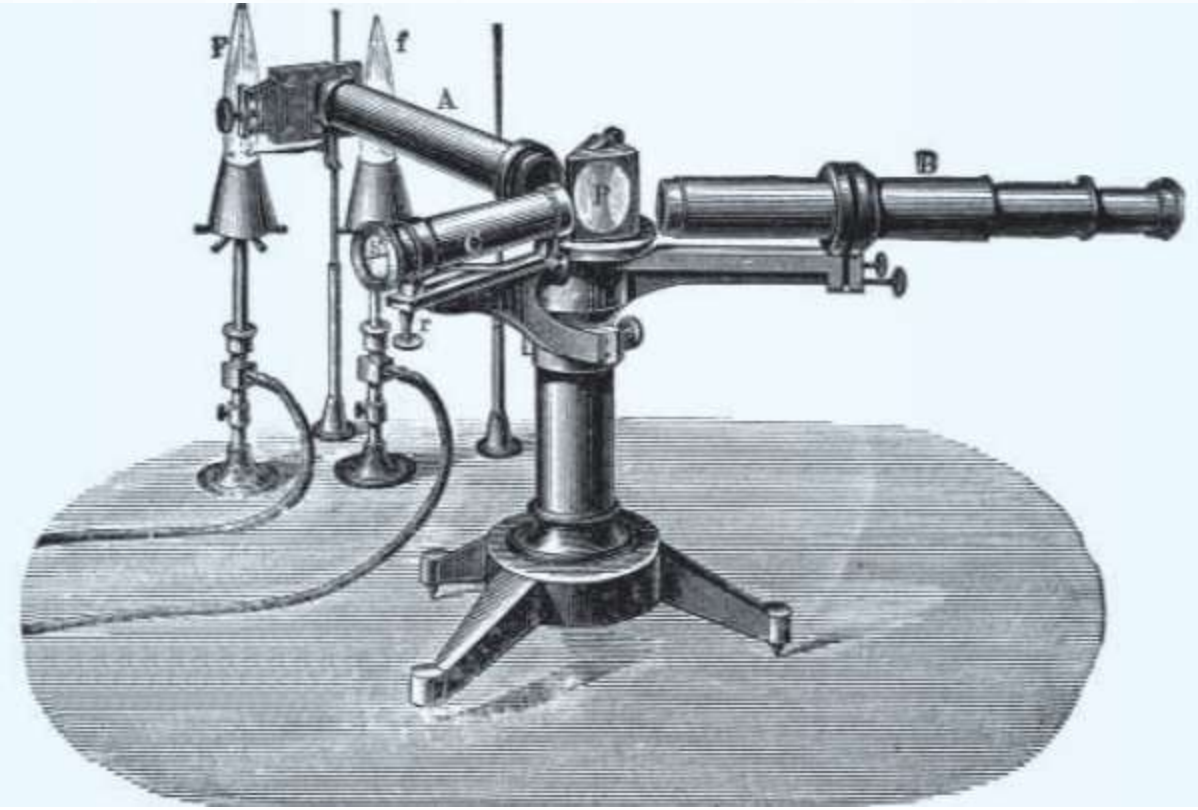
Spectrometric Instrumentation

A **spectrometer or spectrophotometer** is an instrument that will resolve polychromatic radiation into different wavelengths and measure the light intensitry at one or more wavelengths.



Block diagram of spectrometer

All spectrometers require (1) a **source** of continuous radiation over the wavelengths of interest, (2) a **monochromator** for dispersing the light into its component wavelengths and frequently, choosing a narrow band of wavelengths from the source spectrum, (3) a **sample cell**, (4) a **detector, or transducer,** for converting radiant energy into electrical energy, and (5) a device to read out the response of the detector. The sample may precede or follow the monochromator. Each of these, except the readout device, will vary depending on the wavelength region.



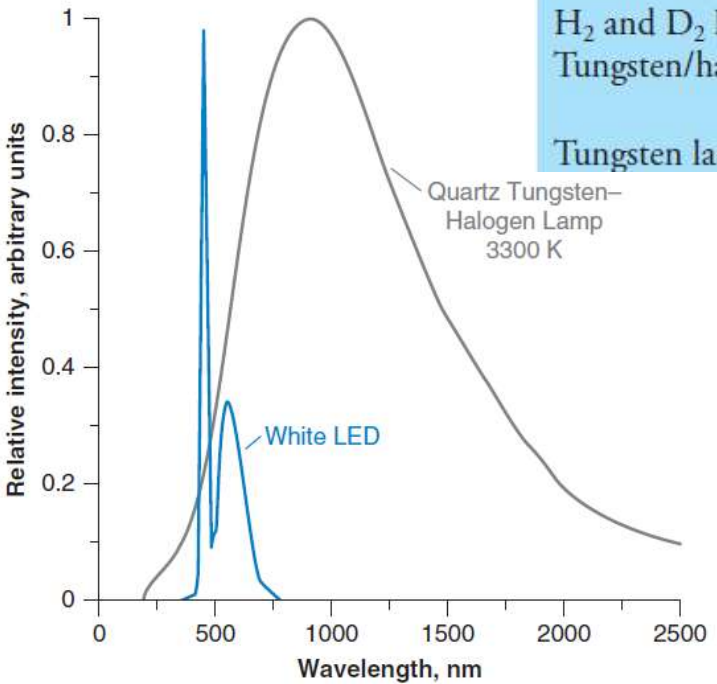
Bunsen burner of the type used in early spectroscopic studies with a prism spectroscope of type used by Kirchhoff.

Sources of Energy

All forms of spectroscopy require a source of energy. In absorption and scattering spectroscopy this energy is supplied by photons. Emission and luminescence spectroscopy use thermal, radiant (photon), or chemical energy to promote the analyte to a less stable, higher energy state. Sources of electromagnetic radiation are classified as either continuum or line sources. A **continuum source** emits radiation over a wide range of wavelengths, with a relatively smooth variation in intensity as a function of wavelength. **Line sources,** on the other hand, emit radiation at a few selected, narrow wavelength ranges.

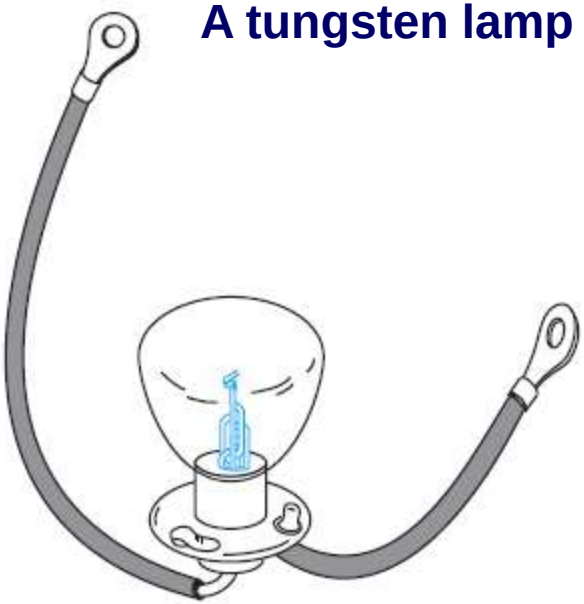
Continuum Sources for Optical Spectroscopy

Source	Wavelength Region, nm	Type of Spectroscopy
Xenon arc lamp	250–600	Molecular fluorescence
H_2 and D_2 lamps	160–380	UV molecular absorption
Tungsten/halogen lamp	240–2500	UV/visible/near-IR molecular absorption
Tungsten lamp	350–2200	Visible/near-IR molecular absorption

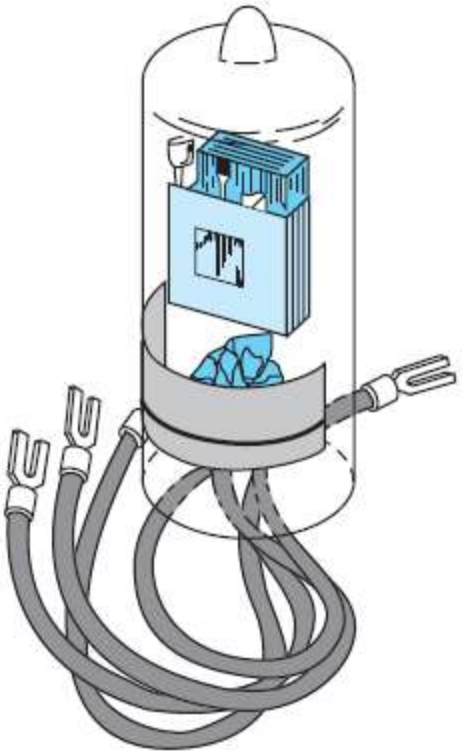


Intensity of radiation as function of wavelength for two typical light sources: Quartz tungsten–halogen lamp operating at 3300 K exhibits useful light intensity from 350–2500 nm. A white LED actually contains a blue InGaN LED emitting at 450 nm that is coated with a broadband phosphor that has peak emission in the green, at 550 nm; this source is useful from 425–700 nm.

A tungsten lamp



Deuterium (and also hydrogen) lamps are most often used to provide continuum radiation in the UV region. A deuterium lamp consists of a cylindrical tube containing deuterium at low pressure with a quartz window from which the radiation exits.



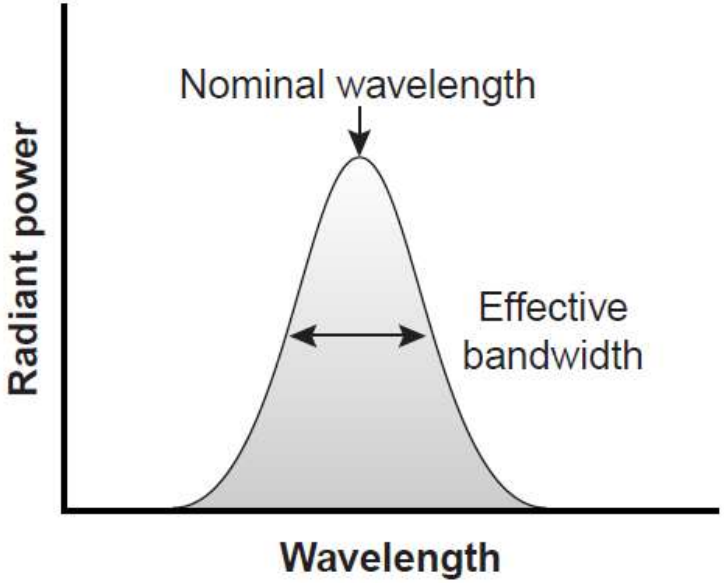
A deuterium lamp

The lamp emits continuum radiation when deuterium (or hydrogen) is stimulated by electrical energy to produce excited molecule of D_2^* (or H_2^*). The excited state species then dissociates to give two hydrogen or deuterium atoms plus an ultraviolet photon.

Wavelength Selection

Unfortunately, we cannot isolate a single wavelength of radiation from a continuum source. Instead, a wavelength selector passes a narrow band of radiation characterized by a **nominal wavelength, an effective bandwidth, and a maximum throughput** of radiation. The effective bandwidth is defined as the width of the radiation at half the maximum throughput.

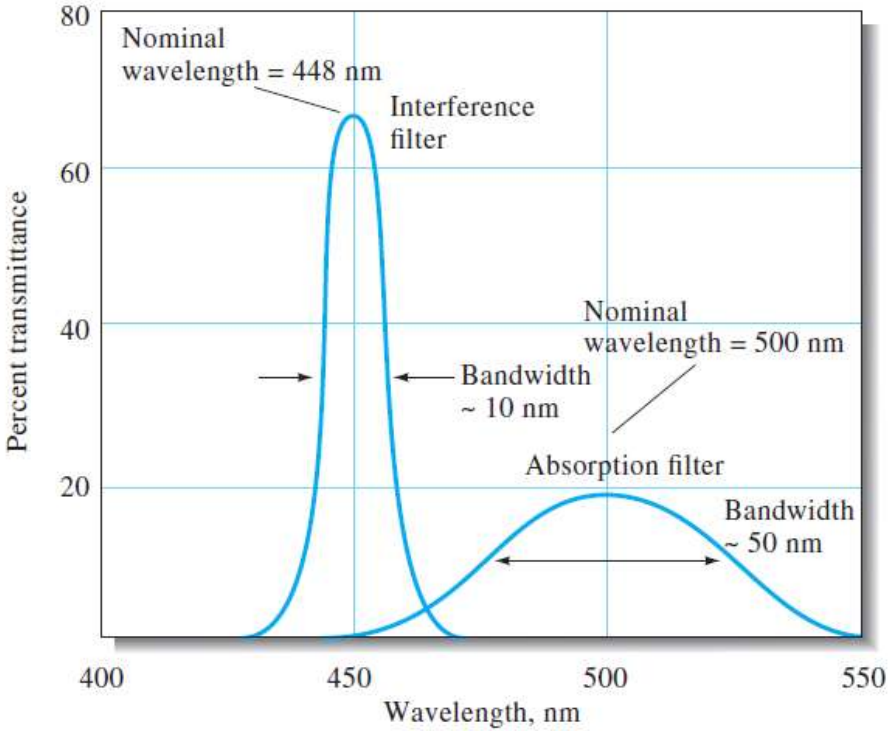
Many instruments use a **monochromator** or a **filter** to isolate the desired wavelength band so that only the band of interest is detected and measured. Others use a **spectrograph** to spread out, or disperse, the wavelengths so that they can be detected with a multichannel detector.



Band of radiation exiting wavelength selector showing the nominal wavelength and effective bandpass.

Wavelength Selection Using Filters

The simplest method for isolating a narrow band of radiation is to use an absorption or interference filter. ***Absorption filters*** work by selectively absorbing radiation from a narrow region of the electromagnetic spectrum. ***Interference filters*** use constructive and destructive interference to isolate a narrow range of wavelengths. A simple example of an absorption filter is a piece of *colored glass*. A purple filter, for example, removes the complementary color green from 500–560 nm.

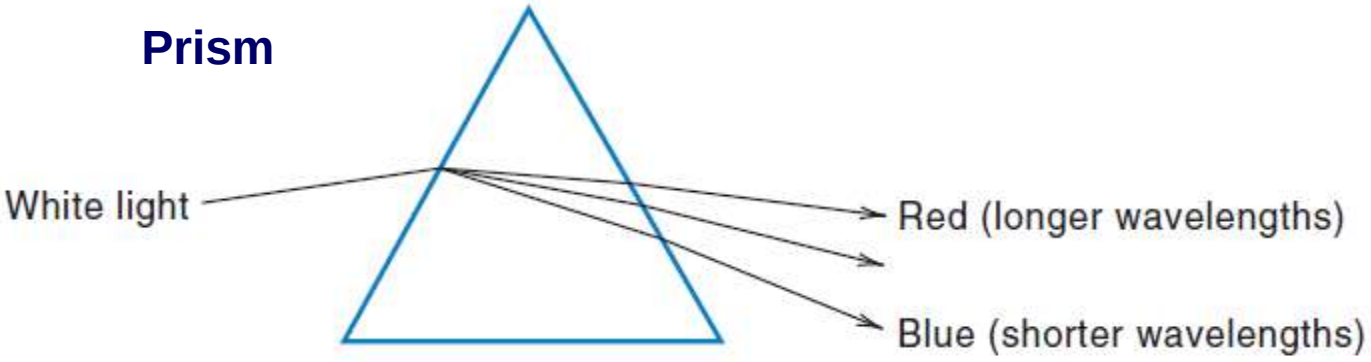


Commercially available absorption filters provide effective bandwidths from 30–250 nm. The maximum throughput for the smallest effective bandpasses, however, may be only 10% of the source's emission intensity over that range of wavelengths. Interference filters are more expensive than absorption filters, but have narrower effective bandwidths, typically 10–20 nm, with maximum throughputs of at least 40%.

An interference filter consists of a very thin layer of a transparent **dielectric** material (frequently calcium fluoride or magnesium fluoride) coated on both sides with a film of metal that is thin enough to transmit approximately half of the radiation striking it and to reflect the other half.

Wavelength Selection Using Monochromators

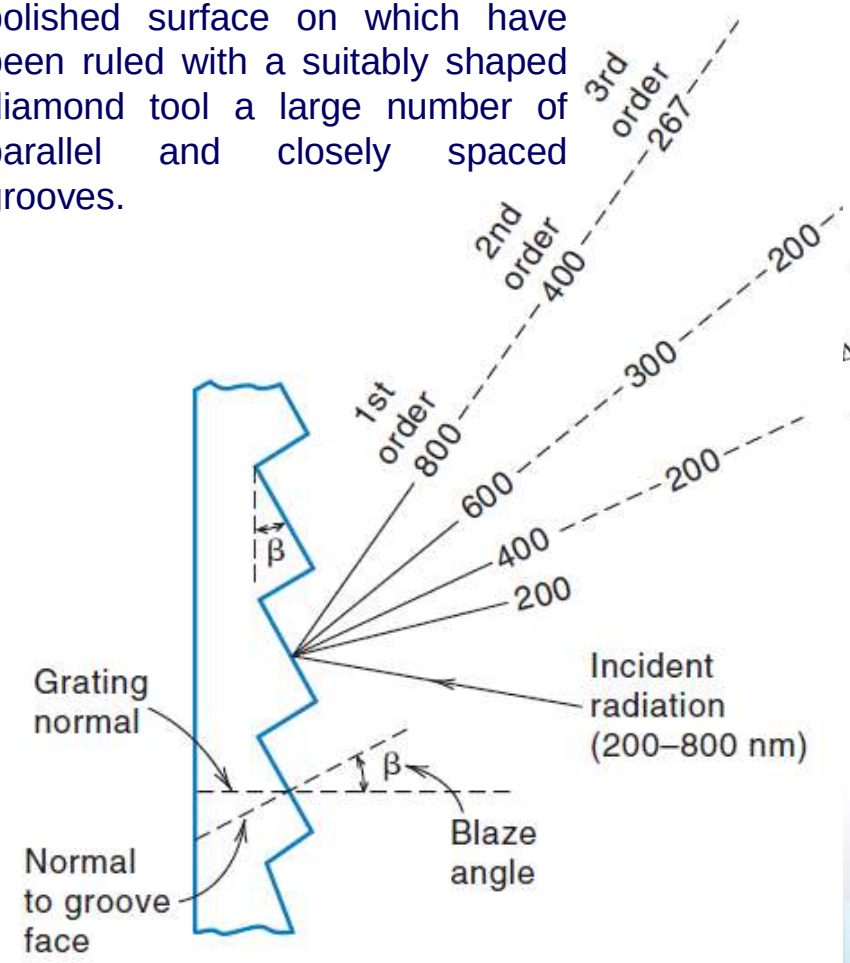
Prism

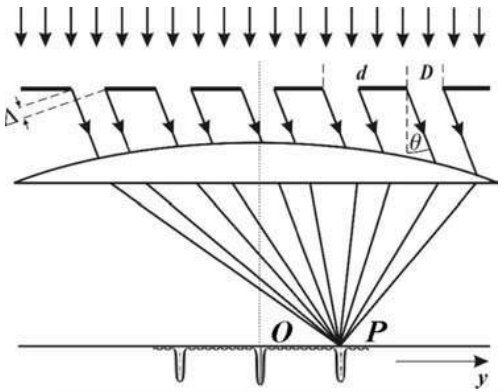


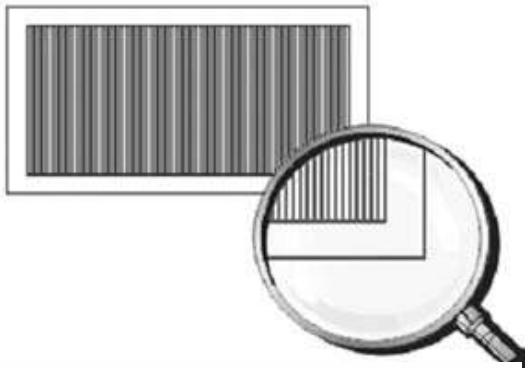
Gratings

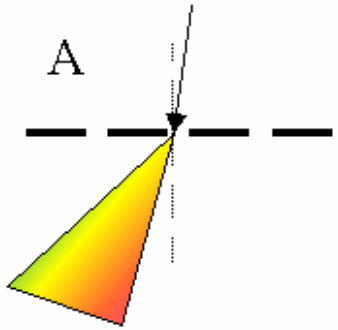
Consists of a hard, optically flat, polished surface on which have been ruled with a suitably shaped diamond tool a large number of parallel and closely spaced grooves.

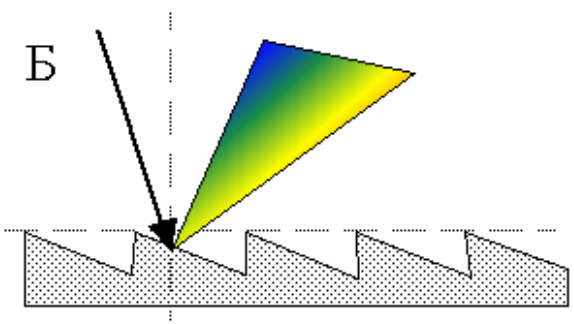
Monochromator-a wavelength selector that uses a ***diffraction grating*** or ***prism***, and that allows for a continuous variation of the nominal wavelength.







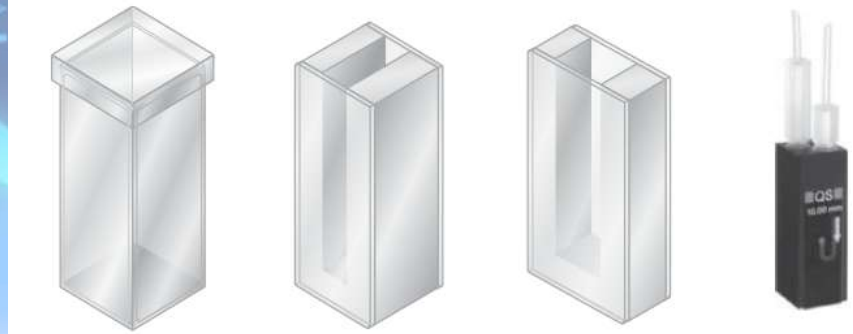


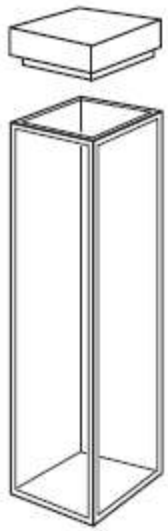


SAMPLE CELLS

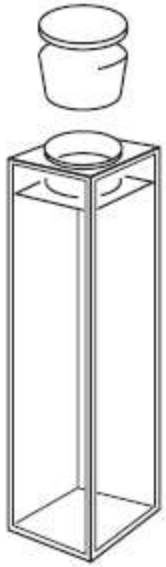
The cell holding the sample (usually a solution) must, of course, be transparent in the wavelength region being measured. Sample containers, which are usually called **cells or cuvettes.** Silicate glass is usually used for the 375–2000 nm region because of its low cost compared to quartz. Plastic cells are also used in the visible.

Fingerprints, grease, or other deposits on the walls may alter significantly the transmission characteristics of a cell. Thus, it is imperative to thoroughly clean cells both before and after use, and the windows must not be touched after cleaning is complete.

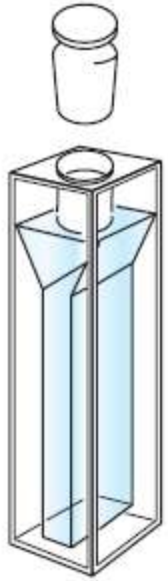




Open-top
normal with lid



Stoppered
normal



Stoppered
semimicro

Detectors

The choice of detectors depend on the wavelength of interest.

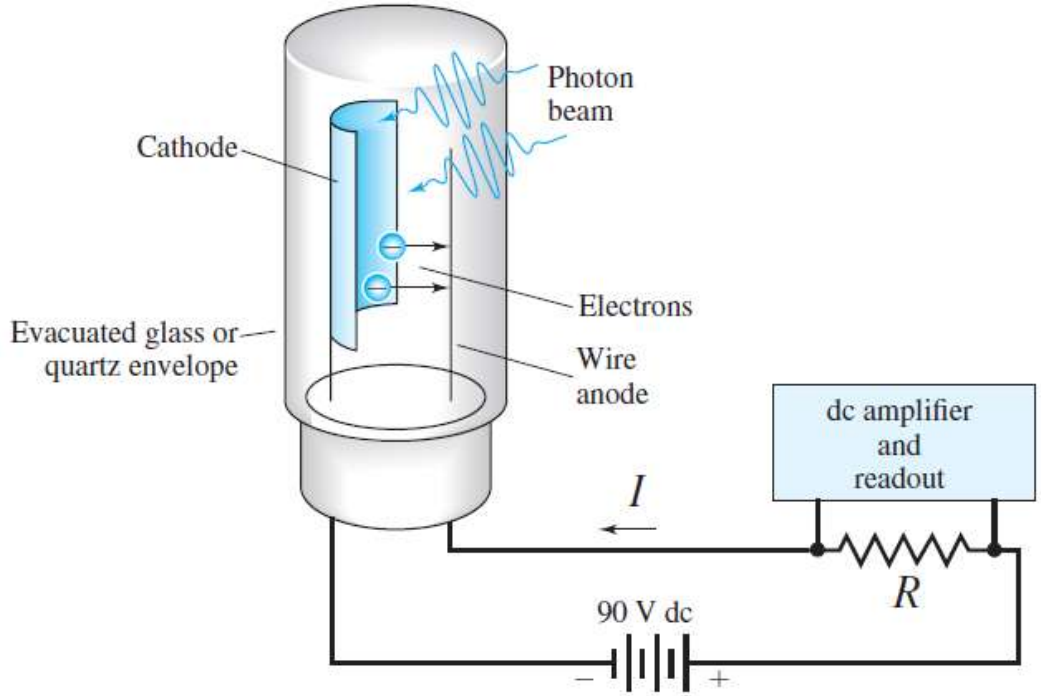
A **detector** is a device that identifies, records, or indicates a change in one of the variables in its environment such as pressure, temperature, or electromagnetic radiation. Familiar examples of detectors include photographic film for indicating the presence of electromagnetic or radioactive radiation, the pointer of a balance for indicating mass differences, and the mercury level in a thermometer for indicating temperature. The human eye is also a detector; it converts visible radiation into an electrical signal that is passed to the brain via a chain of neurons in the optic nerve and produces vision.

Invariably in modern instruments, the information of interest is encoded and processed as an electrical signal. A **transducer** converts nonelectrical quantities (chemical and physical quantities) such as light intensity, pH, mass, and temperature, into **electrical signals** (charge, current, or voltage) that can be subsequently amplified, manipulated, and finally converted into numbers proportional to the magnitude of the original quantity.

There are two general types of transducers: one type responds to photons, the other to heat. All photon detectors are based on the interaction of radiation with a reactive surface either to produce electrons (***photoemission*****)** or to promote electrons to energy states in which they can conduct electricity (***photoconduction*****).** Only UV, visible, and near-IR radiation possess enough energy to cause photoemission to occur; therefore, photoemissive detectors are limited to wavelengths shorter than about 2 mm (2000 nm). Photoconductors can be used in the near-, mid-, and far-IR regions of the spectrum.

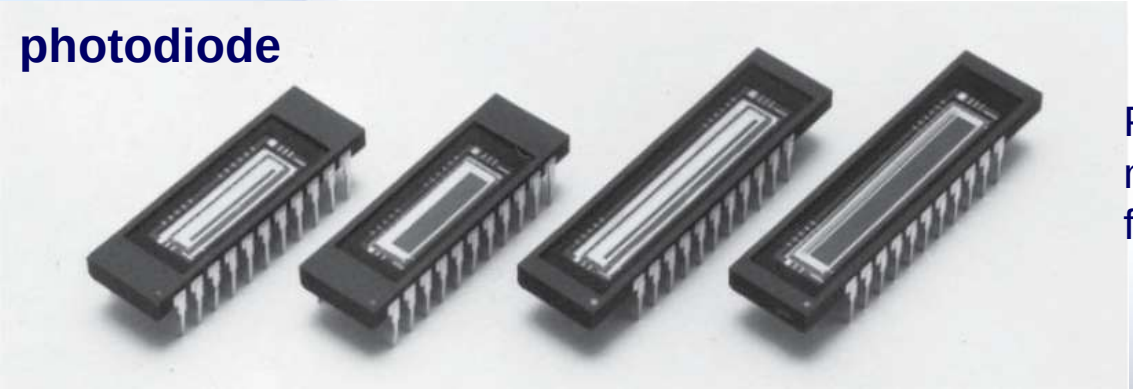
Two general classes of transducers are used for optical spectroscopy. ***Phototubes and photomultipliers*** contain a photosensitive surface that absorbs radiation in the ultraviolet, visible, and near infrared (IR), producing an electric current proportional to the number of photons reaching the transducer. Other photon detectors use a semiconductor as the photosensitive surface. When the semiconductor absorbs photons, valence electrons move to the semiconductor's conduction band, producing a measurable current. One advantage of the Si photodiode is that it is easily miniaturized.

photomultiplier tube



A phototube and accompanying circuit. The photocurrent induced by the radiation causes a voltage *across the measuring* resistor; this voltage is then amplified and measured.

photodiode



Photomultiplier tubes are among the most widely used types of transducers for detecting ultraviolet/visible radiation.

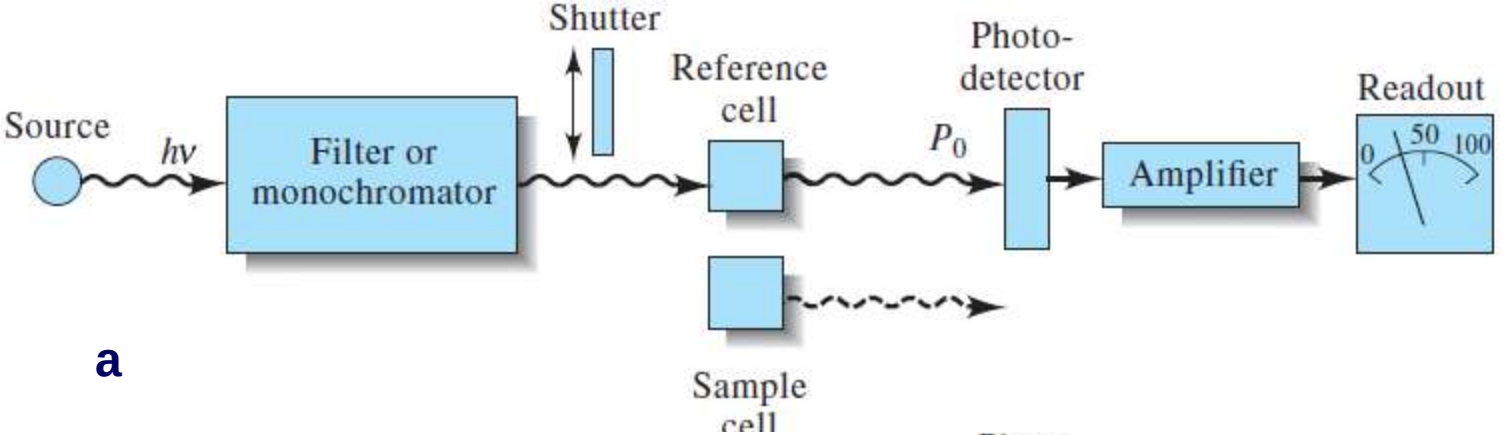
Signal Processors

The electrical signal generated by the transducer is sent to a signal processor where it is displayed in a more convenient form for the analyst. Examples of signal processors include analog or digital meters, recorders, and computers equipped with digital acquisition boards. The signal processor also may be used to calibrate the detector's response, to amplify the signal from the detector, to remove noise by filtering, or to mathematically transform the signal.

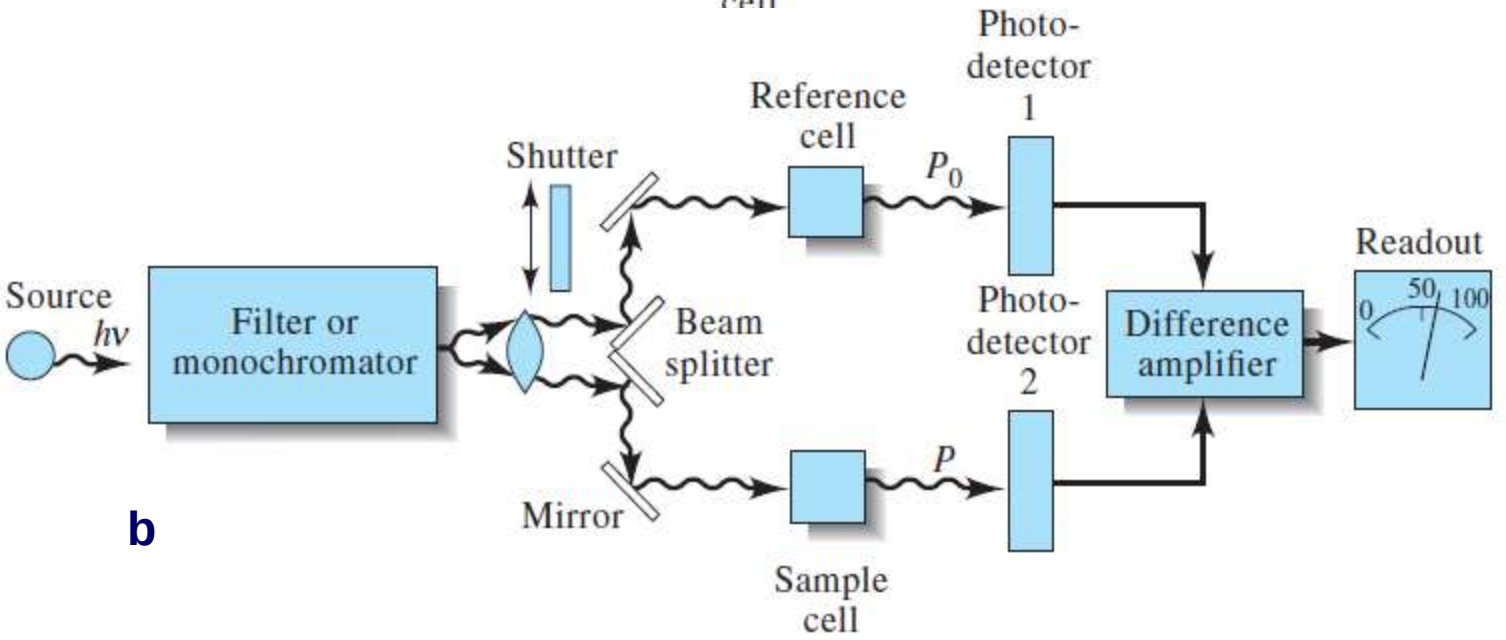
signal processor - A device, such as a meter or computer, that displays the signal from the transducer in a form that is easily interpreted by the analyst.

Types of Instruments

A **spectrometer** is a spectroscopic instrument that uses a monochromator or polychromator in conjunction with a transducer to convert the radiant intensities into electrical signals. **Spectrophotometers** are spectrometers that allow measurement of the ratio of the radiant powers of two beams, a requirement to measure absorbance. ***Photometers*** use a filter for wavelength selection in conjunction with a suitable radiation transducer. Spectrophotometers offer the considerable advantage that the wavelength used can be varied continuously, making it possible to record absorption spectra. Photometers have the advantages of simplicity, ruggedness, and low cost. Several dozen models of spectrophotometers are available commercially. Most spectrophotometers cover the UV/visible and occasionally the near-infrared region, while photometers are most often used for the visible region. Both photometers and spectrophotometers can be obtained in **single- and double-beam** varieties.



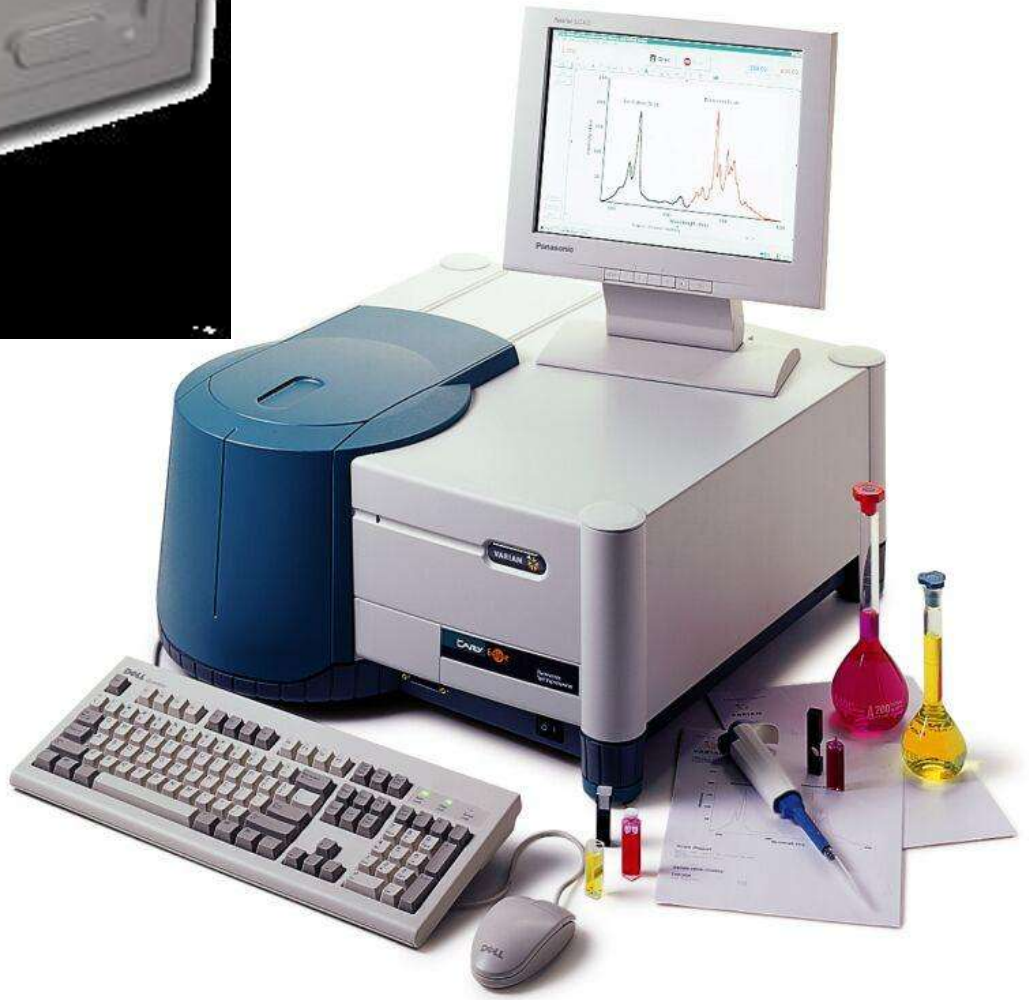
a



b

Instrumental designs for UV/visible photometers or spectrophotometers. In (**a**), a **singlebeam** instrument. Radiation from the filter or monochromator passes through either the reference cell or the sample cell before striking the photodetector. In (**b**), a **doublebeam**- instrument. In this instrument, radiation from the filter or monochromator is split into two beams that simultaneously pass through the reference and sample cells before striking two matched photodetectors.

Miniature fiber-optic spectrometer. Box is the spectrometer. Light source is to right, and fiber-optic cable guides light to cuvet. Second cable takes transmitted radiation to spectrometer.


Panasonic
VARIAN
Cary

Evaluation

• **Scale of Operation**

Molecular UV/Vis absorption is routinely used for the analysis of trace analytes in macro and meso samples. Major and minor analytes can be determined by diluting samples before analysis, and concentrating a sample may allow for the analysis of ultratrace analytes. The scale of operations for infrared absorption is generally poorer than that for UV/Vis absorption.

• **Accuracy**

Under normal conditions relative errors of 1–5% are easily obtained with UV/Vis absorption. Accuracy is usually limited by the quality of the blank. Examples of the type of problems that may be encountered include the presence of particulates in a sample that scatter radiation and interferents that react with analytical reagents. In the latter case the interferant may react to form an absorbing species, giving rise to a positive determinate error. Interferents also may prevent the analyte from reacting, leading to a negative determinate error. With care, it may be possible to improve the accuracy of an analysis by as much as an order of magnitude.

• **Precision**

In absorption spectroscopy, precision is limited by indeterminate errors, or instrumental “noise,” introduced when measuring absorbance. Precision is generally worse with very low absorbances due to the uncertainty of distinguishing a small difference between P_0 *and* P_T, *and for very high absorbances* when *PT approaches 0. We might expect, therefore, that precision will vary with* transmittance.

Evaluation

• **Sensitivity**

The sensitivity of a molecular absorption analysis is equivalent to the slope of a Beer's-law calibration curve and is determined by the product of the analyte's absorptivity and the pathlength of the sample cell. Sensitivity is improved by selecting a wavelength when absorbance is at a maximum or by increasing the pathlength.

• **Selectivity**

Selectivity is rarely a problem in molecular absorption spectrophotometry. In many cases it is possible to find a wavelength at which only the analyte absorbs or to use chemical reactions in a manner such that the analyte is the only species that absorbs at the chosen wavelength. When two or more species contribute to the measured absorbance, a multicomponent analysis is still possible.

• **Time, Cost, and Equipment**

The analysis of a sample by molecular absorption spectroscopy is relatively rapid, although additional time may be required when it is necessary to use a chemical reaction to transform a nonabsorbing analyte into an absorbing form. The cost of UV/Vis instrumentation ranges from several hundred dollars for a simple, manually operated, single-beam instrument equipped with an inexpensive grating, to as much as $50,000 for a computer-controlled, high-resolution, double-beam instrument equipped with variable slits and operating over an extended range of wavelengths.

Atomic Spectroscopy

As in molecular spectroscopy, atomic spectroscopy is divided broadly into ***absorption*** and ***emission spectroscopy***. The notable differences are that atomic spectrometry is always carried out in the gas phase. The measurement conditions require elevated temperatures; with the exception of Hg, Cd and the inert gases, elements are not present as a monoatomic gas at room temperature. Also, as the name implies, we measure atoms; atomic spectroscopy is then a form of elemental analysis. Atomic spectroscopic methods are used for the qualitative and quantitative determination of more than 70 elements. Atomic spectroscopic methods are also rapid, convenient, and usually of high selectivity. These methods can be divided into two groups; **optical atomic spectrometry and atomic mass spectrometry.**

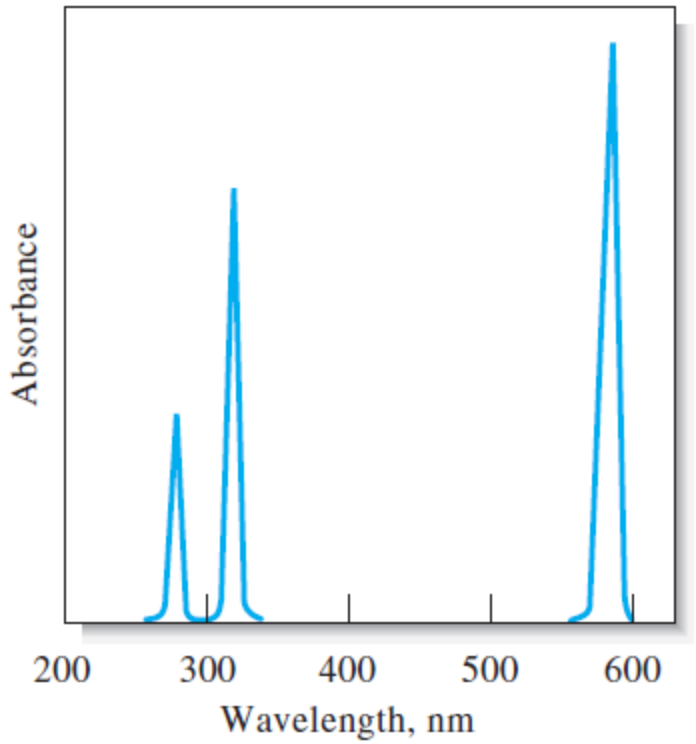
Classification of Atomic Spectroscopic Methods

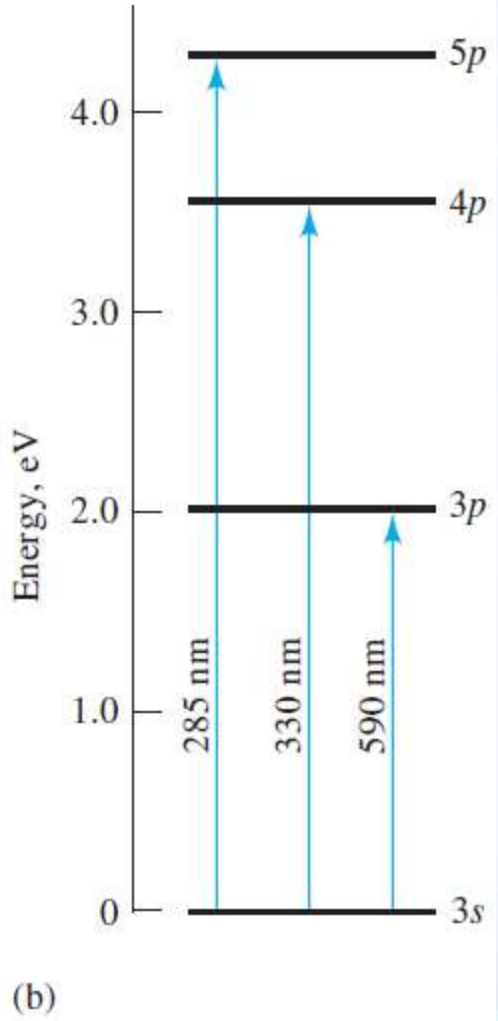
Atomization Method	Typical Atomization Temperature, °C	Types of Spectroscopy	Common Name and Abbreviation
Inductively coupled plasma	6000–8000	Emission	Inductively coupled plasma atomic emission spectroscopy, ICPAES
		Mass	Inductively coupled plasma mass spectrometry, ICP-MS (see Chapter 29)
Flame	1700–3150	Absorption	Atomic absorption spectroscopy, AAS
		Emission	Atomic emission spectroscopy, AES
		Fluorescence	Atomic fluorescence spectroscopy, AFS
Electrothermal	1200–3000	Absorption	Electrothermal AAS
		Fluorescence	Electrothermal AFS
Direct-current plasma	5000–10,000	Emission	DC plasma spectroscopy, DCP
Electric arc	3000–8000	Emission	Arc-source emission spectroscopy
Electric spark	Varies with time and position	Emission	Spark-source emission spectroscopy
		Mass	Spark-source mass spectroscopy

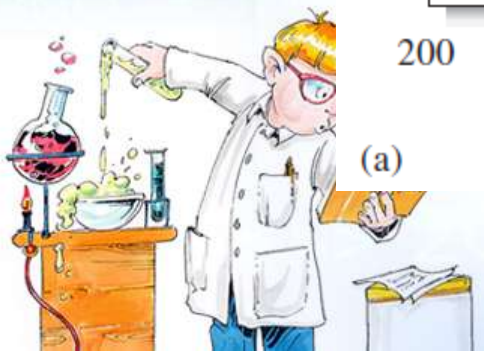
Atomic Spectroscopy

Since atoms are the simplest and purest form of matter and do not have different rotational and vibrational energy states like a molecule, both absorption and emission spectra of atoms consist of sharp lines, corresponding to various wavelengths of light.

Origins of Atomic Spectra

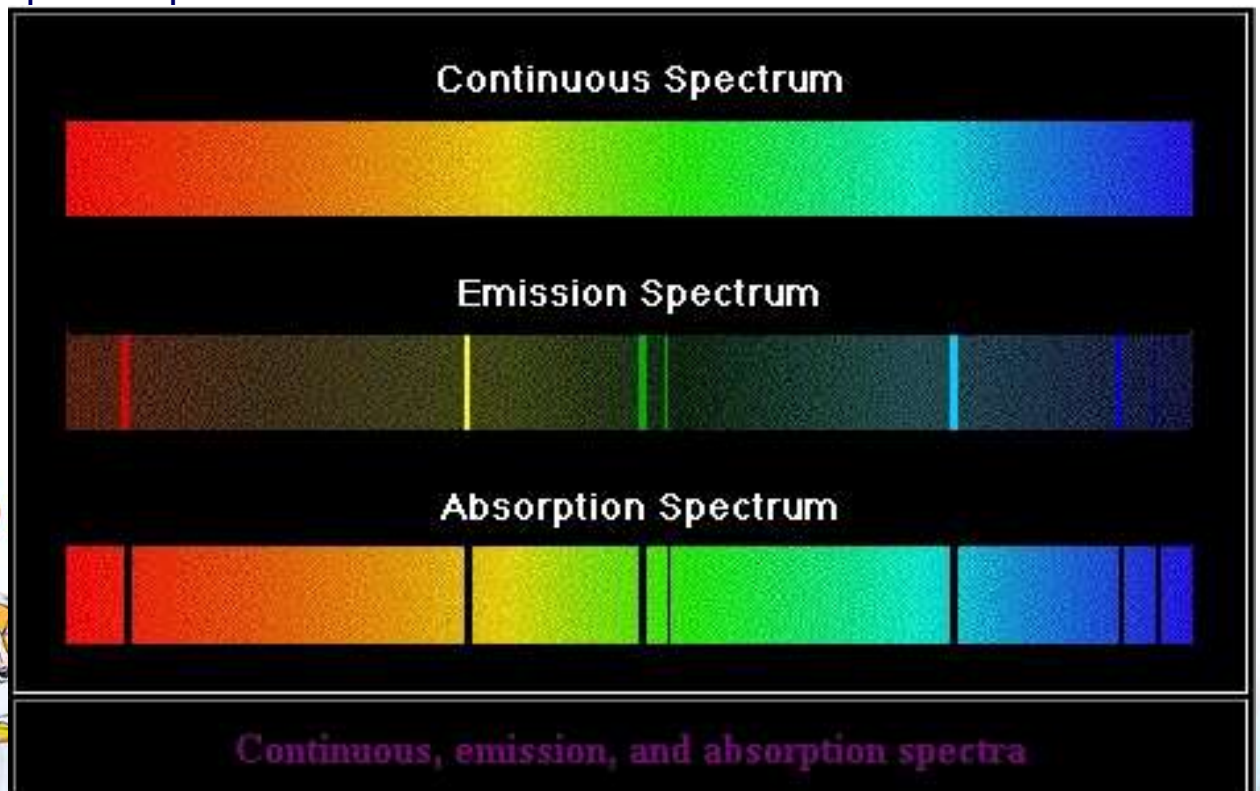


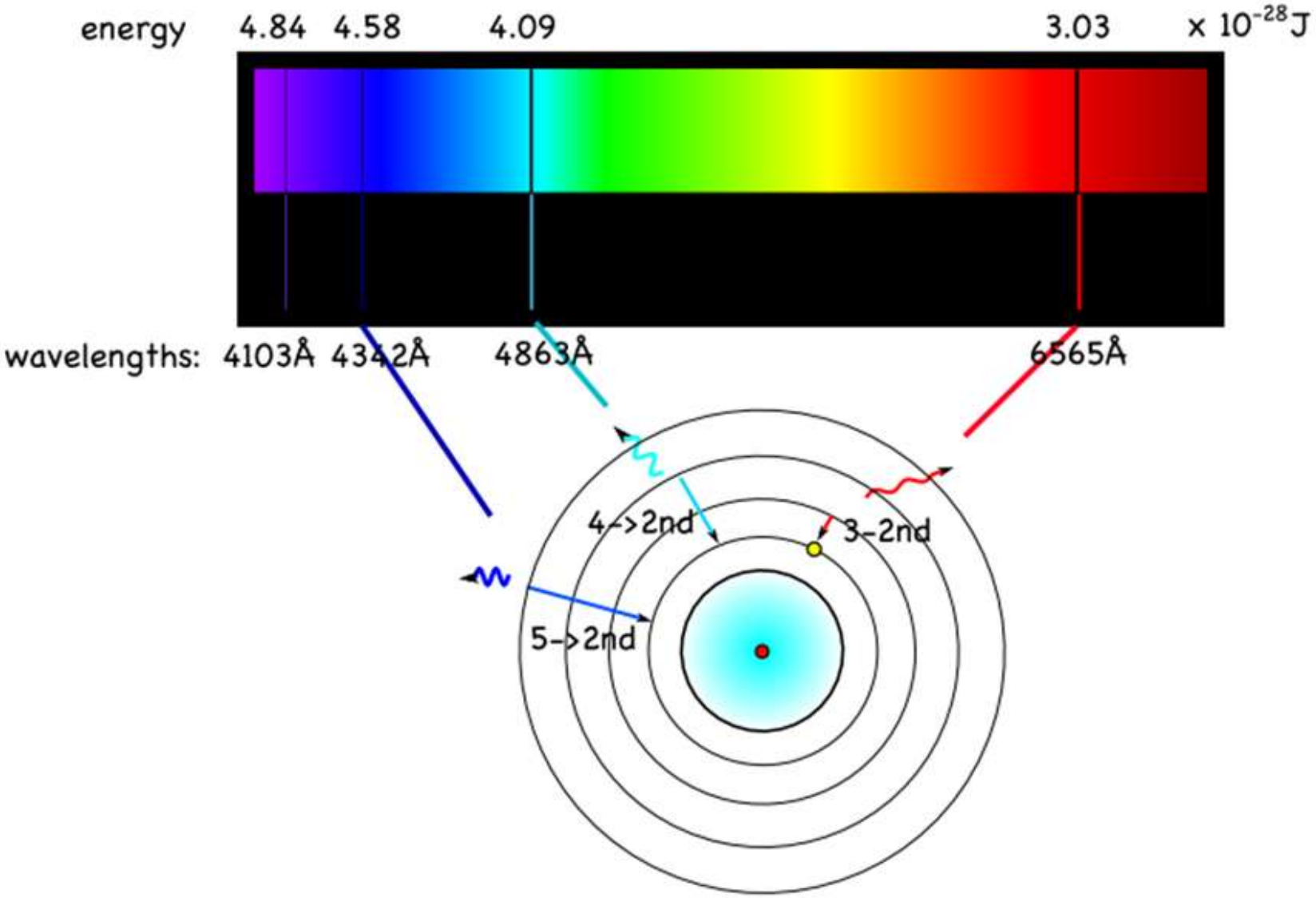




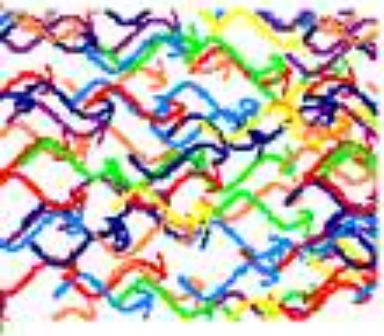
(a) Partial absorption spectrum for sodium vapor. (b) Electronic transitions responsible for the absorption lines in (a).

The energy of ultraviolet and visible electromagnetic radiation is sufficient to cause a change in an atom's valence electron configuration. Sodium, for example, with a valence shell electron configuration of [Ne] $3s^1$, has a single valence electron in its 3s atomic orbital. Absorption of a photon is accompanied by the excitation of an electron from a lower-energy atomic orbital to an orbital of higher energy. Not all possible transitions between atomic orbitals are allowed. For sodium the only allowed transitions are those in which there is a change of ±1 in the orbital quantum number (l); thus transitions from s→p orbitals are allowed, but transitions from s→d orbitals are forbidden. The most obvious feature of this spectrum is that it consists of a few, discrete absorption lines corresponding to transitions between the ground state (the 3s atomic orbital) and the 3p and 4p atomic orbitals.

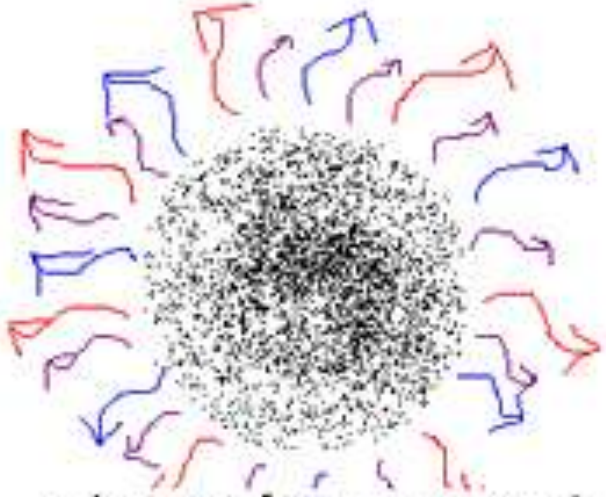



energy
4.84
4.58
4.09
3.03
x 10^-28 J
wavelengths:
4103Å
4342Å
4863Å
6565Å
4->2nd
3->2nd
5->2nd

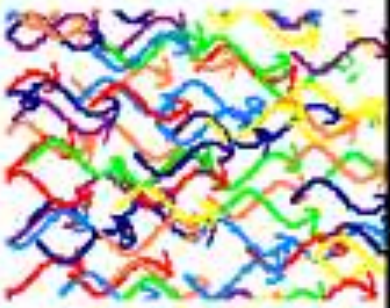
Absorption Spectrum



Photons of white light



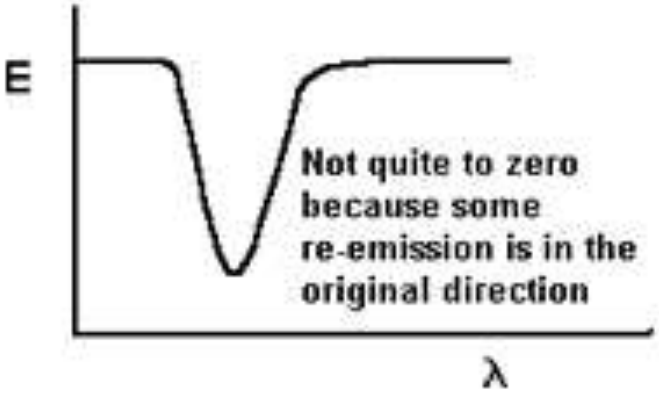
atoms in a sample emitting the absorbed photons in all directions



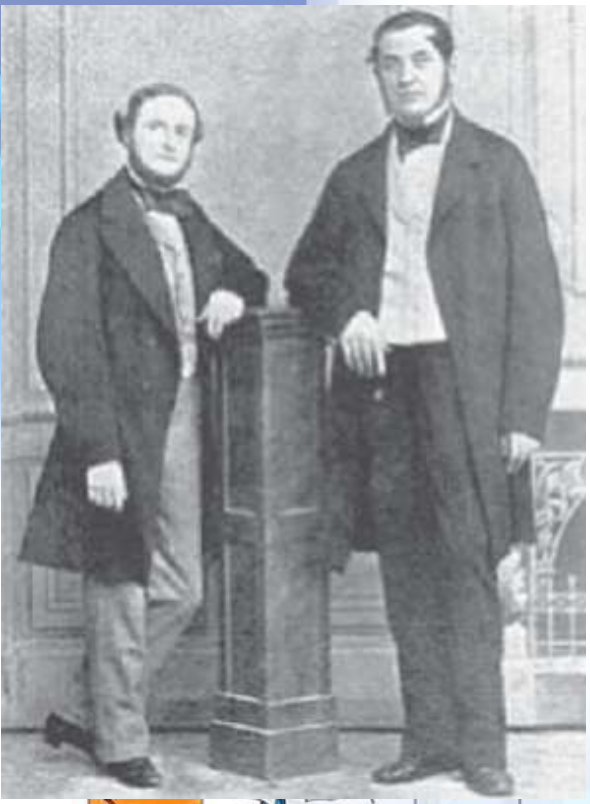
Unabsorbed photons get straight through

Spectrometer to disperse photons into a spectrum

dark lines indicate 'missing' wavelengths (absorbed photons). They are caused by emission not being unidirectional



Imaging of the solar spectrum with high resolution readily reveals the presence of narrow dark lines in the solar continuum. William Hyde Wollaston (otherwise best known for his discovery of palladium and rhodium in 1803) first observed these dark lines in 1802. But it would remain for **Fraunhofer** to independently discover, characterize, and catalog them in detail in 1813–1814. To date, these absorption lines are called Fraunhofer lines and most are still referred with Fraunhofer's original nomenclature.

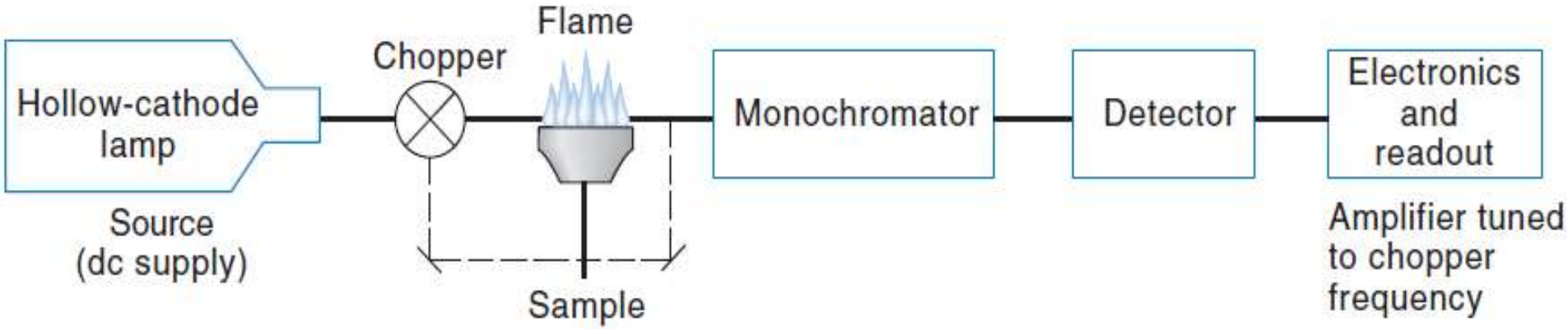


Atomic absorption, along with atomic emission, was first used by ***Guystav Kirchhoff and Robert Bunsen*** in 1859 and 1860, as a means for the qualitative identification of atoms. Although atomic emission continued to develop as an analytical technique, progress in atomic absorption languished for almost a century. Modern atomic absorption spectroscopy was introduced in 1955 as a result of the independent work of A. Walsh and C. T. J. Alkemade. Commercial instruments were in place by the early 1960s, and the importance of atomic absorption as an analytical technique was soon evident.

Instrumentation

Atomization

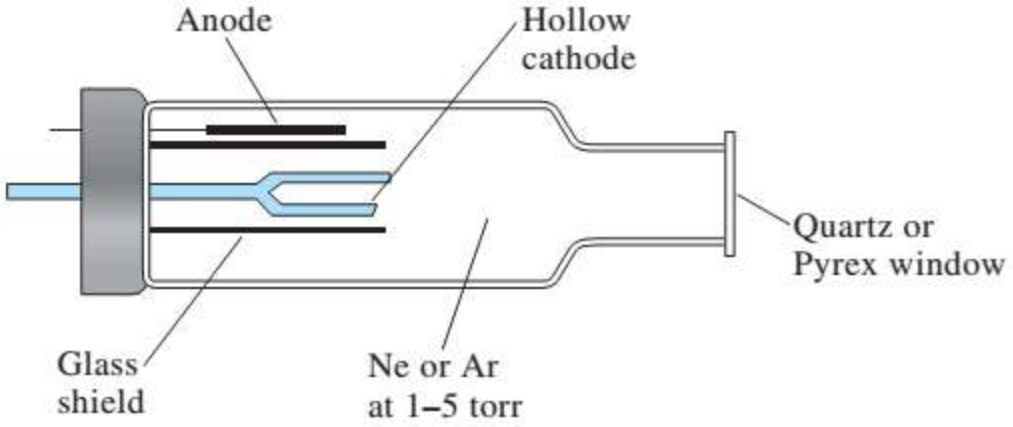
The most important difference between a spectrophotometer for atomic absorption and one for molecular absorption is the need to convert the analyte into a free atom. The process of converting an analyte in solid, liquid, or solution form to a free gaseous atom is called ***atomization***. In most cases the sample containing the analyte undergoes some form of sample preparation that leaves the analyte in an organic or aqueous solution. Two general methods of atomization areused: ***flame atomization and electrothermal atomization***. A few elements are atomized using other methods.



Block diagram of a single-beam atomic absorption spectrometer. Radiation from a **line** source is focused on the atomic vapor in a flame or electrothermal atomizer. The attenuated source radiation then enters a monochromator that isolates the line of interest. Next, the radiant power from the source, attenuated by absorption, is converted into an electrical signal by the photomultiplier tube. The signal is then processed and directed to a computer system for output.

Line Sources

The most useful radiation source for atomic absorption spectroscopy is the ***hollowcathode lamp***. It consists of a tungsten anode and a cylindrical cathode sealed in a glass tube containing an inert gas, such as argon, at a pressure of 1 to 5 torr. The cathode either is fabricated from the ***analyte metal*** or else serves as a support for a coating of that metal.



When a potential is applied across the electrodes, the filler gas is ionized. The positively charged ions collide with the negatively charged cathode, dislodging, or “sputtering,” atoms from the cathode’s surface. Some of the sputtered atoms are in the excited state and emit radiation characteristic of the metal from which the cathode was manufactured.

By fashioning the cathode from the metallic analyte, a hollow cathode lamp provides emission lines that correspond to the analyte’s absorption spectrum.

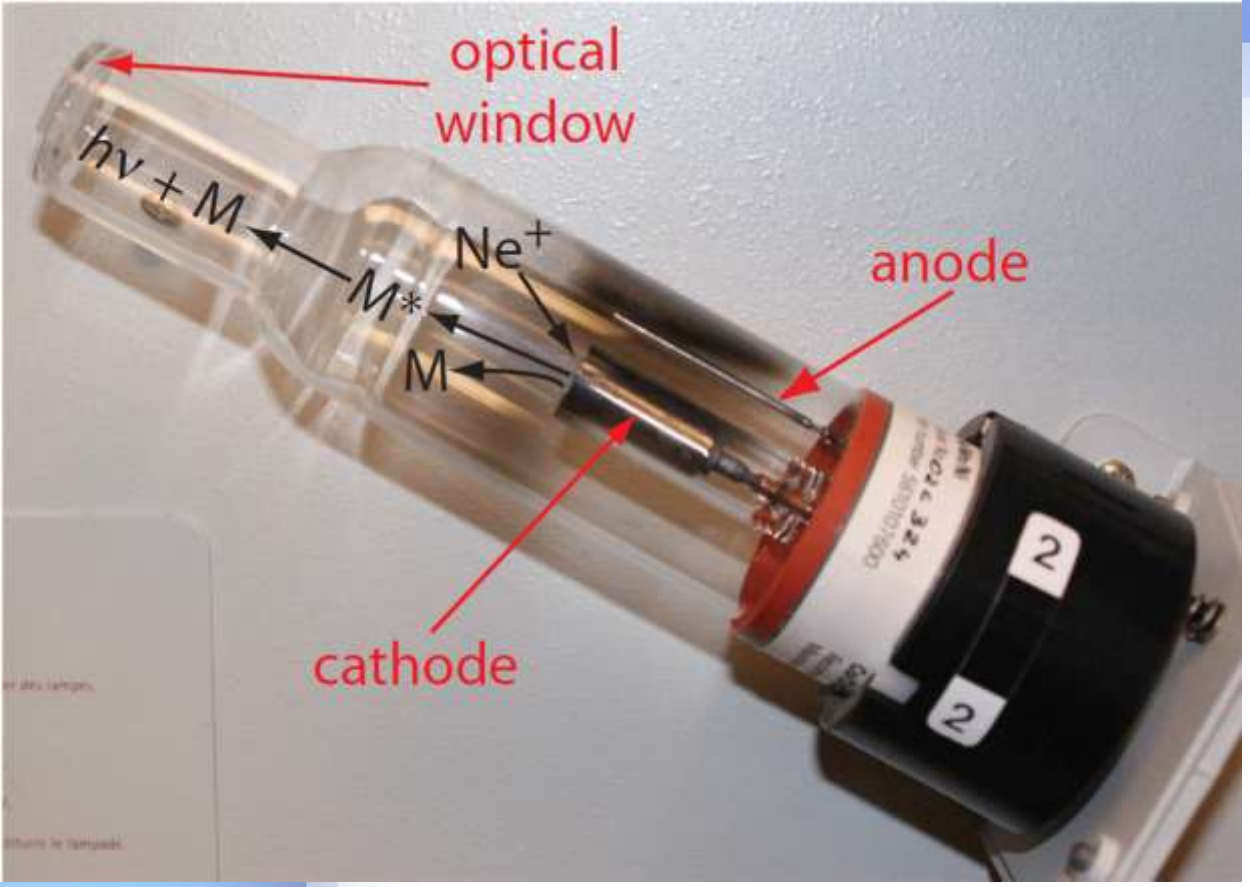
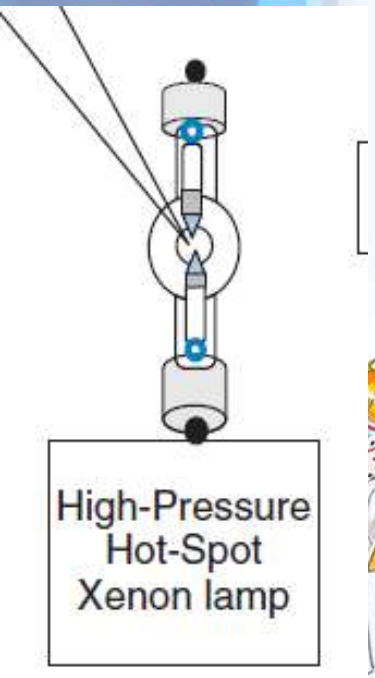


Photo of a typical multielemental hollow cathode lamp. The cathode in this lamp is fashioned from an alloy containing Co, Cr, Cu, Fe, Mn, and Ni, and is surrounded by a glass shield to isolate it from the anode. The lamp is filled with Ne gas. Also shown is the process leading to atomic emission. Each element in a hollow cathode lamp provides several atomic emission lines that we can use for atomic absorption.

In addition to hollow-cathode lamps, **electrodeless-discharge lamps** are useful sources of atomic line spectra. These lamps are often one to two orders of magnitude more intense than their hollow-cathode counterparts. A typical electrodeless- discharge lamp is constructed from a sealed quartz tube containing an inert gas, such as argon, at a pressure of a few torr and a small quantity of the analyte metal (or its salt). The lamp contains no electrodes, but instead it is energized by an intense field of radio-frequency or microwave radiation. The argon ionizes in this field, and the ions are accelerated by the high-frequency component of the field until they gain sufficient energy to excite (by collision) the atoms of the analyte metal. Electrodeless-discharge lamps are available commercially for several elements. They are particularly useful for elements, such as As, Se, and Te, where hollow-cathode lamp intensities are low.

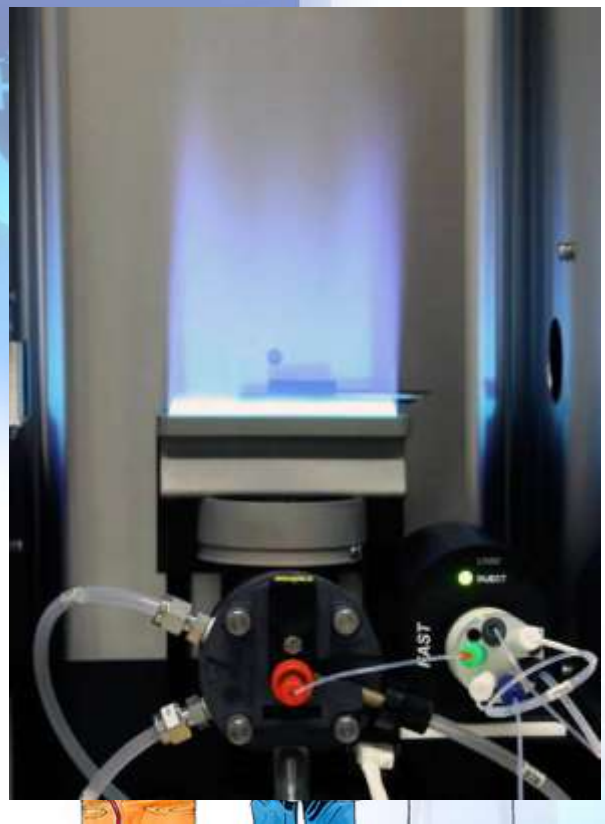


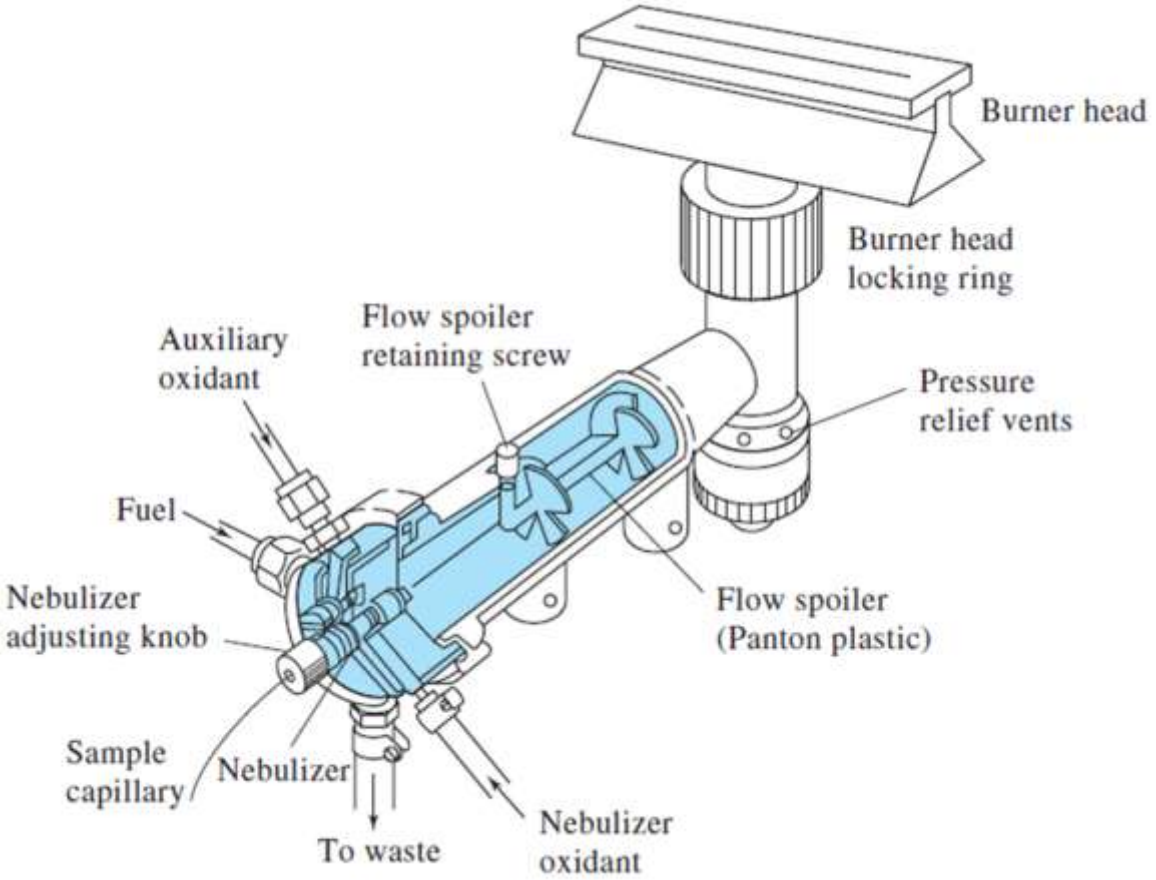
Continuum Source. A popular background correction scheme in commercial AA spectrometers is the continuum lamp technique. In this scheme, a deuterium lamp and the analyte hollow cathode are directed through the atomizer at different times. The hollow-cathode lamp measures the total absorbance, *AT, while the deuterium lamp provides an estimate of the background absorbance, AB. The computer system or processing electronics calculates the difference* and reports the background-corrected absorbance. This method has limitations for elements with lines in the visible because the D_2 lamp intensity becomes quite low in this region.

Atomization

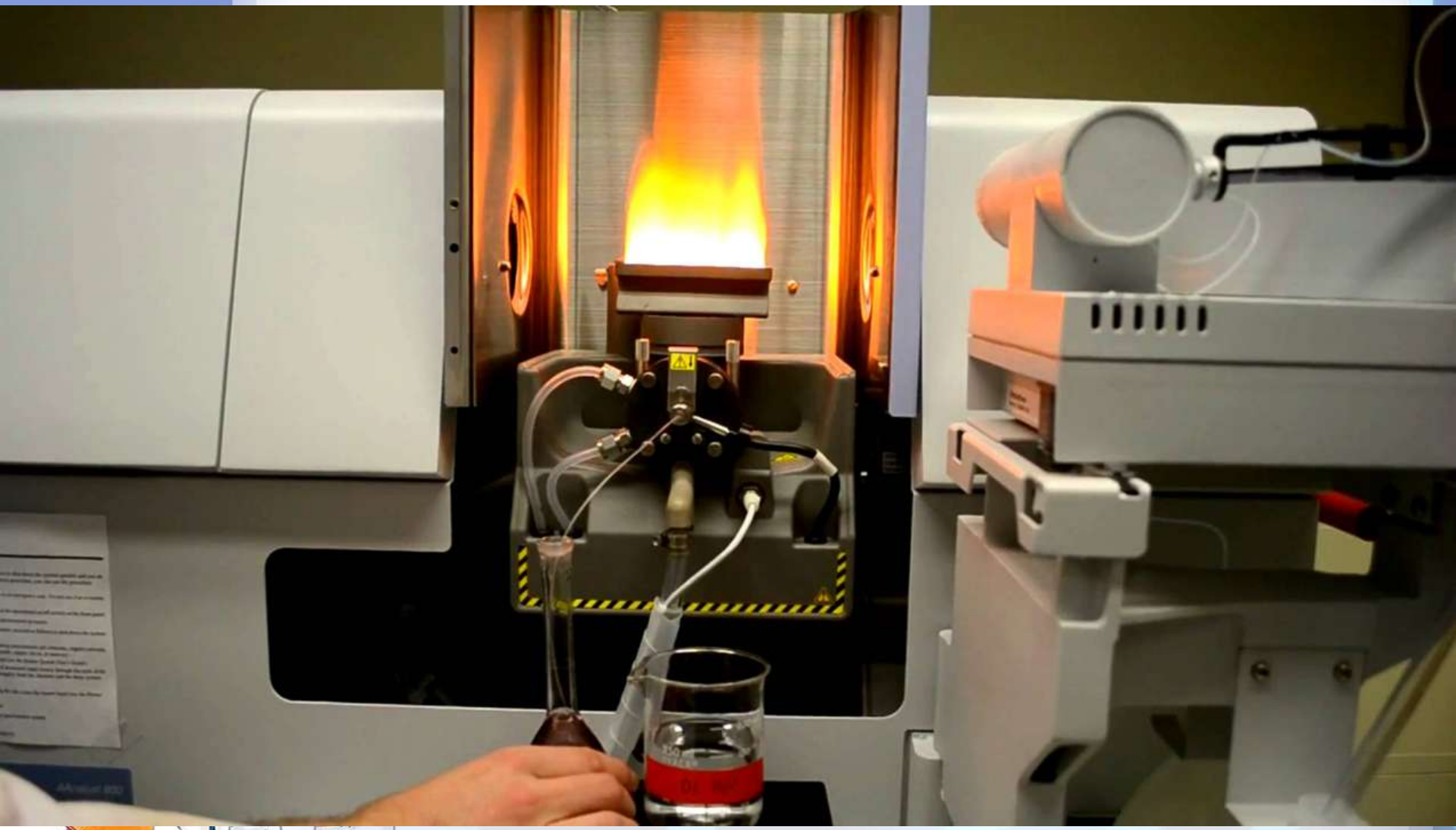
Flame Atomizers

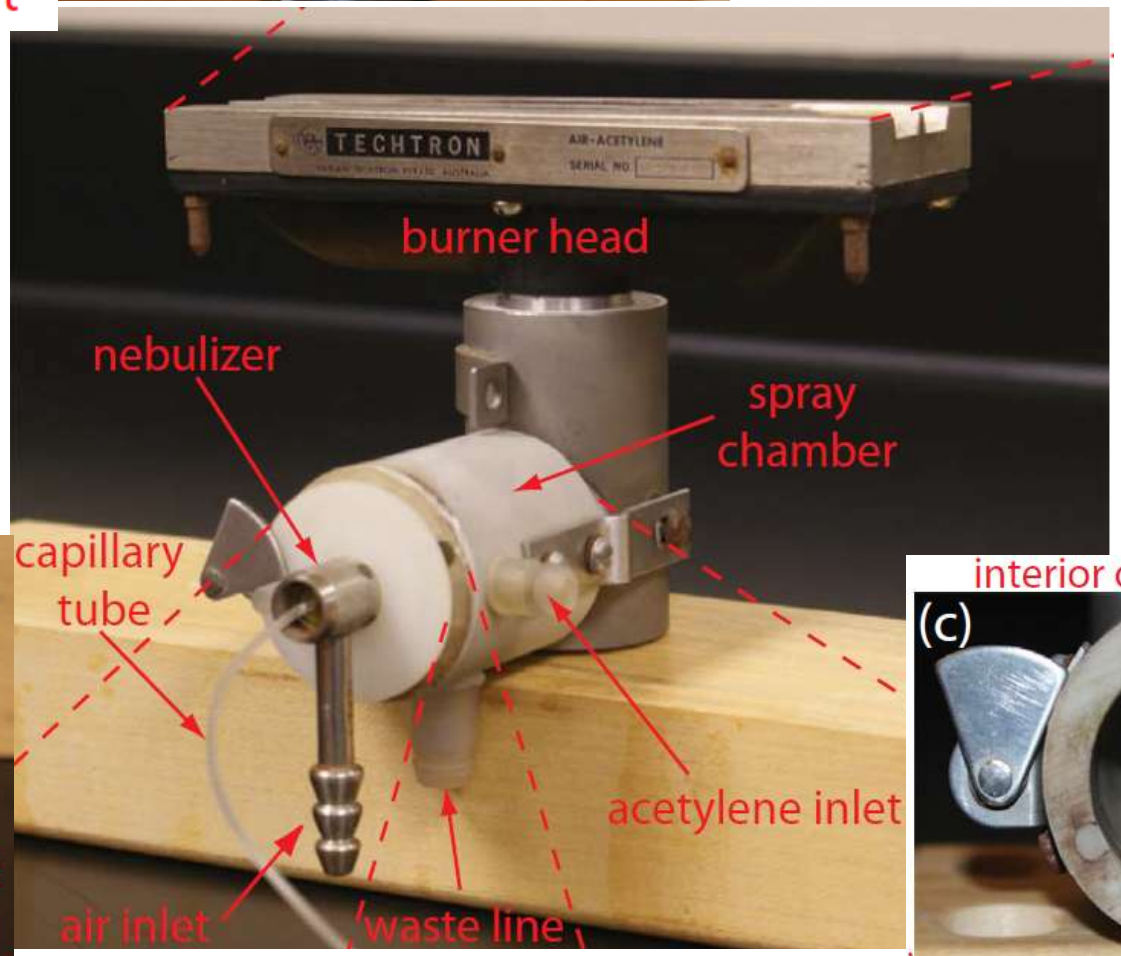
In flame atomization the sample is first converted into a fine mist consisting of small droplets of solution. This is accomplished using a nebulizer assembly. The sample is aspirated into a spray chamber by passing a high-pressure stream consisting of one or more combustion gases, past the end of a capillary tube immersed in the sample. The impact of the sample with the glass impact bead produces an aerosol mist. A flame atomizer consists of a pneumatic nebulizer, which converts the sample solution into a mist, or aerosol, that is then introduced into a burner. The concentric nebulizer is the most popular. In most atomizers, the high-pressure gas is the oxidant, with the aerosol-containing oxidant being mixed subsequently with the fuel.

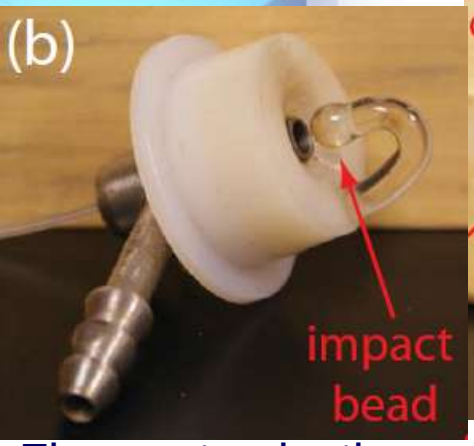


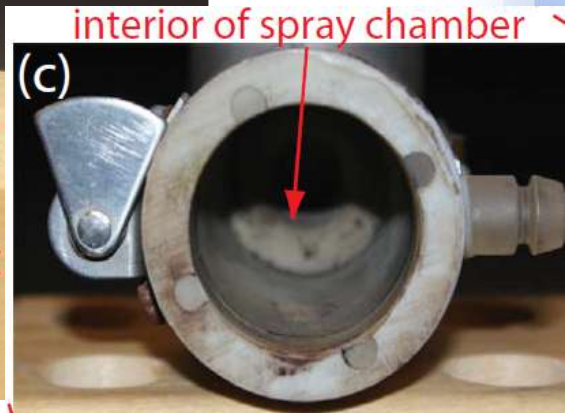


Atomization







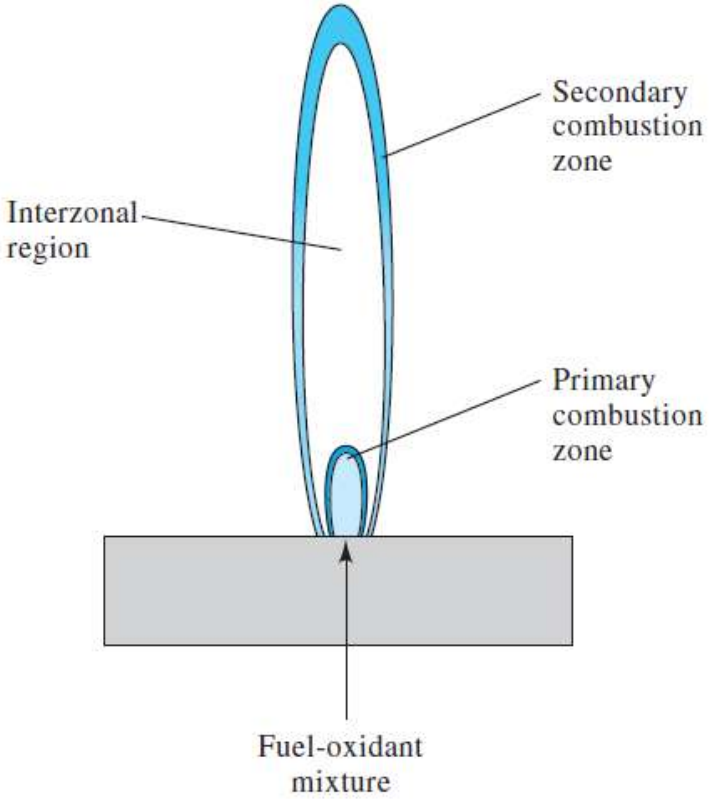


Flame atomization assembly with expanded views of (a) the burner head showing the burner slot where the flame is located; (b) the nebulizer's impact bead; and (c) the interior of the spray chamber.

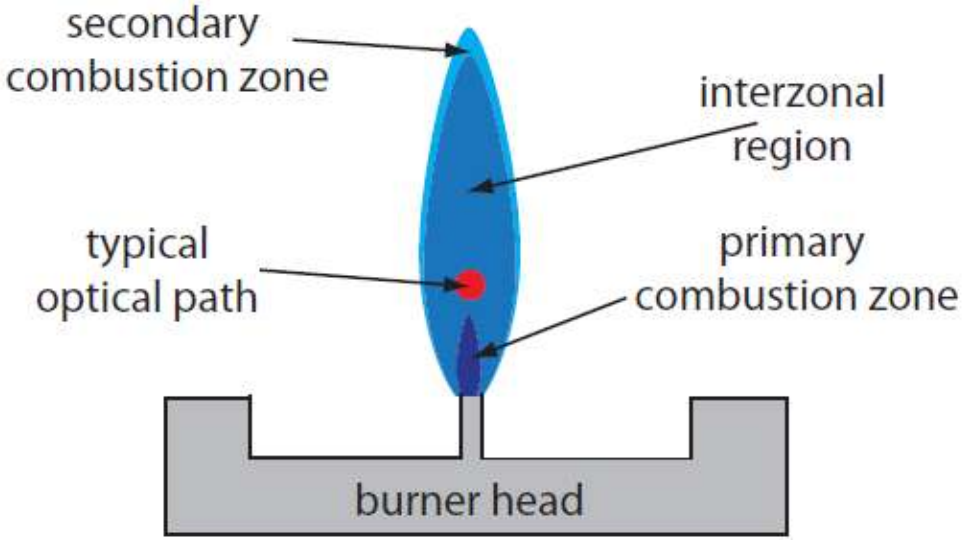
Flames Used in Atomic Spectroscopy

Fuel and Oxidant	Temperature, °C
*Gas/Air	1700–1900
*Gas/O_2	2700–2800
H_2/air	2000–2100
H_2/O_2	2500–2700
†C_2H_2/air	2100–2400
†C_2H_2/O_2	3050–3150
†C_2H_2/N_2O	2600–2800

when the oxidant is air, temperatures are in the range of 1700 to 2400°C. At these temperatures, only easily excitable species, such as the alkali and alkaline earth metals, produce usable emission spectra. For heavy-metal species, which are not so easily excited, oxygen or nitrous oxide must be used as the oxidant. These oxidants produce temperatures of 2500 to 3100°C with common fuels.



When a nebulized sample is carried into a flame, the droplets are desolvated in the ***primary combustion zone***, which is located just above the tip of the burner. The resulting finely divided solid particles are carried to a region in the center of the flame called ***the inner cone***. Here, in this hottest part of the flame, the particles are vaporized and converted to gaseous atoms, elementary ions, and molecular species. Excitation of atomic emission spectra also takes place in this region. Finally, the atoms, molecules, and ions are carried to the outer edge, or ***outer cone***, where oxidation may occur before the atomization products disperse into the atmosphere. Because the velocity of the fuel/oxidant mixture through the flame is high, only a fraction of the sample undergoes all these processes. ately, a flame is not a very efficient atomizer.



Profile of typical flame using a slot burner. The relative size of each zone depends on many factors, including the choice of fuel and oxidant, and their relative proportions.

Advantages and Disadvantages of Flame Atomization

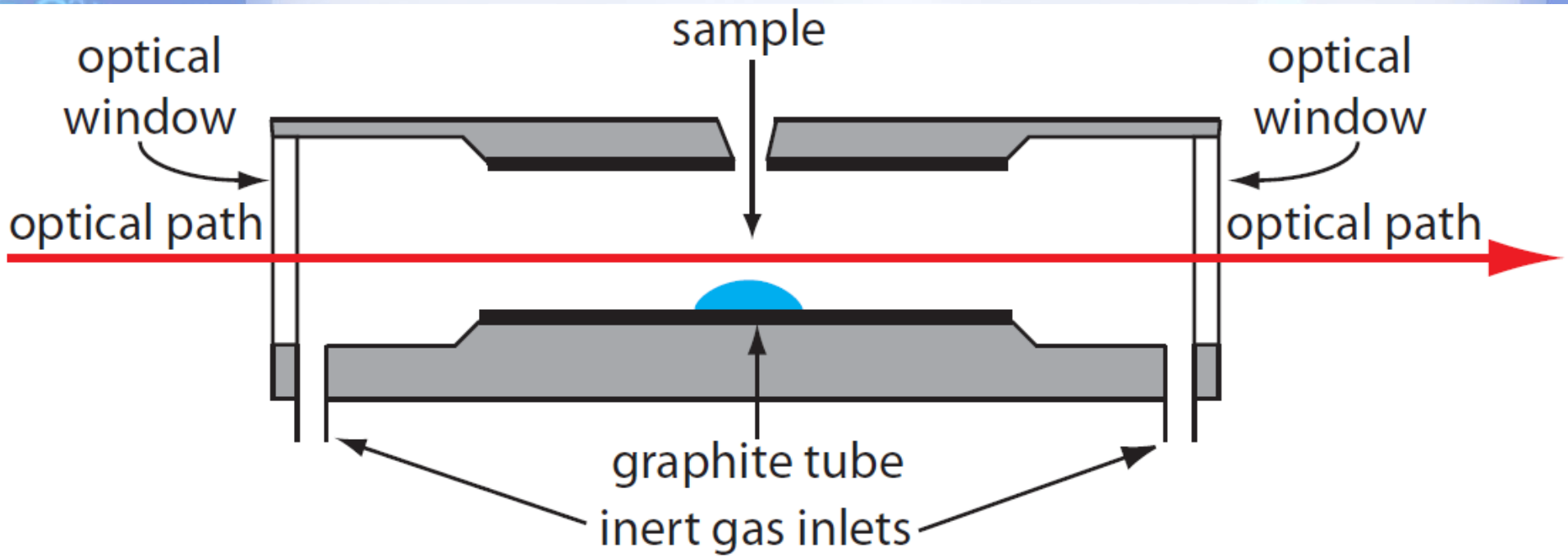
The principal *advantage* of flame atomization is the reproducibility with which the sample is introduced into the spectrophotometer. A significant disadvantage to flame atomizers is that the efficiency of atomization may be quite poor. There are two reasons for poor atomization efficiency. First, the majority of the aerosol droplets produced during nebulization are too large to be carried to the flame by the combustion gases. Consequently, as much as 95% of the sample never reaches the flame. A second reason for poor atomization efficiency is that the large volume of combustion gases significantly dilutes the sample. Together, these contributions to the efficiency of atomization reduce sensitivity because the analyte's concentration in the flame may be a factor of 2.5×10^{-6} less than that in solution.

Electrothermal Atomization

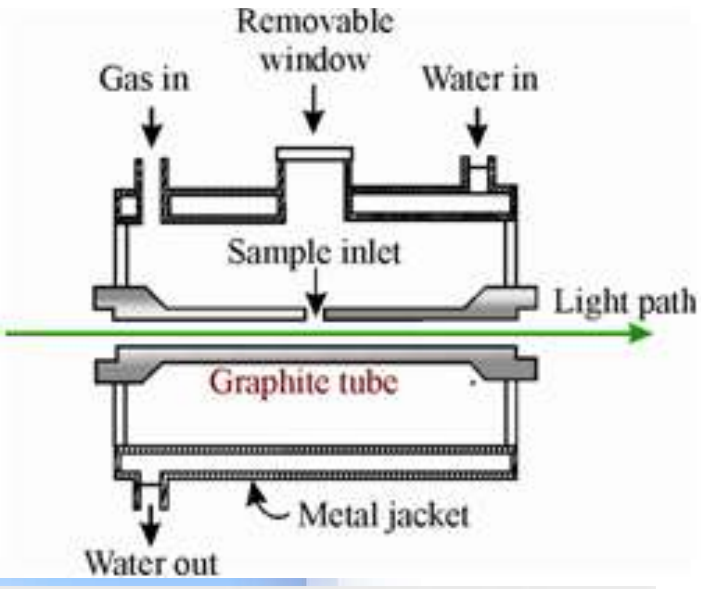
Although aspiration into a flame is the most convenient and reproducible means of obtaining atomic vapor, it is not a particularly efficient means of converting all the analyte into atomic vapor and have it present in the optical path for a long enough time to measure the absorption. From the dissolved molecular/ionic entities in solution, as little as 0.1% of the aspirated analyte may actually be atomized and measured. The volume of solution required for flame atomization is minimally of the order of a milliliter or more.

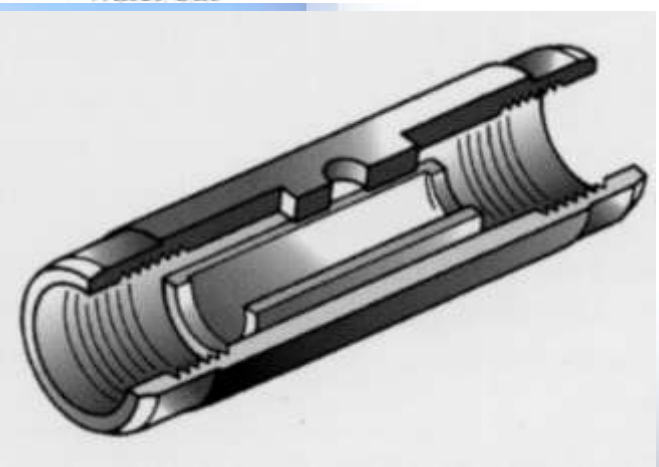
Electrothermal atomization uses some type of a mini-furnace (typically less than 1 cm^3 in volume) in which an aliquot of the sample is put in and dried. The furnace is made of an electrically conductive material. While tantalum and other substances have had utility in specific applications (e.g., for elements that form refractory carbides), presently graphite furnaces are nearly exclusively used. The furnace is then rapidly electrically heated (currents in excess of 100 amperes and heating rates in excess of 1000◦C/s are common) to a very high temperature to produce an atomic vapor cloud.

Diagram showing a crosssection of an electrothermal analyzer



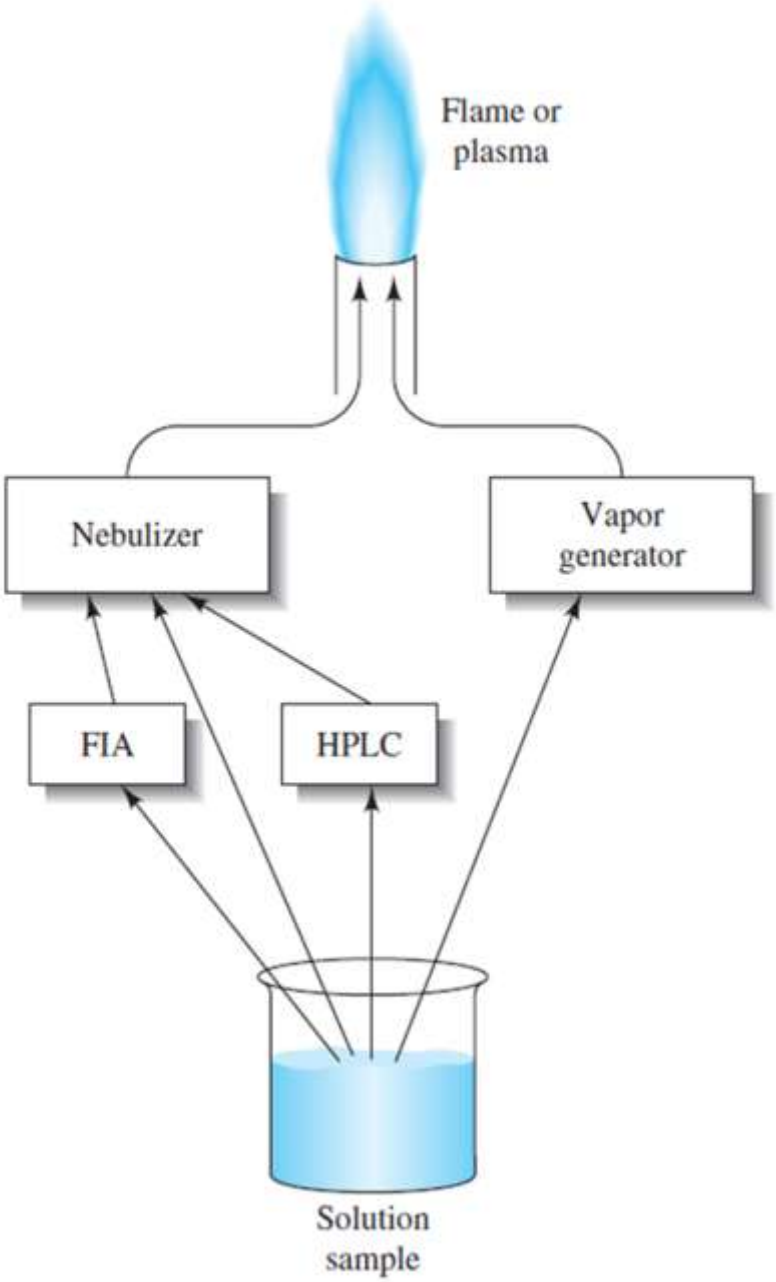
With electrothermal atomizers, a few microliters of sample are deposited in the furnace by syringe or autosampler. Next, a programmed series of heating events occurs: drying, ashing, and atomization. During the drying step, the sample is evaporated at a relatively low temperature, usually 110°C. The temperature is then increased to 300 to 1200°C, and the organic matter is ashed or converted to H_2O and CO_2. After ashing, the temperature is rapidly increased to perhaps 2000 to 3000°C, causing the sample to vaporize and atomize. Atomization of the sample occurs in a period of a few milliseconds to seconds.





Electrothermal atomization provides a significant improvement in sensitivity by trapping the gaseous analyte in the small volume of the graphite tube. The analyte's concentration in the resulting vapor phase may be as much as 1000 times greater than that produced by flame atomization. The improvement in sensitivity, and the resulting improvement in detection limits, is offset by a significant decrease in precision. Atomization efficiency is strongly influenced by the sample's contact with the graphite tube, which is difficult to control reproducibly.

Sample Introduction Systems



The general methods for introducing solution samples into plasma and flames. Direct ***nebulization*** is most often used. In this case, the nebulizer constantly introduces the sample in the form of a fine spray of droplets, called an aerosol. The ***vapor cloud*** produced with electrothermal atomizers is transient because of the limited amount of sample available and the removal of vapor through diffusion and other processes. Solid samples can be introduced into plasmas by vaporizing them with an ***electrical spark*** or with a ***laser beam***. Laser volatilization, often called ***laser ablation***, has become a popular method for introducing samples into inductively coupled plasmas. In laser ablation, a high-powered laser beam, often a Nd:YAG or excimer laser, is directed onto a portion of the solid sample. The sample is then vaporized by radiative heating. The plume of vapor produced is swept into the plasma by means of a carrier gas.

Preparing the Sample

Flame and electrothermal atomization require that the sample be in solution. Solid samples are brought into solution by dissolving in an appropriate solvent. If the sample is not soluble it may be digested, either on a hot-plate or by microwave, using HNO_3, H_2SO_4, or $HClO_4$. Alternatively, we can extract the analyte using a Soxhlet extractor.

Liquid samples may be analyzed directly or extracted if the matrix is incompatible with the method of atomization. A serum sample, for instance, is difficult to aspirate when using flame atomization and may produce an unacceptably high background absorbance when using electrothermal atomization.

A liquid–liquid extraction using an organic solvent and a chelating agent is frequently used to concentrate analytes. Dilute solutions of Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}, for example, can be concentrated by extracting with a solution of ammonium pyrrolidine dithiocarbamate in methyl isobutyl ketone.

Evaluation

1. ***Scale of Operation*** Atomic absorption spectroscopy is ideally suited for the analysis of trace and ultratrace analytes, particularly when using electrothermal atomization. By diluting samples, atomic absorption also can be applied to minor and major analytes. Most analyses use macro or meso samples. The small volume requirement for electrothermal atomization or flame microsampling, however, allows the use of micro, or even ultramicro samples.
2. ***Accuracy*** When spectral and chemical interferences are minimized, accuracies of 0.5–5% are routinely possible. Determinate errors for electrothermal atomization are frequently greater than that obtained with flame atomization due to more serious matrix interferences.
3. ***Precision*** For absorbances greater than 0.1–0.2, the relative standard deviation for atomic absorption is 0.3–1% for flame atomization, and 1–5% for electrothermal atomization. The principal limitation is the variation in the concentration of free analyte atoms resulting from a nonuniform rate of aspiration, nebulization, and atomization in flame atomizers, and the consistency with which the sample is heated during electrothermal atomization.
4. ***Sensitivity*** The sensitivity of an atomic absorption analysis with flame atomization is influenced strongly by the flame's composition and the position in the flame from which absorption is monitored. Normally the sensitivity for an analysis is optimized by aspirating a standard and adjusting operating conditions, such as the fuel-to-oxidant ratio, the nebulizer flow rate, and the height of the burner, to give the greatest absorbance. With electrothermal atomization, sensitivity is influenced by the drying and ashing stages that precede atomization. The temperature and time used for each stage must be worked out for each
type of sample.
5. ***Selectivity*** Due to the narrow width of absorption lines, atomic absorption provides excellent selectivity. Atomic absorption can be used for the analysis of over 60 elements at concentrations at or below the level of parts per million.
6. ***Time, Cost, and Equipment*** The analysis time when using flame atomization is rapid, with sample throughputs of 250–350 determinations per hour when using a fully automated system. Electrothermal atomization requires substantially more time per analysis, with maximum sample throughputs of 20–30 determinations per hour. The cost of a new instrument ranges from $10,000 to $50,000 for flame atomization and $18,000 to $70,000 for electrothermal atomization. The more expensive instruments in each price range include double-beam optics and automatic samplers, are computer controlled, and can be programmed for multielemental analysis by allowing the wavelength and hollow cathode lamp to be changed automatically.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