Spectrophotometric Methods of Analysis

1-Electromegnetic Radiation and its interaction with Matter

المحاضرة الاولى

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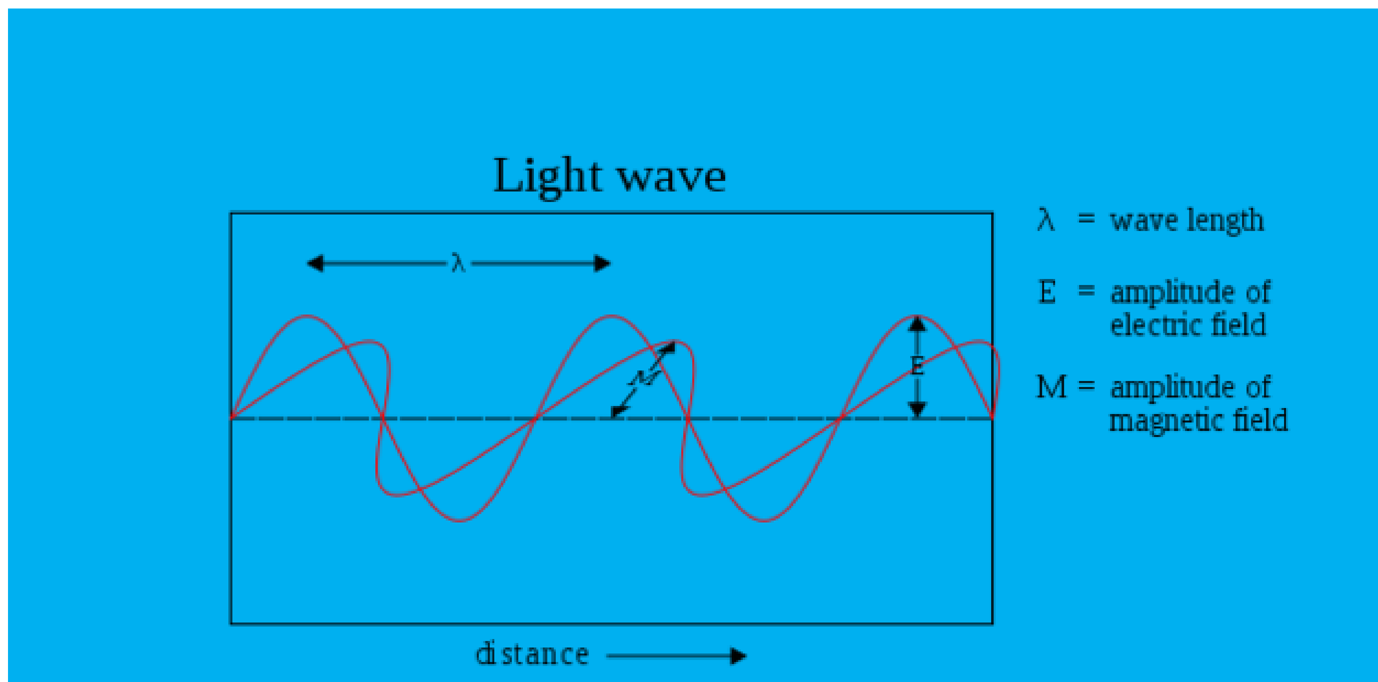
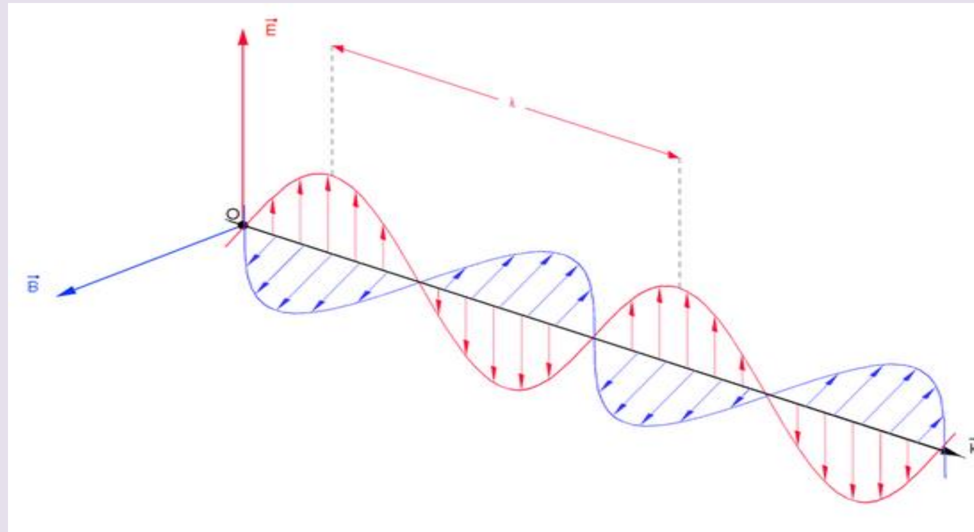
A- Electromegnetic Radiation: is a form of energy that is transmitted through space at enormous velocities. Electromegnetic Radiation can be described as a wave with properties of wave length,frequency,velocity,and amplitude.In contrast to sound wavelight requires no supporting medium for its transmission ,thus ,it easily passes through a vacuum .Light also travels nearly a million times faster than sound

The wave model fails to account for phenomena associated with the absorption and emission of radiant energy.For these processes, electromegnetic radiation can be treated as discrete packets of energy or particles called photon or quanta.These duol views of radiation as particles and waves are not mutually exclusive but are complementary.In fact the energy of a photon is directly proportional to its frequency ,as well shall see. Similarly,this duality app;ies to streams of electrons,protons and other elementary particles,which can produce interference and diffraction effects that are typically associated with wave behavior.

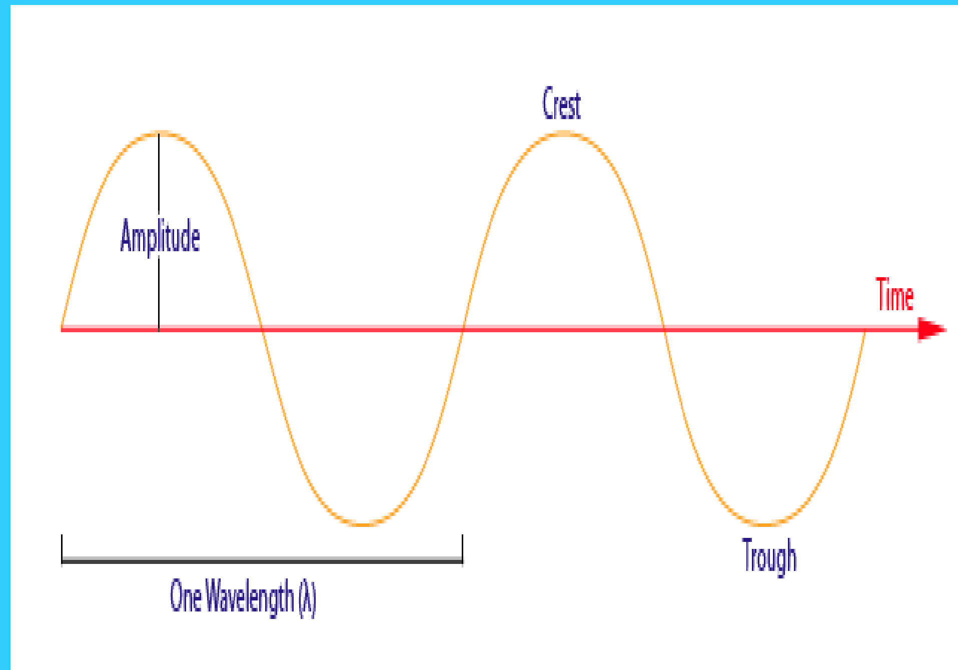
1-Wave Properties

In dealing with phenomena such as reflection ,refraction,interference,and diffraction, electromagnetic radiation,is conveniently mode led as waves consisting of per ascillates electric and magnetic fields as shown in Fig 1





The electric field for single –frequency wave oscillates sinusoid ally in space and time,shown in Fig.2



The electric field is represented as a vector whose length is proportional to the field strength.The x-axis in this plot is either time as the radiation passes affixed point in space or distance at affixed time.Note that the direction in which the field oscillates is perpendicular to the direction in which the radiation propagates.

Wavelength Units for Various Spectral Regions

Region	Unit	Definition
x-ray	Angstrom.A^0	10^{-10} m
Ultraviolet/visible	Nanometer,nm	10^{-9} m
Infrared	Micrometer,µm	10^{-6} m

Period(p):The time in seconds required for the passage of successive maxima or minima through a fixed point in space.

Frequency):Is the number of oscillations of the electric field vector per unit time and equal to 1/p.

Velocity( ): Velocity of the wave front through medium depends on both the medium and the frequency.

Wavelength(λ): The linear distance between successive to maxima or minima of a wave.

Wave number (ύ):It's the number of waves per centimeter and is equal to 1/λ ,the unit of ύ is cm^{-1}.

Example1: Calculate the wavenumber of a beam of infrared radiation with a wavelength of 5.00µm.

Solution:

$$\acute{\upsilon} = \frac{1}{5.00\mu m * 10-6\ cm/\mu m}$$

$= 2000 cm^{-1}$

Amplitude: Is a vector quantity that provides a measure of the electric or magnetic field strength at a maximum point in the wave.

Particle Nature of Light :Photons

In many radiation / matter interaction ,it is most useful to consider light as consisting of photons or quanta.The relation of energy of photon to its wavelength ,frequency,and wavenumber by:

$$E = h\upsilon = \frac{hc}{\lambda} = hc\acute{\upsilon}$$

h= Plank,s constant equal to $6.63*10^{-34}$Js.Note that the wave number and frequency ,in cintrast to the wavelength,are directly proportional to the photon energy.Wavelength is inversely proportional to energy.The radiant power of a beam of radiation is directly proportional to the number of photons per second.

c-Absorption Spectroscopy

If the sample is stimulated by application of an external electromagnetic radiation source ,several processes are possible .For example ,the radiation can be scattered or reflected ,what is important to us is that some of the incident radiation can be absorbed and thus promote some of the analyst species to an excited state .

Photoluminescence Spectroscopy

The most important forms of Photoluminescence for analytical purposes are fluorescence and phosphorescence spectroscopy ,result from absorption of electromagnetic radiation and then dissipation of the energy by emission of radiation in figure above ,the absorption can be cause excitation of the analyst to state 1 or state 2.Once excited,the excess energy can be lost by emission of photon(luminescence).The emission occurs over all angles,and the wavelength emitted correspond to energy differences between levels.The major distinction between fluorescence and phosphorescence in the time scale of emission ,with fluorescence being prompt and phosphorescence being delayed.

e-Radiation absorption

Every molecular species is capable of absorbing its own characteristic frequencies of electromagnetic radiation .In this process transfer energy to the molecule and results in a decrease in the intensity of the incident electromagnetic radiation .Absorption of the radiation ,thus attenuates the beam in accordance with the absorption law described later.

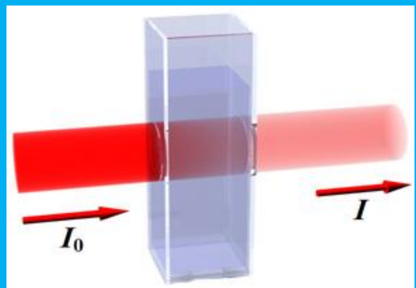
Attuenuate: means to decrease the energy per unit area of abeam of radiation .In terms of the photon model to attenuate means to decrease the number of photons per second in the beam.

d-The absorption Law(Beer-Lambert law or just Beer,s law)

Beer,s law ,tells us quantitatively how the amount of attenuation depends on the concentration of the absorbing molecules and the path length over which absorption occurs.As light traverses a medium containing an absorbing analyte,decrease in intensity occur as the analyte becomes excited.For an analyst solution of a given concentration,the longer the length of light),the more absorbera are in the path ,and the greater the attenuation .Also ,for a given path length of the light ,the higher the concentration of absorbers,the stronger the attenuation.

In the figure ,depicts the attenuation of a parallel beam of monochromatic radiation as it passes through an absorbing solution of thickness contimeters and concentration moles per liter,because of interaction between the photons and absorbing particles the radiant power of the beam decrease from to p_0 or I_0 to P or I.Then transmittance T of the solution is the fraction of incident radiation transmitted by the solution ,as shown in equation 1.transmittance is often expressed as a percentage called the percent transmittance.

$$T = P/P_0$$


I_0
I

Many compounds absorb ultraviolet (UV) or visible (Vis.) light. The diagram below shows a beam of monochromatic radiation of radiant power P_0, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P.

The Beer-Lambert Law

Now let us look at the Beer-Lambert law and explore it's significance. This is important because people who use the law often don't understand it - even though the equation representing the law is so straightforward:

$$A = \varepsilon bc$$

e-Limits to Beer's Law

There are few exception to the linear relationship between absorbance and path length at affixed concentration.We frequently observe deviations from the direct proportionality between absorbance and concentration,however,when the path length bis a constant.Some of these deviations,called real deviation ,are fundamental and represent real limitation to the law.Others are a result of the method that we use to make absorbance measurments(instrumental deviations) or a result of chemical changes that occur when the concentration changes(chemical deviations).

1-Real Limitations to Beer's Law

Beer's Law described the absorption behavior only of dilute solutions and in this sens is a limiting law.At concentration exceeding about0.01M,the average distances between ions or molecules of the absorbing species are diminished to the point where each particle affects the charge distribution ,and thus the extent of absorption,of its neighbors.Because the extent of interaction depends on concentration,the occurrence of this phenomenon causes deviation from the linear relationship between absorbance and concentration.Asimilar effect sometimes occurs in dilute solution of absorbers that contain high concentratios of other species,particularly electrolytes.When ion are very close to one another,the molar absorptivity of the analyst can be altered because of electrostatic interactions,and this can lead to departures from Beer's law.

2- Chemical Deviations

Deviation from Beer׳s law appear when the absorbing species undergoes association ,dissociation,or reaction with the solvent to give products that absorb differently from the analyst.The extent of such deparures can be predicted from the molar absorptivities of the absorbing species and the equilibrium constant for the equilibria involved.Unfortunately,since we are usually unaware that such processes are affecting the analyst,there is often no opportunity to correct the measurement .Typical equilibria that give rise to this effect include monomer-dimer equilibria,metal complexation equilibria when more than one complex is present,acid-base equilibria,and solvent-analyst association equilibria.

Mismatched Cells

Another almost trivial but important deviation from adherence to Beer's law is caused by mismatched cells.If the cells holding the analyte and blank solution are not of equal path length and are not equivalent in optical characteristics ,an intercept will occur in the calibration curve ,and $A=\varepsilon bc+k$ will be the actual equation instead of equation below :

$$A=\varepsilon bc$$

This error can be avoided by using either carefully matched cells or a linear regression procedure to calculate both the slope and the intercept of the calibration curve .In most cases ,this is the best strategy because an intercept can also occur if the blank solution does not totally compensate for interferences .Another way to avoid the mismatched-cell problem with single-beam instruments is to use only one cell and keep it in the same position for both blank and analyte measurements.After obtaining the blank reading ,the cell is emptied by aspiration ,washed ,and filled with analyte solution

The first two design ,for absorption and fluorescence spectroscopy,require an external source of radiation .In absorption measurements (a) the attenuation of the source radiation at the selected wavelength is measured.In fluorescence measurements(b),the source excites the analyte and causes the emission of characteristic radiation ,which is usually measured at a 90 degree angle with respect to the incident source beam.In emission spectroscopy (c),the sample itself is the emitter and no external radiation source is needed.In emission methods ,the samples is usually fed into a plasma or aflame,which provides enough thermal energy to cause the analyte to emit characteristic radiation .

a-Components and configurations of instruments.

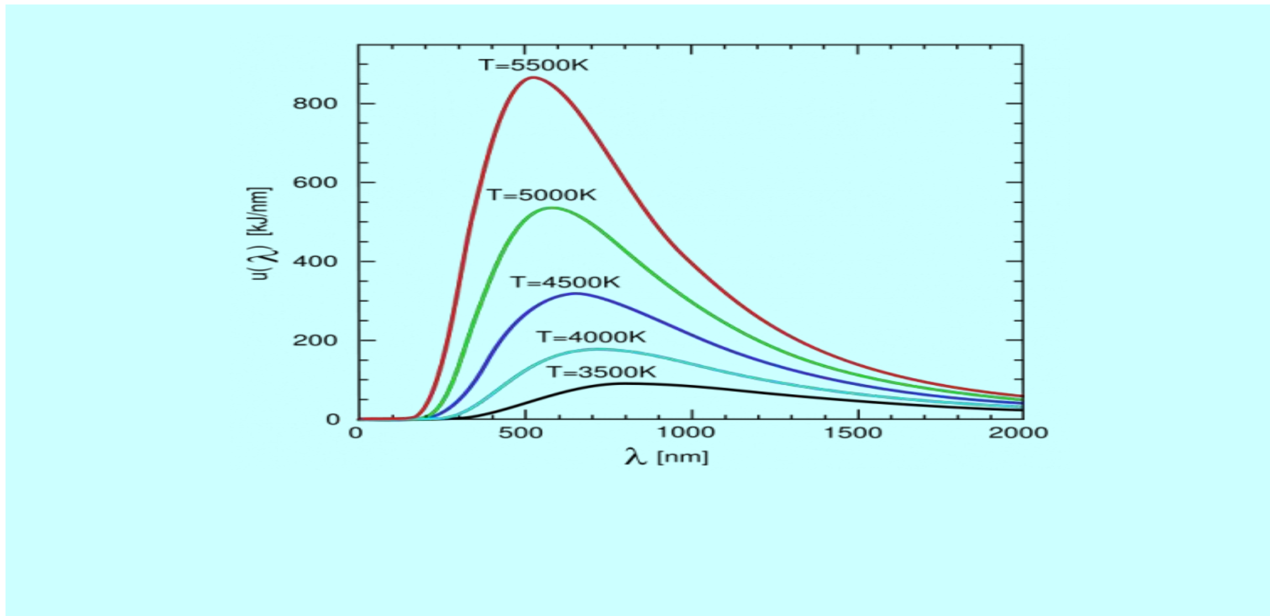
Most spectroscopic instruments for use in the UV/ visible and IR regions are made up of five components:1- a stable source of radiant energy,2-a wavelength selector that isolates a limited region of the spectrum for measurement,3- one or more sample containers ,4-a radiation detector,which converts radiant energy to a measureable electrical signal,and 5- a signal processing and readout unit,usually consisting of electronic hardware and.in modern instruments,a computer.Figure 1 illustrates the three configuration of these components for carrying out optical spectroscopic measurements.As can be seen in the figure,components 3,4,and 5 have similar configurations for each type of measurement.

3-Components of Instruments for Optical Spectroscopy

The basic components of analytical instruments for absorption spectroscopy as well for emission and fluorescence spectroscopy,are remarkably alike in function and in general performance requirements whether the instruments are desigened for ultraviolet(UV),visible,or infrared (IR) radiation.Because of the similarities,such instruments are frequently referred to as optical instruments even though the eye is sensitive only to the visible region.

Effect of Concentration on Line and Band Spectra

The radiant power Pof a line or a band depends directly on the number of excited atoms or molecules,which in turn is proportional to the total concentration c of the species present in the source ,Thus ,we can write $p=kc$, which k constant.



Figuer:Black body radiation curves for various light.

Continuum Spectra

Truly continuous radiation is produced when solids such as carbon and tungsten are heated to incandescence .Thermal radiation of this kind,which is called blackbody radiation,is more characteristic of the temperature of the emitting surface than of its material.Black body radiation is produced by the innumerable atomic and molecular oscillations excited in the condensed solid by the thermal energy .Note that the energy peaks shift to shorter wavelength with increasing temperature.As the figure shows,very high temperatures are required to cause a thermally excited source to emit a substantial fraction of its energy as ultraviolet radiation. Part of the continuum background radiation in the flame spectrum is probably thermal emission from incandescent particles in the flame.Note that this background decreases rapidly as the wavelength approaches the ultraviolet region of the spectrum.

Band Spectra

Band spectra are often produced in spectral sources because of the presence of gaseous radicals or small molecules.For example ,band for OH,MgOH,and MgO are labeled and consist of a series of closly spaced lines that are not fully resolved by the instrument used to obtain the spectrum .Bands arise from the numerous quantized vibrational levels that are superimposed on the ground state electronic energy level of a molecule.

Line Spectra

Line Spectra occur when the radiating species are individual atomic particles that are well separated,as in a gas .The individual particles in a gaseous medium behave independently of one another .and the spectrum in most media consists of a series of sharp lines with widths of 10^{-1} to $10^{-2}A^0$(10^{-2} to 10 nm) .

Emission Spectra

Radiation from a source is conveninently characterized by means of an emission spectrum ,which usually takes the form of plot of the relative power of the emitted radiation as a function of wavelength of frequency .Three typesof spectra:line spectrum,a band spectrum,and a continuum spectrum.The line spectrum is made up of a series of sharp,well-defined peaks caused by excitation of individual atoms.The band spectrum is composed of several groups of lines so closely spaced that are not completely resolved.The source of the bands is small molecules or radicals in the source flame.

Emission of Electromagnetic Radiation

Atoms,ions,and molecules can be excited to one of more higher energy level by any of several processes ,including bombardment with electrons or other elementary particles ;exposure to a high – temperature plasma,flame ,or electric arc;or exposure to a source of electromagnetic radiation .The lifetime of an excited species is generally transitory (10^{-9} to 10^{-6} s) ,and relaxation to a lower energy level or the ground state takes place with a release of the excess energy in the form of electromagnetic radiation ,heat ,or perhaps both.

b-Optical Materials

The cell,window,lenses.mirrors,and wavelength-selecting elements in an optical spectroscopic instrument must tranmit radiation in the wavelength region being in figure down shows the usable wavelength range for several optical materials that are used in the UV,VISIBLE,and IR regions of the spectrum.Ordinary silicate glass is completely adequate for use in the visible region and has the considerable advantage of low coast In the UV region at wavelength shorterthan about 380 nm,glass being to absorb,and fused silica or quartz must be substituted .Also ,in the IR region ,glass,quartz,and fused silica all absorb at wavelength longer than about 2.5µm.Hence ,optical elements for IR spectrometry are typically made from halide salts or ,in some cases ,polymeric materials.

b- Radiation sources for UV, UV,VIS,IR and Laser radiation

To be suitable for spectroscopic studies,a source must generate a beam of radiation that is sufficiently powerful to allow easy detection and measurement .In addition is output power should be stable reasonable periods of time.Typically ,for good stability, a well-regulated power supply must provide electrical power for the source .Spectroscopic source are of two types:continuum sources ,which emit radiation that change in intensity only slowly as a function of wavelength,and line sources ,which emit a limited number of spectral lines,each of wich spans avery limited wavelength range .The distinction between these sources is illustrated in figure below.Sources can also be classified as continuous sources which emit radiation continuously with time

,or pulsed sources,which emit radiation in bursts.

Continum Sources in the Ultraviolet/Visible Region

The most widely used continuum sources in the UV/VIS.range are listed in Table below:

Source	Wavelength Region,nm	Type of Spectroscopy
Xenon arc lamp	250-600	Molecular Fluorescence
H_2 and D_2 lamp	160-380	UV molecular absorption
Tungsten/halogen lamp	240-2500	UV/VIS./near IR molecular absorption
Tungsten lamp	350-2200	UV/VIS./near IR molecular absorption
Nernst glower	400-20,000	IR molecular absorption
Nichrome wire	750-20,000	IR molecular absorption
Globar	1200-40,000	IR molecular absorption

Tungsten /halogen lamps

small Tungsten/halogen lamps, also called quartz/halogen lamps, contain a amount of iodine within the quartz envelope that houses the filament. Quartz allows the filament to be operated at a temperature of about 3500 K, leading to higher intensities and extending the range of the lamp well into the UV. The lifetime of a tungsten/halogen lamp is more than double that of an ordinary tungsten lamp, which is limited by sublimation of tungsten from the filament. In the presence of iodine, the sublimed tungsten reacts to give gaseous WI_2 molecules. These molecules then diffuse back to the hot filament where they decompose, redeposit W atoms on the filament, and release iodine. Tungsten/halogen lamps are finding ever-increasing use in spectroscopic instruments because of their extended wavelength range, greater intensity, and longer life.

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.The lamp emits continuum radiation when deuterium (or hydrogen) is stimulated by electrical energy to produce excited molecule of D2 * (or H2 *). The excitedstate species then dissociates to give two hydrogen or deuterium atoms plus an ultraviolet photon. The reactions for hydrogen are H2 1 Ee S H2*S Hr 1 Hs 1 hn where Ee is the electrical energy absorbed by the molecule. The energy for the overall process is Ee 5 EH2 * 5 EHr1 EHs1 hn where EH2 * is the fixed quantized energy of H2* and EHr and EHs are the kinetic energies of the two hydrogen atoms. The sum of the latter two energies can vary from zero to EH2*. Thus, the energy and the frequency of the photon can also vary within this range of energies. That is, when the two kinetic energies are by chance small, hn is large, and when the two energies are large, hn is small. As a result, hydrogen lamps produce a true spectral continuum from about 160 nm to the beginning of the visible region.

Today, most lamps for generating ultraviolet radiation contain deuterium and are of a low voltage type in which an arc is formed between a heated, oxide-coated filament and a metal electrode .The heated filament provides electrons to maintain a direct current at a potential of about 40 V; a regulated power supply is required for constant intensities. Both deuterium and hydrogen lamps provide a useful spectral continuum in the region from 160 to 375 nm. The deuterium lamp is more widely used than the hydrogen lamp, however, because the deuterium lamp is more intense. At longer wavelengths (360 nm), the lamps generate emission lines that are superimposed on the continuum. For many applications, these lines are a nuisance, but they are useful for wavelength calibration of absorption instruments.

Other Ultraviolet/Visible Sources

In addition to the continuum sources just discussed, line sources are also important for use in the UV/visible region. Low-pressure mercury arc lamps are common sources for use in liquid chromatography detectors. The dominant line emitted by these sources is the 253.7-nm Hg line. Hollow cathode lamps are also common line sources that are specifically used for atomic absorption spectroscopy. Lasers are also used in many spectroscopic applications, both for single wavelength and for scanning purposes.

Laser Sources: The Light Fantastic

Lasers have become widely used as sources in certain types of analytical spectroscopy. To help us understand how a laser works, consider an assembly of atoms or molecules interacting with an electromagnetic wave. For simplicity, we will consider the atoms or molecules to have two energy levels: an upper level 2 with energy E_2 and a lower level 1 with energy E_1. If the electromagnetic wave is of a frequency corresponding to the energy difference between the two levels, excited species in level 2 can be stimulated to emit radiation of the same frequency and phase as the original electromagnetic wave.

Continuum Sources in the Infrared Region

The continuum sources for IR radiation are normally heated inert solids. A **Globar** source consists of a silicon carbide rod. Infrared radiation is emitted when the Globar is heated to about 1500°C by passing electricity through it. Table 25-1 gives the wavelength range of these sources. A **Nernst glower** is a cylinder of zirconium and yttrium oxides that emits IR radiation when heated to a high temperature by an electric current. Electrically heated spirals of nichrome wire also serve as inexpensive IR sources.

Wavelength Selectors

Spectroscopic instruments in the UV and visible regions are usually equipped with one or more devices to restrict the radiation being measured to a narrow band that is absorbed or emitted by the analyte. Such devices greatly enhance both the selectivity and the sensitivity of an instrument. In addition, for absorption measurements, as we saw in Section 24C-3, narrow bands of radiation greatly diminish the chance for Beer's law deviations due to polychromatic radiation. 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.

b-Optical Materials

The cell,window,lenses.mirrors,and wavelength-selecting elements in an optical spectroscopic instrument must tranmit radiation in the wavelength region being in figure down shows the usable wavelength range for several optical materials that are used in the UV,VISIBLE,and IR regions of the spectrum.Ordinary silicate glass is completely adequate for use in the visible region and has the considerable advantage of low coast In the UV region at wavelength shorterthan about 380 nm,glass being to absorb,and fused silica or quartz must be substituted .Also ,in the IR region ,glass,quartz,and fused silica all absorb at wavelength longer than about 2.5µm.Hence ,optical elements for IR spectrometry are typically made from halide salts or ,in some cases ,polymeric materials.

Monochromators and Polychromators

Monochromators generally have a diffraction grating to disperse the radiation into its component wavelengths. Older instruments used prisms for this purpose . By rotating the grating, different wavelengths can be made to pass through an exit slit. The output wavelength of a monochromator is thus continuously variable over a considerable spectral range. The wavelength range passed by a monochromator, called the **spectral bandpass** or **effective bandwidth**, can be less than 1 nm for moderately expensive instruments to greater than 20 nm for inexpensive systems. Because of the ease with which the wavelength can be changed with a monochromator-based instrument, these systems are widely used for spectral scanning applications as well as applications requiring a fixed wavelength. With an instrument containing a **spectrograph**, the sample and wavelength selector are reversed from the configuration shown in Figure 25-1a. Like the monochromator, the spectrograph contains a diffraction grating to disperse the spectrum

Gratings

Most gratings in modern monochromators are replica gratings, which are obtained by making castings of a master grating. The latter 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. A grating for the ultraviolet and visible region typically has from 50 to 6000 grooves/mm, with 1200 to 2400 being most common. The construction of good master grating is tedious, time consuming, and expensive because the grooves must be identical in size, exactly parallel, and equally spaced over the length of the grating (3 to 10 cm). Replica gratings are formed from a master grating by a liquid resin casting process that closely preserves the optical accuracy of the original master grating on a clear resin surface. This surface is usually coated with aluminum or sometimes gold or platinum so that it reflects electromagnetic radiation.

The Echellete Grating. One of the most common types of reflection gratings
is the echellette grating. Figure 25-8 shows a schematic representation of this type of grating, which is grooved or **blazed** such that it has relatively broad faces where reflection occurs and narrow unused faces.4 This geometry provides highly efficient diffraction of radiation. In Figure 25-8, a parallel beam of monochromatic radiation approaches the grating surface at an angle *i* relative to the grating normal. The incident beam is depicted as consisting of three parallel beams that make up a wave front labeled 1, 2, 3. The diffracted beam is reflected at the angle *r*, which depends on the wavelength of the radiation.

Interference Filters. Interference filters are used with ultraviolet and visible radiation, as well as with wavelengths as long as about 14 mm in the infrared region. As the name implies, an interference filter relies on optical interference to provide a relatively narrow band of radiation, typically 5 to 20 nm in width. 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. This array is sandwiched between two glass plates that protect it from the atmosphere.

the central array at a 90-degree angle, approximately half is transmitted by the first metallic layer and the other half. The transmitted radiation undergoes a similar partition when it rereflectedaches the second layer of metal. If the reflected portion from the second layer is of the proper wavelength, it is partially reflected from the inner portion of the first layer in phase with the incoming light of the same wavelength. The result is constructive interference of the radiation of this wavelength and destructive removal of most other wavelengths. As shown in Feature 25-4, the nominal wavelength for an interference filter lmax is given by the equation

$$\lambda_{max}=2\eta t/n$$

where *t* is the thickness of the central fluoride layer, h is its refractive index, and **n** is an integer called the interference order. The glass layers of the filter are often selected to absorb all but one of the wavelengths transmitted by the central layer, thus restricting the transmission of the filter to a single order.

Detecting and Measuring Radiant Energy

To obtain spectroscopic information, the radiant power transmitted, fluoresced or emitted, must be detected in some manner and converted into a measurable quantity. 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.

Diode-Array Detectors. Silicon photodiodes have become important recently because 1000 or more can be fabricated side by side on a single small silicon chip with the width of individual diodes being only about 0.02 mm. With one or two of the diode-array detectors placed along the length of the focal plane of a monochromator, all wavelengths passed can be monitored simultaneously, thus making high speed spectroscopy possible. If the number of light-induced charges per unit time is large compared to thermally produced charge carriers, the current in an external circuit, under reverse-bias conditions, is directly related to the incident radiant power. Silicon photodiode detectors respond extremely rapidly, usually in nanoseconds. Diode arrays can also be obtained commercially with front-end devices called **image intensifiers** to provide gain and allow the detection of low light levels.

Charge-Transfer Devices. Photodiode arrays cannot match the performance of photomultiplier tubes in terms of sensitivity, dynamic range, and signal-to-noise ratio. Thus, their use has been limited to situations where the multichannel advantage outweighs their other shortcomings. In contrast, performance characteristics of **charge-transfer device** (CTD) detectors approach or sometimes surpass those of photomultiplier tubes in addition to having the multichannel advantage. As a result, this type of detector is now appearing in ever-increasing numbers in modern spectroscopic instruments.8 A further advantage of charge-transfer detectorsis that they are two dimensional in the sense that individual detector elements are arranged in rows and columns.

Charge-coupled devices are also available with front-end image intensifiers to provide gain. Such intensified CCDs (ICCDs) can be gated on and off at selected intervals to provide time resolution for lifetime studies or for chemical kinetics experiments or to discriminate against undesirable signals. A recent development in CCD cameras is the electron-multiplying CCD (EMCCD) in which a gain register is inserted prior to the output amplifier. Both ICCDs and EMCCDs are capable of single photon detection. Because of the image intensifier, ICCDs are more expensive than EMCCDs. However, the EMCCD must be cooled to low temperatures (<170K), which leads to additional expense and often condensation problems. CCDs and CIDs are appearing in ever-increasing numbers in modern spectroscopic instruments. In spectroscopic applications, charge-transfer devices are used in conjunction with multichannel instruments as discussed in Section 25B-3. In addition to spectroscopic applications, charge-transfer devices find widespread applications in digital cameras, in solid-state television cameras, in microscopy, and in astronomical applications, such as the Hubble Space Telescope.

ThermalDetectors

The convenient photon detectors discussed in the previous section cannot be used to measure infrared radiation because photons in this region lack sufficient energy to cause photoemission of electrons. Historically, thermal detectors, such as thermocouples, bolometers, and pneumatic devices, were used to detect all but the shortest IR wavelengths. These detectors are still found in older dispersive IR spectrometers. The characteristics of most thermal detectors are, however, much inferior to those of

the photon detectors used in the UV/visible region.

Signal Processors and Readout Devices

A signal processor is an electronic device that may amplify the electrical signal from the detector (see Feature 25-6). In addition, the signal processor may convert the signal from dc to ac (or the reverse), change the phase of the signal, and filter it to remove unwanted components. The signal processor may also perform such mathematical operations on the signal as differentiation, integration, or conversion to logarithms. Several types of readout devices are found in modern instruments. Digital meters and computer monitors are two examples. Computers are often used to control various instrumental parameters, to process and store data, to print results and spectra, to compare results with various databases, and to communicate with other computers and network devices.

Utraviolet/Visible Photo meters and Spect rophoto meters

The optical components have been combined in various ways to produce two types of instruments for absorption measurements. Several common terms are used to describe complete 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 (recall from Chapter 24, Equation 24-6 on page 659 that A 5 log P0/P < log Psolvent/Psolution).

Single-Beam Instrument

Tthe design of a simple and inexpensive spectrophotometer, the Spectronic 20, which is designed for the visible region of the spectrum. This instrument first appeared on the market in the mid-1950s, and the modified version shown in the figure is still being manufactured and widely sold. More of these instruments are currently in use throughout the world than any other single spectrophotometer model. The Spectronic 20 reads out in transmittance or in absorbance on a **liquid-crystal display (LCD)**; older analog instruments read out in transmittance on a meter. The instrument is equipped with an **occluder**, which is a vane that automatically falls between the beam and the detector whenever the cylindrical cell is removed from its holder. The light control device consists of a V-shaped aperture that is moved in and out of the beam to control the amount of light reaching the exit slit.

Double-BeamInstruments

Many modern photometers and spectrophotometers are based on a double-beam
design. two double-beam designs (b and c) compared with a single-beam system (a). A double-beam-in-space instrument in which two beams are formed by a V-shaped mirror called a **beam-splitter**. One beam passes through the reference solution to a photodetector, and the second simultaneously passes through the sample to a second, matched photodetector. The two outputs are amplified, and their ratio, or the logarithm of their ratio, is obtained electronically or computed and displayed on the output device. A double-beam-in-time spectrophotometer. In this design, the beams are separated in time by a rotating sector mirror that directs the entire beam through the reference cell and then through the sample cell. The pulses of radiation are then recombined by another mirror that transmits the reference beam and reflects the sample beam to the detector. The double-beam-in-time approach is generally preferred over the double-beam-in-space because of the difficulty in matching two detectors.

Molecular Absorption Spectrometry UV-VIS Absorption Measurements

The absorption of ultraviolet, visible, and infrared radiation is widely used to identify and determine many inorganic, organic, and biochemical species. Ultraviolet and visible molecular absorption spectroscopy is used primarily for quantitative analysis and is probably applied more extensively in chemical and clinical laboratories than any other single technique. Infrared absorption spectroscopy is a very powerful tool for determining the identity and structure of both inorganic and organic compounds. In addition, it now plays an important role in quantitative analysis, particularly in the area of environmental pollution.

Ultraviolet and Visible Molecular Absorption Spectroscopy

Several types of molecular species absorb ultraviolet and visible radiation. Molecular absorption by these species can be used for qualitative and quantitative analyses. UVvisible absorption is also used to monitor titrations and to study the composition of complex ions.

Absorbing Species

absorption of ultraviolet and visible radiation by molecules generally occurs in one or more electronic absorption bands, each of which is made up of many closely packed but discrete lines. Each line arises from the transition of an electron from the ground state to one of the many vibrational and rotational
energy states associated with each excited electronic energy state. Because there are so many of these vibrational and rotational states and because their energies differ only slightly, the number of lines contained in the typical band is quite large and their separation from one another is very small. the visible absorption spectrum for1,2,3,4-tetrazine vapor shows the fine structure that is due to the numerous rotational and vibrational levels associated with the excited electronic states of this aromatic molecule. In the gaseous state, the individual tetrazine molecules are sufficiently separated from one another to vibrate and rotate freely, and many individual absorption lines appear as a result of the large number of vibrational and rotational energy states. As a pure liquid or in solution, however, the tetrazine molecules have little freedom to rotate, so lines due to differences in rotational energy levels disappear. Furthermore, when solvent molecules surround the tetrazine molecules.

Absorption by Organic Compounds

Absorption of radiation by organic molecules in the wavelength region between

180 and 780 nm results from interactions between photons and electrons that either participate directly in bond formation (and are thus associated with more than one atom) or that are localized about such atoms as oxygen, sulfur, nitrogen, and the halogens. The wavelength of absorption of an organic molecule depends on how tightly its electrons are bound. The shared electrons in carbon-carbon or carbon-hydrogen single bonds are so firmly held that their excitation requires energies corresponding to wavelengths in the vacuum ultraviolet region below 180 nm. Single-bond spectra have not been widely exploited for analytical purposes because of the experimental difficulties of working in this region. These difficulties occur because both quartz and atmospheric components absorb in this region, which requires that evacuated spectrophotometers with lithium fluoride optics be used.

Absorption by Inorganic Species

In general, the ions and complexes of elements in the first two transition series absorb broad bands of visible radiation in at least one of their oxidation states. As a result, these compounds are colored . Absorption occurs when electrons make transitions between filled and unfilled d-orbitals with energies that depend on the ligands bonded to the metal ions. The energy differences between these d-orbitals (and thus the position of the corresponding absorption maxima) depend on the position of the element in the periodic table, its oxidation state, and the nature of the ligand bonded to it.

Absorption spectra of ions of the lanthanide and actinide series differ substantially from those shown in Figure 26-2. The electrons responsible for absorption by these elements (4f and 5f, respectively) are shielded from external influences by electrons that occupy orbitals with larger principal quantum numbers. As a result, the bands tend to be narrow and relatively unaffected by the species bonded by the outer electrons.

Qualitative Applications of Ultraviolet/ Visible Spectroscopy

Spectrophotometric measurements with ultraviolet radiation are useful for detecting chromophoric groups, such as those shown in Table 26-1.2 Because large parts of even the most complex organic molecules are transparent to radiation longer than180 nm, the appearance of one or more absorption bands in the region from 200 to400 nm is clear indication of the presence of unsaturated groups or of atoms such as sulfur or halogens. Often, you can get an idea as to the identity of the absorbing groups by comparing the spectrum of an analyte with those of simple molecules containing various chromophoric groups.

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of simple molecules containing various chromophoric groups.

Usually, however, ultraviolet spectra do not have sufficient fine structure to permit an analyte to be identified unambiguously. Thus, ultraviolet qualitative data must be supplemented with other physical or chemical evidence such as infrared, nuclear magnetic resonance, and mass spectra as well as solubility and melting- and boiling-point information.

Solvents

Ultraviolet spectra for qualitative analysis are usually measured using dilute solutions of the analyte. For volatile compounds, however, gas-phase spectra are often more useful than liquid-phase or solution spectra (for example, compare Figure 24-14a and 24-14b). Gas-phase spectra can often be obtained by allowing a drop or two of the pure liquid to evaporate and equilibrate with the atmosphere in a stoppered cuvette A solvent for ultraviolet/visible spectroscopy must be transparent in the region of the spectrum where the solute absorbs. The analyte must be sufficiently soluble in the solvent to give a well-defined analyte. In addition, we must consider possible interactions of the solvent with the absorbing species. For example, polar solvents, such as water, alcohols, esters, and ketones, tend to obliterate vibrational fine structure and should thus be avoided to preserve spectral detail.

Quantitative applications

Ultraviolet and visible molecular absorption spectroscopy is one of the most useful tools available for quantitative analysis. The important characteristics of spectrophotometric and photometric methods are:

■■*Wide applicability.* A majority of inorganic, organic, and biochemical species absorb ultraviolet or visible radiation and are thus amenable to direct quantitative determination. Many nonabsorbing species can also be determined after chemical conversion to absorbing derivatives. Of the determinations performed in clinical laboratories, a large majority is based on ultraviolet and visible absorption spectroscopy.

■■ *High sensitivity*. Typical detection limits for absorption spectroscopy range from1024 to 1025 M. This range can often be extended to 1026 or even 1027 M with procedural modifications.

■■*Moderate to high selectivity*. Often a wavelength can be found at which the analyte alone absorbs. Furthermore, where overlapping absorption bands do occur, corrections based on additional measurements at other wavelengths sometimes eliminate the need for a separation step. When separations are required, spectrophotometry often provides the means for detecting the separated species.

■■ *Good accuracy.* The relative errors in concentration encountered with a typical spectrophotometric or photometric procedure lie in the range from 1% to 5%. Such errors can often be decreased to a few tenths of a percent with special precautions.

■■ *Ease and convenience*. Spectrophotometric and photometric measurements are easily and rapidly performed with modern instruments. In addition, the methods lend themselves to automation quite nicely.

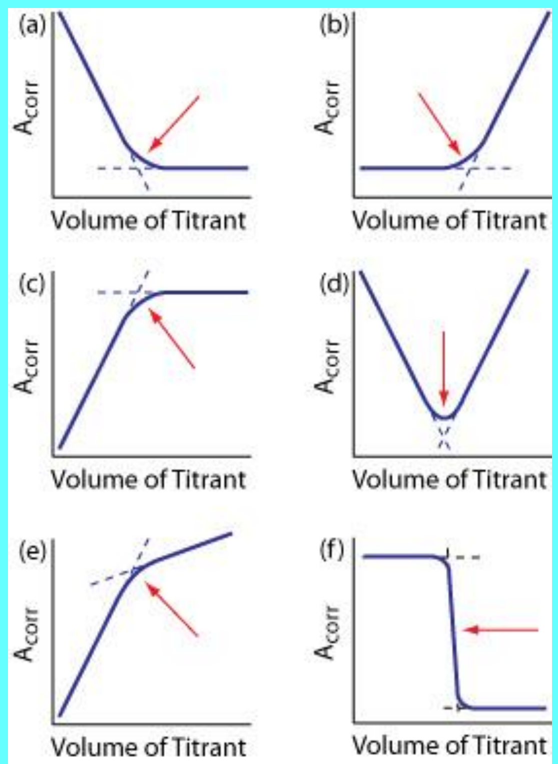
The Relationship between Absorbance and Concentration. The calibration standards for a photometric or a spectrophotometric method should approximate as closely as possible the overall composition of the actual samples and should encompass a reasonable range of analyte concentrations. A calibration curve of absorbance versus the concentrations of several standards is usually obtained to evaluate the relationship. It is seldom, if ever, safe to assume that Beer's law holds and to use only a single standard to determine the molar absorptivity. Unless there is no other choice, it is never a good idea to base the results of a determination solely on a literature value for the molar absorptivity. In cases where matrix effects are a problem, the standard addition method may improve results by providing compensation for some of these effects.

Photometric and Spectrophotometric Titrations

Photometric and spectrophotometric measurements are useful for locating the equivalence points of titrations.10 This application of absorption measurements requires that one or more of the reactants or products absorb radiation or that an absorbing indicator be added to the analyte solution.

TitrationCurves

A photometric titration curve is a plot of absorbance (corrected for volume change) as a function of titrant volume. If conditions are chosen properly, the curve consists of two straight-line regions with different slopes, one occurring prior to the equivalence point of the titration and the other located well beyond the equivalence-point region. The end point is taken as the intersection of extrapolated linear portions of the two lines.



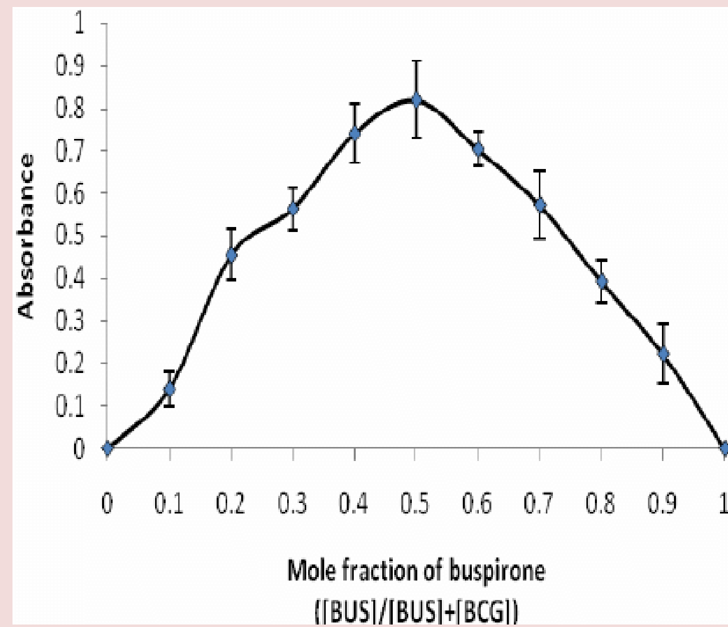
(a)
Acorr
Volume of Titrant
(b)
Acorr
Volume of Titrant
(c)
Acorr
Volume of Titrant
(d)
Acorr
Volume of Titrant
(e)
Acorr
Volume of Titrant
(f)
Acorr
Volume of Titrant

Spectrophotometric Studies of Complex Ions

Spectrophotometry is a valuable tool for determining the composition of complex ions in solution and for determining their formation constants. The power of the technique lies in the fact that quantitative absorption measurements can be performed without disturbing the equilibria under consideration. Although in many spectrophotometric studies of systems of complexes, a reactant or a product absorbs, nonabsorbing systems can also be investigated successfully. For example, the composition and formation constant for a complex of iron(II) and a nonabsorbing ligand may often be determined by measuring the absorbance decreases that occur when solutions of the absorbing iron(II) complex of 1,10-phenanthroline are mixed with various amounts of the nonabsorbing ligand. The success of this approach depends on the well-known values of the formation constant (*K*f 5 2 3 1021) and the composition of the 1,10-phenanthroline (3:1) complex of iron(II). The three most common techniques used for complex-ion studies are (1) the method of continuous variations, (2) the mole-ratio method, and (3) the slope-ratio method.We illustrate these methods for metal ion-ligand complexes, but the principles apply to other types.

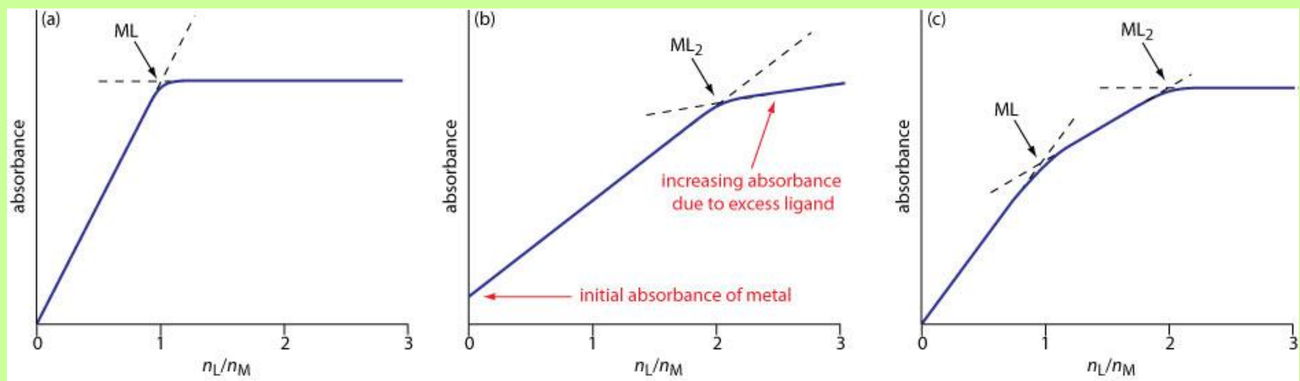
1-The Method of Continuous Variations

In the method of continuous variations, cation and ligand solutions with identical analytical concentrations are mixed in such a way that the total volume and the total moles of reactants in each mixture are constant but the mole ratio of reactants varies systematically (for example, 1:9, 8:2, 7:3, and so forth). The absorbance of each solution is then measured at a suitable wavelength and corrected for any absorbance the mixture might exhibit if no reaction had occurred. The corrected absorbance is plotted against the volume fraction of one reactant, that is, VM /(VM + VL), where VM is the volume of the cation solution and VL is the volume of the ligand solution.


Absorbance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Mole fraction of buspirone
([BUS]/[BUS]+[BCG])

2-The Mole-Ratio Method

In the mole-ratio method, a series of solutions is prepared in which the analytical concentration of one reactant (usually the metal ion) is held constant while that of the other is varied. A plot of absorbance versus mole ratio of the reactants is then prepared. If the formation constant is reasonably favorable, two straight lines of different slopes that intersect at a mole ratio that corresponds to the combining ratio in the complex are obtained.



(a)
ML
absorbance
0
1
2
3
n_L/n_M
(b)
ML_2
absorbance
increasing absorbance
due to excess ligand
initial absorbance of metal
0
1
2
3
n_L/n_M
(c)
ML_2
ML
absorbance
0
1
2
3
n_L/n_M

3-The Slope-Ratio Method

The slope-ratio approach is particularly useful for weak complexes but is applicable only to systems in which a single complex is formed. The method assumes (1) that the complex-formation reaction can be forced to completion by a large excess of either reactant, (2) that Beer's law is followed under these circumstances, and (3) that only the complex absorbs at the wavelength chosen.

Infrared Absorption Spectroscopy

Infrared spectroscopy is a powerful tool for identifying pure organic and inorganic compounds because, with the exception of a few homonuclear molecules such as O2, N2, and Cl2, all molecular species absorb infrared radiation. In addition, with the exception of chiral molecules in the crystalline state, every molecular compound has a unique infrared absorption spectrum. Therefore, an exact match between the spectrum of a compound of known structure and the spectrum of an analyte unambiguously identifies the analyst. Infrared spectroscopy is a less satisfactory tool for quantitative analyses than its ultraviolet and visible counterparts because of lower sensitivity and frequent deviations from Beer's law.

Instruments for Infrared Spectrometry

Three types of infrared instruments are found in modern laboratories; dispersive spectrometers (spectrophotometers), Fourier transform spectrometers, and filter photometers. The first two are used for obtaining complete spectra for qualitative identification, while filter photometers are designed for quantitative work. Fourier transform and filter instruments are nondispersive in the sense that neither uses a grating or prism to disperse radiation into its component wavelengths.

Dispersive Instruments

With one difference, dispersive infrared instruments are similar in general design to the double-beam (in time) spectrophotometers shown in Figures 25-20c. The difference lies in the location of the cell compartment with respect to the monochromator. In ultraviolet/visible instruments, cells are always located between the monochromator and the detector in order to avoid photochemical decomposition, which may occur if samples are exposed to the full power of an ultraviolet or visible source.

Fourier Transform Spectrometers

Fourier transform infrared (FTIR) spectrometers offer the advantages of high sensitivity, resolution, and speed of data acquisition (data for an entire spectrum can be obtained in 1 s or less). In the early days of FTIR, instruments were large, intricate, costly devices controlled by expensive laboratory computers. Since the 1980s, the instrumentation has evolved, and the price of spectrometers and computers have dropped dramatically. Today, FTIR spectrometers are commonplace, having replaced older, dispersive instruments in most laboratories.

Fluorescence is a photoluminescence process in which atoms or molecules are excited by absorption of electromagnetic radiation (recall Figure 24-6). The excited species then relax to the ground state, giving up their excess energy as photons. One of the most attractive features of molecular fluorescence is its inherent sensitivity, which is often one to three orders of magnitude better than absorption spectroscopy. In fact, single molecules of selected species have been detected by fluorescence spectroscopy under controlled conditions. Another advantage is the large linear concentration ranges of fluorescence methods, which are significantly broader than linear concentration ranges in absorption spectroscopy. Fluorescence methods are, however, less widely applicable than absorption methods because of the smaller number of chemical systems that show appreciable fluorescence.

Theory of Molecular Fluorescence

Molecular fluorescence is measured by exciting the sample at an absorption wavelength, also called the excitation wavelength, and measuring the emission at a longer wavelength called the emission or fluorescence wavelength. For example, the reduced form of the coenzyme nicontinamide adenine dinucleotide (NADH) absorbs radiation at 340 nm, and the molecule emits photoluminescence radiation with an emission maximum at 465 nm. Usually photoluminescence emission is measured at right angles to the incident beam to avoid measuring the incident radiation (recall Figure 25-1b). The short-lived emission that occurs is called **fluorescence**, while luminescence that is much longer lasting is called **phosphorescence**.

Fluorescence Instrumentation

There are several different types of fluorescence instruments. All follow the general block diagram of Figure 25-1b. Optical diagrams of typical instruments .If the two wavelength selectors are both filters, the instrument is called a **fluorometer**.

If both wavelength selectors are monochromators, the instrument is a **spectrofluorometer**. Some instruments are hybrids and use an excitation filter along with an emission monochromator. Fluorescence instruments can incorporate a double-beam design in order to compensate for changes in the source radiant power with time and wavelength. Instruments that correct for the source spectral distribution are called **corrected spectrofluorometers**. Radiation sources for fluorescence are usually more powerful than typical absorption sources.

fluorescence methods are generally one to three orders of magnitude more sensitive than methods based on absorption. Mercury arc lamps, xenon arc lamps, xenon-mercury arc lamps, and lasers are typical fluorescence sources. Monochromators and transducers are typically similar to those used in absorption spectrophotometers. Photomultipliers are still widely used in high-sensitivity spectrofluorometers, but CCDs and photodiode arrays have become popular in recent years. The sophistication, performance characteristics, and cost of fluorometers and spectrofluorometers vary widely as with absorption spectrophotometers. Generally, fluorescence instruments are more expensive than absorption instruments of corresponding quality.

Applications of Fluorescence Methods

Fluorescence spectroscopy is not a major structural or qualitative analysis tool because molecules with subtle structural differences often have similar fluorescence spectra. Also, fluorescence bands in solution are relatively broad at room temperature. However, fluorescence has proved to be a valuable tool in oil spill identification. The source of an oil spill can often be identified by comparing the fluorescence emission spectrum of the spill sample to that of a suspected source. The vibrational structure of polycyclic hydrocarbons present in the oil makes this type of identification possible. Fluorescence methods are used to study chemical equilibria and kinetics in much the same way as absorption spectrophotometry.

it is possible to study chemical reactions at lower concentrations because of the higher sensitivity of fluorescence methods. In many cases where fluorescence monitoring is not feasible, fluorescent probes or tags can be bound covalently to specific sites in molecules such as proteins, thus making them detectable via fluorescence. These tags can be used to provide
information about energy transfer processes, the polarity of the protein, and the distances between reactive sites (see for example Feature 27-1). Quantitative fluorescence methods have been developed for inorganic, organic,
and biochemical species.

Inorganic fluorescence methods can be divided into two classes: direct methods and indirect methods. Direct methods are based on the reaction of the analyte with a complexing agent to form a fluorescent complex. Indirect methods depend on the decrease in fluorescence, also called **quenching**, as a result of interaction of the analyte with a fluorescent reagent. Quenching methods are primarily used for the determination of anions and dissolved oxygen. Some fluorescence reagents for cations are shown in **Figure 27-9**. Nonradiative relaxation of transition-metal chelates is so efficient that these species seldom fluoresce. It is worth noting that most transition metals absorb in the UV or visible region, while nontransition-metal ions do not. For this reason, fluorescence is often considered complementary to absorption for the determination.

Among the compound types that can be determined by fluorescence are amino acids, proteins, coenzymes, vitamins, nucleic acids, alkaloids, fluorescence are amino acids, proteins, coenzymes, vitamins, nucleic acids, alkaloids, porphryins, steroids, flavonoids, and many metabolites.2 Because of its sensitivity, fluorescence is widely used as a detection technique for liquid chromatographic methods for flow analysis methods, and for electrophoresis. In addition to methods that are based on measurements of fluorescence intensity, there are many methods involving measurements of fluorescence lifetimes. Several instruments have been developed that provide microscopic images of specific species based on fluorescence lifetimes.

Fluorescence methods are 10 to1000 times more sensitive than absorption methods.

Atomic Spectroscopy

Atomic spectroscopic methods are used for the qualitative and quantitative determination of more than 70 elements. Typically, these methods can detect parts-per-million to parts-per-billion amounts, and in some cases, even smaller concentrations. Atomic spectroscopic methods are also rapid, convenient, and usually of high selectivity. These methods can be divided into two groups; Spectroscopic determination of atomic species can only be performed on a gaseous medium in which the individual atoms or elementary ions, such as Fe1, Mg1, or Al1, are well separated from one another. Consequently, the first step in all atomic spectroscopic

procedures is **atomization.**

atomization, a process in which a sample is volatilized and decomposed in such a way as to produce gas-phase atoms and ions. The efficiency and reproducibility of the atomization step can have a large influence on the sensitivity, precision, and accuracy of the method. In short, atomization is a critical step in atomic spectroscopy.

Atomic Absorption Spectrometry

Flame atomic absorption spectroscopy (AAS) is currently the most widely used of all the atomic methods because of its simplicity, effectiveness, and relatively low cost. The technique was introduced in 1955 by Walsh in Australia and by Alkemade and Milatz in Holland.4 The first commercial atomic absorption (AA) spectrometer was introduced in 1959, and use of the technique grew explosively after that. The reason that atomic absorption methods were not widely used until that time was directly related to problems created by the very narrow widths of atomic absorption lines, see color plate 17 for the solar spectrum and some atomic absorption lines).

Flame Atomizers

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 same types of nebulizers that are used with ICPs are used with flame atomizers. 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. The burners used in flame spectroscopy are most often premixed, laminar flow burners.

The aerosol, oxidant, and fuel are then burned in a slotted burner, which provides a flame that is usually 5 or 10 cm in length. Laminar flow burners of the type shown in Figure 28-10 provide a relatively quiet flame and a long path length. These properties tend to enhance sensitivity for atomic absorption and reproducibility. The mixing chamber in this type of burner contains a potentially explosive mixture, which can be ignited by flashback if the flow rates are not sufficient. Note that, for this reason, the burner in

Figure 28-10 is equipped with pressure relief vents.

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. Unfortunately, a flame is not a very efficient atomizer.

Effects of Flame Temperature

Both emission and absorption spectra are affected in a complex way by variations in flame temperature. In both cases, higher temperatures increase the total atom population of the flame and thus the sensitivity. With certain elements, such as the alkali metals, however, this increase in atom population is more than offset by the loss of atoms by ionization.

Flame temperature determines to a large extent the efficiency of atomization,

which is the fraction of the analyte that is desolvated, vaporized, and converted to free atoms and/or ions. The flame temperature also determines the relative number of excited and unexcited atoms in a flame. In an air/acetylene flame, for example, calculations show that the ratio of excited to unexcited magnesium atoms is about1028, whereas in an oxygen/acetylene flame, which is about 700°C hotter, this ratio is about 1026. Hence, control of temperature is very important in flame emission methods.

For example, with a 2500°C flame, a temperature increase of 10°C causes the number of sodium atoms in the excited 3*p* state to increase by about 3%. In contrast, the corresponding *decrease* in the much larger number of ground state atoms is only about 0.002%. Therefore, at first glance, emission methods, based as they are on the population of *excited atoms*, require much closer control of flame temperature than do absorption procedures in which the analytical signal depends upon the number of *unexcited atoms*. However, in practice because of the temperature dependence of the atomization step, both methods show similar dependencies.

The number of unexcited atoms in a typical flame exceeds the number of excited atoms by a factor of 103 to 1010 or more. This fact suggests that absorption methods should show lower detection limits (DLs) than emission methods. In fact, however, several other variables also influence detection limits, and the two methods tend to complement each other in this regard.

Other Atomizers

Many other types of atomization devices have been used in atomic spectroscopy. Gas discharges operated at reduced pressure have been investigated as sources of atomic emission. The **glow discharge** is generated between two planar electrodes in a cylindrical glass tube filled with gas to a pressure of a few torr. High-powered lasers have been employed to vaporize samples and to cause **laser-induced breakdown**. In the latter technique, dielectric breakdown of a gas occurs at the laser focal point. A laser-induced breakdown spectrometer (LIBS) is part of the Mars Science Laboratory aboard the rover Curiosity which arrived on Mars in August 2012. In the early days of atomic spectroscopy, dc and ac arcs and high-voltage sparks were popular sources for exciting atomic emission. Such sources have almost entirely been replaced by the ICP.

Hollow-cathode lamps for about 70 elements are available from commercial sources. For some elements, high-intensity lamps are available that provide about an order of magnitude higher intensity than normal lamps. Some hollow cathode lamps have a cathode containing more than one element and thus provide spectral lines for the determination of several species. The development of the hollow-cathode lamp is widely regarded as the single most important event in the evolution of atomic absorption spectroscopy.

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.

Pulsed Hollow-Cathode Lamp Background Correction. In this technique,

often called **Smith-Hieftje background correction**, the analyte hollow cathode is pulsed at a low current (5 to 20 mA) for typically 10 ms and then at a high current(100 to 500 mA) for 0.3 ms. During the low current pulse, the analyte absorbance plus the background absorbance is measured (AT). During the high-current pulse, the hollow-cathode emission line becomes broadened. The center of the line can be strongly self-absorbed so that much of the line at the analyte wavelength is missing. Hence, during the high-current pulse, a good estimate of the background absorbance, AB, is obtained. The instrument computer then calculates the difference which is an estimate of AA, the true analyte absorption.

Continuum Source Background Correction.

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, A_T, while the deuterium lamp provides an estimate of the background absorbance, A_B. 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.

Zeeman Effect Background Correction. Background correction with electrothermal atomizers can be done by means of the Zeeman effect. In Zeeman background correction, a magnetic field splits spectral lines that are normally of the same energy (degenerate) into components with different polarization characteristics. Analyte and background absorption can be separated because of their different magnetic and polarization behaviors

Interferences in Atomic Absorption

Flame atomic absorption is subject to many of the same chemical and physical interferences as flame atomic emission .Spectral interferences by elements that absorb at the analyte wavelength are rare in AA. Molecular constituents and radiation scattering can cause interferences, however. These are often corrected by the background correction schemes discussed in Section 28D-2. In some cases, if the source of interference is known, an excess of the interferent can be added to both the sample and the standards. The added substance is sometimes called a **radiation buffer**.

Atomic Fluorescence Spectrometry

Atomic fluorescence spectrometry (AFS) is the newest of the optical atomic spectroscopic methods. Like atomic absorption, an external source is used to excite the element of interest. However, instead of measuring the attenuation of the source, the radiation emitted as a result of absorption is measured, often at right angles to avoid measuring the source radiation. r most elements, atomic fluorescence with conventional hollow-cathode or electrodeless-discharge sources has no significant advantages over atomic absorption or atomic emission.

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Atomic Mass Spectrometry

Atomic mass spectrometry has been around for many years, but the introduction of the inductively coupled plasma (ICP) in the 1970s and its subsequent development for mass spectrometry4 led to the successful commercialization of ICPMS by several instrument companies. Today, ICPMS is a widely used technique for the simultaneous determination of over 70 elements in a few minutes. The ion source is the major difference between atomic and molecular mass spectrometry. For atomic mass spectrometry, the ion source must be very energetic to convert the sample into simple gas phase ions and atoms. In molecular mass spectrometry, the ion source is much less energetic and converts the sample into molecular ions and fragment ions.

The Inductively Coupled Plasma

The inductively coupled plasma is described extensively in Section 28B-2 in connection with its use in atomic emission spectrometry. The axial geometry shown in Figure28-7 is most often used in ICPMS. In MS applications, the ICP serves as both anatomizer and an ionizer. Solution samples may be introduced by a conventional or an ultrasonic nebulizer. Solid samples can be dissolved in solution or volatized by means of a high-voltage spark or high-powered laser prior to introduction into the ICP. Ions formed in the plasma are then introduced into the mass analyzer, often a quadrupole, where they are sorted according to mass-to-charge ratio and detected. Extracting ions from the plasma can present a major technical problem in ICPMS.

Atomic Mass Spectra and Interferences

Because the ICP source predominates in atomic mass spectrometry, we focus our discussion on ICPMS. The simplicity of ICPMS spectra, such as the cerium spectrum shown in Figure 29-6b, led early workers in the field to have hopes of an “interference-free method.” Unfortunately, this hope was not realized in further studies, and serious interference problems are sometimes encountered in atomic mass spectrometry, just as in optical atomic spectroscopy. Interference effects in atomic mass spectroscopy fall into two broad categories: spectroscopic interferences and matrix interferences.