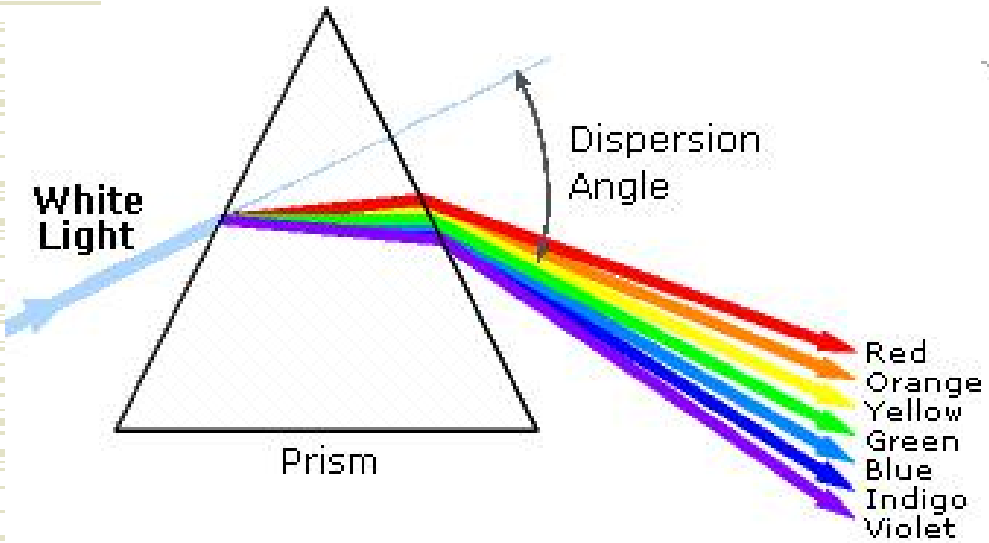
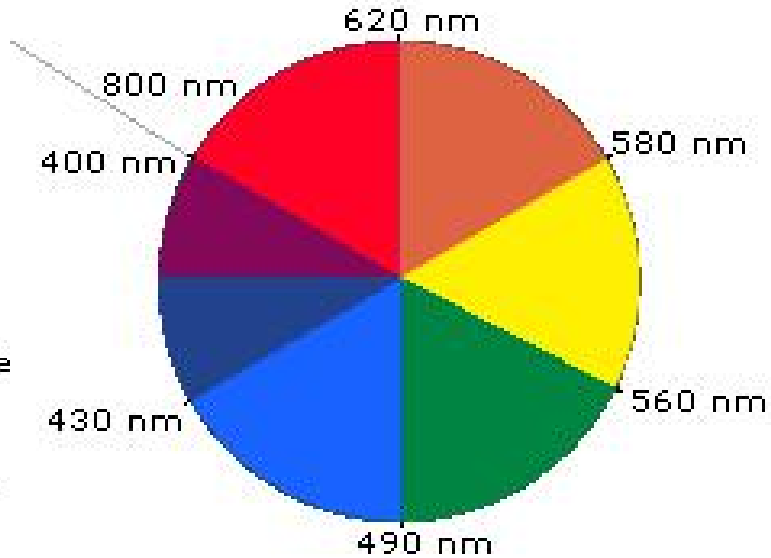
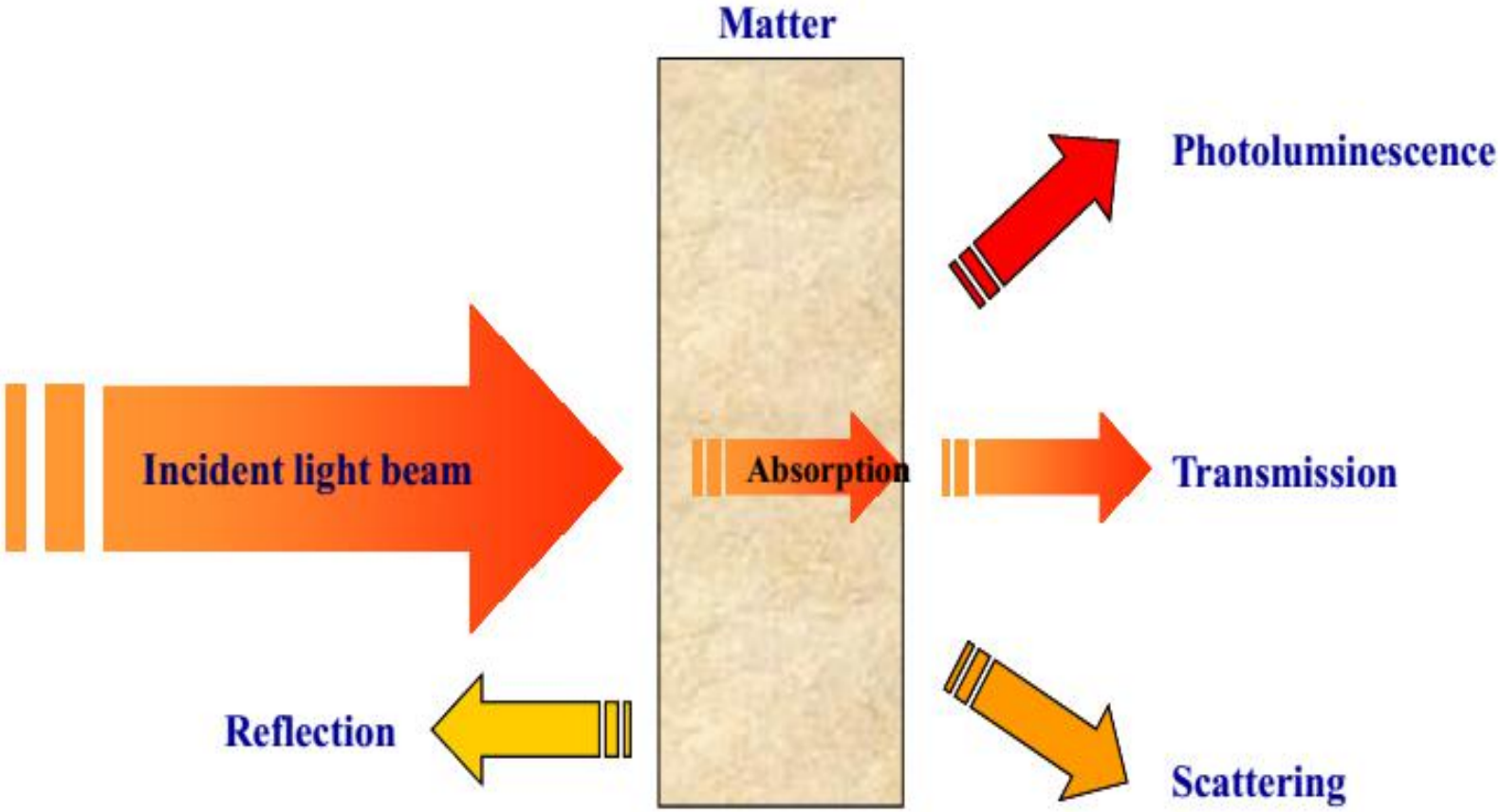
Introduction to Spectroscopy

Chapter One





If matter is exposed to electromagnetic radiation, e.g. infrared light, the radiation can be absorbed, transmitted, reflected, scattered or undergo photoluminescence.



Spectroscopy

- ✓ It is a science that study about the interactions of electromagnetic radiation (radiant energy) and matter (molecules, atoms, or ions)
- ✓ Spectroscopic analytical methods, covered in this course, are based on measuring the amount of radiation (intensity of radiation) produced or absorbed by molecular or atomic species of interest.
- ✓ It has played a vital role in the development of modem atomic theory.
- ✓ In addition, it provides perhaps the most widely used tools for the elucidation of molecular structure as well as the quantitative and qualitative determination of both inorganic and organic compounds.

Interactions of Electromagnetic Radiation

- **Physical Interactions:** Not dependent on the characteristic of electromagnetic radiation
  1. Reflection of Radiation
  2. Refraction of Radiation
  3. Diffraction of Radiation
  4. Scattering of Radiation
  5. Polarization of Radiation
- **Chemical Interaction:** Dependent of the characteristics of electromagnetic radiation
  1. Absorption
  2. Emission
  3. photoluminescence
  4. Chemiluminescence

- Historically, the interactions of interest were between electromagnetic radiation and matter, but now spectroscopy has been broadened to include interactions between matter and other forms of energy, such as acoustic waves and beams of particles such as ions and electrons.
- In this section we will see about what is electromagnetic radiation, how matter absorbs and emits EMR and what is a quantitative relation between the absorbed or emitted light and matter.
- We will give more emphasize on atomic emission and absorption, uv/vis, infrared, NMR spectroscopy.
- Before going into details about these techniques first it is wise to see about the properties of electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity.

- The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation.
- Electromagnetic radiation, unlike sound waves, requires no supporting medium for its transmission and passes readily through a vacuum.
- Light also travels nearly a million times faster than sound.
- We call electromagnetic radiation in the UV/visible and sometimes in the IR region light, although strictly speaking the term refers only to visible radiation.

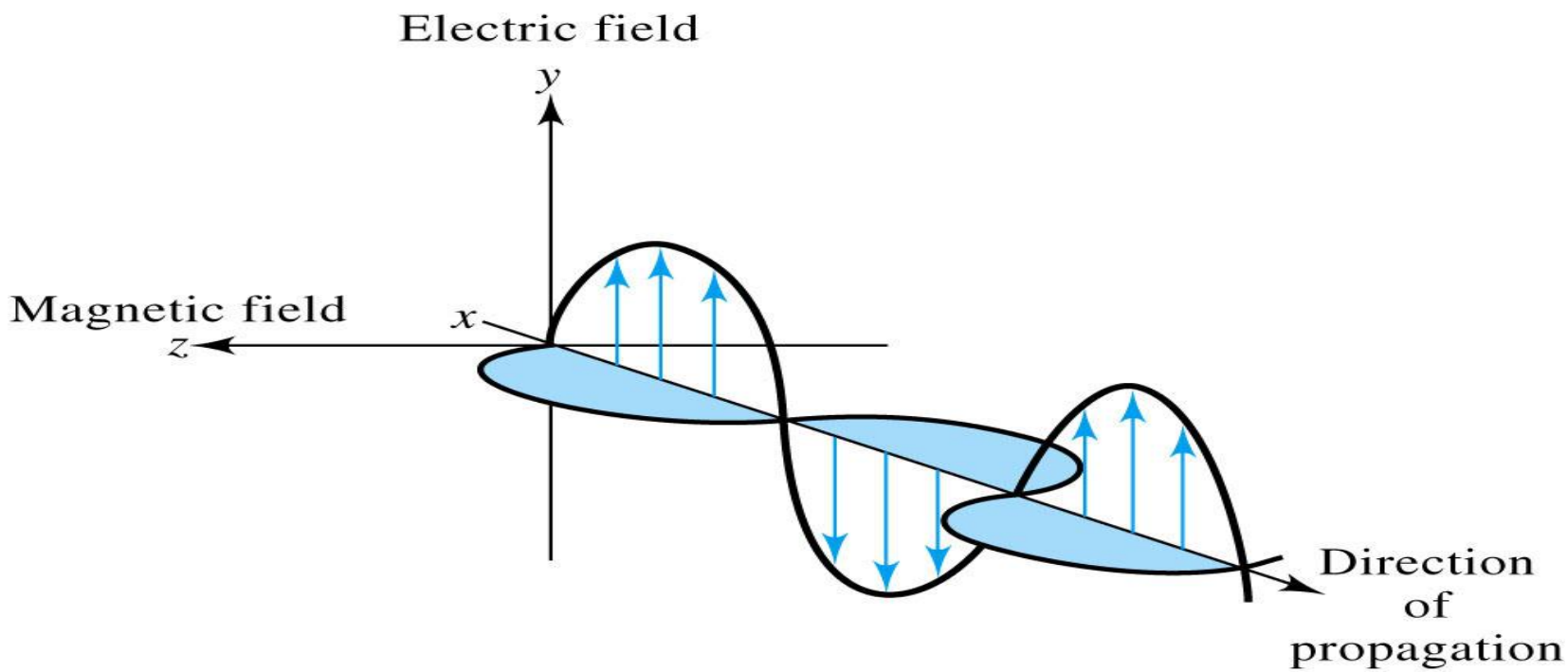
- EMR can be considered to have dual natures
  - **Wave nature**
  - **Particle nature**

- Diffraction, refraction, reflection of EMR is explained by the wave nature of light.
- The wave model fails to account for phenomena associated with the absorption and emission of radiant energy.
- To understand these processes, it is necessary to invoke a particle model in which electromagnetic radiation is viewed as a stream of discrete particles, or wave packets, of energy called photons (which is its particle nature).
- These dual views of radiation as particles and as waves are not mutually exclusive but, rather, complementary.

Light as a Wave

EMR is conveniently represented as an electric and magnetic fields that undergo in – phase sinusoidal oscillations at right angles to each other and to the direction of propagation.

- It is emission and transmission of energy in the form of electromagnetic waves.



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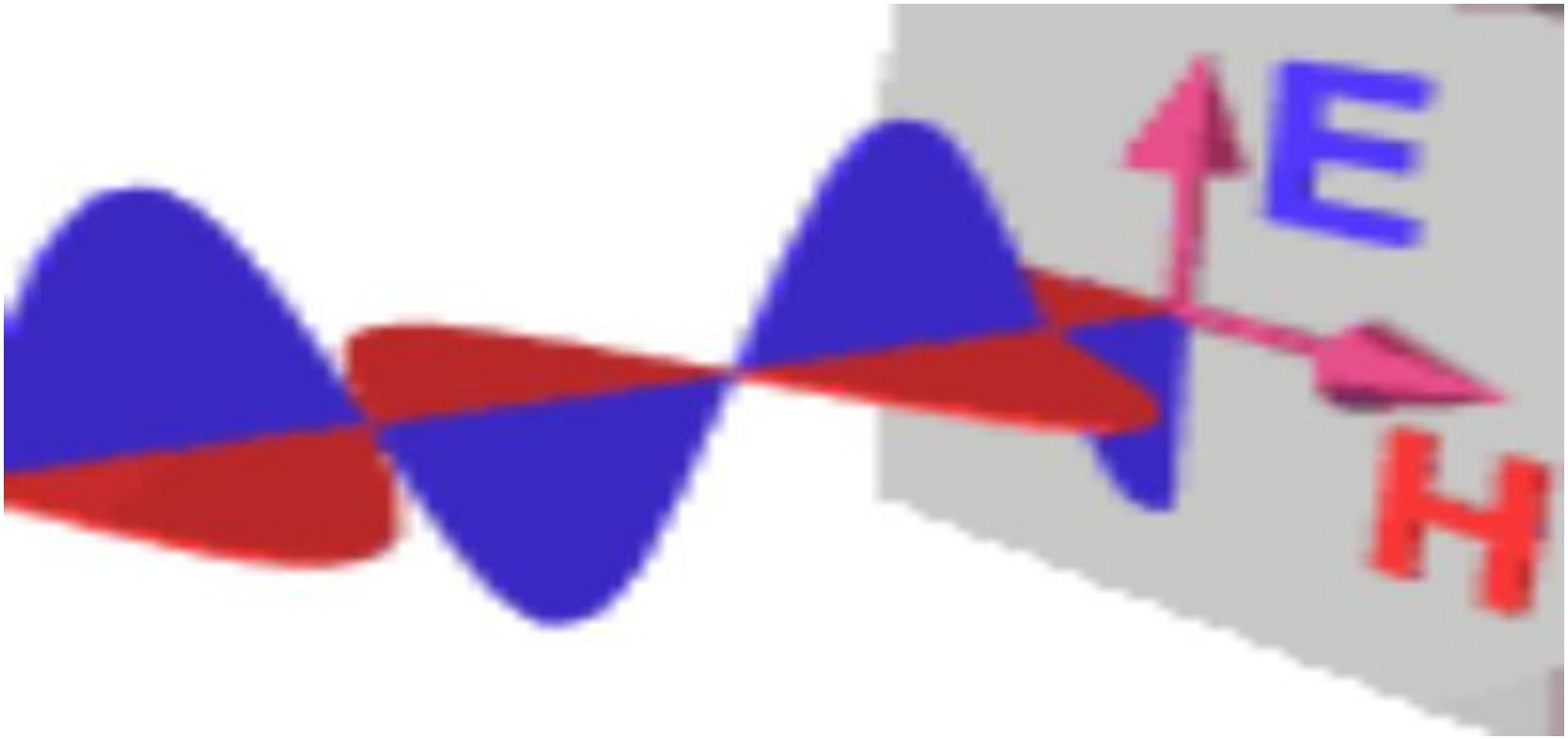
- Radiation can be thought of as a traveling transverse wave.
- Both have the same frequency and wave length hence they have the same speed

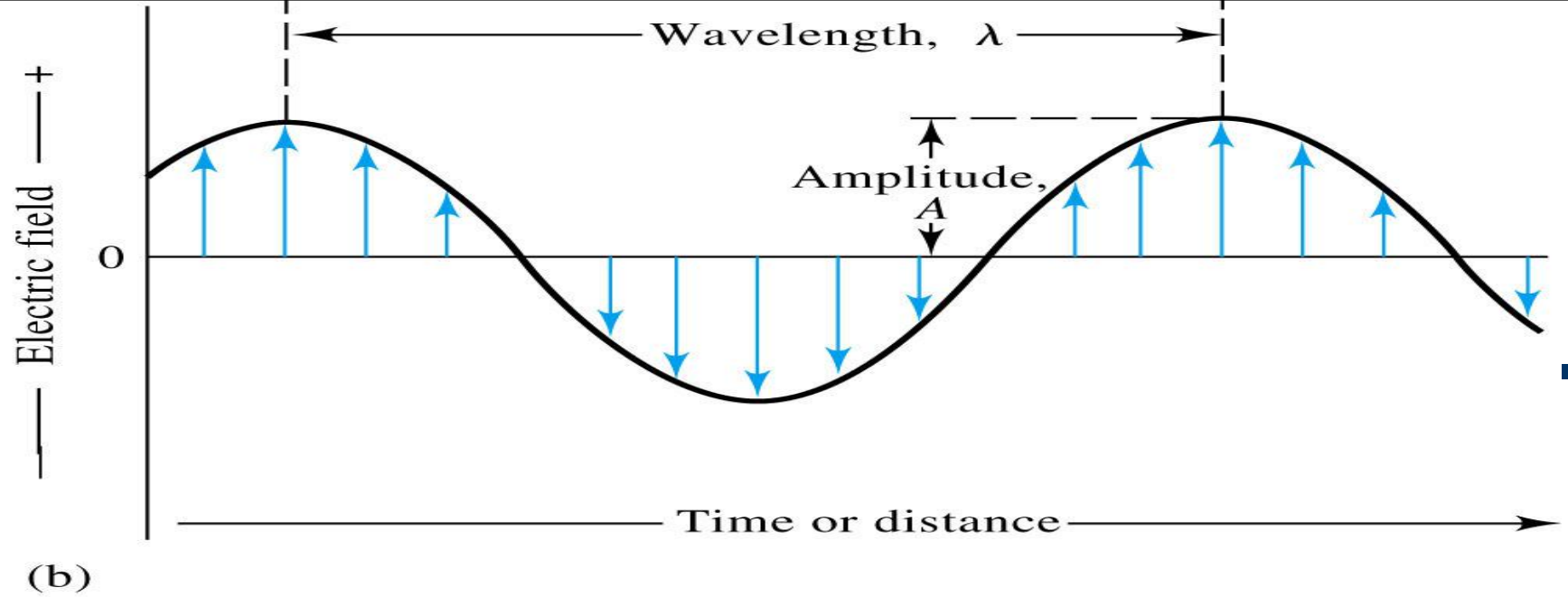


- The electric component of the radiation is in the form of an oscillating electric field of strength E and the magnetic component is in the form of an oscillating magnetic field of strength H at a time t .
- These oscillating fields are at right angles to each other, as shown, and, if the directions of the vectors E and H are y and z respectively, then

$$E_y = A\sin(2\pi\upsilon t - kx)$$

$$H_z = A\sin(2\pi\nu t - kx)$$

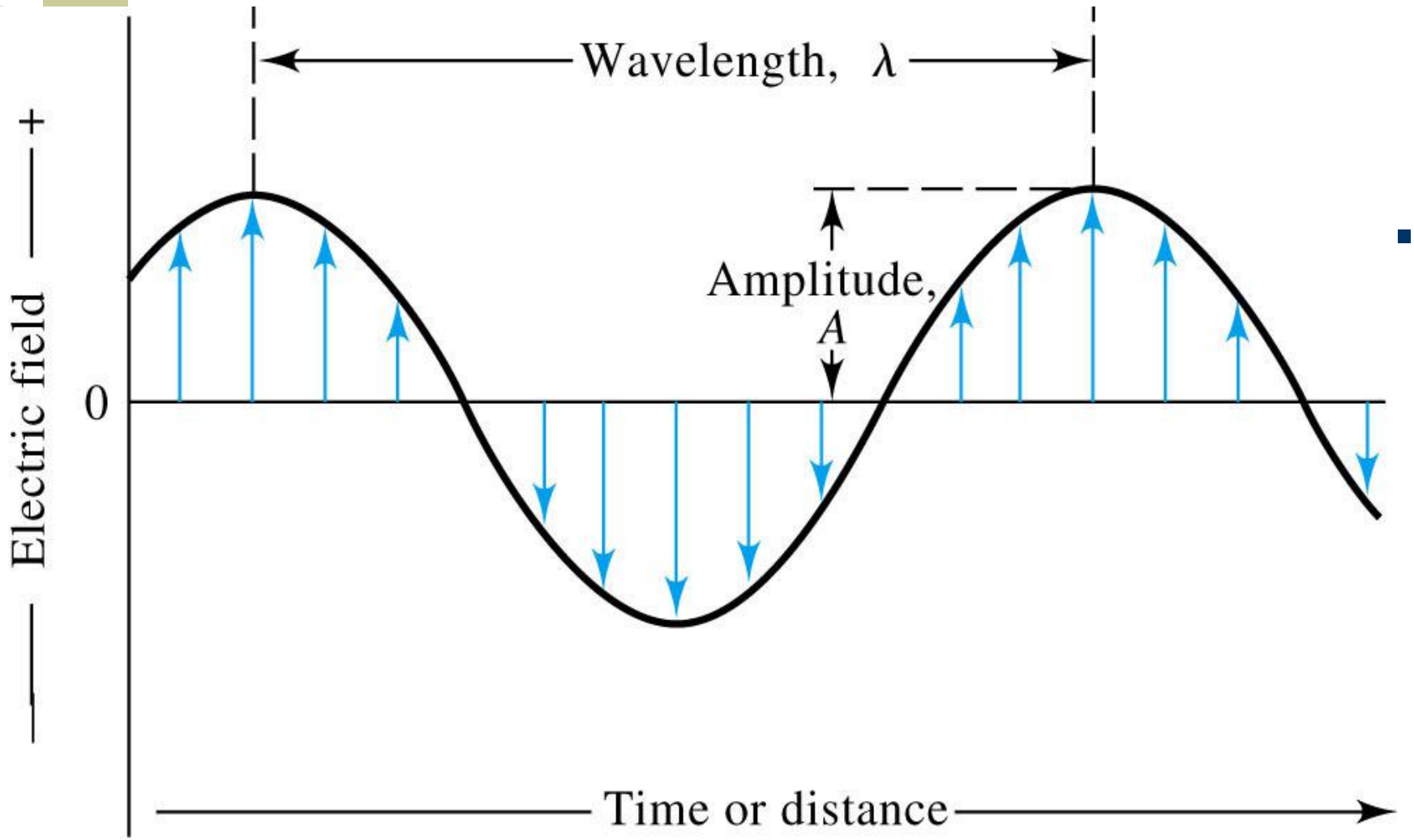
Where A is the amplitude. Therefore, the fields oscillate sinusoidally with an angular frequency of $2\pi\nu$ and, because k is the same for each component, they are in-phase. (kx is phase angle ϕ)



- Throughout this chapter and most of the remaining chapters only the electric component of radiation will be considered because the electric field is responsible for most of the phenomena that are of interest to us, including transmission, reflection, refraction, and absorption.
- Note, however, that the magnetic component of electromagnetic radiation is responsible for absorption of radio-frequency waves in nuclear magnetic resonance.

Wave Parameters

- **Amplitude (A):** Length of the electric vector at a maximum in the wave.
- **Period (P):** The time in seconds required for the passage of successive maxima or minima through a fixed point in space.
- **Frequency (ν):** The number of oscillations of the field that occur per second and is equal to 1/P. (s^{-1} or Hz).
- **Wavelength (λ):** The linear distance between any two equivalent points on successive waves (successive maxima or minima). (A, nm, etc.).



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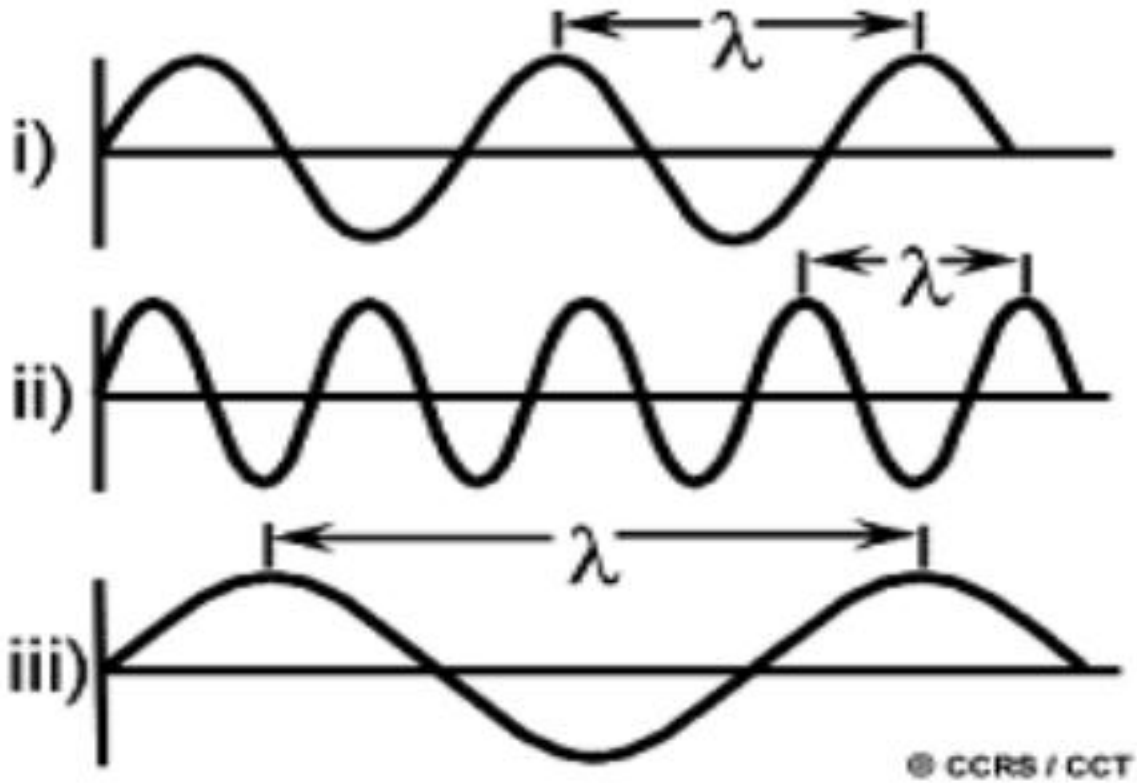
λ
i)
λ
ii)
λ
iii)
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- The SI unit of wavelength is meter (m). Since the values of most EMR wavelengths are small most conveniently we use centimeter (cm), micro meter (μm) and nanometer (nm).
- For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (nm, 10^{-9} m), and the wavelength for infrared radiation is given in microns (μm, 10^{-6} m).

$$1 \text{ cm} = 10^{-2} \text{ m or } 1 \text{ m} = 100 \text{ cm}$$
$$1 \ \mu\text{m} = 10^{-6} \text{ m or } 1 \text{ m} = 10^{6} \ \mu\text{m}$$
$$1 \text{ nm} = 10^{-9} \text{ m or } 1 \text{ m} = 10^{9} \text{ nm}$$

Prefix	Symbols	Multiplier
giga-	G	10^{9}
mega-	M	10^{6}
kilo-	k	10^{3}
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	µ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}
atto-	a	10^{-18}

Example

Convert 500 nm into meter and micrometer.

- Light of only a single wavelength is called **monochromatic light**.
- Light that consists of more than one wavelength is called **polychromatic light**. White light (visible light from the sun) is an example of polychromatic light since it contains emr with wavelengths range from 350 nm to 750 nm).

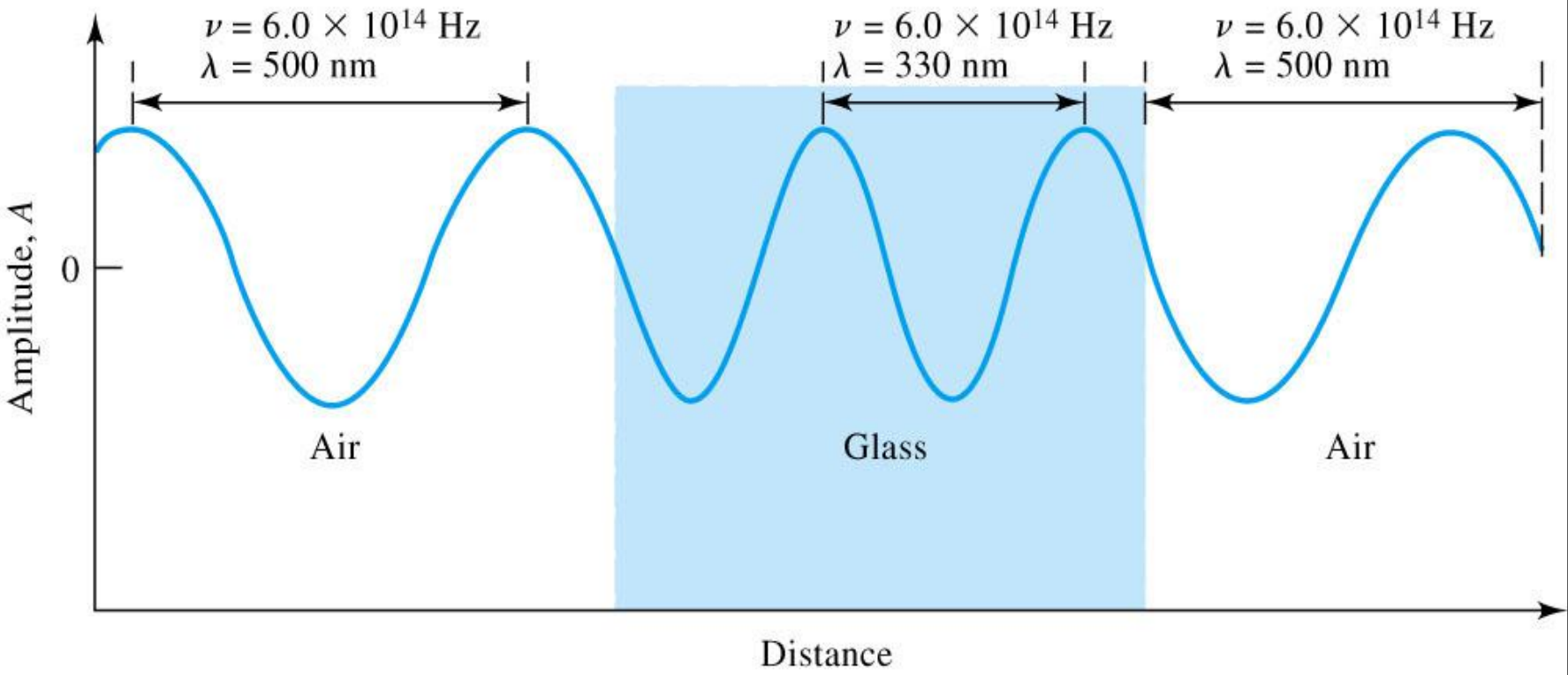
- Multiplication of the frequency in cycles per second by the wavelength in meters per cycle gives the velocity of propagation V, in meters per second:

$$V_i = \upsilon . \lambda_i$$

- It is important to realize that the frequency of a beam of radiation is determined by the source and remains invariant with the medium it passes.
- In contrast, the velocity of radiation depends upon the composition of the medium through which it passes. Thus, the equation implies that the wavelength of radiation also depends on the medium.
- The subscript i in the equation indicates these dependencies.

Effect of the Medium on a Light Wave

- Frequency remains the same.
- Velocity and Wavelength change.



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The Speed of Light

In a vacuum, the velocity (c) of light is 2.99792×10^{8} m s^{-1} and the velocity of light in air is about 0.03% less. Thus, for a vacuum, or for air, the velocity of light:

$$c = \nu\lambda = 3.00 \times 10^{8} \text{m s}^{-1} = 3.00 \times 10^{10} \text{ cm s}^{-1}$$

In a medium containing matter, light travels with a velocity less than c because of interaction between the electromagnetic field and electrons in the atoms or molecules of the medium. Since the frequency of the radiation is constant, the wavelength must decrease as the light passes from a vacuum to a medium containing matter.

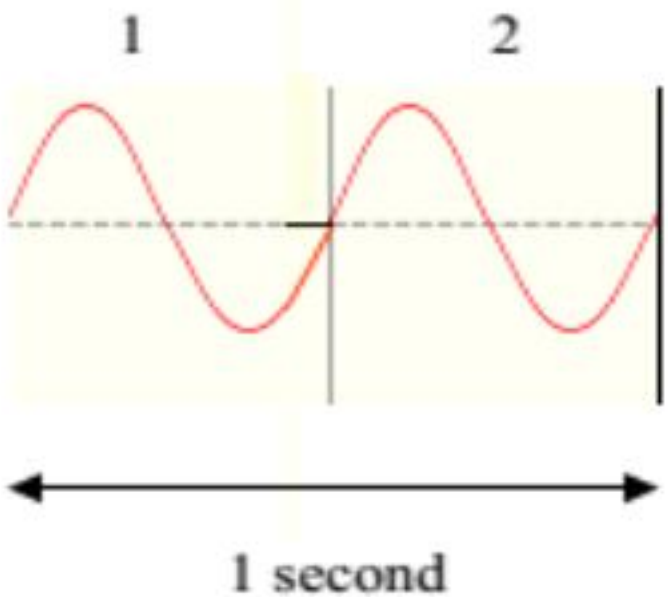
- **Velocity of propagation:** $V_i = \nu \times \lambda_i$

  In vacuum, the velocity of radiation is independent of wavelength and given by the symbol c.

  $c = \nu\lambda = 3.00 \times 10^8$ m/s $= 3.00 \times 10^{10}$ cm/s

- In vacuum all types of radiation travels at speed of light.
- This extraordinarily fast speed accounts for the seemingly instantaneous manner with which light fills a room when the light switch is switched on.
- **Wave number ($\bar{\nu}$):** The reciprocal of the wavelength in centimeters (cm^{-1}).
- The wave number is a useful unit because, in contrast to wavelength, it is directly proportional to the frequency, and thus the energy, of radiation.
- The **power P** of radiation is the energy of the beam that reaches a given area per second,
- whereas the **intensity I** is the power per unit solid angle

Example: Frequency = 2/s (2 Hz)



Example

Calculate the frequency of a beam of visible radiation with a wavelength of 700 nm in vacuum.

Example

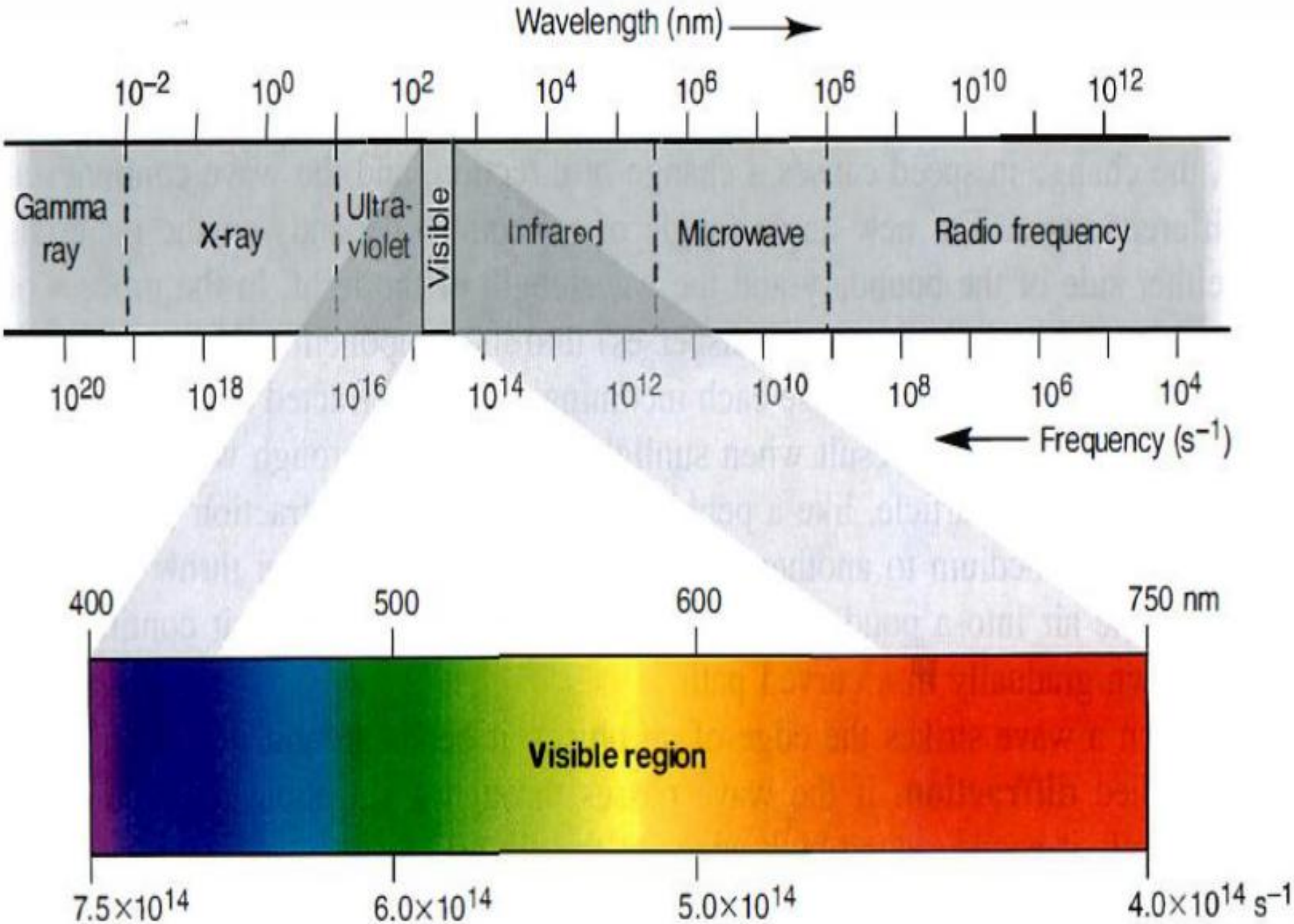
Which one has the larger wave number. An EMR with wave length

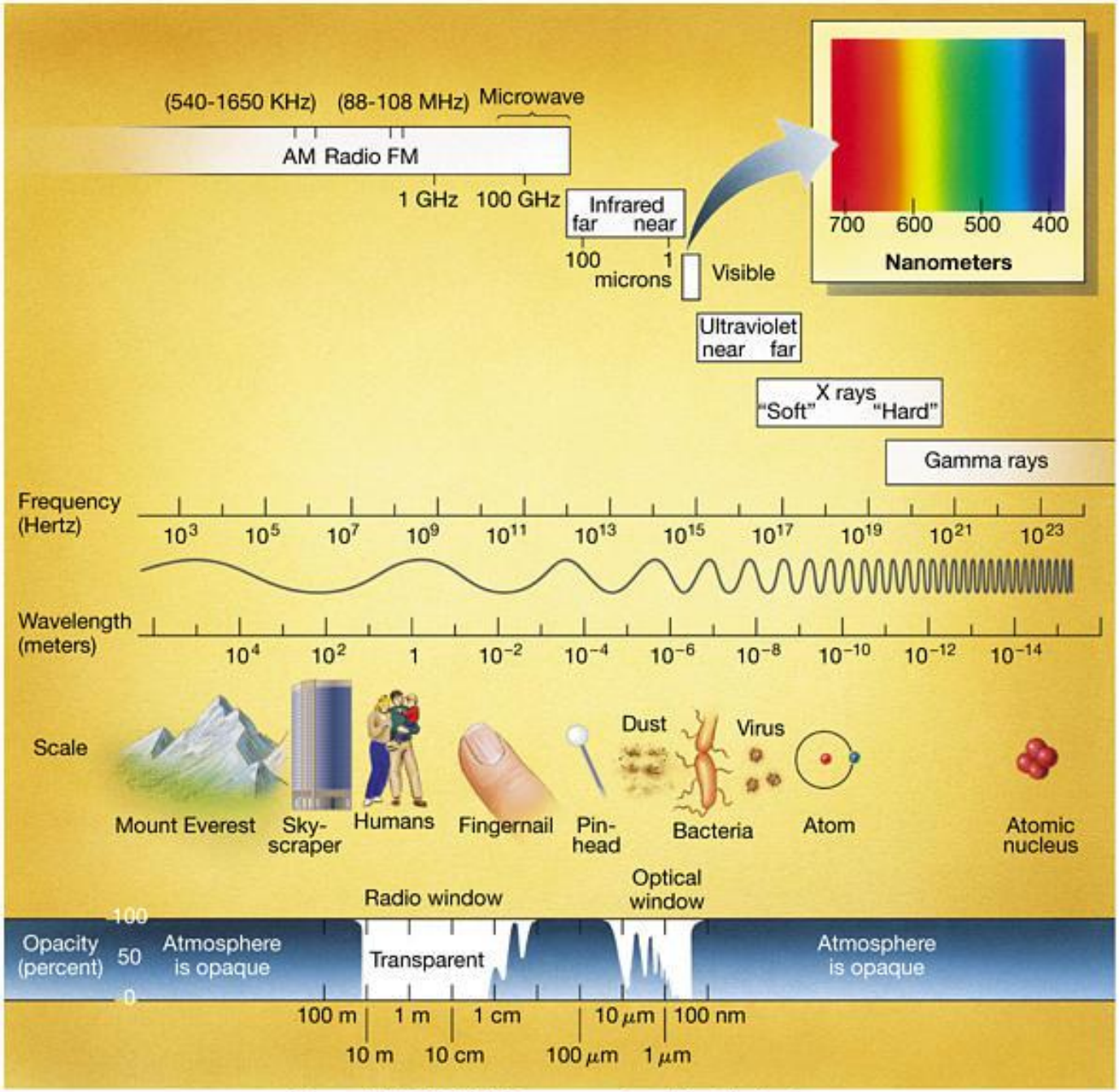
a. 1000 μm

b. 1000 nm

- **The Electromagnetic Spectrum:** It encompasses an enormous range of wavelength and frequencies.

- The divisions are based on the methods used to generate and detect the various kinds of radiation.
- Several overlaps are incident. Note that the portion of the spectrum visible to the human eye is tiny when compared with other spectral regions.


Wavelength (nm)
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
10^{6}
10^{10}
10^{12}
Gamma ray
X-ray
Ultra-violet
Visible
Infrared
Microwave
Radio frequency
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
Frequency (s^{-1})
400
500
600
750 nm
Visible region
7.5×10^{14}
6.0×10^{14}
5.0×10^{14}
4.0×10^{14} s^{-1}



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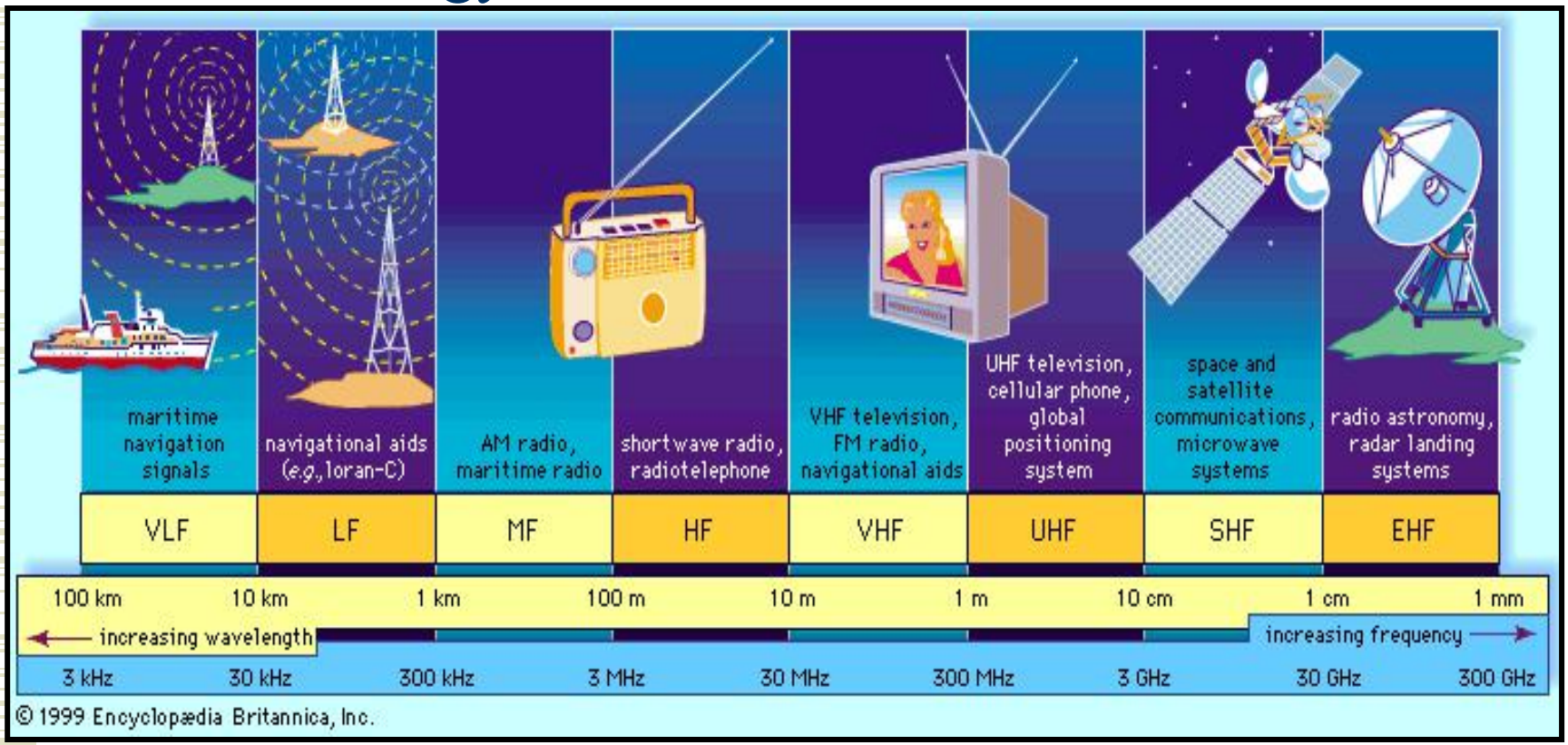
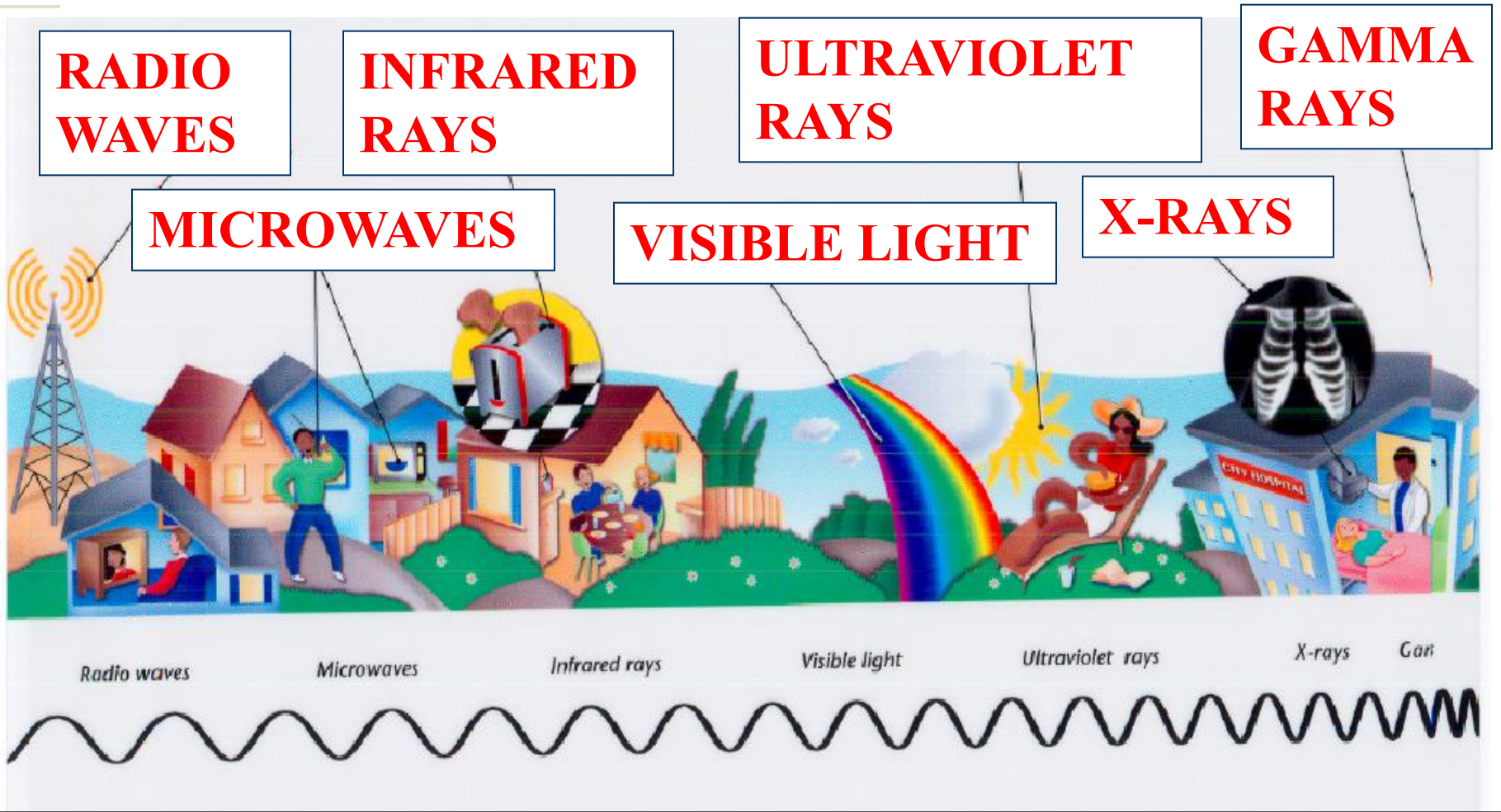
Types of EM Radiation

- Radiowaves
  - lowest energy EM radiation

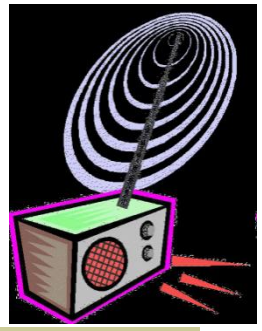


B. Waves of the Electromagnetic Spectrum

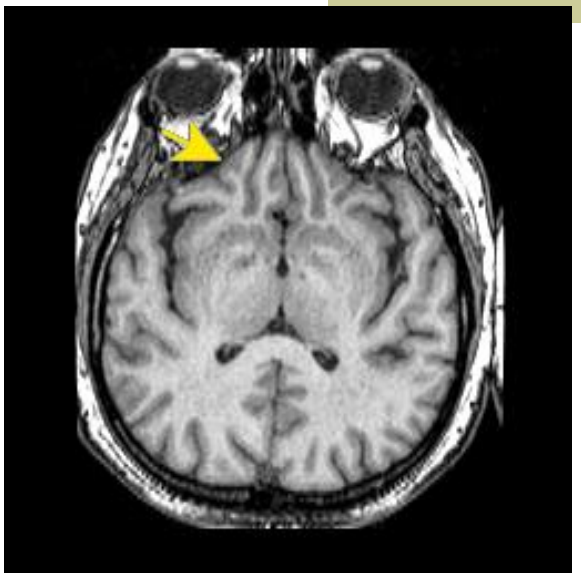
- **Electromagnetic Spectrum**—name for the range of electromagnetic waves when placed in order of increasing frequency

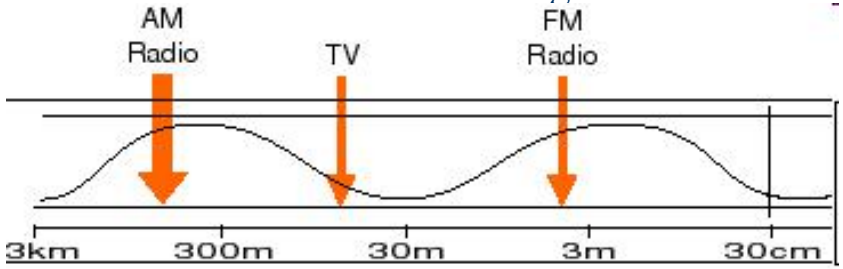


Radio waves



- Longest wavelength EM waves
- Uses:
  - TV broadcasting
  - AM and FM broadcast radio
  - Heart rate monitors
  - Cell phone communication
  - MRI (MAGNETIC RESONACE IMAGING)
    - Uses Short wave radio waves with a magnet to create an image



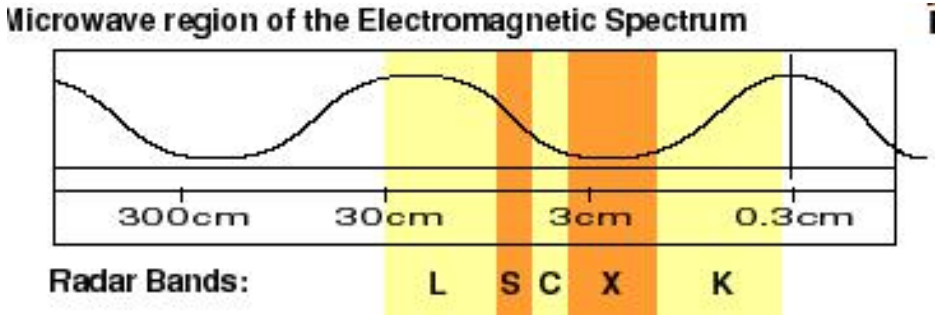


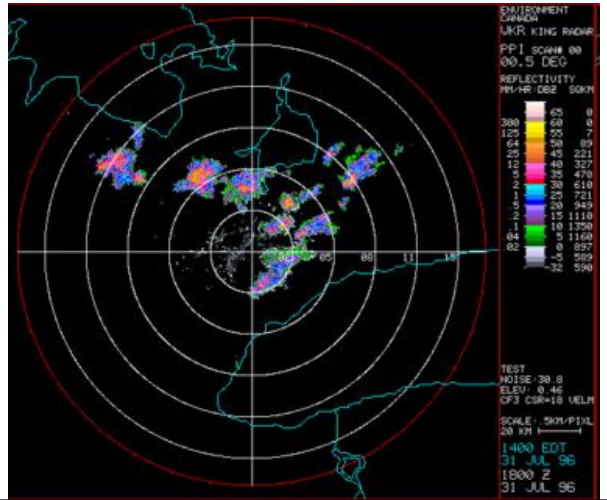
Radio Wave Region of the Electromagnetic Spectrum

- Radio and television waves are on the long end of the electromagnetic spectrum, on the order of kilometers long.
- These are very low energy waves (remember: long wavelength = low energy) that do not harm as far as our health and safety are concerned.
- That is a good thing, because the atmosphere in which we live is full of these wavelengths transporting the radio and television sound and pictures from every studio on Earth ultimately to our personal radios and televisions.

Microwaves

- Wavelengths from 1 mm- 1 m
- Uses:
  - Microwave ovens
  - Bluetooth headsets
  - Broadband Wireless Internet
  - Radar
  - GPS



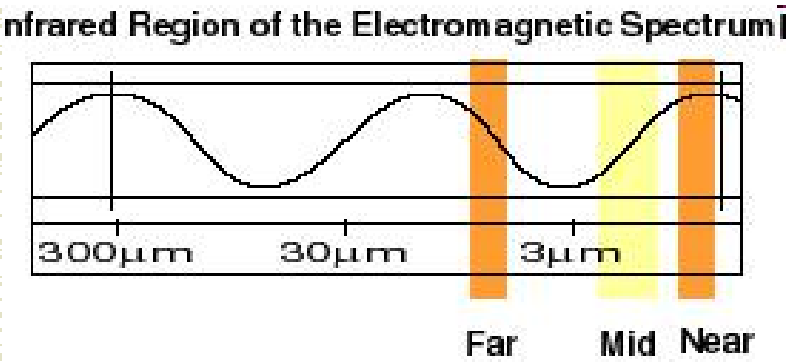


- Microwaves have wavelengths on the order of a centimeter and are also of low energy, but they can be dangerous because their absorption causes the generation of much internal heat.

- Microwave ovens are used in our kitchens, but they are also used in an analytical laboratory for drying samples.

Infrared Radiation

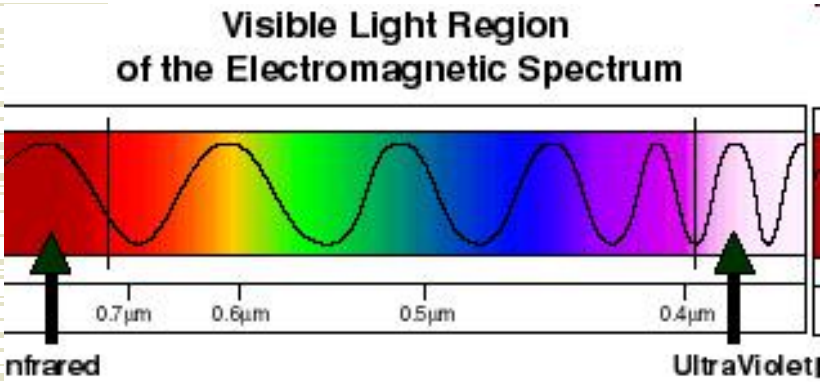
- Wavelengths in between microwaves and visible light
- Uses:
  - Night vision goggles
  - Remote controls
  - Heat-seeking missiles



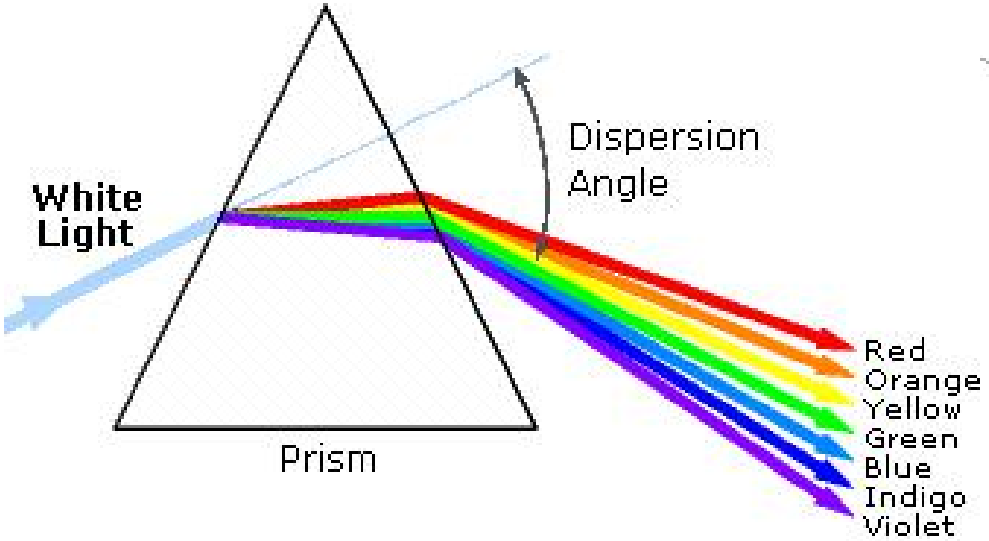
- In the infrared region, the wavelengths are extremely short by comparison.
- Wavelengths in this range are so short that we cannot represent them on paper or measure them with common measuring tools.
- While the wavelengths are shorter and have higher energy than radio and television waves or microwaves, they also cause us no harm.
- Indeed, the remote controls we use to control our stereos and VCRs utilize infrared light

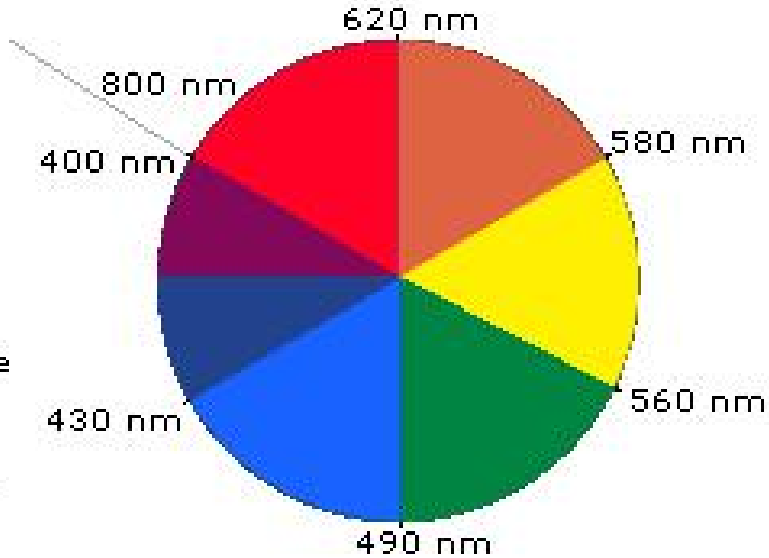
Visible light

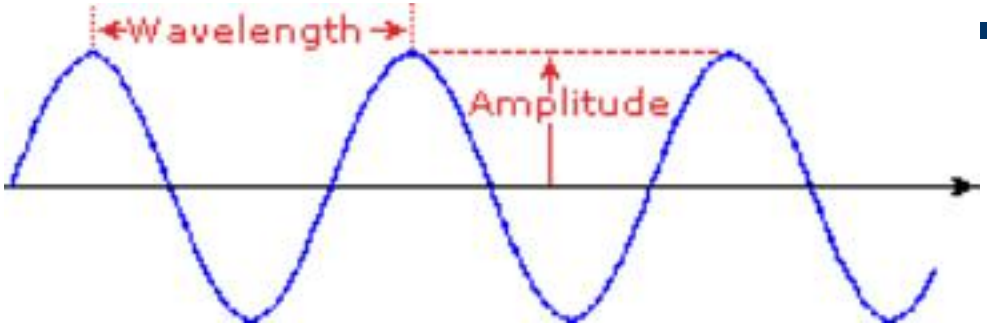
- Only type of EM wave able to be detected by the human eye
- Violet is the highest frequency light
- Red light is the lowest frequency light
- It is located approximately in the middle of the electromagnetic spectrum and a very narrow region compared to the entire spectrum and to the other regions.

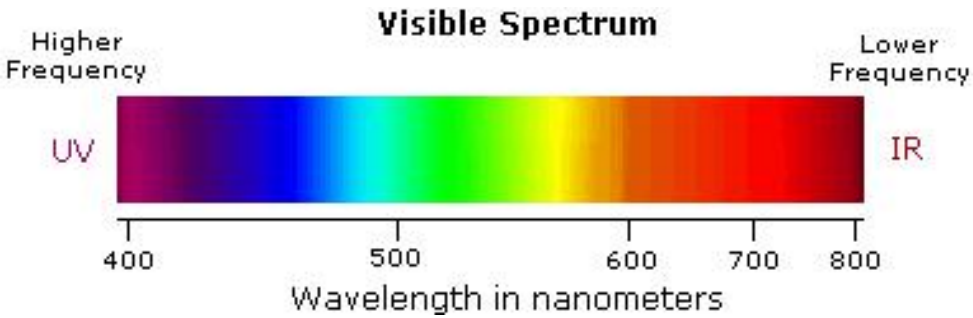


Visible and Ultraviolet Spectroscopy





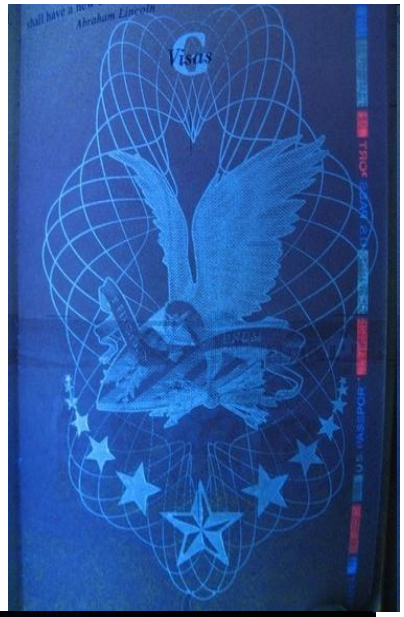


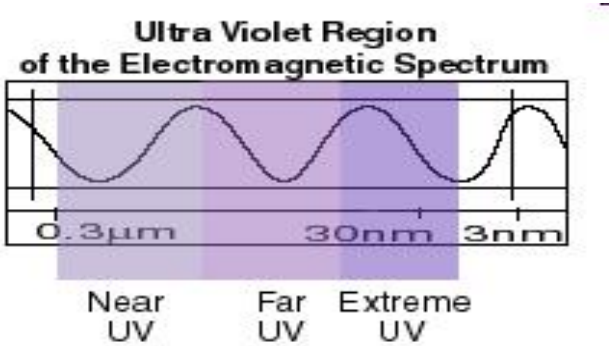


- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

Ultraviolet

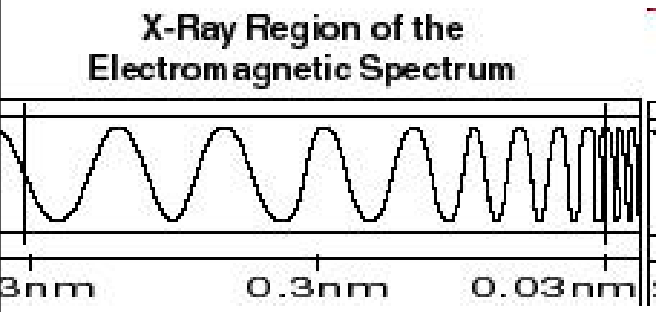
- Shorter wavelengths than visible light
- Uses:
  - Black lights
  - Security images on money
  - Harmful to living things
    - Used to sterilize medical equipment
    - Too much causes sun burn
    - Extremely high exposure can cause skin cancer





X-rays

- Tiny wavelength, high energy waves
- Uses:
  - Medical imaging
  - Airport security
    - Moderate dose can damaging to cells



X-rays are extremely short wavelengths of extremely high energy, penetrating our skin and tissue and causing harm, hence the reason for the lead aprons used by doctors and dentists when our bodies are x-rayed.

Gamma Rays

- Smallest wavelengths, highest energy EM waves
- Uses
  - Sterilizes medical equipment
  - Cancer treatment to kill cancer cells
    - Kills nearly all living cells.

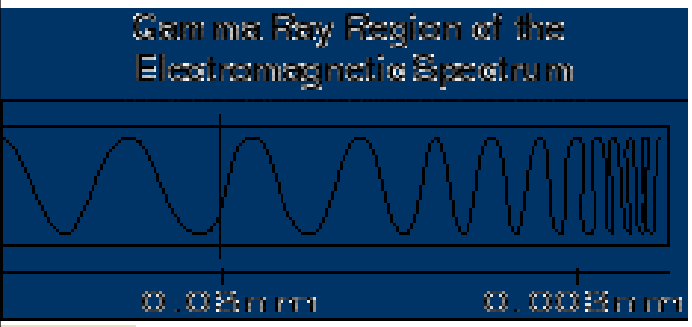


TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type of Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	—	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	—	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet-visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 μm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–375 mm	13–0.03	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^3	Spin of nuclei in a magnetic field

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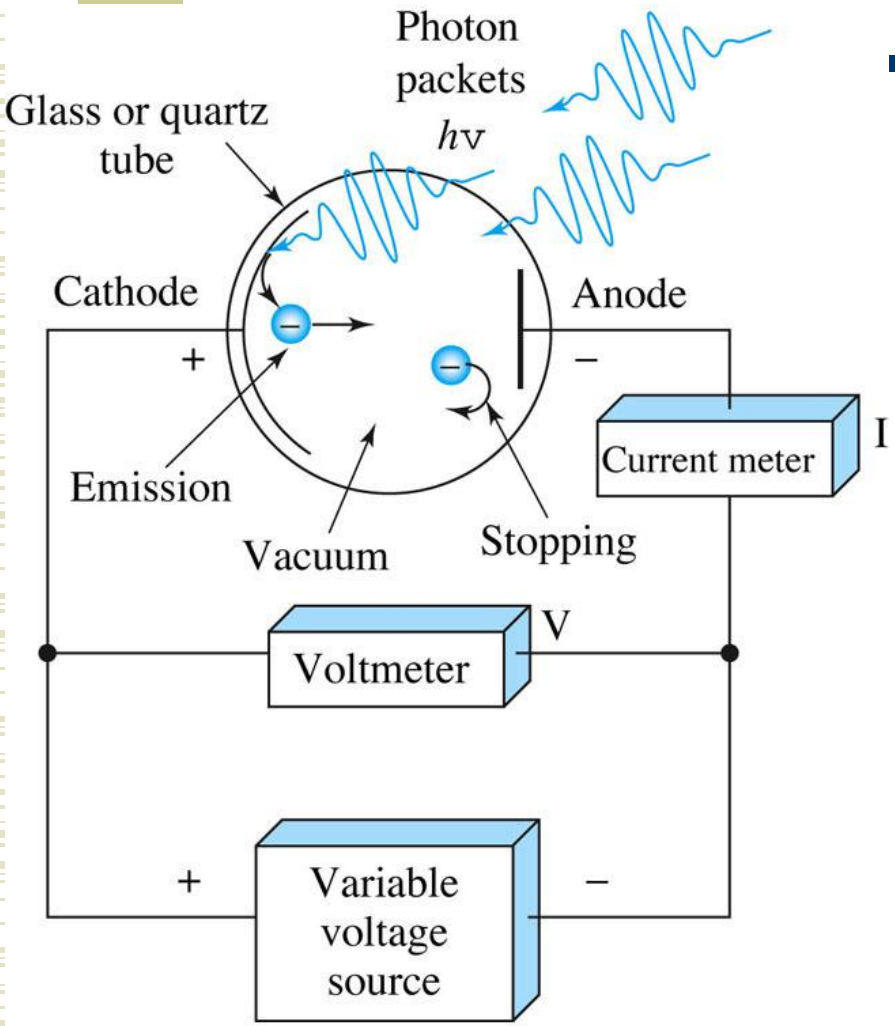
- When electromagnetic radiation is emitted or absorbed, a permanent transfer of energy from the emitting object or to the absorbing medium occurs.

- To describe these phenomena, it is necessary to treat electromagnetic radiation not as a collection of waves but rather as a stream of discrete particles called ***photons or quanta***.

Electromagnetic radiation can be treated as discrete packets of energy or particles called ***photons*** or ***quanta***.

According to particle nature of emr, they are a stream of discrete bundle of energy called **photon**.

The Photoelectric Effect



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Vo: Stopping voltage (the negative voltage at which the photocurrent is zero)

$$eV_0 = h\nu - \omega$$

ω: work needed to remove e^-

The surface of the large photocathode on the left usually is coated with an alkali metal or one of its compounds, but other metals may be used.

- When monochromatic radiation impinges on the photocathode, electrons are emitted from its surface with a range of kinetic energies.
- As long as the voltage V applied between the anode and the cathode is positive, the electrons are drawn from left to right through the photo tube to produce a current I in the circuit.
- When the voltage across the phototube is adjusted so that the anode is slightly negative with respect to the cathode, the photoelectrons are repelled by the anode, and the photocurrent decreases as expected.
- At this point in the experiment, however, some of the electrons have sufficient kinetic energy to overcome the negative potential applied to the anode, and a current is still observed.

- The negative voltage at which the photocurrent is zero is called the stopping voltage. It corresponds to the potential at which the most energetic electrons from the cathode are just repelled from the anode.

$$eV_0 = h\nu - \omega$$

- If we multiply the stopping voltage by the charge on the electron, $e = 1.60 \times 10^{-19}$ coulombs, we have a measure of the kinetic energy in joules of the most energetic of the emitted electrons.

1. When light of constant frequency is focused on the anode at low applied negative potential, the photocurrent is directly proportional to the intensity of the incident radiation.
2. The magnitude of the stopping voltage depends on the frequency of the radiation impinging on the photocathode.
3. The stopping voltage depends on the chemical composition of the coating on the photocathode.
4. The stopping voltage is independent of the intensity of the incident radiation.

- This equation shows that the energy of an incoming photon is equal to the kinetic energy of the ejected photoelectron plus the energy required to eject the photoelectron from the surface being irradiated.
- That is the energy of the radiation must be equal to ω to eject the electron and the excess energy will be converted into kinetic energy.

$$KE_e + \omega = h\upsilon$$

- ω is the work function, a constant that is characteristic of the surface material and represents the minimum energy binding electron in the metal.

The energy of one photon of light is given by

$$E = h\upsilon$$

- Where h is Planck's constant i.e. equals to 6.626×10^{-34} J.s and υ is the frequency of light.
- When this equation is expressed in terms of wave length and wave number respectively it becomes

$$E = \frac{hC}{\lambda} \qquad E = hC\bar{\nu}$$

- If we have n number of photon, the total energy is equals to

$$E = nh\nu$$

$$E = \frac{nhC}{\lambda}$$

As indicated the energy of a photon of radiation is directly proportional to the frequency and wave number of the radiation and inversely proportional to the wave length of the radiation.

Exercise

1. Arrange different EMR in the increasing order of their energy
2. Calculate the energy of a photon whose
   A. Frequency is 1.5×10^{5} Hz
   B. Wave length of 1 m
   C. Wave number is 5.2×10^{10} m^{-1}

How does Electromagnetic Radiation Interact with Matter?

- The interaction of electromagnetic radiation and matter conforms to well established quantum mechanical laws.
- Atoms, ions, and molecules exist only in certain discrete states with specific energies.
- The same quantum mechanical laws dictate that a change in state requires the absorption or emission of energy, ΔE, exactly equal to the difference in energy between the initial and final states.

$$\Delta E = E_{final} - E_{initial} = h\nu$$

- For atoms or ions in the elemental state, the energy of any given state arises from the motion of electrons around the positively charged nucleus.
- As a consequence the various energy states are called electronic states.
- In addition to having electronic states, molecules also have quantized vibrational states that are associated with the energy of interatomic vibrations and quantized rotational states that arise from the rotation of molecules around their centers of mass.
- The lowest energy state of an atom or molecule is its ground state. Higher energy states are termed excited states. Generally. at room temperature chemical species are in their ground state.

- A change in any form of motion or electron energy level involves a change in the energy of the molecule. Such a change in energy is called a transition;
  - ✓ The chemical nature of matter (its composition),
  - ✓ its physical state, and
  - ✓ the arrangement of the atoms or molecules in the physical state with respect to each other

  affect the way in which any given material interacts with electromagnetic radiation.

Absorption of Radiation

- **Absorption of Radiation:** Absorption occurs only if :

a. There is an interaction between the electromagnetic radiation and the material.

b. The energy of the electromagnetic radiation must exactly corresponds to the energy of transition in the molecule.

When material (atoms, ions or molecules) changes its state (from lower to higher energy), it absorbs an amount of energy exactly equal to the energy difference between the states.

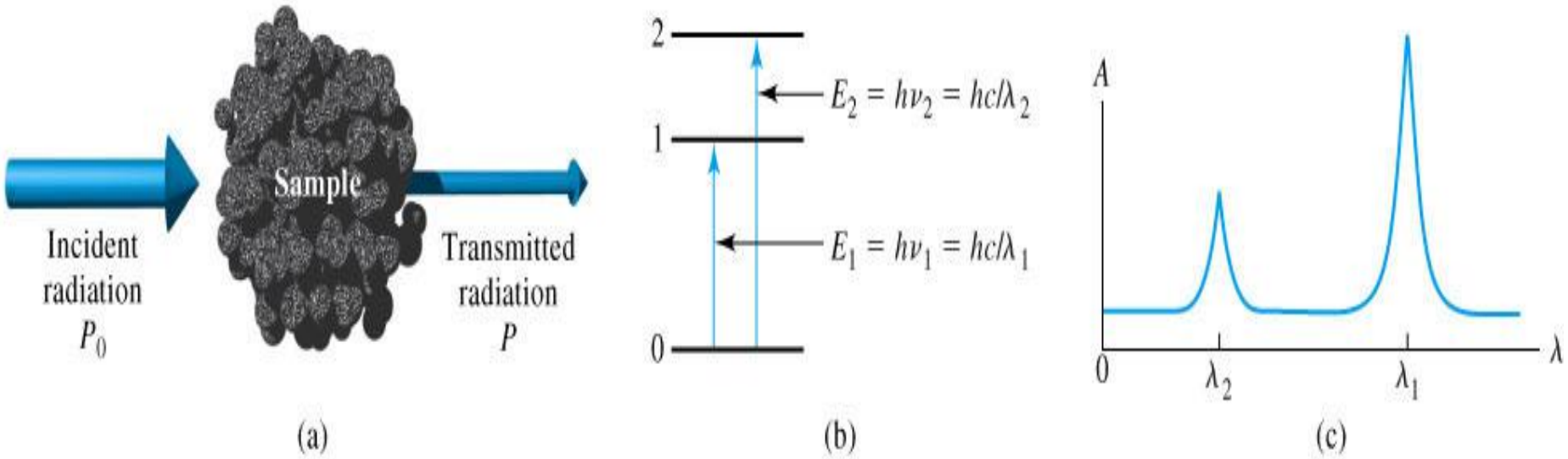
$$E_1 - E_o = h\nu = hc/\lambda$$

where, E_1 = energy of the higher state,

E_o = energy of the lower state.

Absorption of Radiation

When radiation passes through a sample certain frequency may be selectively removed by **absorption**, a process in which electromagnetic energy is transferred to the atoms, ions or molecules. Absorption promotes these particles from ground state to one or more higher energy states. The energy of the exciting photon must exactly match the energy difference between the ground state and one of the excited states of the absorbing species. Since these energy differences are unique for each species, a study of the frequencies of absorbed radiation provides a means of characterizing the constituents of a sample of matter.



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Molecular transition

- There are three basic processes by which a molecule can absorb radiation; all involve raising a molecule to a higher internal energy level, the increase in energy being equal to the energy of the absorbed radiation
- In molecules the electronic states are subdivided into vibrational states and each vibrational states are subdivided into rotational states.
- The energy of a band in a molecular absorption spectrum is the sum of three different energy components.

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

- Transitions between electronic-vibrational-rotational states give rise to spectra that appear to have bands.

- In all the three types internal energy is quantized; that is, they exist at discrete levels.
- First, a molecule rotates about various axes; the energy of the rotation being at definite energy levels, so a molecule can absorb radiation and be raised to a higher rotational energy level.

The transition of a molecule from lower molecular energy level into higher molecular energy level is called rotational transition.

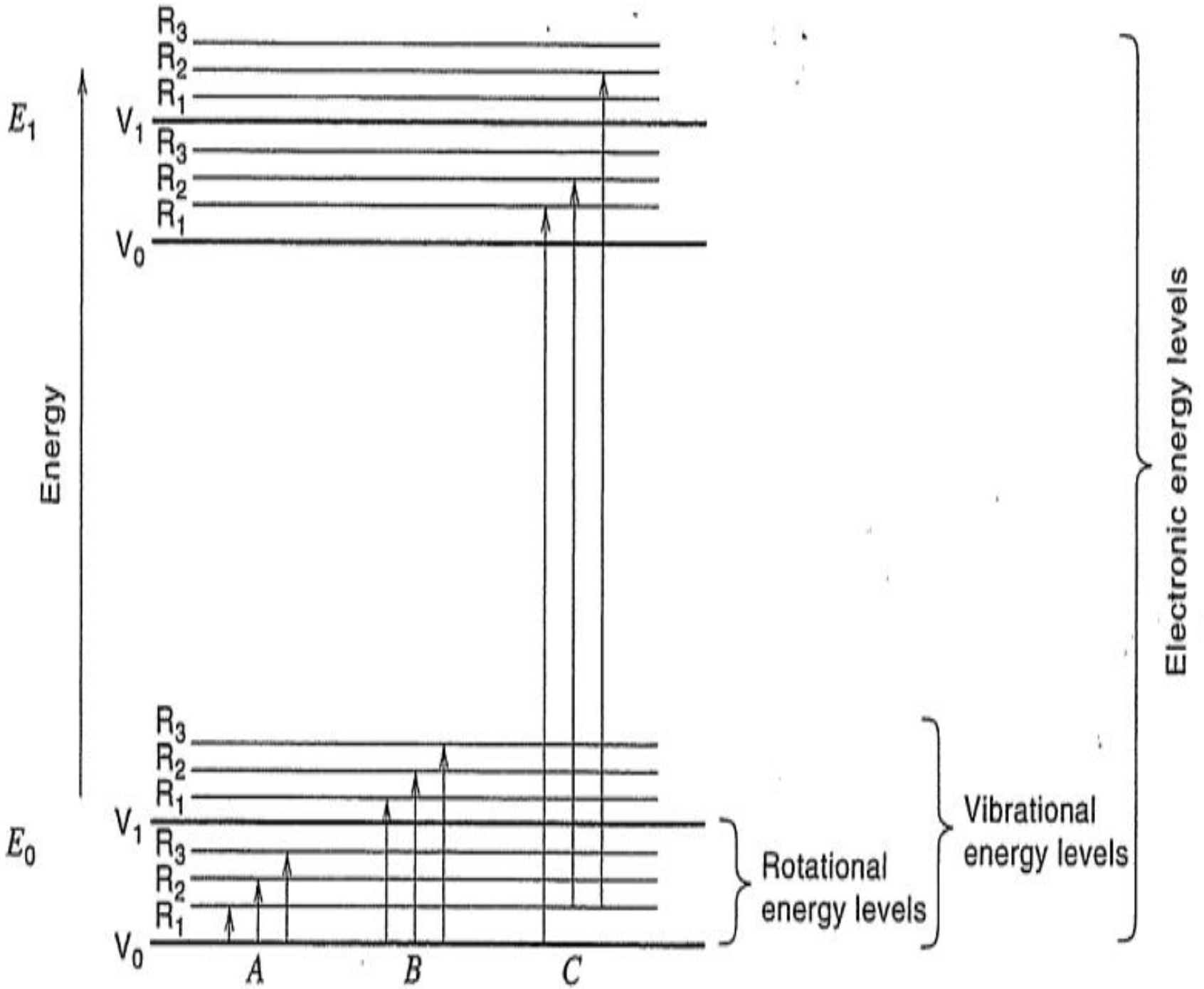
- The atoms or the groups of atoms within a molecule vibrate relative to each other, and the energy of this vibration occurs at definite quantized Levels.
- The molecule may then absorb a discrete amount of energy and be raised to a higher vibrational energy level, in a vibrational transition.
- The third one is the transition of the electrons of the molecule from lower electronic energy level into higher electronic energy level. This is called electronic transition.

- $E_{electronic}$ describes the electronic energy of the molecule that arises from the energy states of its several bonding electrons.
- $E_{vibration}$ refers to the total energy associated with the multitude of interatomic vibrations that are present in molecular species.
- Generally, a molecule has many more quantized vibrational energy levels than it does electronic levels.
- $E_{rotation}$ is the energy caused by various rotational motions within a molecule; again the number of rotational states is much larger than the number of vibrational states

- Since each of these internal energy transition is quantized, they will occur only at definite wavelengths corresponding to an energy $h\nu$, equal to the quantized jump in the internal energy.
- There are, however, many different possible energy levels for each type of transitions, and several wavelengths may be absorbed. The relative energies of the three transition processes are in the following order:

Electronic > Vibrational > Rotational

- Because of this, these transitions take place by different radiations with different energy.
- Example, rotational transition can takes place by absorption of microwave or far IR.
- Vibrational transition requires a little beat larger energy radiation, near IR. But electronic transitions occur while the molecule absorbs Uv/Vis radiation.


R3
R2
R1
E1
V1
R3
R2
R1
V0
Energy
R3
R2
R1
E0
V1
R3
R2
R1
V0
A
B
C
Rotational energy levels
Vibrational energy levels
Electronic energy levels

Atomic Absorption

- In atoms, there are no rotational and vibrational transitions.
- The absorption of EMR by atoms will result an electronic transition of electrons of the atom from lower electronic energy level to higher one.
- Ultraviolet and visible radiation have enough energy to cause transitions of the outermost, or bonding, electrons only.
- X-ray frequencies, on the other hand, are several orders of magnitude more energetic and are capable of interacting with electrons that are closest to the nuclei of atoms.
- Absorption peaks that correspond to electronic transitions of these innermost electrons are thus observed in the X-ray region.

- A specific molecule, such as hexane, or a specific atom, such as mercury, can absorb only certain frequencies of radiation.
- All hexane molecules will absorb and emit light with the same frequencies, but these frequencies will differ from those absorbed by a different molecule, such as benzene.
- All mercury atoms will absorb the same frequencies of incident light, but these will differ from the frequencies of light absorbed by atoms of lead or copper.
- Not only are the frequencies unique, but also the degree to which the frequency is absorbed or emitted is unique to a species.
- This degree of absorption or emission results in light of a given intensity.

- The uniqueness of the frequencies and amount of each frequency absorbed and emitted by a given chemical species is the basis for the use of spectroscopy for identification of chemicals.
- We call the set of frequencies and the associated intensities at which a species absorbs or emits its Spectrum

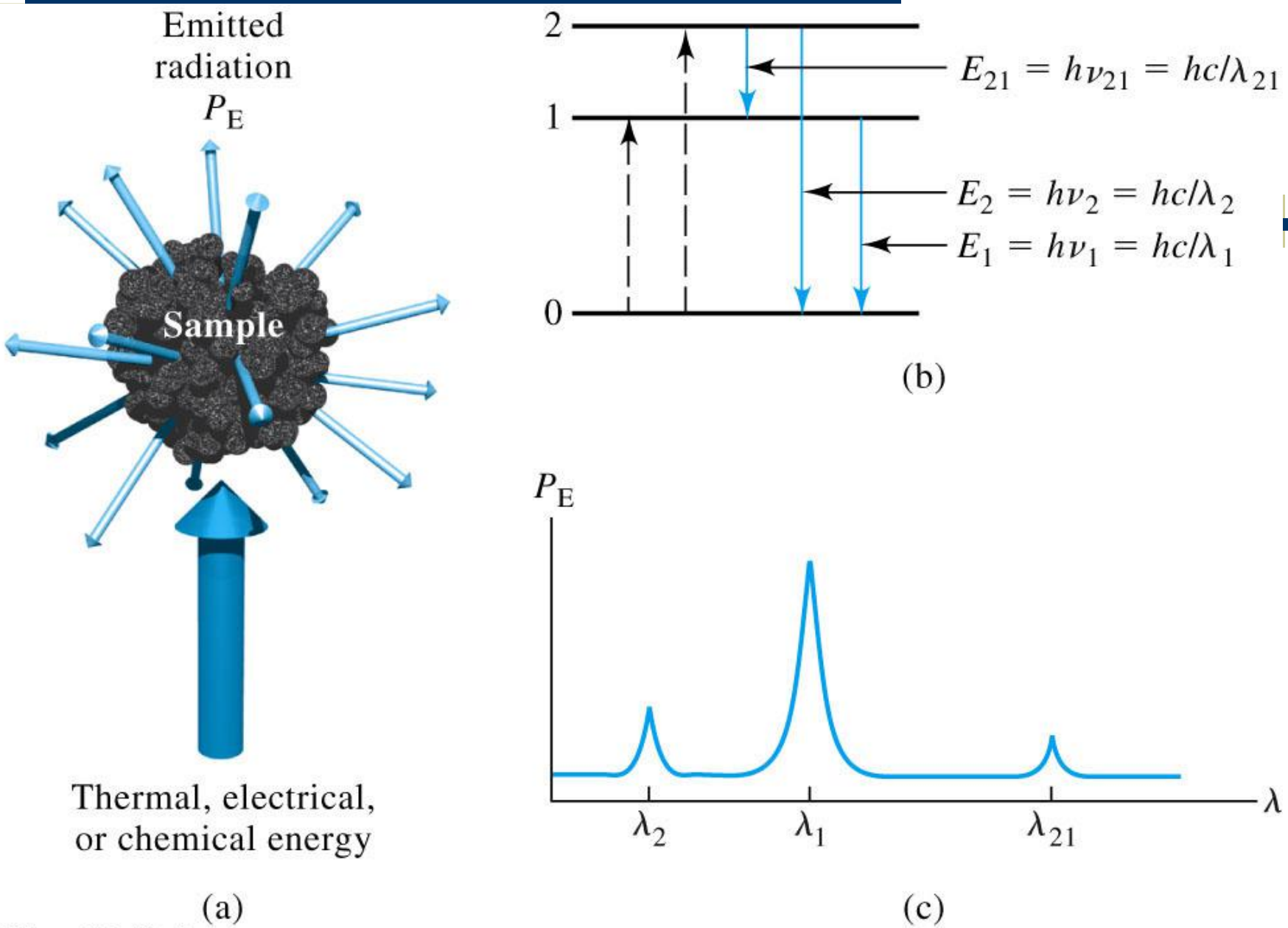
- **Emission of Radiation:** Electromagnetic radiation is produced when excited particle (atoms, ions, or molecules) relax to lower energy levels by giving up their excess energy as photons. Radiation from an excited source is characterized by means of an emission spectrum.

$X \rightarrow X^* \rightarrow X + h\nu$

Excitation can be done by –

1. Bombardment with electrons
2. Electric current ac spark
3. Heat of a flame
4. An arc or a furnace (produce Uv, Vis or IR radiation)
5. Beam of electromagnetic radiation

- The sample is usually stimulated by applying energy in the form of
  - ✓ heat,
  - ✓ electrical energy,
  - ✓ light,
  - ✓ particles, or a
  - ✓ chemical reaction.
- Prior to applying the stimulus, the analyte is predominantly in its lowest energy state, or ground state.
- The stimulus then causes some of the analyte species to undergo a transition to a higher energy, or excited state.



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Chapter Two

QUANTITATIVE ASPECTS OF SPECTROCHEMICAL MEASUREMENTS

Quantitative Relation for Emission Techniques

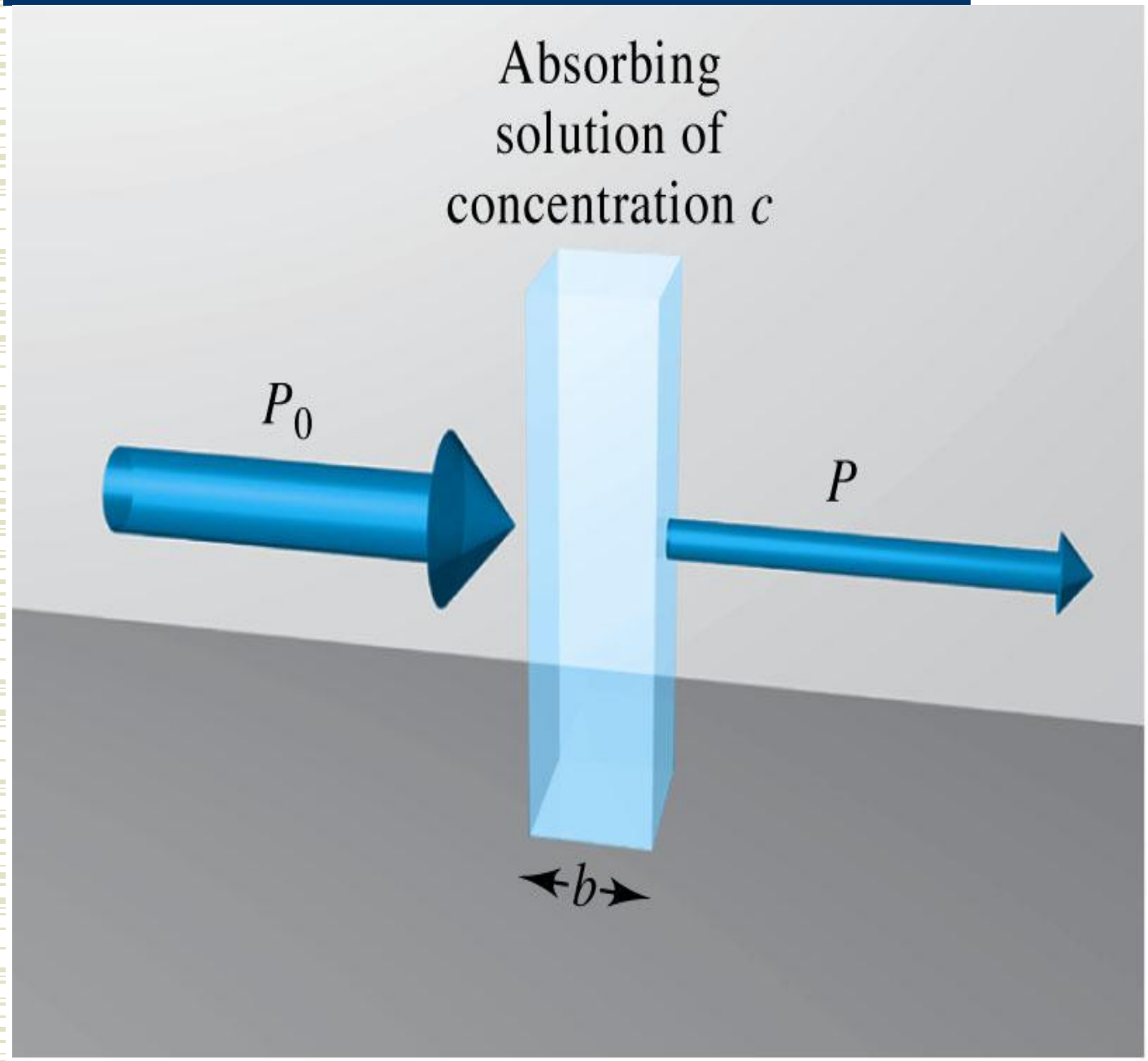
- the power or intensity of the emitted radiation is measured using different detectors that convert a radiant energy into electrical signal commonly current and voltage.
- The current or voltage produced is directly proportional to the power or intensity of the radiation.
- The power or intensity of the radiation is directly proportional to the number of atoms that are excited and finally on the concentration of the analyte.
- The measured signal, S, is directly proportional to the concentration of the substance being determined by the following equation,

$$S = k`C$$

Where k` is a constant which is determined from a calibration curve plotted by measuring on different standard samples.

Quantitative Relation for Absorption Techniques

- Quantitative absorption methods require two power measurements:
- one before a beam has passed through the medium that contains the analyte (P_o) and the other after the beam has passed through the sample (P).
- Two terms, which are widely used in absorption spectrometry and related to the ratio of P_o and P, are **transmittance** and **absorbance**.



$$T = \frac{P}{P_0}$$

$$A = \log \frac{P_0}{P}$$

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- When light passes through an absorbing sample, the power of the light emerging from the sample is decreased.
- Assume the power of a beam of monochromatic (i.e. single wavelength) radiation is P_0. This beam is passed through a sample that can absorb radiation of this wavelength
- The emerging light beam has a power equal to P, where $P_0 > P$.

- **Transmittance:** The transmittance T of the medium is the fraction of incident radiation transmitted by the medium.

$$T = \frac{P}{P_o} \qquad \text{(value from 0 to 1)}$$

- where, P_o is the incident power of the beam and P is the power of the beam after absorbed by the sample.
- Transmittance is often expressed as a percentage,

$$\%T = \frac{P}{P_o} x100 \qquad \text{(value from 0 to 100)}$$

1. If no radiation is absorbed by the sample, $P = P_0$.

thus $T = 1$ or $\%T = 100$

1. If any amount of radiation is absorbed, $P < P_0$.

- An important fact to recognize concerning transmittance is that it is not linear with concentration.
- In other words, a plot of transmittance or percent transmittance vs. concentration would not be an acceptable standard curve because it is not a straight line. Rather, its logarithmic relationship can be used .
- Because it is logarithmic, the logarithm of the transmittance can be expected to be linear with concentration.
- Thus, we define the parameter of absorbance as the negative logarithm of the transmittance and give it the symbol A:

- **Absorbance:** The absorbance A of a medium is defined by the equation,

$$A = -\log T$$

$$A = -\log \frac{P}{P_o}$$

$$A = \log \frac{P_o}{P}$$

$$A = \log \frac{1}{T}$$

Beer's Law

- Bouguer, and later Lambert, observed that the fraction of the energy, or the intensity of radiation, absorbed in a thin layer of material depends on the absorbing substance and on the frequency of the incident radiation, and is proportional to the thickness of the layer.
- At a given concentration of the absorbing species, summation over a series of thin layers, or integration over a finite thickness, leads to an exponential relationship between transmitted intensity and thickness.

Beer's Law

- **Beer's Law:** For monochromatic radiation, absorbance is directly proportional to the path length "b" through the medium and the concentration "c" of the absorbing species. These relationships are given by,

$$A = \alpha bc$$

where, α is a proportionality constant called the absorptivity. The magnitude of "α" will clearly depend upon the units used for "b" and "c". For solutions of an absorbing species, "b" is often given in terms of centimeters, and "c" in grams per liter.

Absorptivity then has units of $Lg^{-1}cm^{-1}$,

- when the concentration is expressed in moles/liter and cell length is in centimeters, the absorptivity is called the molar absorptivity and is given the spectral symbol ε. Thus when b is in centimeters and c is in moles per liter,

$$A = \varepsilon bc$$

where ε has the units L $mol^{-1}cm^{-1}$

- This equation that summarizes the relationship between absorbance, concentration of the species measured, sample path length, and the absorptivity of the species is known as the Beer – Lambert – Bouguer Law or, more commonly, as Beer's Law, which serves as the basis for quantitative analyses by both atomic and molecular absorption measurements.

Example

A sample in a 1.0 cm cell is determined with a spectrometer to transmit 70% light at certain wavelength. If the absorptivity of this substance at this wavelength is 1.5 $Lcm^{-1}g^{-1}$, what is the concentration of this substance?

Solution

The percent transmittance is 70%, and so T = 0.70

According to Beer`s law

$$A = abc = \log\frac{1}{T}$$

$$(1.5\,Lcm^{-1}g^{-1})(1.0\,cm)c = \log\frac{1}{0.70}$$

$$c = \frac{0.155}{1.5} = 0.103\ \frac{g}{L}$$

Example

A solution containing 2.00 mg iron (as thiocyanate complex) in 200 mL was observed to transmit 80.0% of the incident light compared to an appropriate blank.

a) What is the absorbance of the solution at this wavelength?
b) What fraction of light would be transmitted by a solution of iron which is half of the previous?

Solution

a) The percent transmittance is 80.0%, and so T = 0.800

$$A = \log\left(\frac{1}{T}\right) = \log\left(\frac{1}{0.80}\right) = 0.097$$

b)

$$m_{Fe} = 2\ mg\ x\ \frac{1\ x\ 10^{-3}\ g}{mg} = 0.002\ g$$

$$V = 200\ mL\ x\ \frac{1\ x\ 10^{-3}\ L}{mL} = 0.2\ L$$

$$c = \frac{0.002\ g}{0.2\ L} = 0.01\ \frac{g}{L}$$

$$A_1 = abc_1$$

$$0.097 = ab\ x\ 0.01$$

$$ab = \frac{0.097}{0.01} = 9.7$$

$$c_2 = 0.5\ x\ c_1 = 0.5\ x\ 0.01\ \frac{g}{L} = 0.005\ \frac{g}{L}$$

$$A_2 = abc_2 = 9.7x\ 0.005 = 0.0485\ \frac{g}{L}$$

Exercise

Amines, RNH_2, react with picric acid to form amine picrates, which absorb strongly at 359 nm ($\epsilon = 1.25 \times 10^4$). An Unknown amine (0.09265 g) is dissolved in water and diluted to 100 mL. A 1 mL aliquot this diluted to 250 mL for measurement. If this final solution exhibits an absorbance of 0.545 at 359 nm using a 1.00 cm cell, what is the formula weight of the amine? What is the probable formula?

Mixtures of Absorbing species

- It is possible to make quantitative calculations when two absorbing species in solution have overlapping spectra.
- It is apparent from Beer`s law that the total absorbance A at a given wavelength will be equal to the sum of the absorbances of all absorbing species.
- For two absorbing species x and y, then, if c is in gram per liter,

$$A = \alpha_x b c_x + \alpha_y b c_y \quad \text{at} \quad \lambda$$

- or if c is in mole per liter,

$$A = \varepsilon_x b c_x + \varepsilon_y b c_y \quad \text{at} \quad \lambda$$

- Where the subscripts refer to substances x and y, respectively.

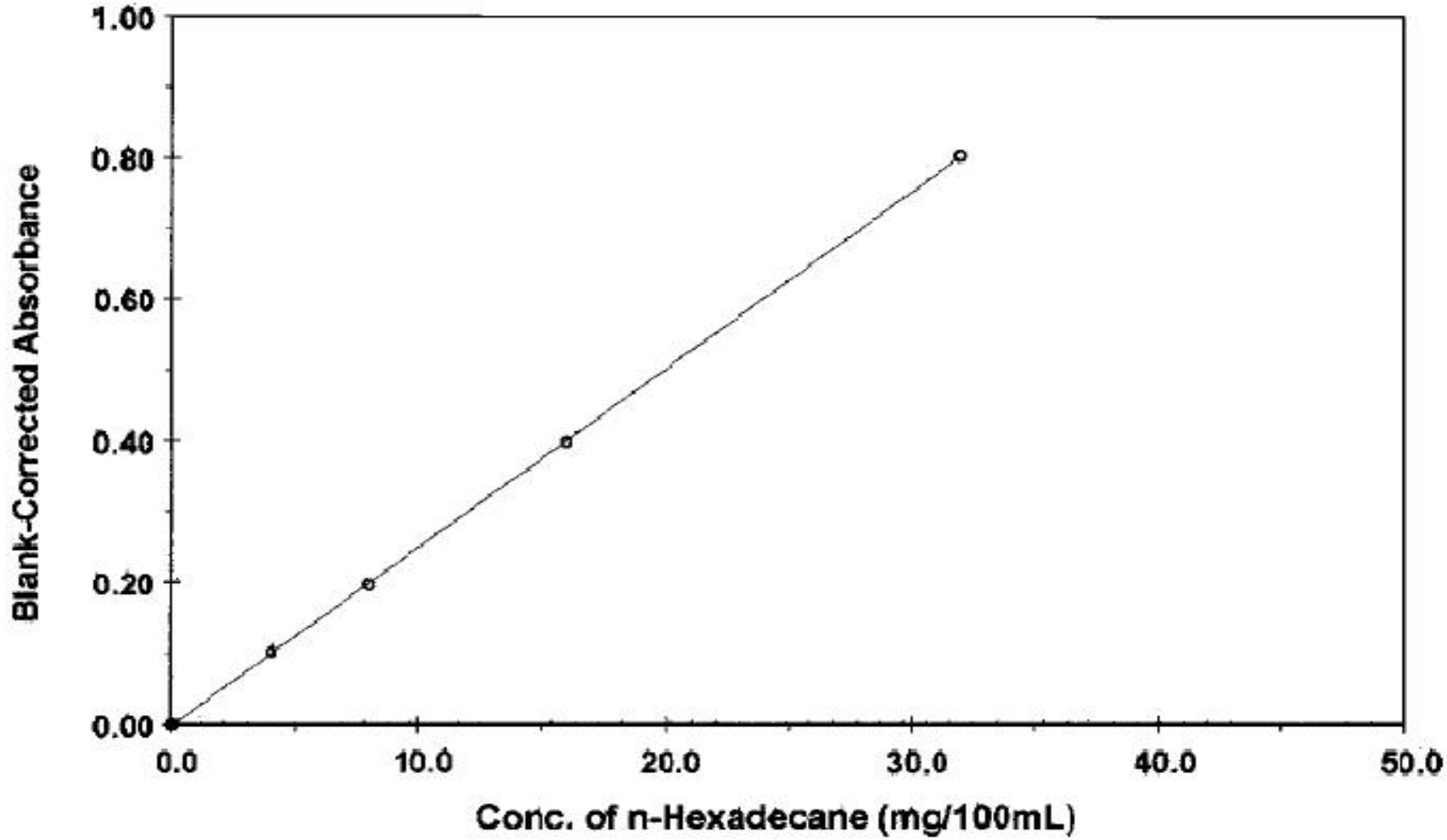
- For determination of a mixture of two substances, since there are two unknowns, two measurements will have to be made.
- The technique is to choose two wavelengths for measurement, one occurring at the absorption maximum for x (λ_1) and the other at the maximum for y (λ_2). We can write, then,

$$A_1 = A_{x1} + A_{y1} = \epsilon_{x1} b c_x + \epsilon_{y1} b c_y$$

$$A_2 = A_{x2} + A_{y2} = \epsilon_{x2} b c_x + \epsilon_{y2} b c_y$$

Where A_1 and A_2 are the absorbances at wavelength 1 and 2, respectively (for the mixture): A_{x1} and A_{y1} are the absorbances contributed by x and y, respectively, at wave length 1; and A_{x2} and A_{y2} are the absorbances contributed by x and y, respectively, at wavelength 2. Similarly, ϵ_{x1} and ϵ_{y1} are the molar absorptivities of x and y, respectively, at wavelength1; while ϵ_{x2} and ϵ_{y2} are the molar absorptivities of x and y, respectively, at wavelength 2. These molar absorptivities are determined by making absorbance measurements on pure solutions (known molar concentrations) of x and y at wavelength 1 and 2. So c_x and c_y become the only two unknowns in the equation and they can be calculated from the solution of the two simultaneous equations.

- Beer`s law is used to determine the concentration of different substances.
- As the equation shows absorbance is linearly proportional to the concentration where ϵb is constant.
- Ideally when we plot A vs C, it will be linear with slope equals to ϵb and y intercept equals to zero.
- This is done by measuring the absorbance of a set of standard solutions and plotting a calibration curve A vs C.
- The absorbance of the unknown solution is measured and its concentration is derived from the calibration curve.


1.00
0.80
0.60
0.40
0.20
0.00
Blank-Corrected Absorbance
0.0
10.0
20.0
30.0
40.0
50.0
Conc. of n-Hexadecane (mg/100mL)

Deviations from Beer's Law

- Beer's law states that a plot of absorbance versus concentration should give a straight line passing through the origin with a slope equal to a*b*. However, deviations from direct proportionality between absorbance and concentration are sometimes encountered.
- Beer`s law is fulfilled at low concentrations.
- These deviations are a result of one or more of the following three things ;
  - ☞real (fundamental) limitations,
  - ☞chemical factors (deviations)
  - ☞instrumental factors (deviations)

Real (Fundamental) Limitations,

- Beer's law is successful in describing the absorption behavior of dilute solutions only ; in this sense it is a limiting law.
- There are two contributions to this fundamental limitation to Beer's law.

1. At high concentrations (> 0.01M),the average distance between the species responsible for absorption is diminished to the point where each affects the charge distribution of its neighbors.
   - the individual particles of analyte no longer behave independently of one another.
   - This interaction, in turn, can alter the species' ability to absorb at a given wavelength of radiation and may change the value of ϵ thus leading to a deviation from Beer's law.

2. The absorptivity, **a**, and molar absorptivity, **ϵ**, depend on the sample's refractive index.

- Since the refractive index varies with the analyte's concentration, the values of **a** and **ϵ** will change.
- For sufficiently low concentrations of analyte, the refractive index remains essentially constant, and the calibration curve is linear

Chemical Factors (Deviations)

- Chemical deviations from Beer's law are caused by shifts in the position of a chemical or physical equilibrium involving the absorbing species. (i.e. when the absorbing species is involved in an equilibrium reaction)
- Deviations from Beer's law arise when an analyte dissociates, associates, or reacts with a solvent to produce a product with a different absorption spectrum than the analyte.

Example

- During analysis of a weak acid, HA, to construct a Beer's law calibration curve, several standards containing known total concentrations of HA, C_{tot}, are prepared and the absorbance of each is measured at the same wavelength.

- Since HA is a weak acid, it exists in equilibrium with its conjugate weak base, A^-

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- If both HA and A^- absorb at the selected wavelength, then Beers law is written as

$$A = \varepsilon_{HA} b c_{HA} + \varepsilon_{A^-} b c_{A^-}$$

- where C_{HA} and C_{A^-} are the equilibrium concentrations of HA and A^-. Since the weak acid's total concentration, C_{tot}, is

$$c_{tot} = c_{HA} + c_{A^-}$$

The concentrations of HA and A^- can be written as

$$c_{HA} = \alpha_{HA} c_{tot}$$

$$c_{A^-} = \alpha_{A_} c_{tot}$$

- where α_{HA} and α_{A-} is the fraction of weak acid present as HA and A^- respectively. Substituting these equations into previous equation and rearranging, gives

$$A = \left(\varepsilon_{HA}\alpha_{HA} + \varepsilon_{A^-} - \varepsilon_{A^-}\alpha_{HA}\right) b c_{tot}$$

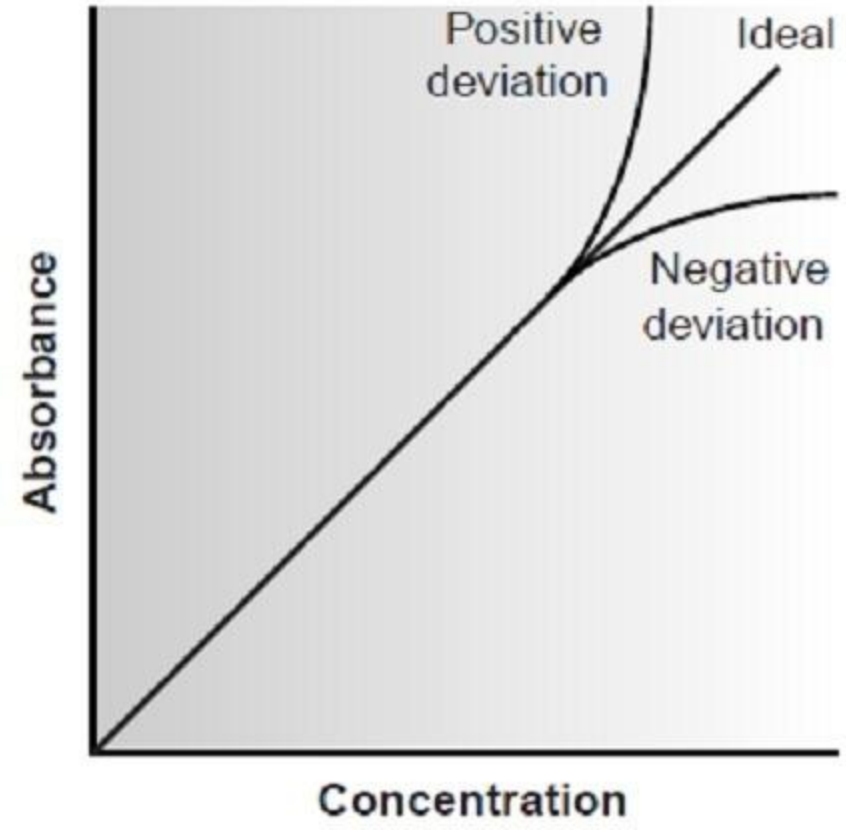
- Because values of α_{HA} may depend on the concentration of HA, the above equation may not be linear.
- A Beer's law calibration curve of absorbance (A) versus C_{tot} will be linear if one of two conditions is met.

1. If the wavelength is chosen such that ϵ_{HA} and ϵ_{A^-} are equal, then the above equation simplifies to the following and a linear Beer's law calibration curve is realized

$$A = \varepsilon_{A^-} b c_{tot}$$

2. if α_{HA} is held constant for all standards, then the previous equation will be a straight line at all wavelengths.

- Because HA is a weak acid, values of α_{HA} change with pH.
- To maintain a constant value for α_{HA}, therefore, we need to buffer each standard solution to the same pH.
- Depending on the relative values of ϵ_{HA} and ϵ_{A^-}, the calibration curve will show a positive or negative deviation from Beer's law if the standards are not buffered to the same pH.



Calibration curves showing positive and negative deviations from Beer's law.

instrumental factors (deviations)

- There are two principal instrumental limitations to Beer's law

1. Strict adherence to Beer's law is observed only with truly monochromatic radiation, that is, for radiation consisting of only one wavelength.
   - even the best wavelength selector passes radiation with a small, but finite effective bandwidth.
   - Using polychromatic radiation always gives a negative deviation from Beer's law, but is minimized if the value of ϵ is essentially constant over the wavelength range passed by the wavelength selector.

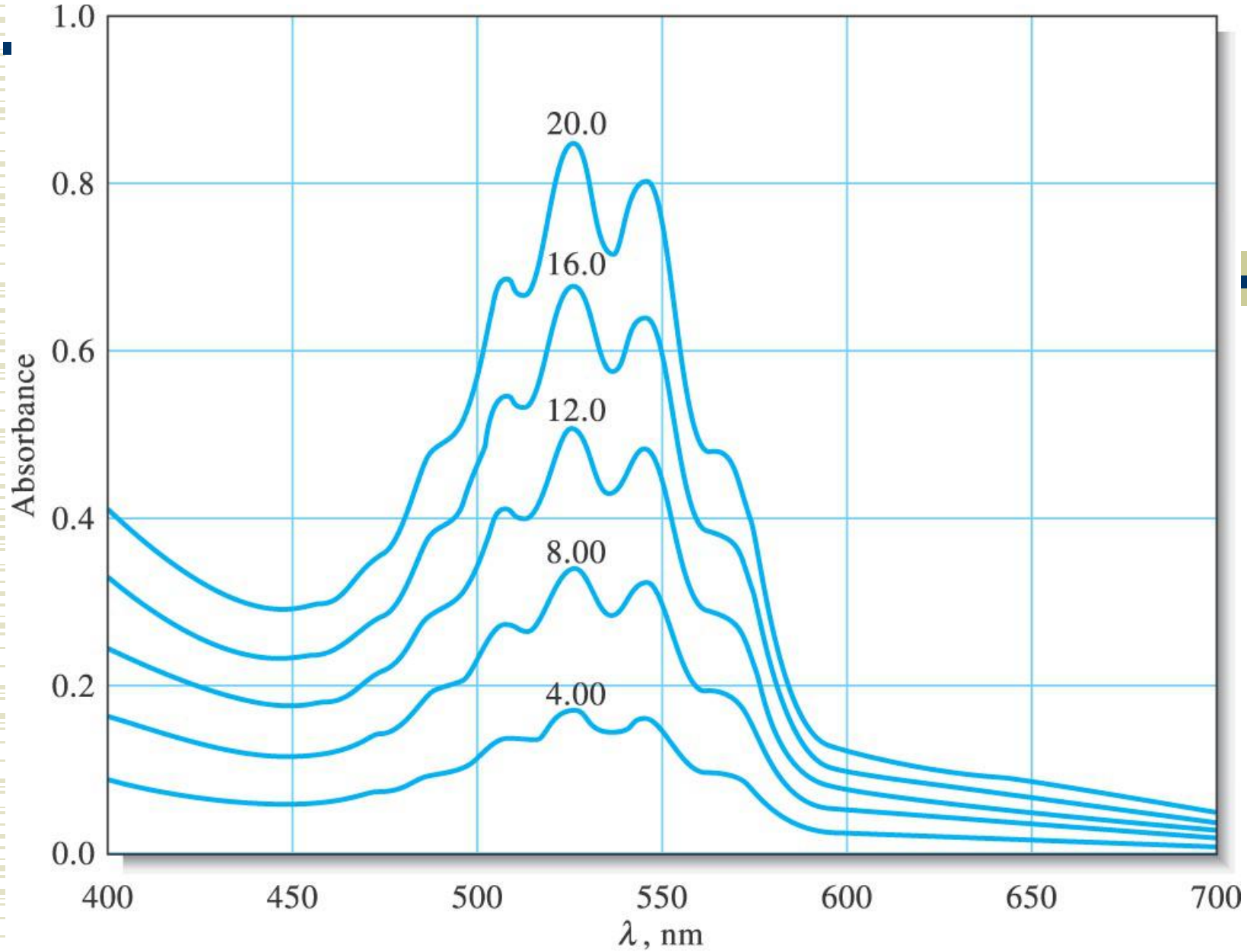
2. Stray radiation

- It arises from imperfections within the wavelength selector that allows extraneous light to leak into the instrument.
- Stray radiation adds an additional contribution, P_{stray}, to the radiant power reaching the detector; thus

$$A = \log\left(\frac{p_o + p_{stray}}{p_T + p_{stray}}\right)$$

Absorption spectra

- It is a plot that is used to show the overall absorption of a radiation
- An absorption spectrum is sometimes plotted absorbance versus wavelength.
- Absorbance could also be plotted absorbance against wave number or frequency. Most modern scanning instruments can produce such an absorption spectrum directly.
- Older instruments often display transmittance and produce plots of %T versus wavelength.
- In IR spectroscopy commonly % transmittance vs wave number is plotted.



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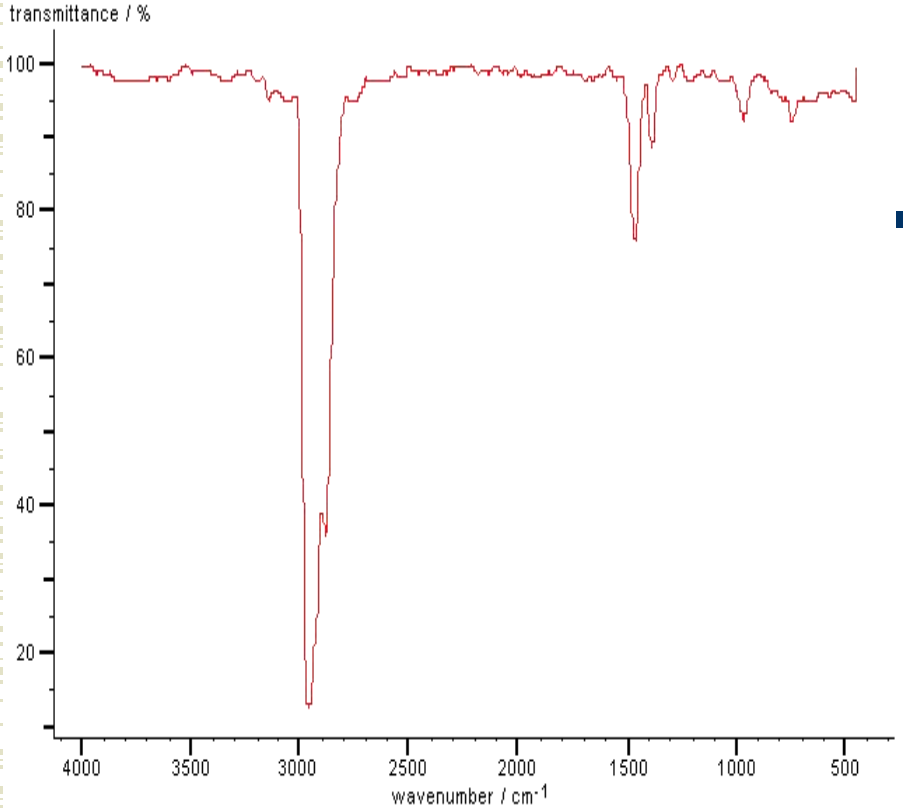
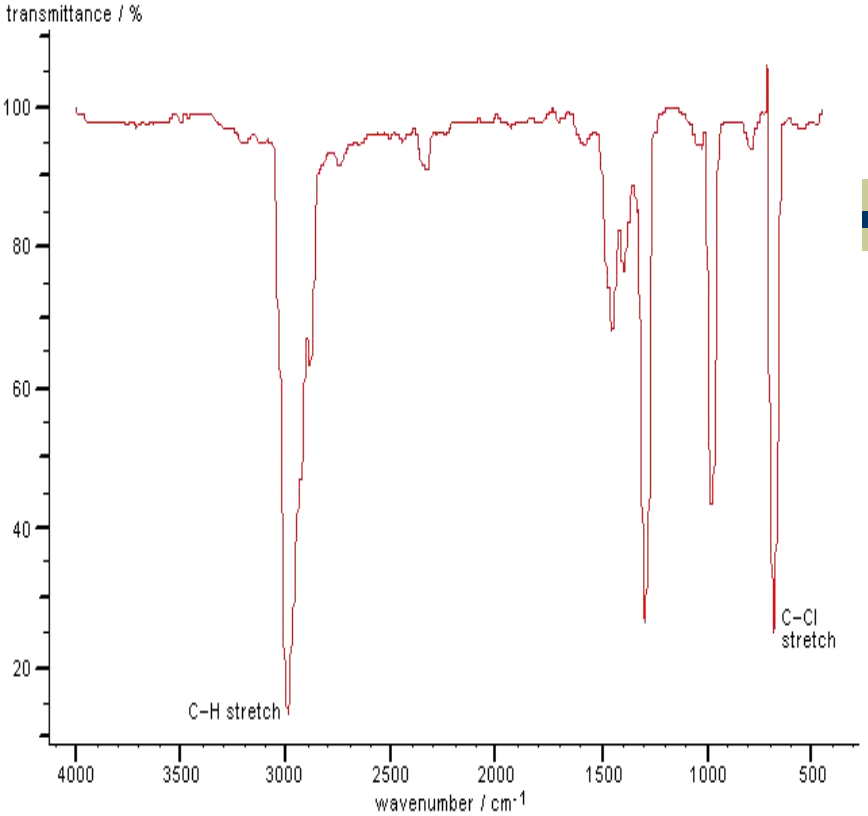
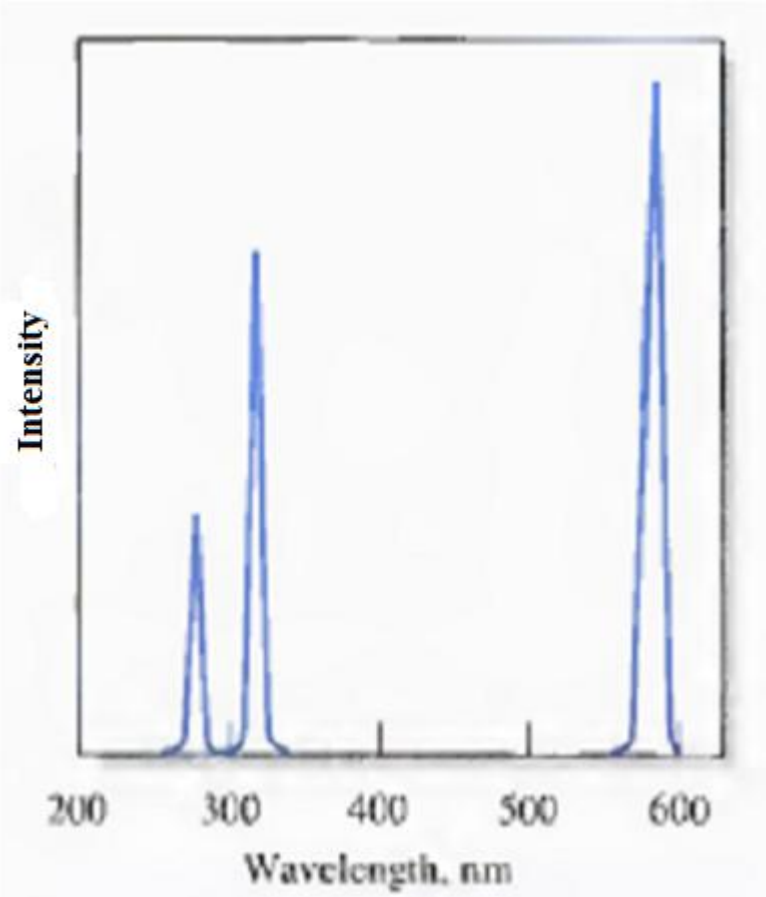


Ethane



Chloroethane



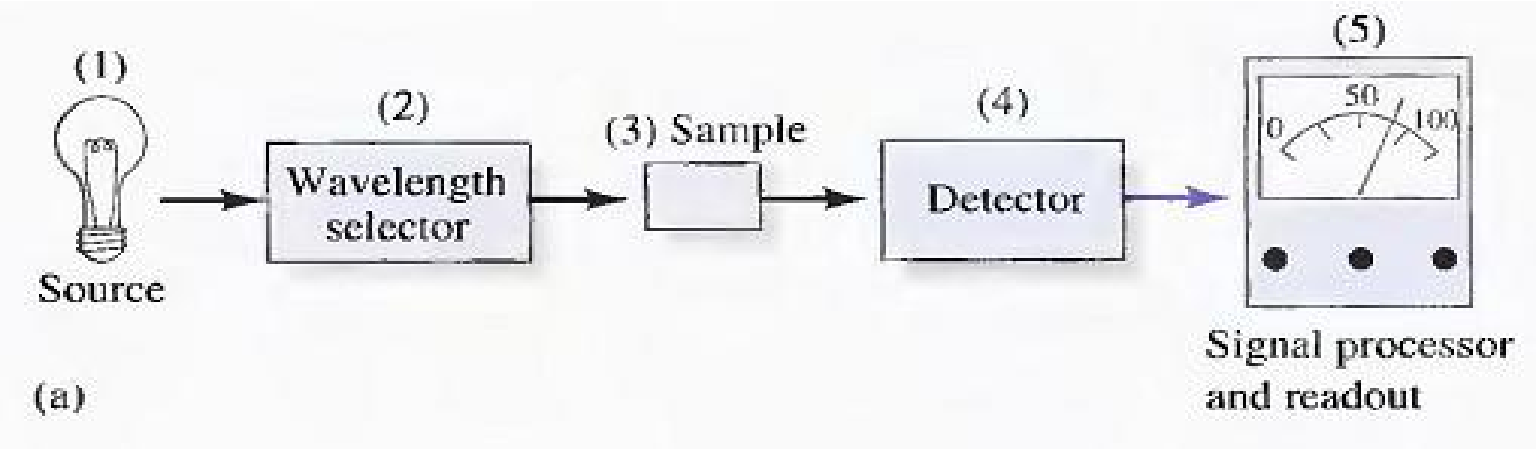
- emission spectra is plotted commonly intensity of the emitted radiation Vs wave length

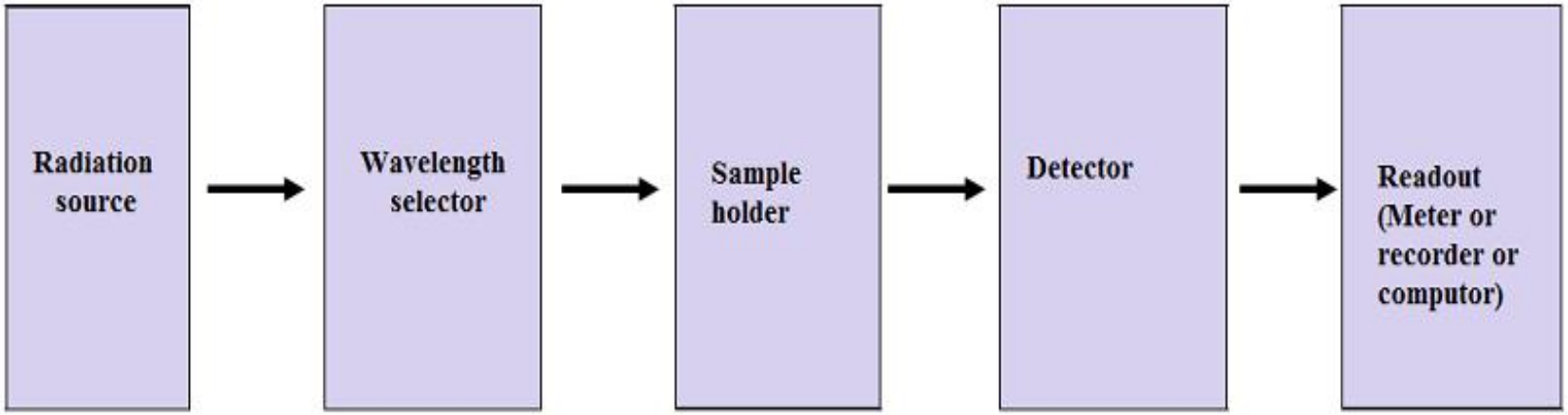
Chapter Three
Instruments for optical spectroscopy

- The instrumentation and their order of spectroscopic measurements depends on whether it is based on absorption or emission technique

- ✓ Typical spectroscopic instruments that involve absorption techniques contain five components:
  1. a stable source of radiant energy
  2. a transparent container for holding the sample
  3. a device that isolates a restricted region of the spectrum for measurement
  4. a radiation detector, which converts radiant energy to a usable electrical signal
  5. a signal processor and readout, which displays the transduced signal on a meter scale, a computer screen, a digital meter, or another recording device.

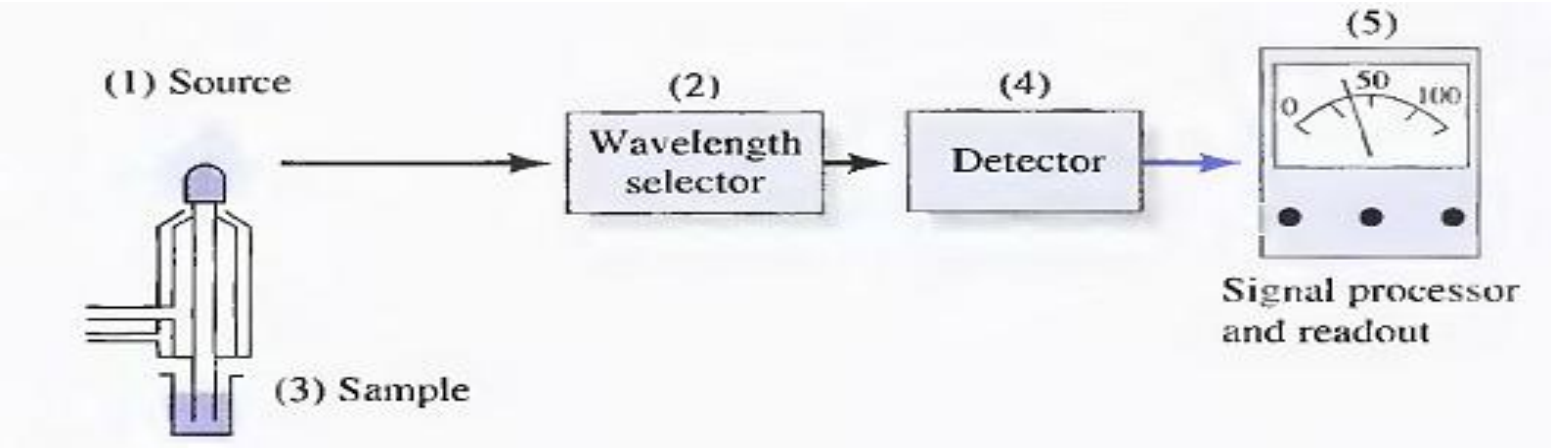
Components and arrangement of instruments for absorption spectroscopy.





- radiation of the selected wavelength is sent through the sample, and the transmitted radiation is measured by the detector-signal processing-readout unit.
- With some instruments, the position of the sample and wavelength selector is reversed.

Components and arrangement of instruments for emission spectroscopy.



- In emission spectroscopy, the sample itself is the emitter and no external radiation source is needed.
- In emission methods, there is no need for sample holder.
- The sample is usually fed into a plasma or a flame, which provides enough thermal energy to cause the analyte to emit characteristic radiation.

Radiation Sources

- An ideal radiation source for spectroscopy should have the following characteristics:
  - The source must emit radiation over the entire wavelength range to be studied.
  - The intensity of radiation over the entire wavelength range must be high enough so that extensive amplification of the signal from the detector can be avoided.
  - The intensity of the source should not vary significantly at different wavelengths.
  - The intensity of the source should not fluctuate over long time intervals.

.

The source of radiation can be classified into two class

A. Continuum Sources
B. Line sources

A. Continuum Sources

- These are radiation sources that produces radiation over a wide range of wavelengths, with a relatively smooth variation in intensity as a function of wavelength.
- These are commonly used in Uv-vis spectroscopy, IR spectroscopy and NMR. It produces a radiation in the required region that contains broad wavelengths.
- Enable us to measure absorbance at several wavelengths (Scanning the wave length)

: Common continuum radiation sources in spectroscopy

Source	Wavelength	Region Useful for
H_2 and D_2 lamp (Deuterium lamp)	continuum source from 160–380 nm	UV molecular absorption
Tungsten lamp	continuum source from 320–2400 nm	Vis molecular absorption
Xe arc lamp	continuum source from 200–1000 nm	molecular fluorescence
Nernst glower	continuum source from 0.4–20 mm	IR molecular absorption
Globar	continuum source from 1–40 mm	IR molecular absorption
Nichrome wire	continuum source from 0.75–20 mm	IR molecular absorption

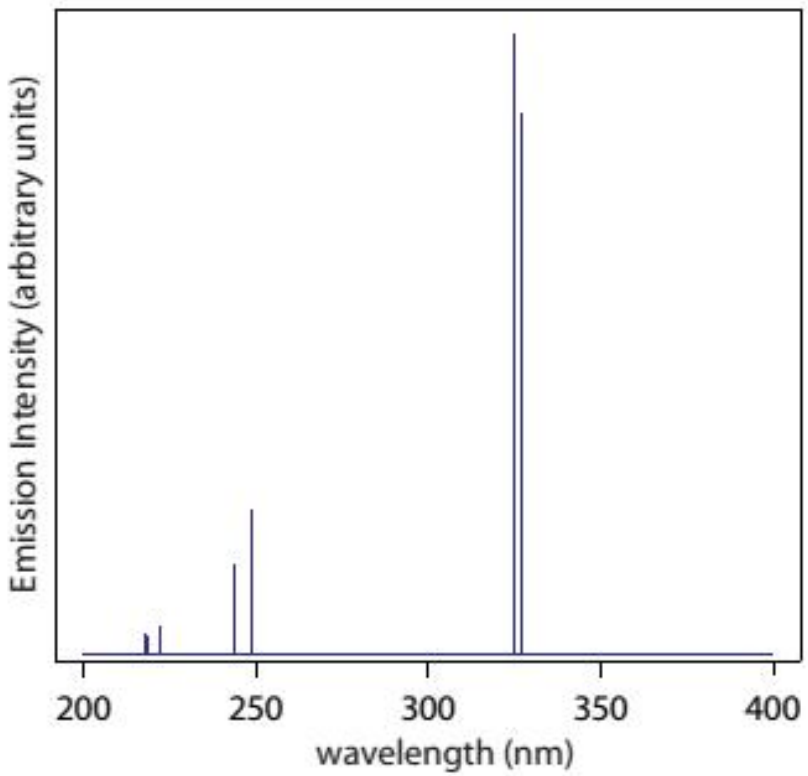
Deutrium lamp

Tungsten lamp

B. Line Sources

- These are source that emits radiation at only selected wavelengths (very narrow bands of wavelengths).
- It has widely used in atomic absorption and atomic and molecular fluorescence spectroscopy.

Source	Wavelength	Region Useful for
hollow cathode lamp	line source in UV/Vis	atomic absorption
Hg vapor lamp	line source in UV/Vis	molecular fluorescence
laser	line source in UV/Vis	atomic and molecular absorption, fluorescence and scattering



Emission spectrum from a Cu hollow cathode lamp. This spectrum consists of seven distinct emission lines (the first two differ by only 0.4 nm and are not resolved in this spectrum). Each emission line has a width of approximately 0.01 nm at ½ of its maximum intensity.

Wavelength Selectors

- In order to plot the absorption spectrum of a compound or complex ion, we must be able to carefully control the wavelengths from the broad spectrum of wavelengths emitted by the source so that we can measure the absorbance at each wavelength.
- Additionally, in order to perform quantitative analysis by Beer's law, we need to be able to carefully select the wavelength of maximum absorption, also from this broad spectrum of wavelengths, in order to plot the proper absorbance at each concentration.
- These facts dictate that we must be able to filter out the unwanted wavelengths and allow only the wavelength of interest to pass.

- Wave length selectors are devices that control a radiation that passes through the container that contains the sample.
- Or they are devices which selects a radiation that will be detected
- Most quantitative analysis based on absorption is based on measurement of absorbance at a single wave length.
- In emission technique, quantitation takes place by measuring the intensity of a single wave length that is emitted by the analyte.
- So, wave length selector is basic device in both absorption and emission techniques.

- In reality, there is no such thing as a single wavelength.
- In the visible region, the spectrum of colors is continuous, meaning that there is no sharp delineation between green light and blue light
- The electromagnetic spectrum is a continuous wavelength band.
- Thus wavelength selection in a spectro-chemical instrument actually consists of the selection of a narrow wavelength band from the larger band.
- The width of the band that is allowed to pass is called the bandwidth.
- The narrowness of the band that is allowed to pass varies from one design to another and is called the resolution.
- Thus a high resolution (narrow bandwidth) is ideal, although many applications do not require the best available resolution and money is often saved by purchasing instruments with a low resolution (wide bandwidth).

There are two general types of wavelength selectors

I. Filters
II. Monochromators

I. Filters

- In this group of wavelength selector we have two types of filters
  a. Absorption filters
  b. Interference filters

Absorption filters

- The most common type consists of colored glass or of a dye suspended in gelatin and sandwiched between glass plates.
- It is based on a principle that colored glass absorb certain wave length and transmitted other wave lengths
- What we want is the transmitted ones

- Absorption filters can be as simple as a piece of colored glass.
- Blue glass transmits blue wavelengths of the visible spectrum but absorb red and yellow wavelengths. So blue glass can be used to isolate blue region of a visible radiation.
- These filters are
  - ☞stable,
  - ☞simple, and
  - ☞cheap,

  so they are excellent for use in portable spectrometers designed to be carried into the field.

- The biggest limitation is that the range of wavelengths transmitted is broad compared with prisms and gratings.
- The transmission range may be 50–300 nm for typical absorption filters.
- Absorption filters are limited to the visible region of the spectrum and the X-ray region.
- they are also difficult to be used in applications where we use variable wave lengths
- If you want to change the wave length you have to take away the filter and replace by anothers

II. Monochromators

- One limitation of an absorption or interference filter is that they do not allow for a continuous selection of wavelength.
- If measurements need to be made at two wavelengths, then the filter must be changed in between measurements.
- For many spectroscopic methods, it is necessary or desirable to be able to continuously vary the wavelength of radiation over a broad range which is called scanning a spectrum.
- A further limitation is that filters are available for only selected nominal ranges of wavelengths.
- Monochromators offer an alternative approach to wavelength selection, which provides for a continuous variation of wavelength

- The word “monochromator” is derived from the Latin language,

  “mono” meaning one

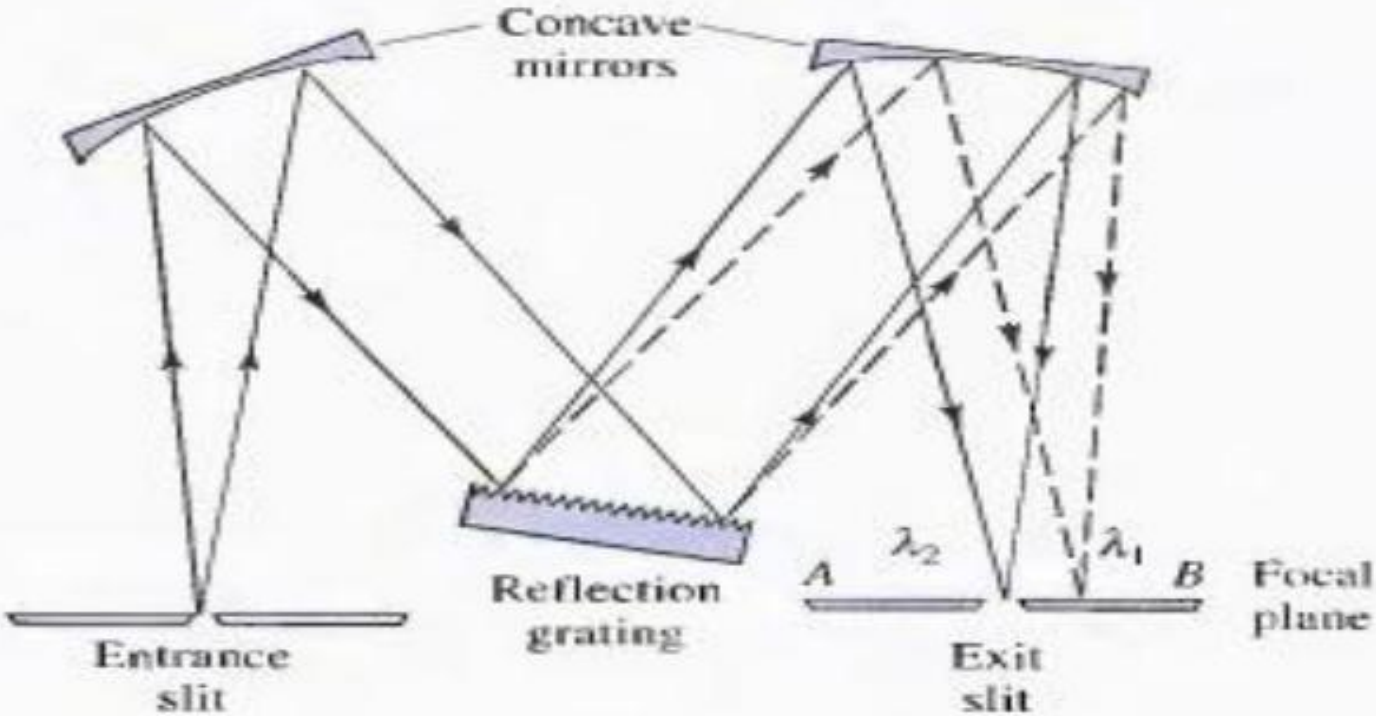
  and

  “chromo” meaning color

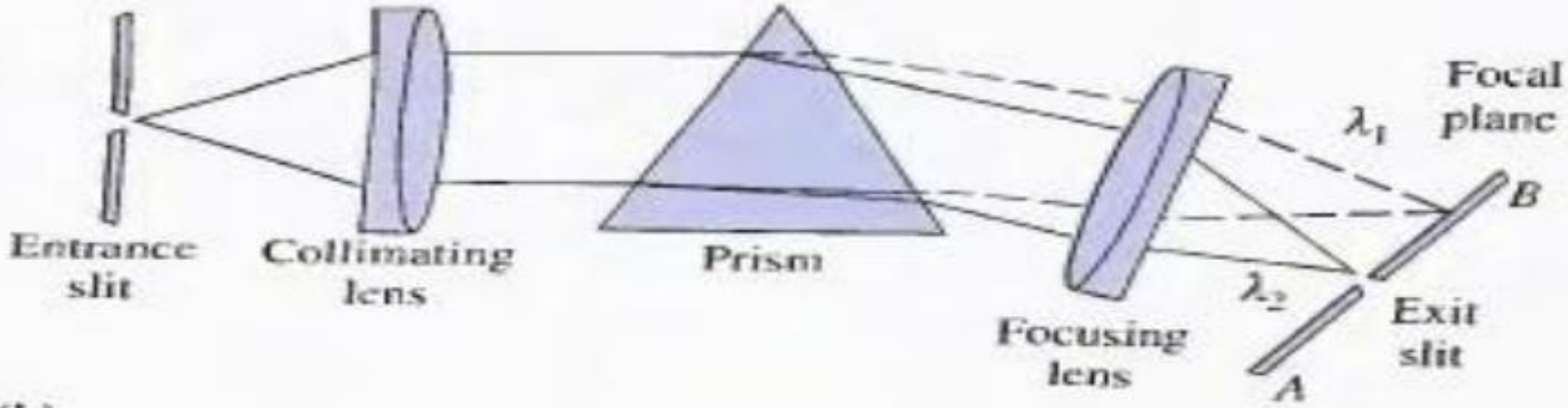
- It is a device more sophisticated than an absorption filter that isolates the narrow band of wavelengths.

- A monochromator is made up of the following parts:
  - an entrance slit,
  - a dispersing element, and
  - an exit slit.
  - In addition to these, there is often a network of mirrors situated for the purpose of aligning or collimating a beam of light before and after it contacts the dispersing element.

  - Collimating means making rays of light or particles accurately parallel


Concave mirrors
Reflection grating
Entrance slit
Exit slit
A
B
λ_2
λ_1
Focal plane

(a)


Entrance slit
Collimating lens
Prism
Focusing lens
Focal plane
λ_1
λ_2
B
A
Exit slit

(b)

A slit

- It is a small circular or rectangular hole cut in an otherwise opaque plate, such as a black metal plate, where the light enters into and leave the monochromator.
- The size of the opening is often variable - a variable slit width.
- The entrance slit is where light enters the monochromator from the source.
- Its purpose is to create a unidirectional beam of light of appropriate intensity from the multidirectional light emanating from the source.
- Its slit width is usually variable so that the intensity of the beam can be adjusted - the wider the opening the more intense the beam.

dispersing element.

- After passing through the entrance slit, the beam encounters a dispersing element.
- The dispersing element is a device which disperses the light into its component wavelengths.
- For visible light, a beam of white light is dispersed into a spray of rainbow colors, the violet–blue wavelengths on one end to the red wavelengths on the other, like a rainbow.
- The narrow band of the spectrum is then selected by the exit slit.
- As the dispersing element is rotated, the spray of colors moves across the exit slit such that a different narrow wavelength range emerges from the exit slit at each position of rotation.

- The function of the exit slit is to permit only a very narrow band of light to pass through to the sample and detector.
- One way to accomplish this is to rotate the dispersion element to allow dispersed light of different wavelengths to fall on the exit slit in sequence.
- The exit slit width can be variable too, but making it wider would result in a wider wavelength band (a wider bandwidth) passing through, which can be undesirable.
- The light emerging from this exit slit is therefore monochromatic and is passed on to the sample compartment to pass through the sample.

- We have two types of dispersing element:
  1. Prisms
  2. Gratings

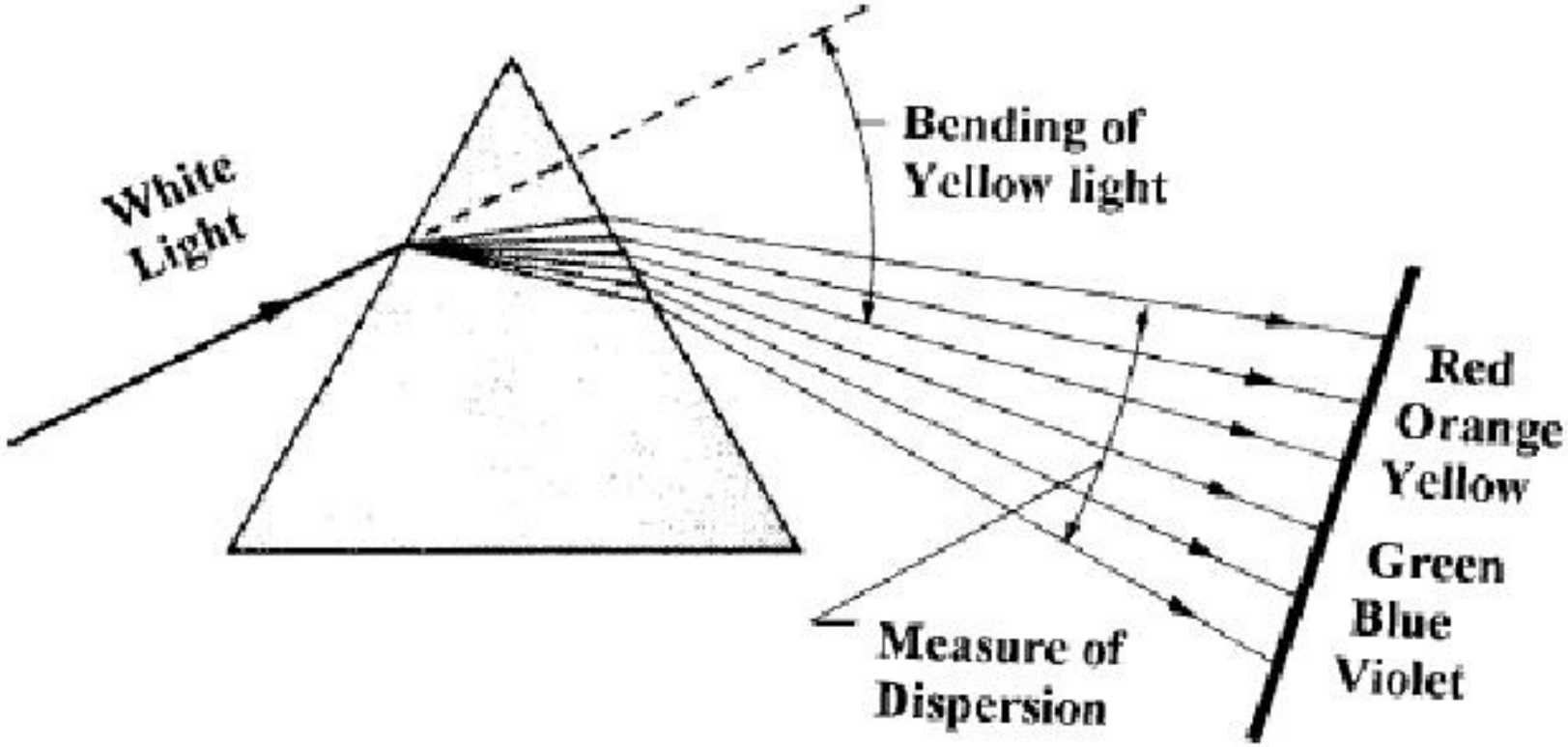
Prisms

- This dispersing element is common for you.
- When a white light passes through a prism it will disperse into its components, the seven rainbow colors, violet, indigo, blue, green, yellow, orange and red.
- A prism is a three-dimensional triangularly shaped glass or quartz block.
- When the light beam strikes one of the three faces of the prism, the light emerging through another face is dispersed.

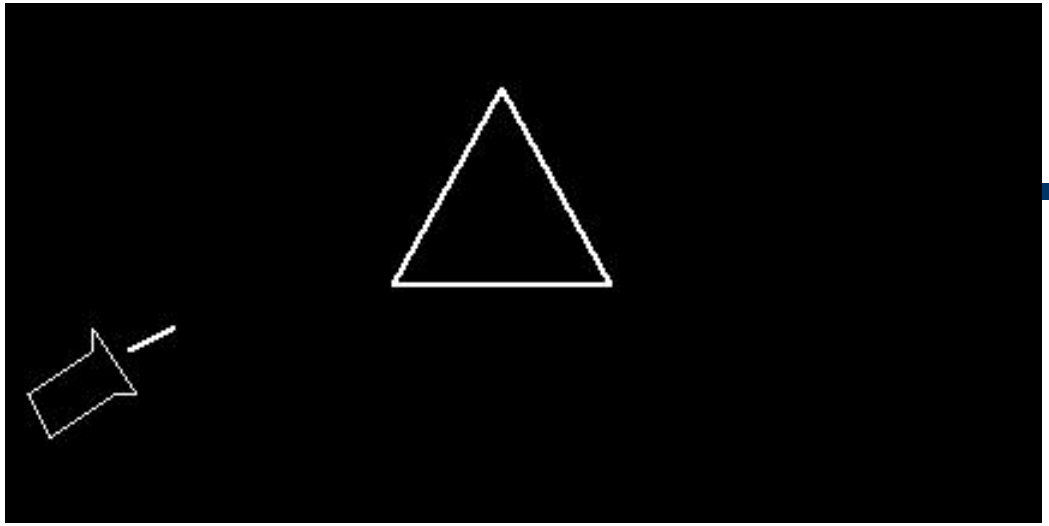
- When electromagnetic radiation passes through a prism, it is refracted because of the difference in the refractive index of the material in which the prism is made up of and the air.

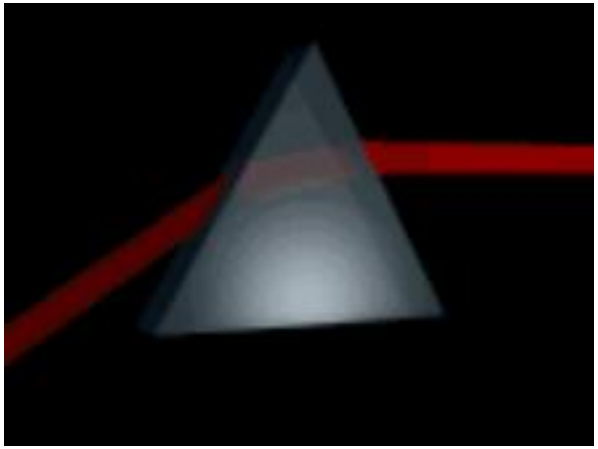
- The refractive index depends on the wavelength and, therefore, so does the degree of refraction.
- Shorter wavelengths are refracted more than longer wavelengths.
- The effect of refraction is to spread the wavelengths apart into different wavelengths.
- By rotation of the prism, different wavelengths of the spectrum can be made to pass through an exit slit and the sample.
- Prisms are used to disperse IR, visible, and UV radiation. However, because of its non linear dispersion, it works more effectively for the shorter wavelengths.

- Prisms and lenses that are made up of glasses can be used to disperse visible radiation.
- Prisms made up of quartz or fused silica be used in the ultraviolet region.
- Since glasses and fused silica transmit low in the infrared radiation, they have low application in IR regions.
- To disperse IR we use prisms made up of crystals of alkali halides since they are transparent in the IR region.
- Sodium chloride (rock salt) is used in most instruments and is useful for the entire region from 2.5 to 15.4 μm (4000 to 650 cm^{-1}). For longer wavelengths, KBr (20 to 25 μm) or CsI (10 to 38 μm) can be used . Due to solubility effect they must be kept dry.



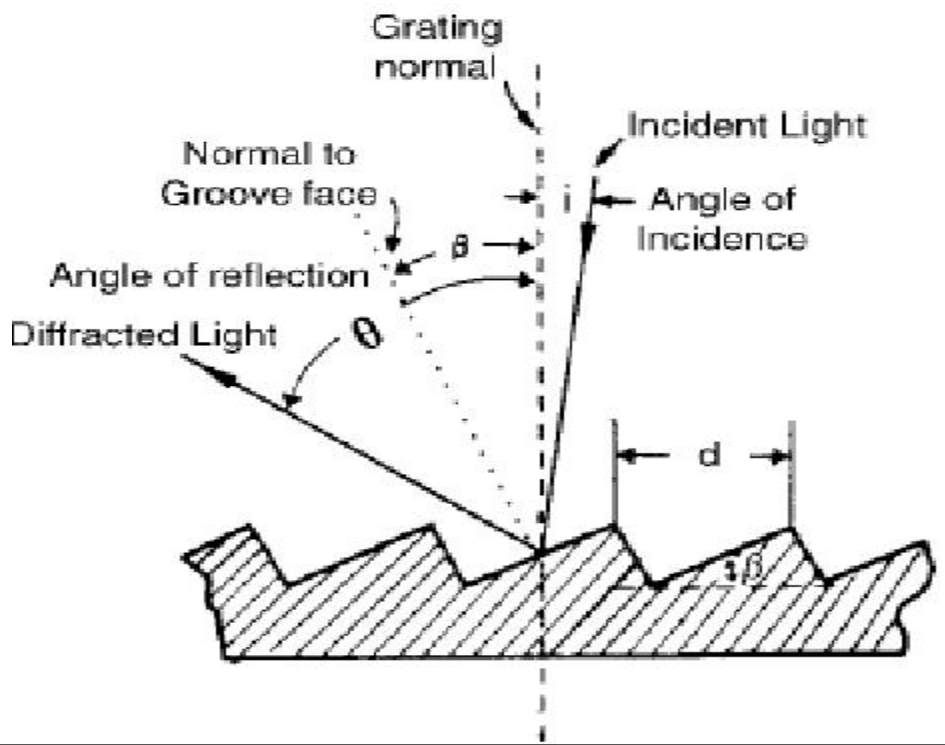
4: Dispersion of visible light by a prism.

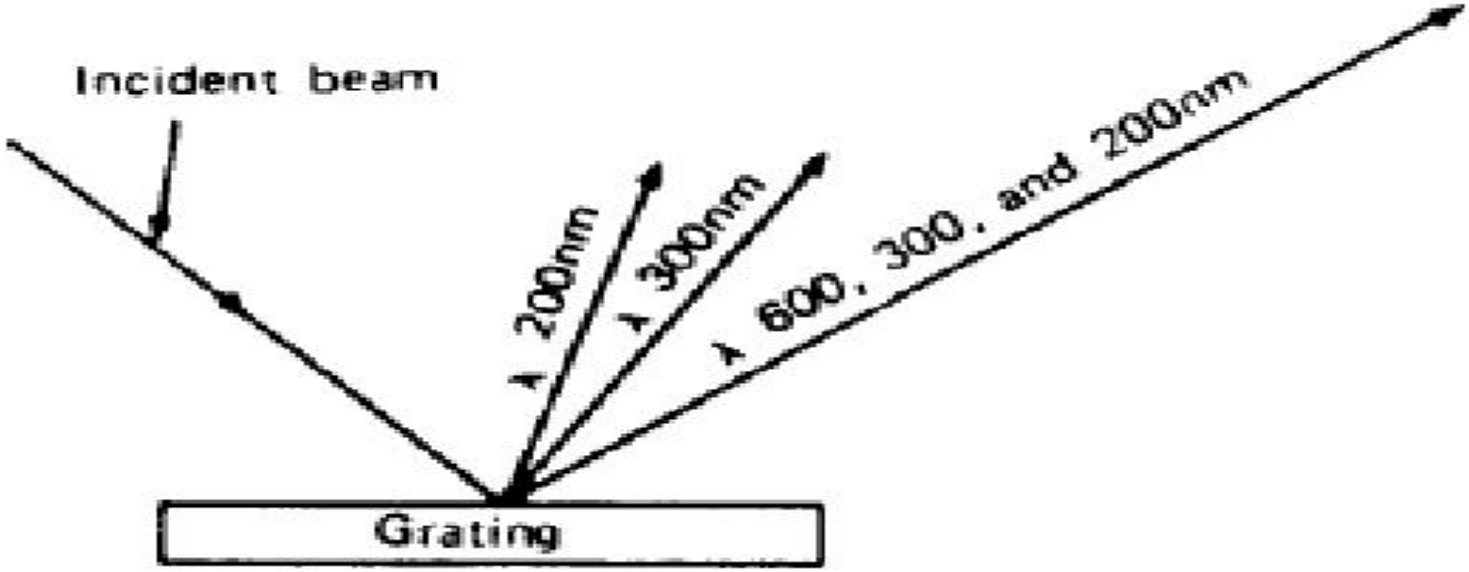




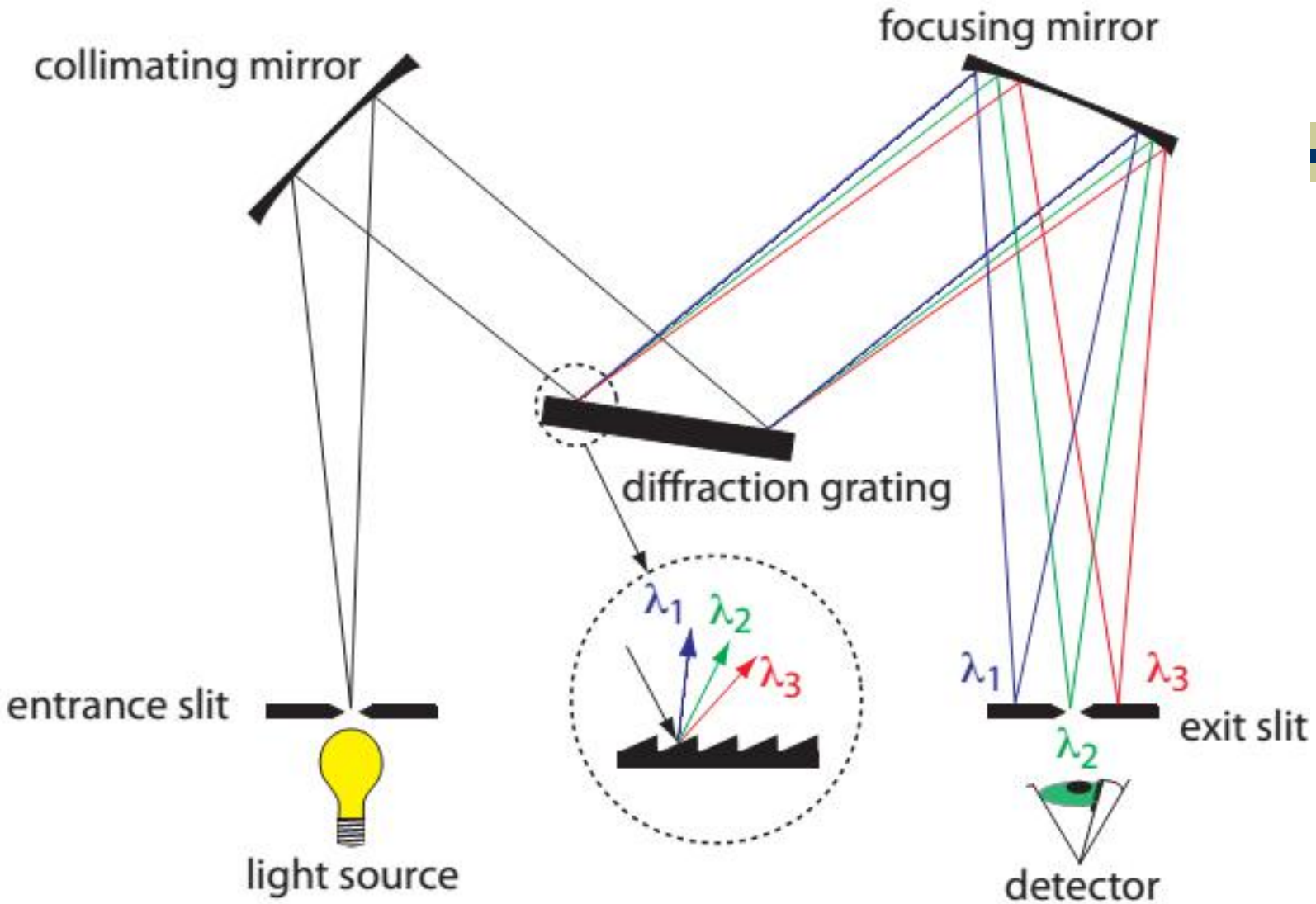
Gratings

- A diffraction grating consists of a series of closely spaced parallel grooves cut (or ruled) into a hard glass, metallic, or ceramic surface
- The surface may be flat or concave, and is usually coated on the ruled surface with a reflective coating.





- UV, visible, and IR radiation can be dispersed by a diffraction grating.
- A grating for use in the UV and visible regions will contain between 500 and 5000 grooves/mm,
- while a grating for the IR region will have between 50 and 200 grooves/mm.


collimating mirror
focusing mirror
diffraction grating
λ_1
λ_2
λ_3
entrance slit
light source
exit slit
detector

3. Sample Holder

- In molecular spectroscopy we usually use sample holder.
- We don`t use them in atomic absorption and emission techniques because they are not necessary
- They are used to hold the sample .
- They are placed after the wavelength selector and the detector.
- In some instruments it is placed between the radiation source and the wavelength selector.
- They usually are called *cells* or cuvettes.

- The materials in which these sample holders are made up of depend on the type of radiation used.
- The major criterion for a material to be used as a sample holder is that it must be transparent in the region of radiation used.
- In the region of UV and visible we usually use sample holders that are made up of glasses and quartz.
- Silica glass is ordinarily used in the region from 375 to 200 nm region because of its low cost compared with quartz.
- Plastic containers can also be used in the visible region.

Exercise

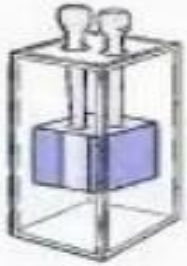
- Comment on usage of sample holders made up of colored glasses in the visible region?

Open-top
normal with lid

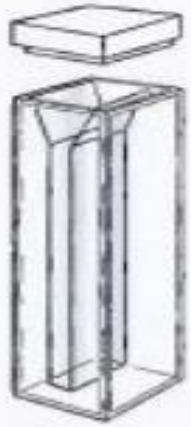
Stoppered
normal

Stoppered
semimicro

Cylindrical

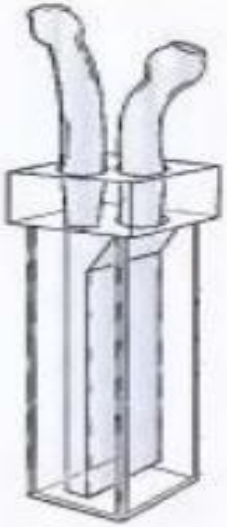


Semimicro
flow

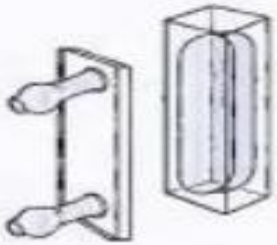


Tall micro

Minimum height
micro



Sampling



Demountable
flow

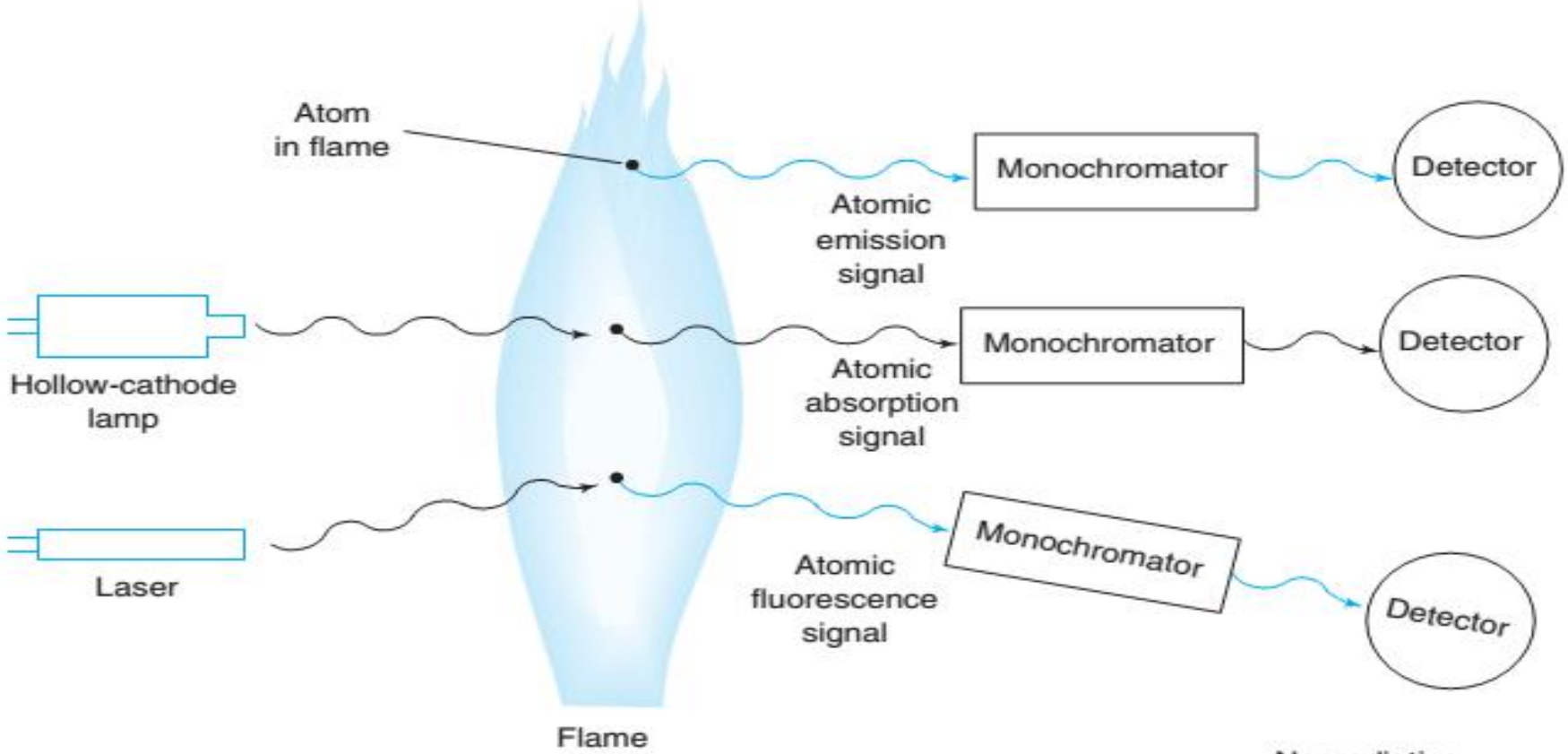
- Glasses and quartz are not fairly transparent in the IR region. So they are not usually used in the IR spectroscopy .
- For IR region sample containers that are made up of crystal of alkali halides are usually used.
- The quality of spectroscopic data is critically dependent on the way that cells are used and maintained.
- Finger prints, grease, or other deposits on the walls rnarkedly alter the transmission characteristics of a cell. Thus, thorough cleaning before and after use is imperative, and care must be taken to avoid touching the windows after cleaning is complete.

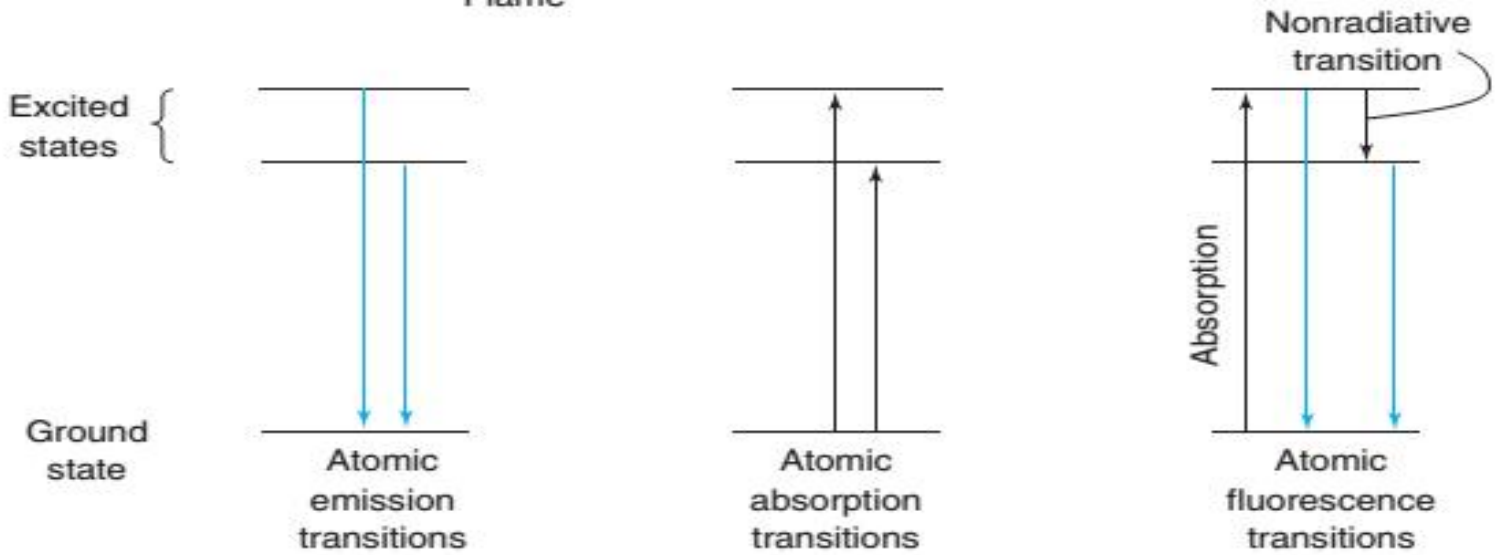
Spe

Chapter Four
Atomic Spectroscopy

- Samples are vaporized and decomposed into atoms.
- Concentrations of atoms in the vapor are measured by emission or absorption characteristic
- wavelengths of radiation.
- Atomic spectroscopy refers to the
  - ☞ absorption, (Atomic absorption spectroscopy AAS)
  - ☞ emission or (Atomic Emission Spectroscopy AES)
  - ☞ fluorescence (Atomic Fluorescence spectroscopy AFS)

  of ultraviolet–visible (UV-VIS) light by atoms and monoatomic ions.


Atom
in flame
Monochromator
Detector
Atomic
emission
signal
Hollow-cathode
lamp
Monochromator
Detector
Atomic
absorption
signal
Laser
Monochromator
Detector
Atomic
fluorescence
signal
Flame


Nonradiative
transition
Excited
states
Absorption
Ground
state
Atomic
emission
transitions
Atomic
absorption
transitions
Atomic
fluorescence
transitions

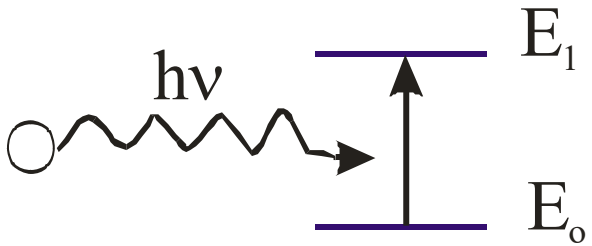
- Based on the breakdown of a sample into atoms, followed by the measurement of the atom's absorption or emission of light.

- In optical spectrometry, the elements present in a sample are converted to gaseous atoms or elementary ions by a process called atomization. The ultraviolet-visible absorption, emission, or fluorescence of the atomic species in the vapor is then measured.
- It deals with absorbance, fluorescence or emission (luminescence) of atoms or elemental ions rather than molecules
- Provides information on elemental composition of sample or compound
  - ✓ UV/Vis, IR, Raman gives molecular functional group information, but no elemental information.

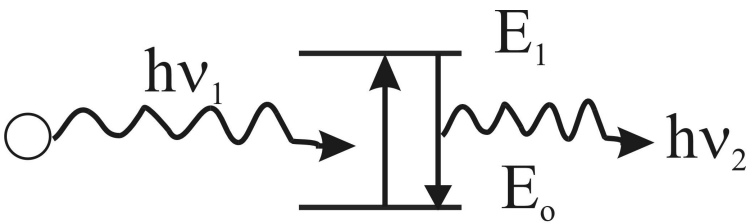
major types of atomic spectroscopy:

- Absorption – light of a wavelength characteristic of the element of interest radiates through the atom vapor. The atoms absorb some of the light. The amount absorbed is measured.
- Emission – sample is heated to excitation/ionization of the sample atoms. Excited and ionized atoms decay to a lower energy state through emission. Intensity of the light emitted is measured.
- Fluorescence – a short wavelength is absorbed by the sample atoms, a longer wavelength (lower energy) radiation characteristic of the element is emitted and measured

- Basic process the same as in UV/Vis, fluorescence etc. for molecules



Absorbance



Fluorescence

- Differences from Molecular Spectroscopy
  - no vibration levels → much sharper absorbance, fluorescence, emission bands
  - position of bands are well-defined and characteristic of a given element
  - qualitative analysis is easy in atomic spectroscopy (not easy in molecular spectroscopy)

- Molecular (UV-VIS and IR) spectroscopy: deals with inorganic or organic molecules in solution

- Atomic spectroscopy: mainly deals with high energy absorption/emission of individual atoms

Atomic Absorption Spectroscopy

- Atomic absorption spectroscopy is based on absorption of an emr (usually in the UV – Vis region) by ground state atoms after the sample is converted into atom.
- A light of a wavelength characteristic of the element of interest radiates through the atom vapor. The atoms absorb some of the light. The amount absorbed is measured.

- AAS is an elemental analysis technique capable of providing quantitative information on > 70 elements in almost any type of sample, practically independent of the chemical form of the element in the sample.
- A determination of cadmium in a water sample is a determination of the total cadmium concentration.
- It does not matter whether the cadmium exists as the chloride, sulfate, or nitrate, or even if it exists as a complex or an organometallic compound,
- Concentrations as low as ppt levels of some elements in solution can be determined and AAS is used routinely to determine ppb and ppm concentrations of most metal elements.

- a given element can be determined in the presence of other elements, which do not interfere by absorption of the analyte wavelength. Therefore it is not necessary to separate the analyte from the rest of the sample (the matrix).
- This results in rapid analysis times and eliminates some sources of error.
- This is not to say that AAS measurements are completely free from interferences; both chemical and spectral interferences do occur and must be compensated for.

- The major disadvantages of AAS are that no information is obtained on the chemical form of the analyte (no speciation) and
- only one element can be determined at a time.

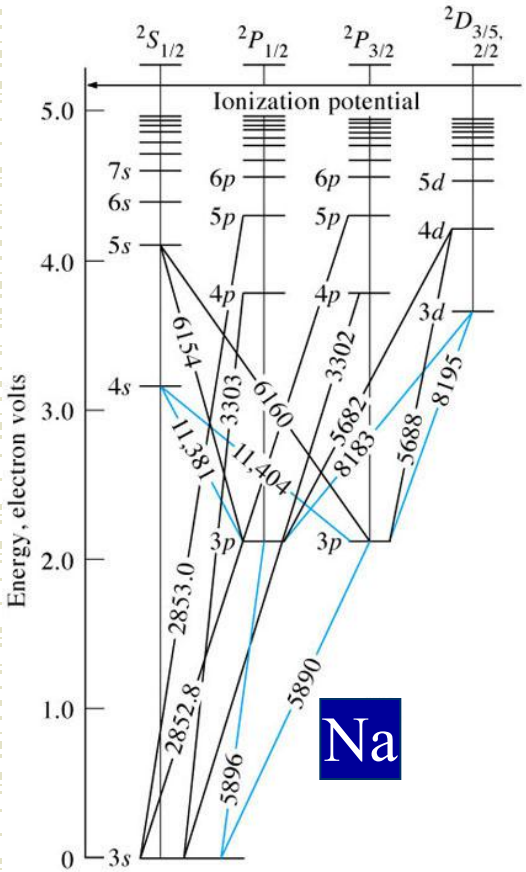
How Atoms Absorb EMR?

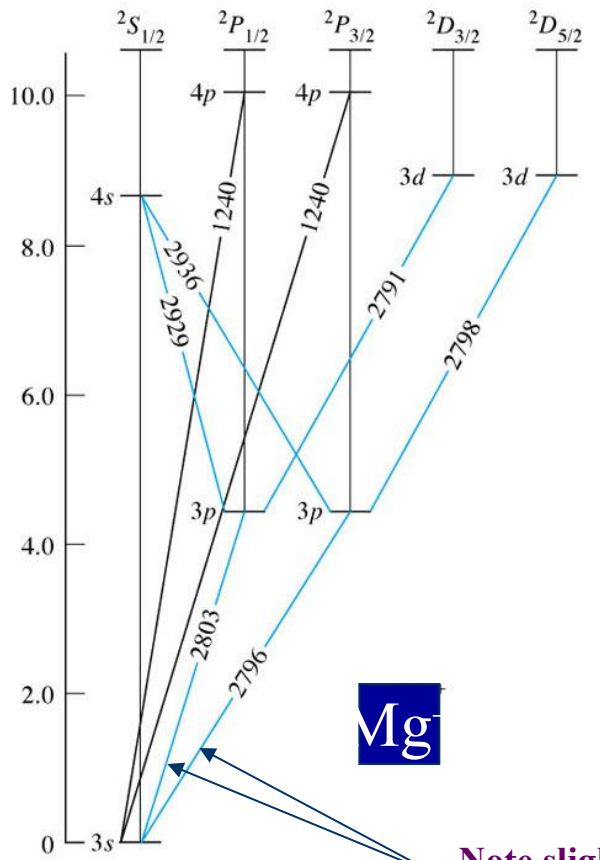
- An atom consists of a nucleus surrounded by electrons.
- Every element has a unique number of electrons, equal to its atomic number for a neutral atom of that element.
- The electrons are located in atomic orbitals of various types and energies and the electronic energy states of atoms are quantized.
- The lowest energy, most stable electron configuration of an element is its ground state.
- When an external source of radiation impinges on the analyte vapor and if the external source radiation is of the appropriate frequency (wavelength), it can be absorbed by the analyte atoms and promote them to excited states.

Energy Level Diagrams

energy level diagram for the outer electrons of an element describes atomic spectroscopy process.

i. every element has a unique set of atomic orbitals
ii. p, d, f split by spin-orbit coupling
iii. Spin (s) and orbital (l) motion create magnetic fields that perturb each other (couple)
- parallel → higher energy; antiparallel → lower energy





- **Similar pattern between atoms but different spacing**
- **Spectrum of ion different to atom**
- **Separations measured in electronvolts (eV)**

  $1eV = 1.602 \times 10^{-19}$ J

  $= 96.484$ kJ $\times$ mol^{-1}
- **As number of electrons increases, number of levels increases**

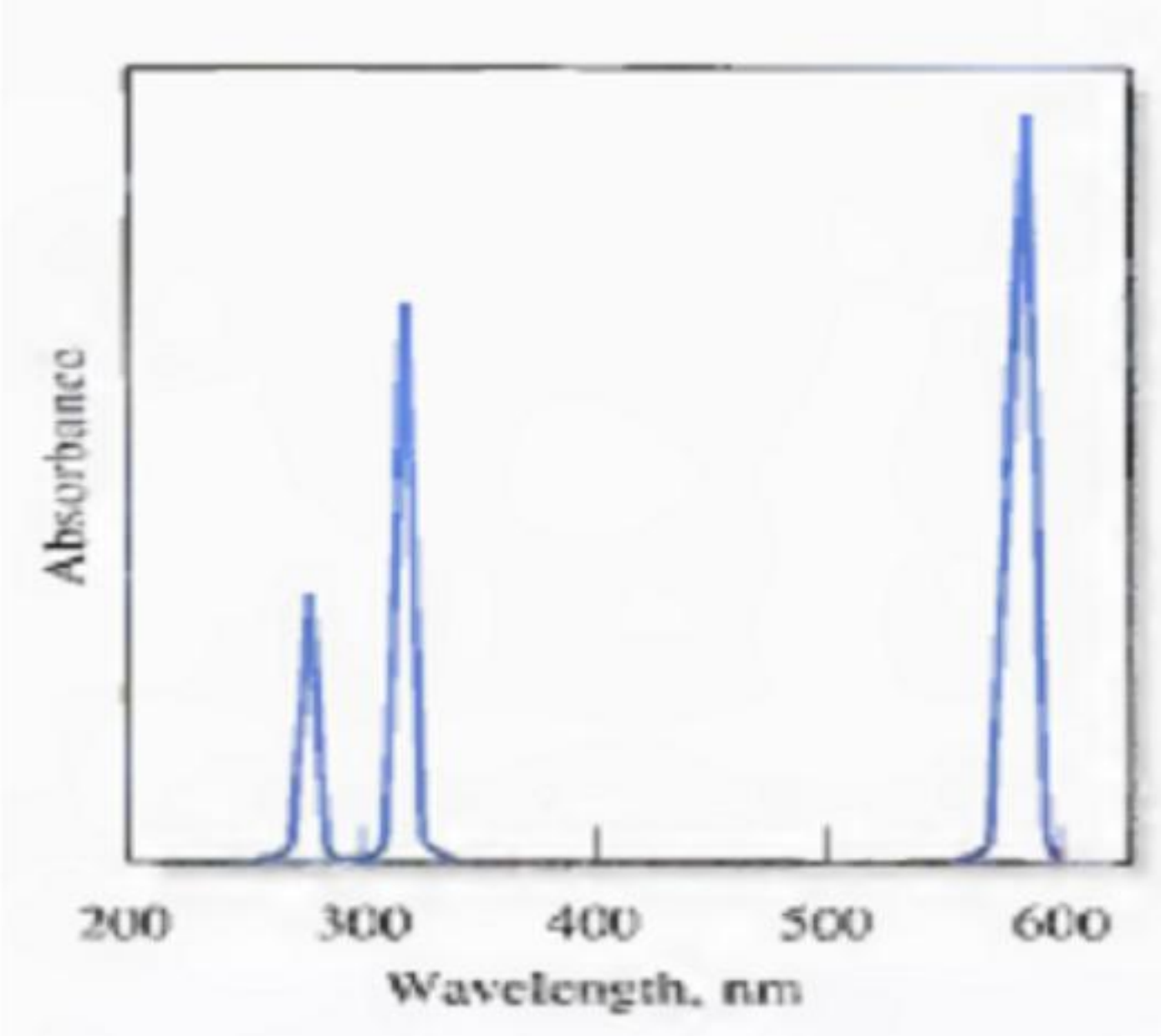
  emission spectra more complex

  Li 30 lines
  Cs 645 lines
  Cr 2277 lines

Note slight differences in energy due to magnetic fields caused by spin

- It is this outer shell electron that is involved in atomic absorption transitions.
- UV and visible wavelengths are the range of radiant energies absorbed in AAS.
- UV/VIS radiation does not have sufficient energy to excite the inner shell electrons, only the electrons in the outermost (valence) shell are excited.
- This is true of all elements: only the outermost electrons (valence electrons) are excited in AAS.
- For elements that have several outer electrons that can be excited absorption and emission spectra m ay be much more complex.

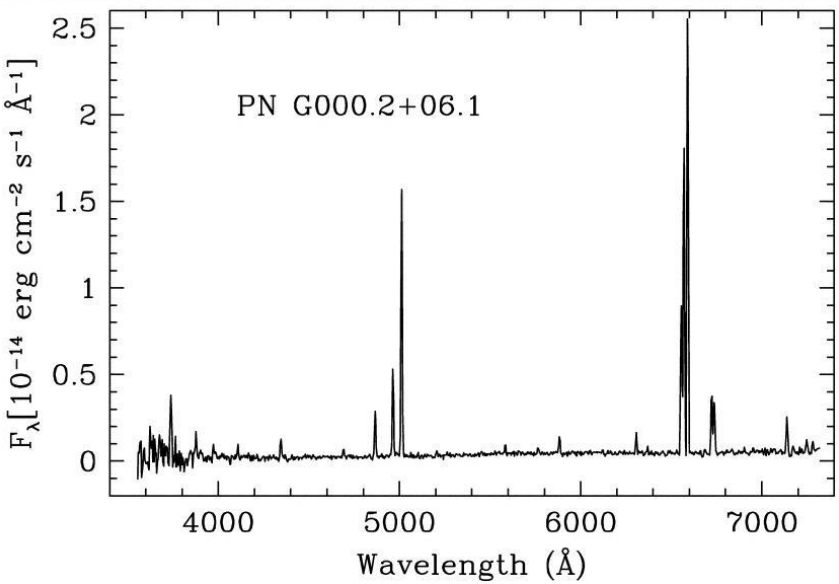
- Gas phase atoms do not vibrate in the same sense that molecules do. Also, they have virtually no rotational energy.
- Hence no vibrational or rotational energy is involved in the electronic excitation of atoms.
- As a result, atomic absorption spectra consist of a few very narrow absorption lines, in contrast to the wide bands of energy absorbed by molecules in solution.


Absorbance
200
300
400
500
600
Wavelength, nm

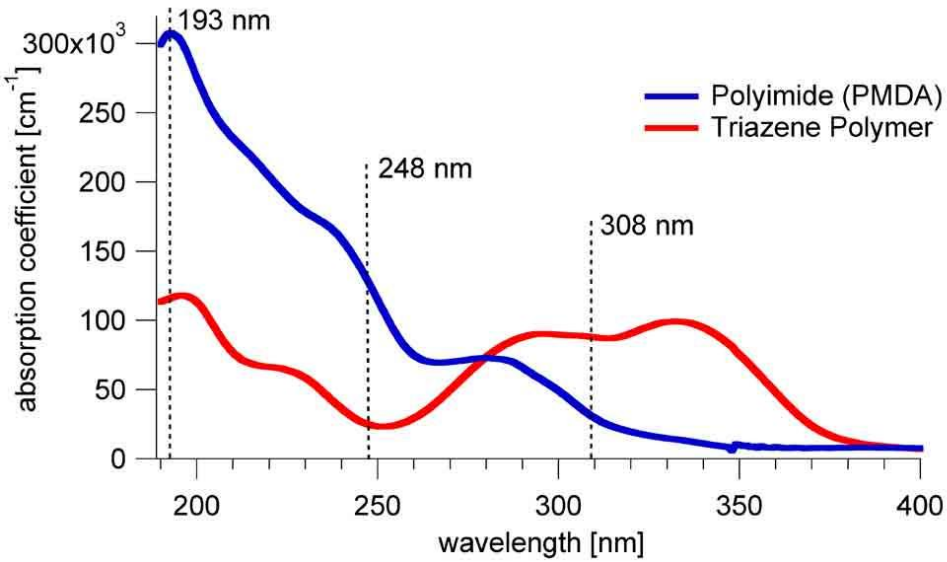
Atomic spectra vs molecular spectra:

- Lines

Bands



Typical atomic spectrum
e.g. acquired by AAS

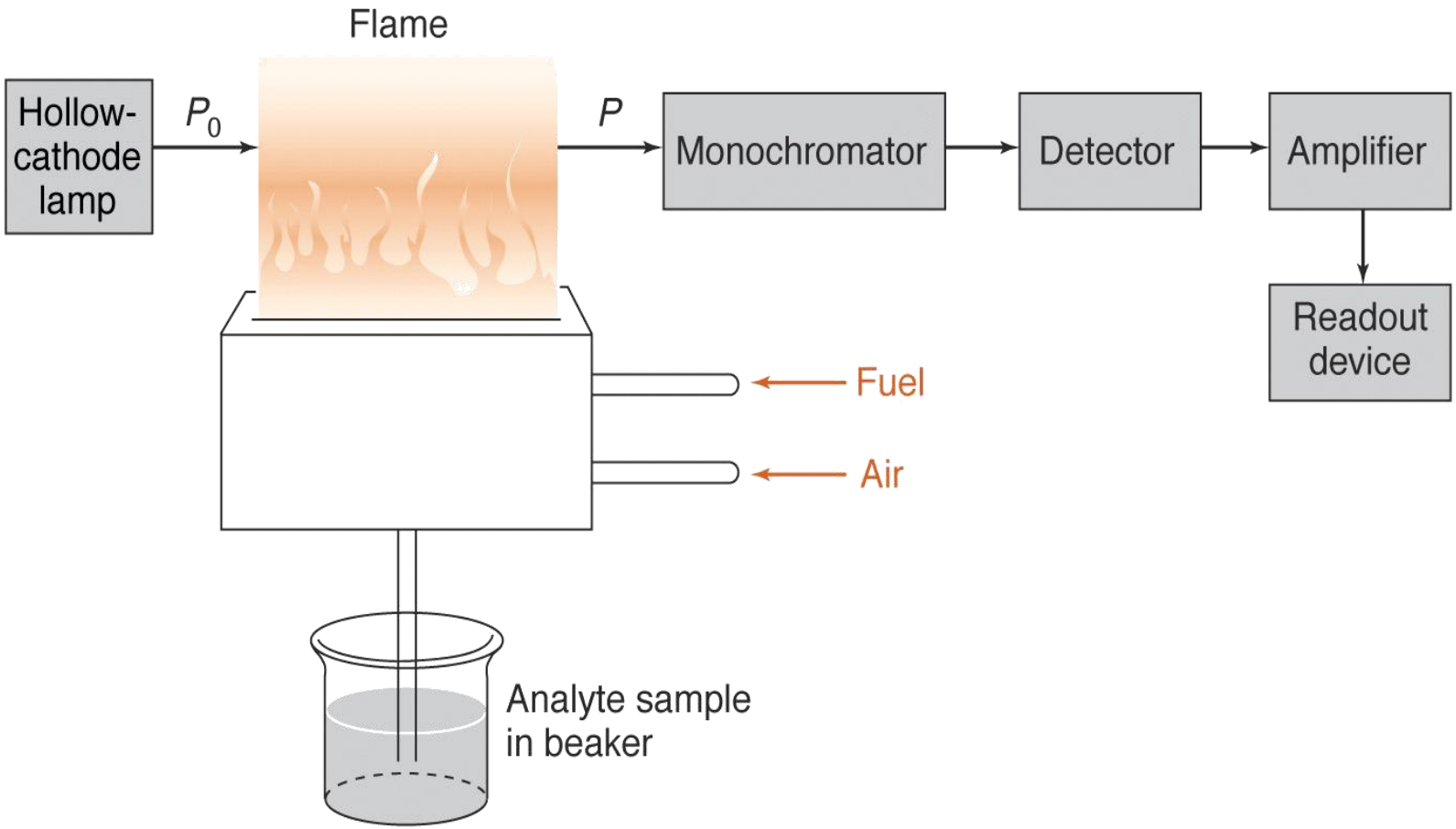


Two typical molecular spectra
Acquired by UV-Vis spectroscopy

Y axes: intensity of absorbed light. Under ideal conditions proportional to analyte concentration ($I \equiv c$; Beer's law).

- According to the Bohr model of the atom, atomic absorption and emission line widths should be infinitely narrow, because there is only one discrete value for the energy of a given transition.
- However, there are several factors that contribute to line broadening.
    1. Natural broadening
    2. Pressure broadening
    3. Doppler broadening
    4. Electric or magnetic field effect

Instrumentation



Atomization

- In atomic spectroscopy the constituents of a sample must be converted to gaseous atoms or ions, which can then be determined by emission, absorption, fluorescence, or mass spectral measurements.
- The precision and accuracy of atomic methods depend critically on the atomization step and the method of introduction of the sample into the atomization region.
- Atomization is the process of converting an analyte in solid, liquid, or solution form to a free gaseous atom
- The device is called atomizer.

Atomization is separation of particles into individual molecules and breaking molecules into atoms .This is done by exposing the analyte to high temperatures in a flame or graphite furnace .

- 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 atomizer is the sample cell of the AAS system.
- The atomizer must produce the ground state free gas phase atoms necessary for the AAS process to occur.
- The analyte atoms are generally present in the sample as salts, molecular compounds, or complexes.
- The atomizer must convert these species to the reduced, free gas phase atomic state.

Sample Atomization – expose sample to flame or high-temperature

i. Need to break sample into atoms to observe atomic spectra

ii. Basic steps:

a) nebulization – solution sample, get into fine droplets by spraying through thin nozzle or passing over vibrating crystal.

b) desolvation - heat droplets to evaporate off solvent just leaving analyte and other matrix compounds

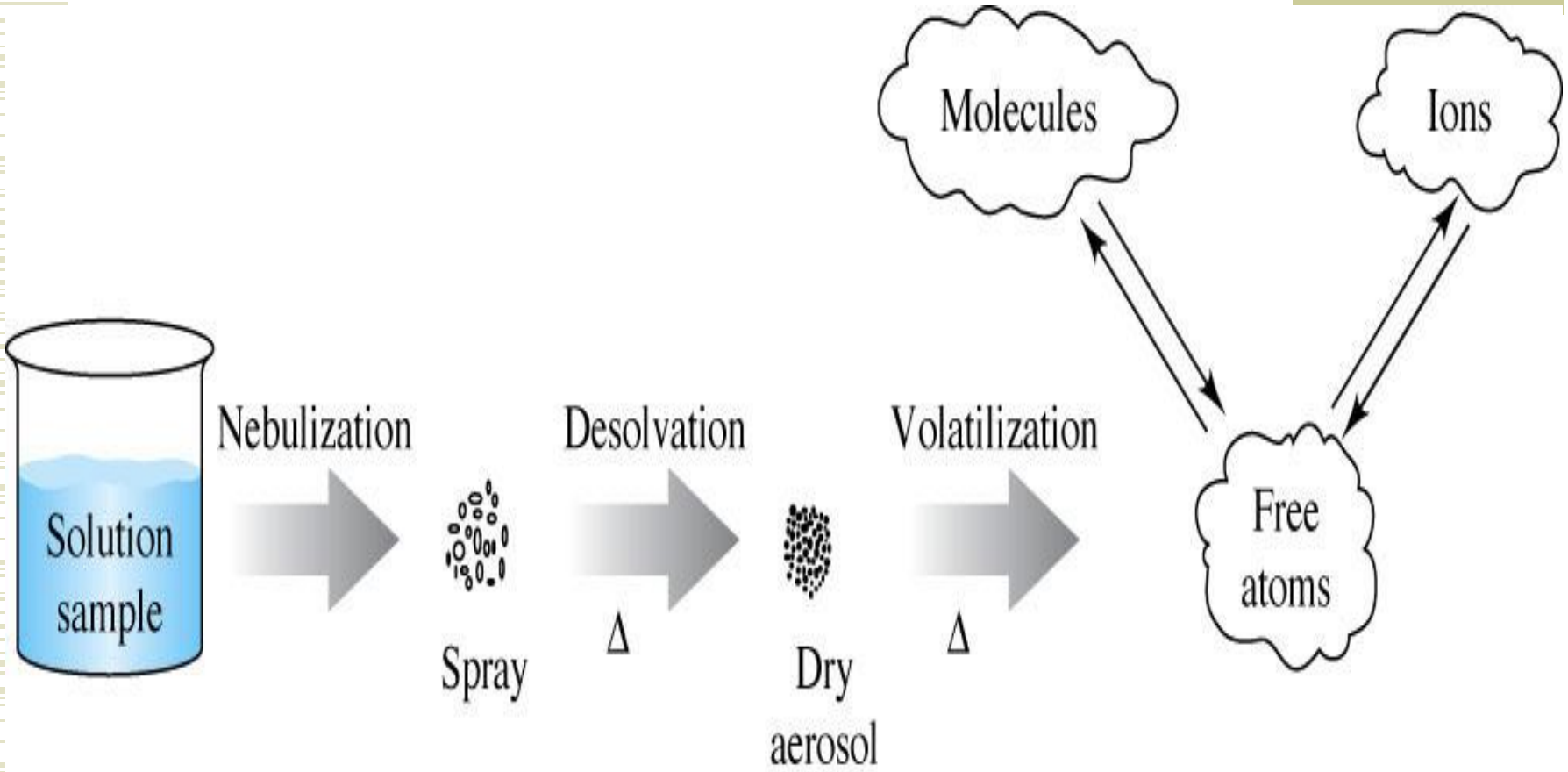
c) volatilization – convert solid analyte/matrix particles into gas phase

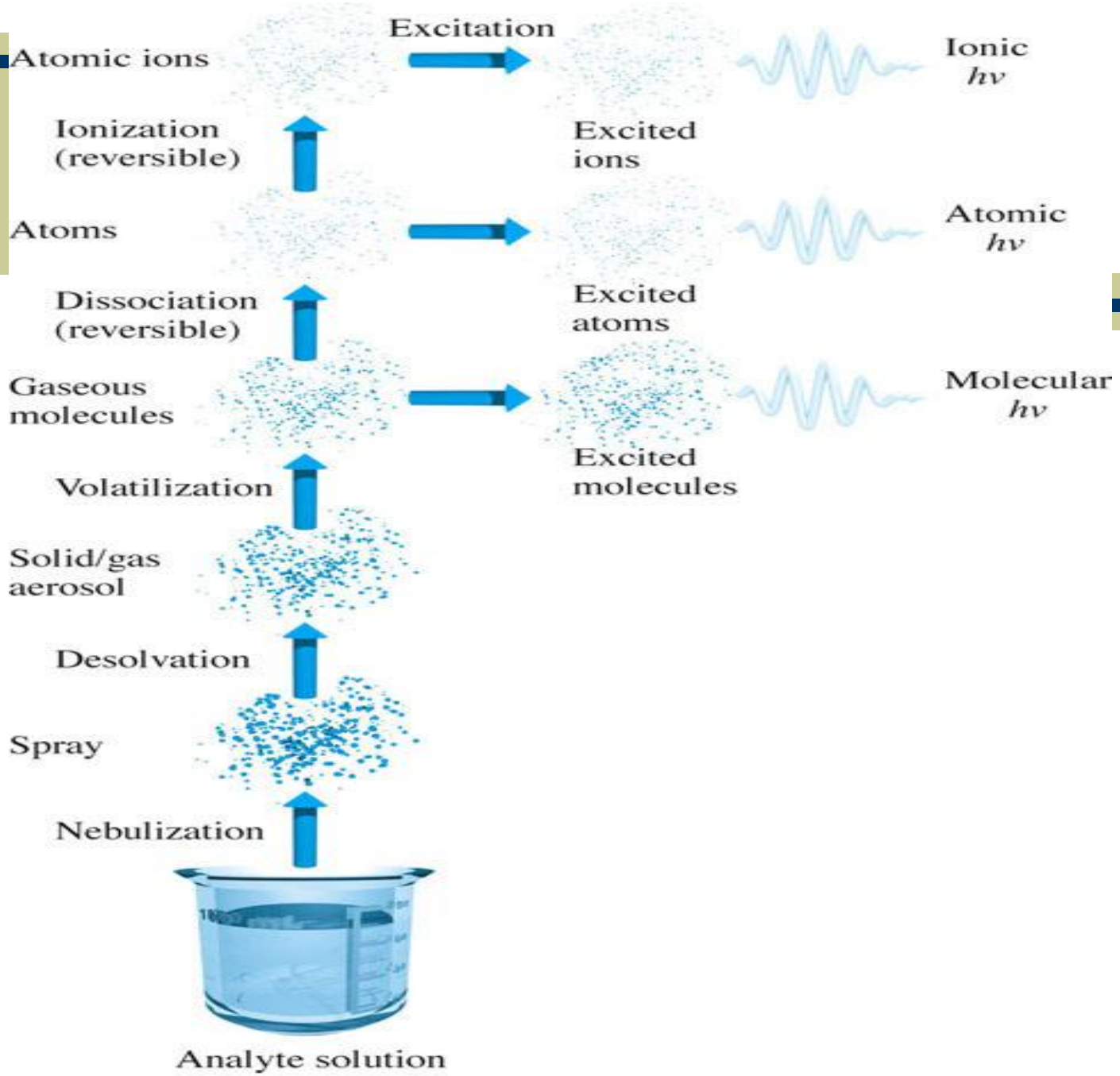
d) dissociation – break-up molecules in gas phase into atoms.

e) ionization – cause the atoms to become charged

f) excitation – with light, heat, etc. for spectra measurement.

Cont'd


Molecules
Ions
Solution sample
Nebulization
Spray
Desolvation
Δ
Dry aerosol
Volatilization
Δ
Free atoms



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Types of Atomizers Used for Atomic Spectroscopy

Type of Atomizer	Typical Atomization Temperature, °C
Flame	1700–3150
Electrothermal vaporization (ETV)	1200–3000
Inductively coupled argon plasma (ICP)	4000–6000
Direct current argon plasma (DCP)	4000–6000
Microwave-induced argon plasma (MIP)	2000–3000
Glow-discharge plasma (GD)	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)

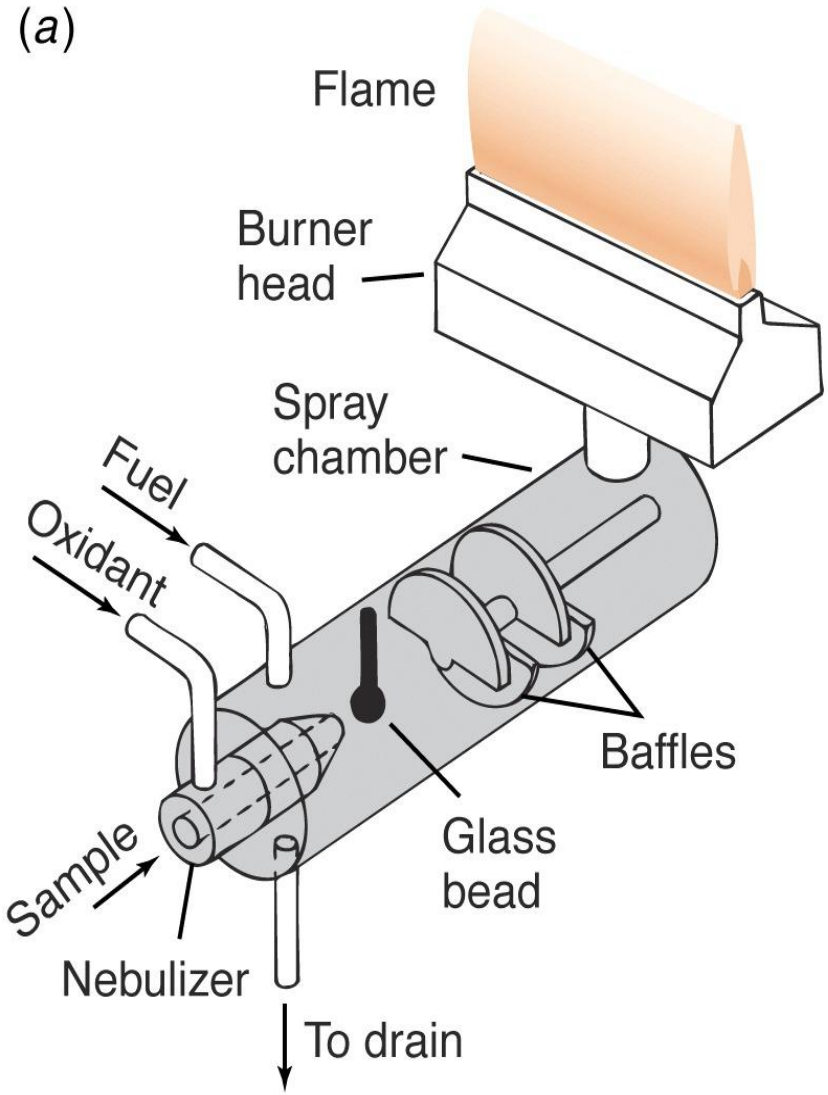
Flame Atomizer

- The general AA method that uses flame atomizer is called flame atomic absorption spectroscopy. (FAAS)
- a solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame as fine mist where atomization occurs.
- To create a flame, we need to mix an oxidant gas and a fuel gas, and light the mixture.
- In modern commercial flame AAS, two types of flames are used. The first is the air – acetylene flame, where air is the oxidant and acetylene is the fuel.
- The second type of flame is the nitrous oxide–acetylene flame, where nitrous oxide is the oxidant and acetylene is again the fuel.

- Selection of flame type depends on the volatilization temperature of the atom of interest.

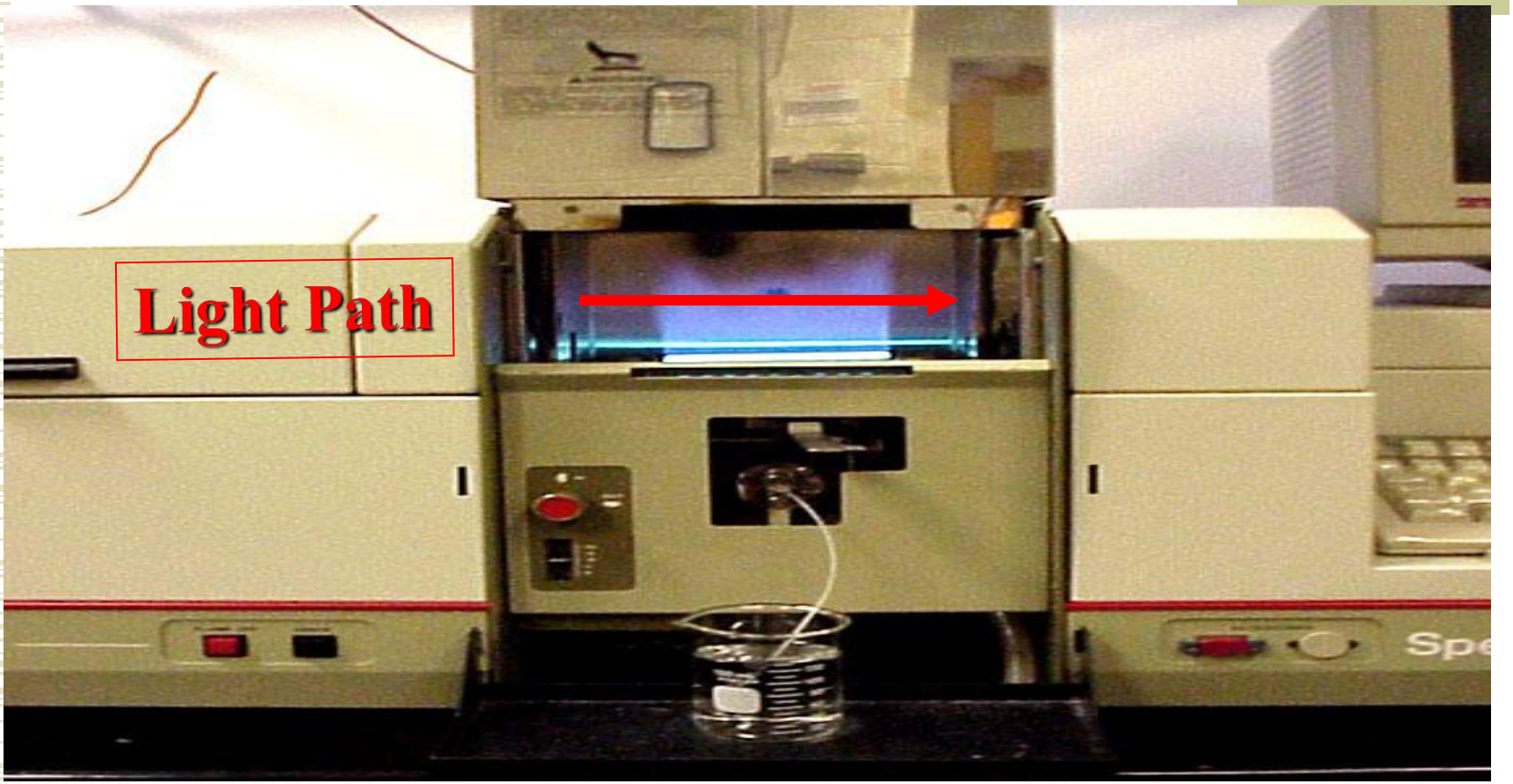
- Different mixes and flow rates give different temperature profile in flame
- gives different degrees of excitation of compounds in path of light source

Fuel	Oxidant	Temperature Range (°C)
natural gas	air	1700–1900
hydrogen	air	2000–2100
acetylene	air	2100–2400
acetylene	nitrous oxide	2600–2800
acetylene	oxygen	3050–3150

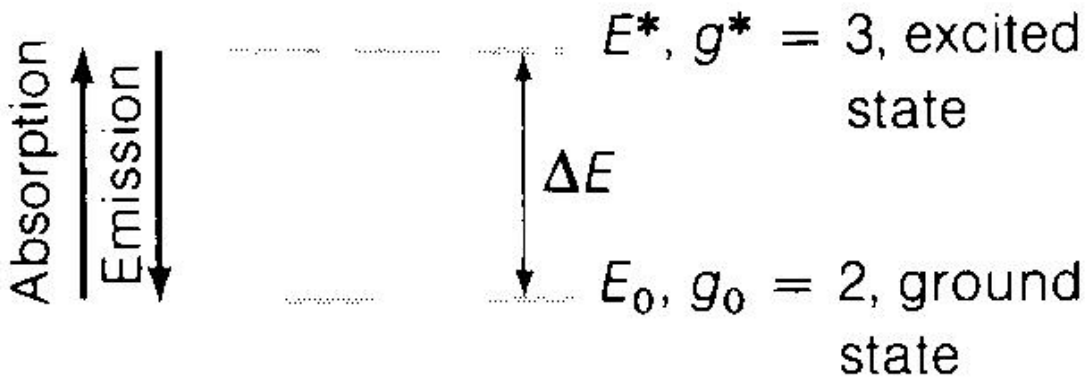

(a)
Flame
Burner head
Spray chamber
Fuel
Oxidant
Baffles
Glass bead
Sample
Nebulizer
To drain

Flame Atomic absorption spectrometer

- In this method, light from a source is directed through the sample to a detector.



Effect of flame temperature on excited state population



atoms in Excited state

Boltzmann constant

$$\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E/kT}$$

Temperature

atoms in Ground state

Energy difference

Statistical factor

- Where
  - N^* and N are the number of atoms in an excited state and the ground state,
  - k = Boltzmann constant (1.38×10^{-23} J/K),
  - T = Temperature (K),
  - $\Delta E = E^* - E$ is the energy difference between excited and ground states,
  - g^* and g are the statistical weights of the excited and ground states respectively (determined by the no. states having equal energy at each quantum level n)

Advantages

- ✓ equipment relatively cheap
- ✓ easy to use (training easy compared to furnace)
- ✓ good precision
- ✓ high sample throughput
- ✓ relatively facile method development
- ✓ cheap to run

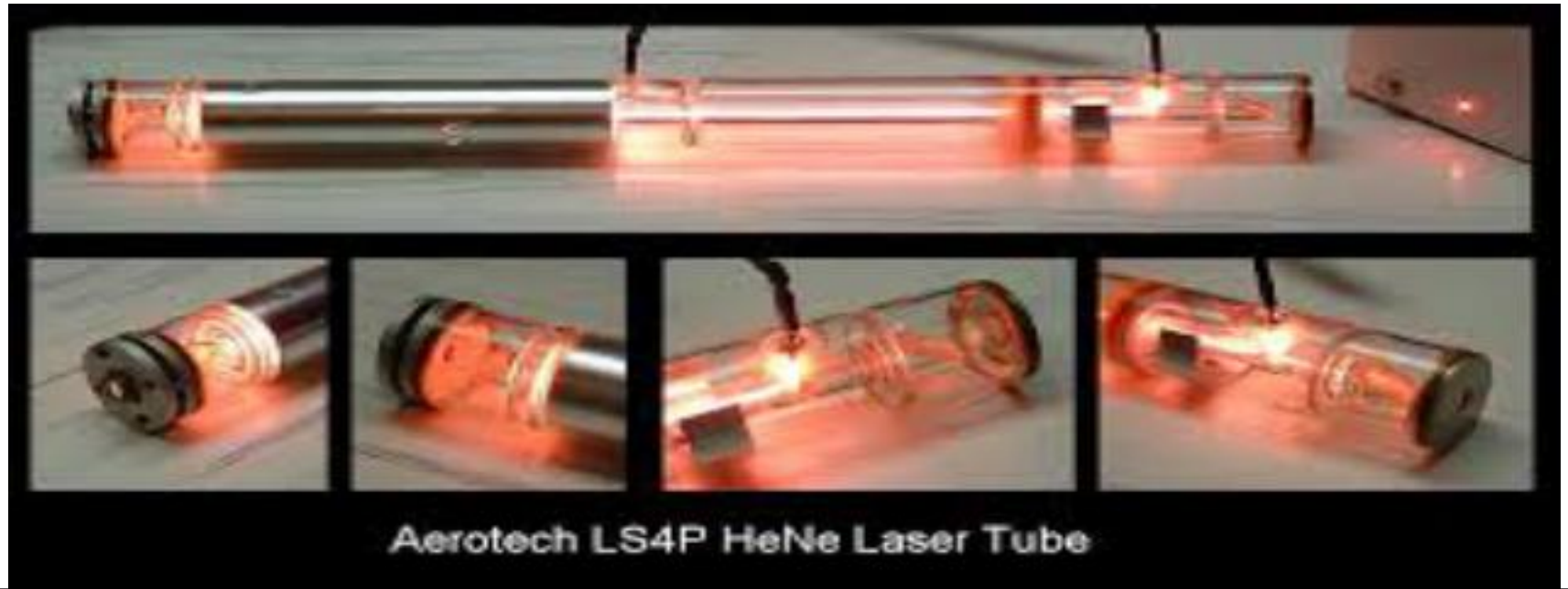
Disadvantages

- ➢ lack of sensitivity (compared to furnace)
- ➢ problems with refractory elements
- ➢ require large sample size
- ➢ sample must be in solution

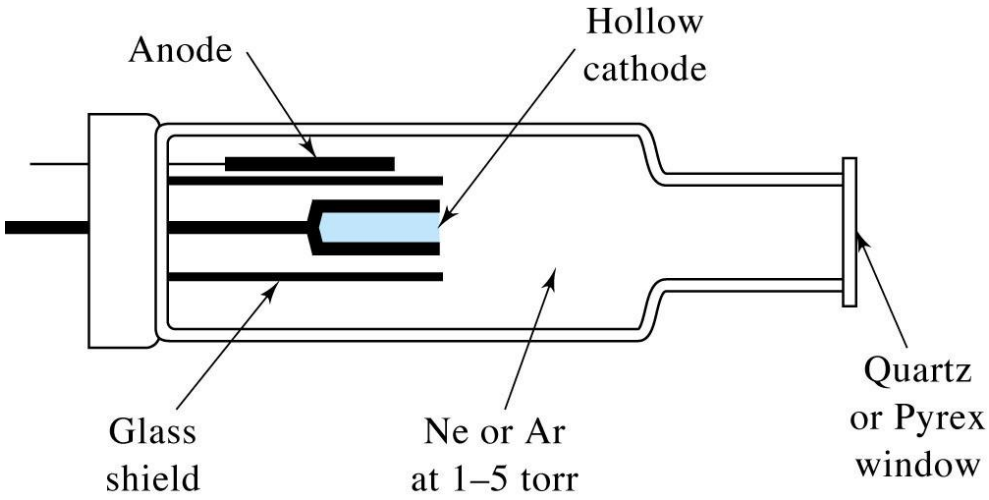
Radiation Sources

- In AAS, line sources of radiation are used because of the absorption line of atoms is very narrow, a few thousands to one - hundredths of a nano meter

Hollow Cathode Lamp (HCL)

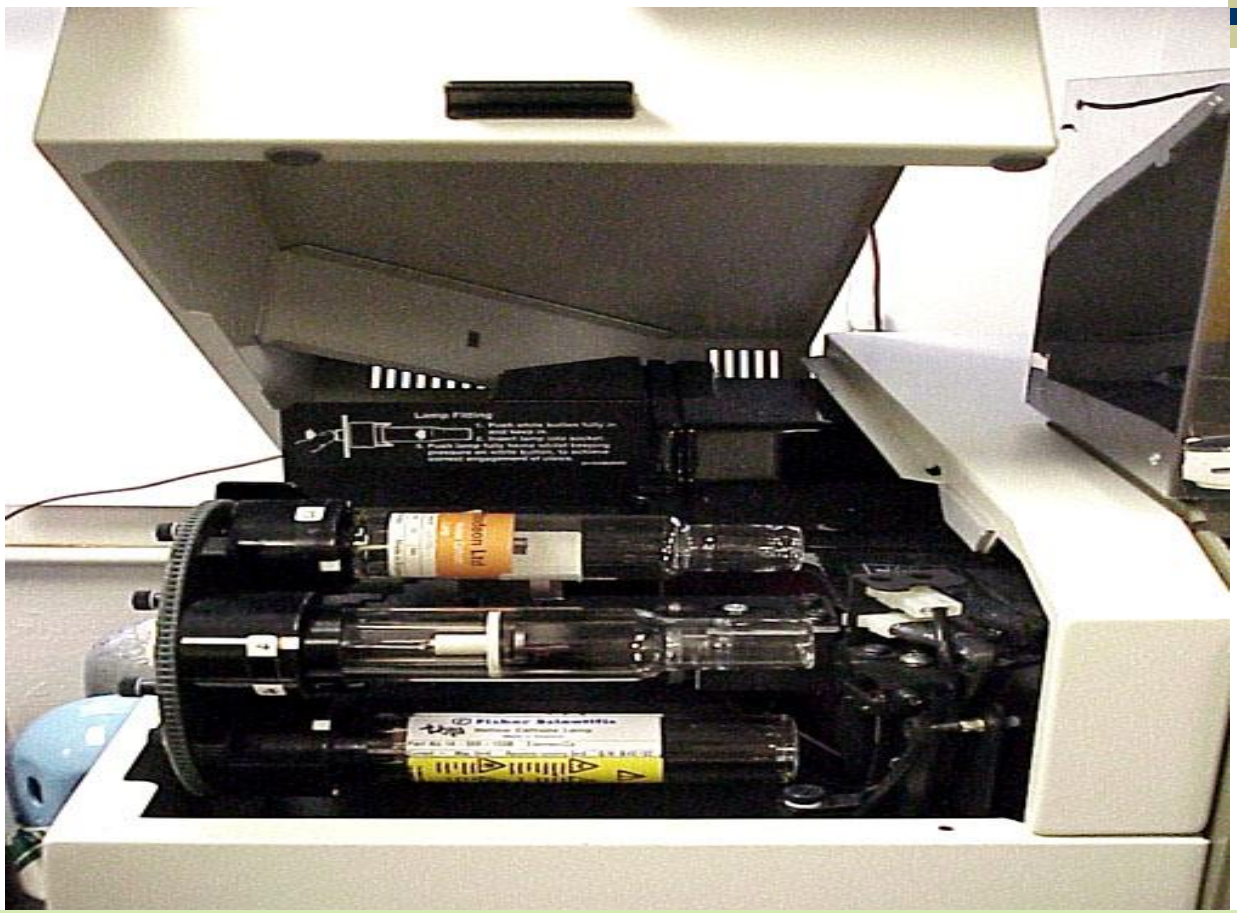


What is needed for a light source in AAS is a source that produces very narrow emission lines at the exact wavelengths capable of being absorbed by analyte atoms.



- ✓a tungsten anode and a cylindrical cathode
- ✓neon or argon at a pressure of 1 to 5 torr is used as filler gas
- ✓The cathode is constructed of the metal whose is being analyzed
- ✓Therefore the atomic radiation emitted by the HCL has the same frequency as that absorbed by the analyte atoms in the flame or furnace.

The lamp is housed inside the lamp compartment of the instrument.



- If we want to determine Cu, the lamp cathode must be a copper cylinder; if we want to determine gold, the cathode must be a gold cylinder, and so on.
- The cathode and an inert anode are sealed in a glass cylinder filled with Ar or Ne at low pressure (the - filler gas).
- A window of quartz or glass is sealed onto the end of the lamp; a quartz window is used if UV wavelengths must be transmitted.
- Most HCLs have quartz windows, because most elements have emission and absorption lines in the UV.
- Glass can be used for some elements, such as sodium, where all the strong absorption lines are in the visible region of the spectrum.

- The HCL is filled with inert filler gases such as argon
- When a potential is applied atoms of the filler gas become ionized and are attracted and accelerated toward the cathode.

$$Ne + e^- \rightleftharpoons Ne^+ + 2e^-$$

- The fast moving ions strike the surface of the cathode and physically dislodge some of the surface metal atoms (a process called —sputtering).

$$M_{(s)} + Ne^+ \rightleftharpoons M_{(g)} + Ne^+$$

- Repeated bombardment of the metal atom the gases causes it to be excited.

$$M_{(g)} + Ne^{+} \rightleftharpoons M^{*}_{(g)} + Ne^{+}$$

- When the excited elements relax to ground state, they emits the characteristic radiation of the metal

$$M^{*}_{(g)} \longrightarrow M_{(g)} + h\nu$$

- Eventually, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are re-deposited

- Narrow line sources such as the HCL provide not only high sensitivity, but also specificity. If only Cu atomic emission lines are produced by the Cu HCL, there are few species other than Cu atoms that can absorb these lines. Therefore, there is little spectral interference in AAS.
- Each hollow cathode emits the spectrum of metal used in the cathode.
- For this reason, a different HCL must be used for each different element to be determined. This is an inconvenience in practice and is the primary factor that makes AAS a technique for determining only one element at a time.
- The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the metal tube; this design also enhances the probability that redeposition will occur at the cathode rather than on the glass walls

Sample Preparation in Atomic Absorption measurement

- A disadvantage of flame spectroscopic methods is the requirement that the sample be introduced into the atomization and excitation source in the form of a solution. Most commonly an aqueous one.
- Unfortunately, many materials of interest, such as soils, animal tissues, plants, petroleum products and minerals are not directly soluble in common solvents, and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization.

- Some of the common methods used for decomposing and dissolving samples for atomic absorption methods include
  1. treatment with hot mineral acids; oxidation with liquid reagents, such as sulfuric, nitric, or perchloric acids (wet ashing);
  2. combustion in an oxygen bomb or other closed container to avoid loss of analyte;
  3. ashing at a high temperature; and
  4. high-temperature fusion with reagents such as boric oxide, sodium carbonate, sodium peroxide, or potassium pyrosulfate.

- Decomposition of materials such as those just cited usually requires rigorous treatment of the sample at high temperatures accompanied by a risk of losing the analyte by volatilization or as particulates in smoke.
- Furthermore, the reagents used in decomposing a sample often introduce the kinds of chemical and spectral interferences that were discussed earlier. Additionally, the analyte may be present in these reagents as an impurity

Atomic Emission Spectroscopy

- I t is a spectroscopic technique which is based on emission of electromagnetic radiation by atoms
- It id based on measurement of the emission from excited atoms.
- Atomic emission spectroscopy is a multi element technique with the ability to determine metals, metalloids, and some nonmetal elements simultaneously.
- During atomic emission the following processes occur

I. production of an aerosol from solution (nebulization)

$$\text{Sample} \longrightarrow S_a$$

I. removal of solvent MA(aq) ÆMA (solid)

$$S_a \longrightarrow S_s$$

I. vaporization of sample MA(solid) ÆMA(vapour)

$$S_s \longrightarrow S_g$$

I. atomization

$$S_g \longrightarrow A_g$$

I. excitation

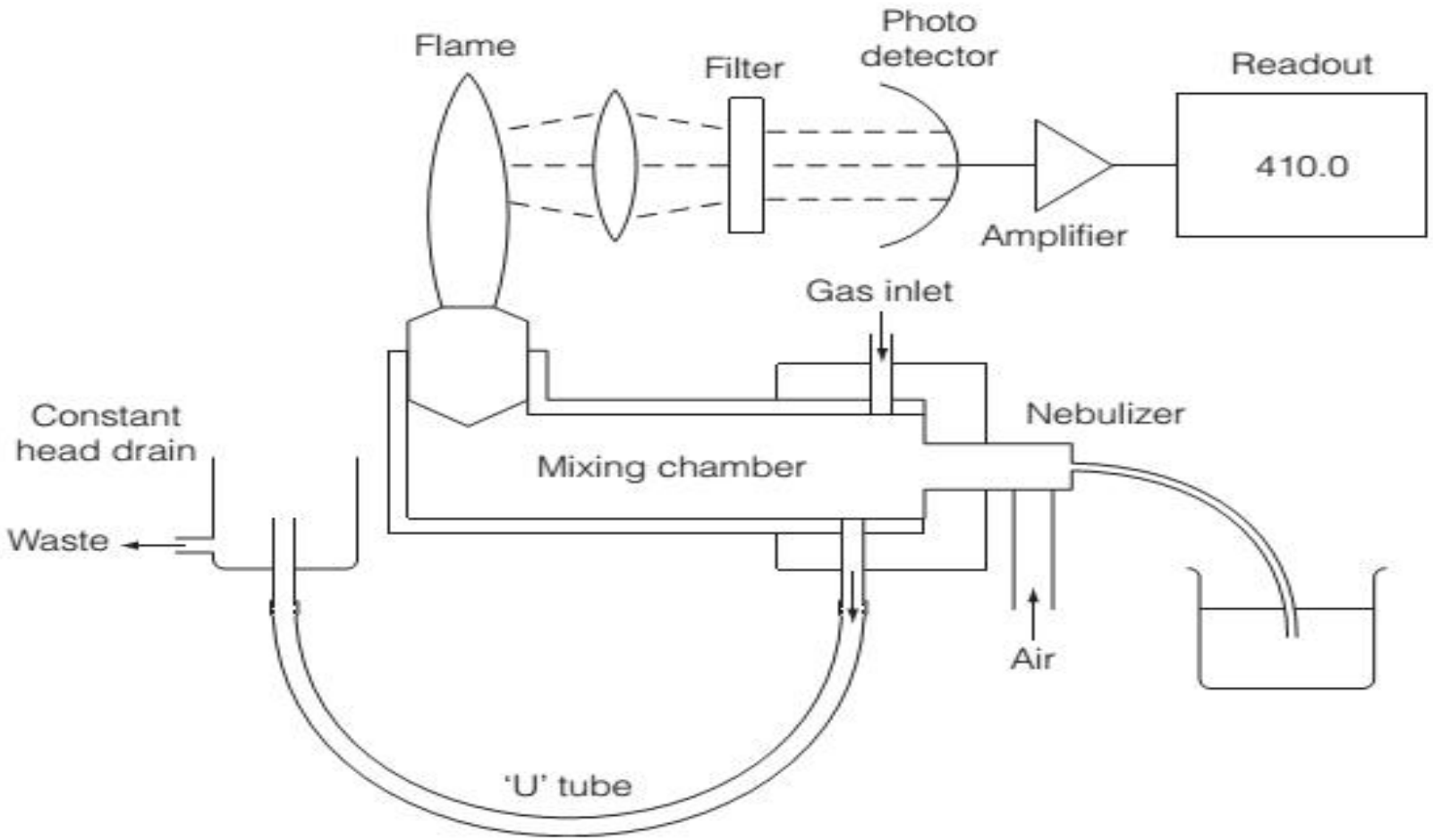
$$A_g \longrightarrow A^*$$

I. emission

$$A_g^* \longrightarrow A_g + h\upsilon$$

Instrumentation

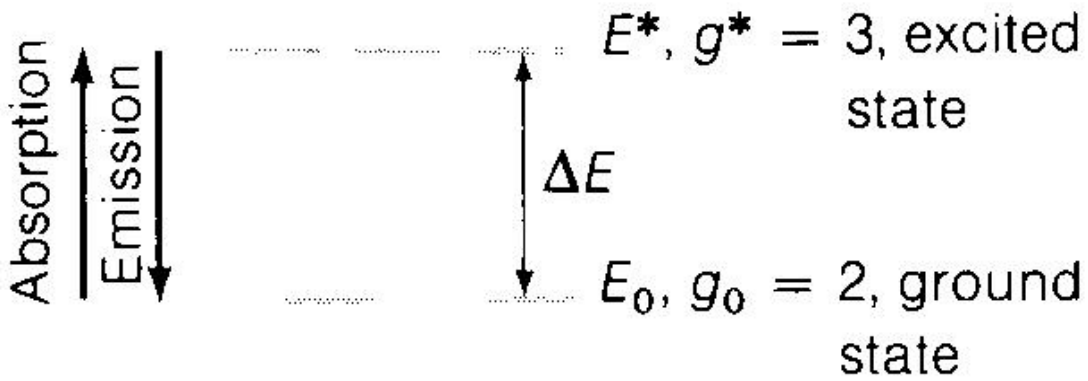
- Instrumentation for AES is similar with AAS except the absence of radiation source in AES



Excitation sources

- Generally; the atomizers used in AAS not only convert the components of samples to atoms or elementary ions but, in the process, excites fraction of these species to higher electronic states.
- As the excited species rapidly relax back lower states, ultraviolet and visible line spectra arise (emission spectra) that are useful for qualitative and quantitative elemental analysis.
- The major difference between the various types of atomic emission spectroscopy techniques lies in the source of excitation and the amount of energy imparted to t he atoms or ions (i.e., the excitation efficiency of the source).

Effect of flame temperature on excited state population



atoms in Excited state

Boltzmann constant

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Temperature

atoms in Ground state

Energy difference

Statistical factor

- Where
  - N^* and N are the number of atoms in an excited state and the ground state,
  - k = Boltzmann constant (1.38×10^{-23} J/K),
  - T = Temperature (K),
  - $\Delta E = E^* - E$ is the energy difference between excited and ground states,
  - g^* and g are the statistical weights of the excited and ground states respectively (determined by the no. states having equal energy at each quantum level n)

This law shows several features useful for analytical spectrometry:

- ☞ the greater the energy difference, the smaller the ratio of the population of the upper level with respect to the lower;
- ☞ the higher the temperature the larger the ratio;
- ☞ the higher the degeneracy ratio (g^*/g), the larger the ratio

☞ For AES large ratio of N^*/N_o is required in order to have large emission

- In atomic Emission the sample is atomized and the analyte atoms are excited to higher energy levels all in the atomizer
- Practically we have several methods used to excite atoms. These include flame, Spark, arc and etc.

Source	Temperature (^oC)
Flame	1700-3150
Plasma	4,000-6,000
Arc/Spark	4,000-5,000

Flame Atomic Emission Spectroscopy

- It, also called flame photometry, is based on the measurement of the emission spectrum produced when a solution containing metals or some nonmetals such as halides, sulfur, or phosphorus is introduced into a flame

The Functions of Flame:

1. To convert the constituents of liquid sample into the vapor state.
2. To decompose the constituents into atoms or simple molecules:
3. To excite a fraction of the resulting atomic or molecular species

$$M \rightarrow M^*$$

- A flame is the result of the exothermic chemical reaction between two gases, one of which serves as the fuel and the other as the oxidant.
- The reaction is an oxidation–reduction reaction, with the oxidant oxidizing the fuel.
- In the process, the reaction generates a great deal of heat.
- Common oxidants for modern AAS/OES systems are air and nitrous oxide.
- The only fuel used in modern AAS/OES systems is acetylene, although commercial filter photometer systems can use propane, natural gas, or butane as fuel.

- Flame temperature is probably the most important single variable in flame photometry.
- The type of fuel and oxidant used controls the temperature.
- In general, an increase in flame temperature causes an increase in emission intensity for most elements.
- This does not happen with elements that ionize easily, such as sodium, potassium, and lithium.
- If these elements are heated at too high a temperature, they become ionized; the outer electrons move to higher and higher energy states until they leave the atom completely, forming an ion.
- If the atoms ionize, the valence electrons are lost and therefore cannot return to the ground state and emit atomic radiation in the process. A loss of atomic emission intensity results. These elements must be determined in low-temperature flames to minimize ionization.

- Flame sources impart relatively low quantities of energy to the atoms produced in the flame. Electrons are promoted to only a few low-energy excited states in flames; this results in simple and few emission spectra.

- It is used mostly for easily excited alkali metals
  > easily excited even at low temperatures
  - Na, K
  - need internal standard (Cs usually) to correct for variations flame

<u>Advantages</u>

- cheap

<u>Disadvantage</u>

- not high enough temperature to extend to many other elements

Instrumentation of Flame atomic spectrometer (photometer)

- Instrumentation for atomic emission spectroscopy is similar in design to that used for atomic absorption.
- In fact, most flame atomic absorption spectrometers are easily adapted for use as flame atomic emission spectrometers by turning off the hollow cathode lamp and monitoring the difference between the intensity of radiation emitted when aspirating the sample and that emitted when aspirating a blank

Analytical Applications of Flame Atomic Emission Spectroscopy

- Multi elemental Analysis Atomic emission spectroscopy is ideally suited for multi elemental analysis because all analytes in a sample are excited simultaneously.
- A scanning monochromator can be programmed to move rapidly to an analyte's desired wavelength, pausing to record its emission intensity before moving to the next analyte's wavelength.

- Electrical discharges such as arcs and sparks provide significantly more energy than flames.
- Most elements can be atomized and ionized in these discharges;
- the higher energy input causes electrons to populate many higher-energy levels. This results in spectra with many emission lines.
- Plasma sources, such as the ICP and the direct current plasma (DCP), are high-energy sources that permit the excitation of most elements, both metals and nonmetals, and result in very line-rich spectra.
- advantages of emission spectroscopy; many elements, as atoms and ions, emit multiple wavelengths simultaneously.
- The analyst has a choice of several wavelengths for each element and the ability to measure multiple elements concurrently.

- The disadvantage is that as the number of emission wavelengths increases, so does the spectral interference from overlapping lines.
- This mandates the use of high resolution spectrometers, which are more expensive than the spectrometers needed for flame emission systems or for atomic absorption.

Inductively Coupled Plasma (ICP)

- Makes use of plasma (partially ionized gas)

- Similar to flame photometry but reaches much higher temperatures (greater than 10000 K)

-More sensitive
-Multi element analysis
-Spectral overlap

- Over 70 elements (in principle simultaneously) Including non-metals such as sulfur, phosphorus, and halogens (not possible with AAS) ppm to ppb range