Chapter 18

Fundamentals of Spectrophotometry

Properties of Light

Electromagnetic Radiation

- energy radiated in the form of a WAVE caused by an electric field interacting with a magnetic field
- result of the acceleration of a charged particle
- does not require a material medium and can travel through a vacuum

Properties of Electromagnetic Radiation

$v_i = \nu \lambda_i$

where v_i => velocity
ν => frequency
λ_i => wavelength

Properties of Electromagnetic Radiation

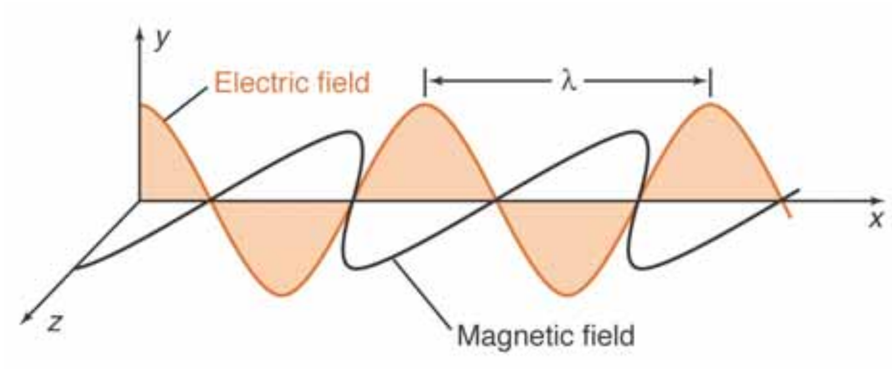
in vacuum, velocity is independent of frequency,

maximum value

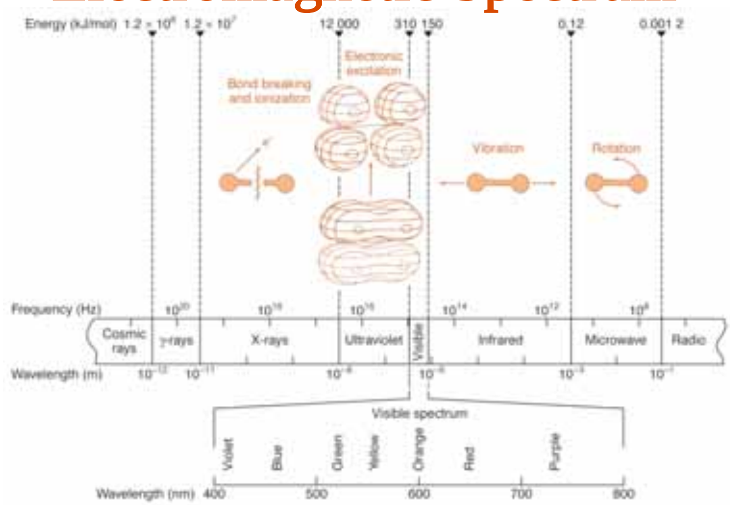
$c = \nu\lambda = 2.998 \times 10^8$ m/s

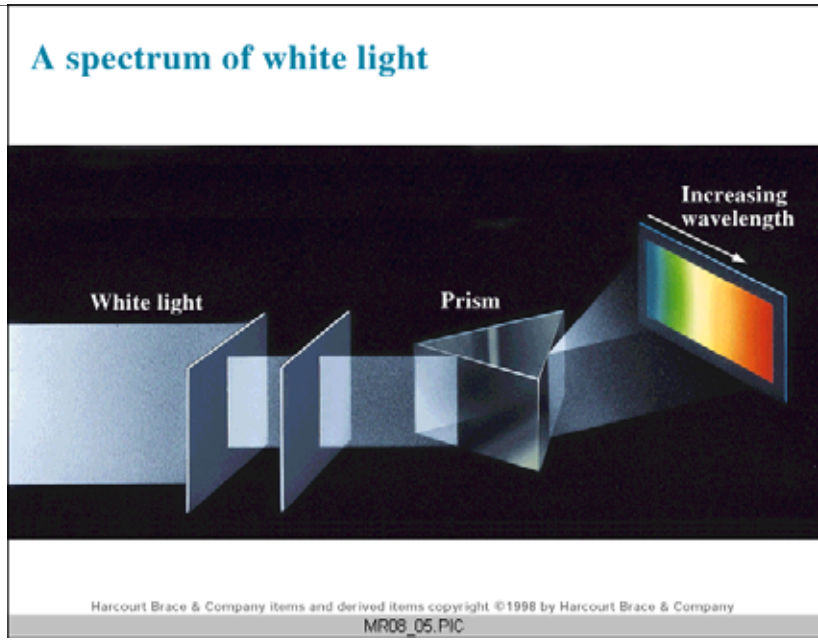
Properties of Electromagnetic Radiation

Fig. 19-1, pg. 511 ”Plane-polarized electromagnetic radiation of wavelength λ, propagating along the x axis. The electric field of the plane-polarized light is confined to a single plane. Ordinary, unpolarized light has electric field components in all planes."



Regions of Electromagnetic Spectrum





Line Spectrum

A spectrum produced by a luminous gas or vapor and appearing as distinct lines characteristic of the various elements constituting the gas.

Emission Spectrum

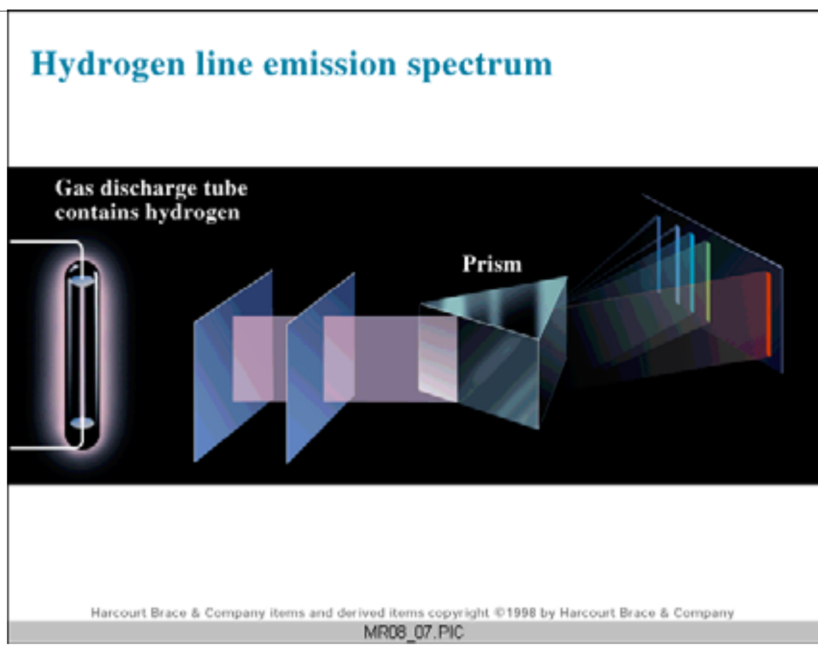
The spectrum of bright lines, bands, or continuous radiation characteristic of and determined by a specific emitting substance subjected to a specific kind of excitation.

Ground State

The state of least possible energy in a physical system, as of elementary particles. Also called *ground level.*

Excited State

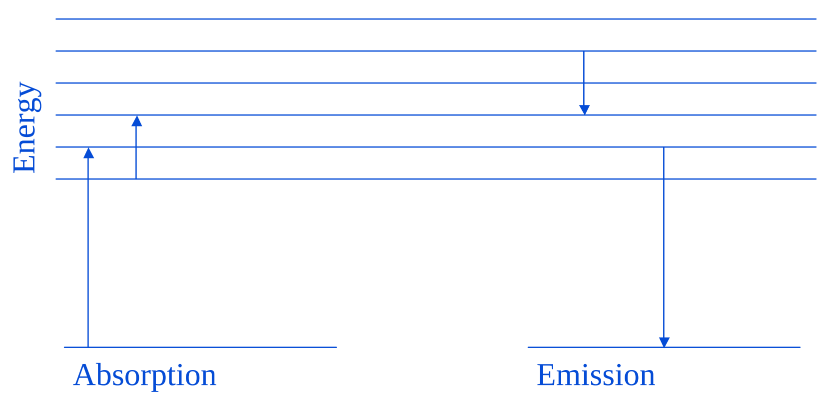
Being at an energy level higher than the ground state.



Absorption Spectrum

- Light shinning on a sample causes electrons to be excited from the ground state to an excited state
- wavelengths of that energy are removed from transmitted spectra

Absorption and Emission of Light



Absorption Methods, Transmittance

$T = P/P_o$

where T => transmittance

P => power of transmitted radiation

P_o => power of incident radiation

$\%T = (P/P_o)*100$

where $\%T$ => percent transmittance

Absorption Methods, Absorbance

$A = -\log_{10}T = -\log_{10}(P/P_o)$

where A => absorbance

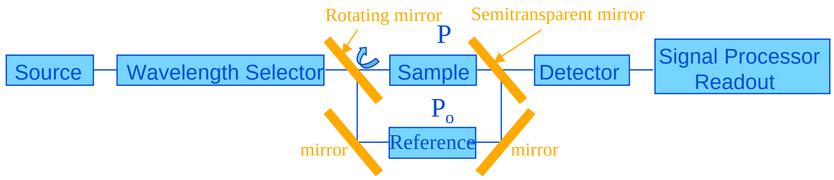
Relation Between Transmittance and Absorbance

P/P_o	%T	A
1	100	0
0.1	10	1
0.01	1	2

Colors of Visible Light

Wavelength	Absorbed	Observed
380-420	violet	green-yellow
420-440	violet-blue	yellow
440-470	blue	orange
470-500	blue-green	red
500-520	green	purple
520-550	yellow-green	violet
550-580	yellow	violet-blue
580-620	orange	blue
620-680	red	blue-green
680-780	purple	green

Components of Optical Instruments



Absorption Spectrometer

Emission Flame Photometer

Flame Atomic Absorption Spectrometer

Fluorescence and/or Scattering Spectrometer

Absorption Methods, Beer's Law

$A = abc = \varepsilon bc$

where a => absorptivity

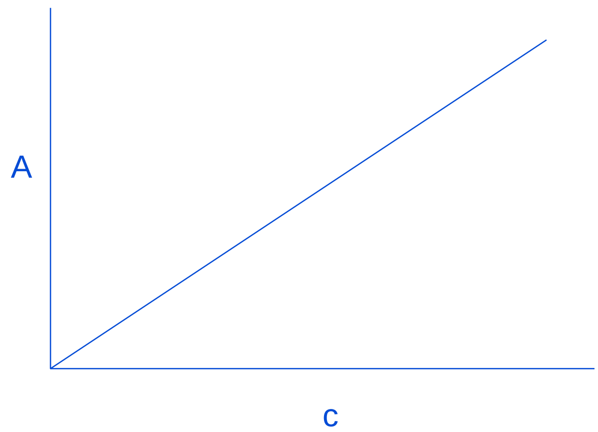
b => path length

c => concentration

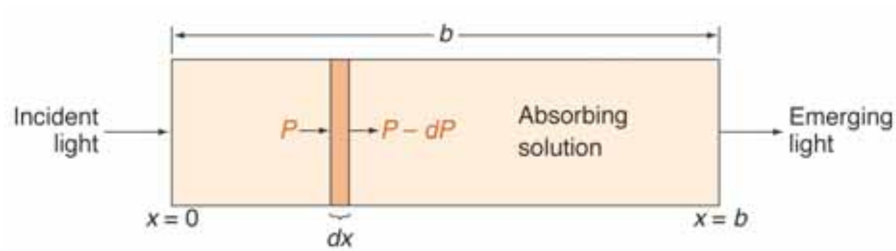
ε => molar absorptivity

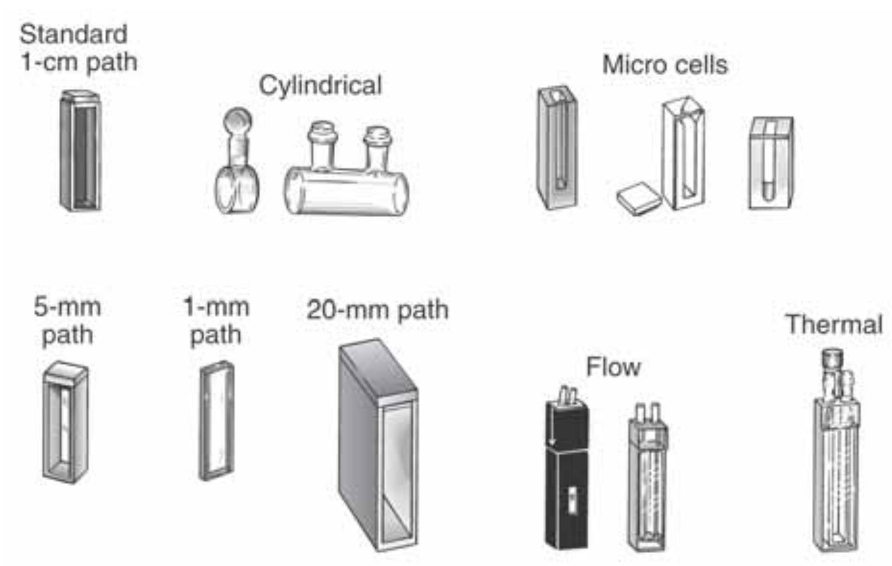
Beer's Law

$A = abc = \varepsilon bc$



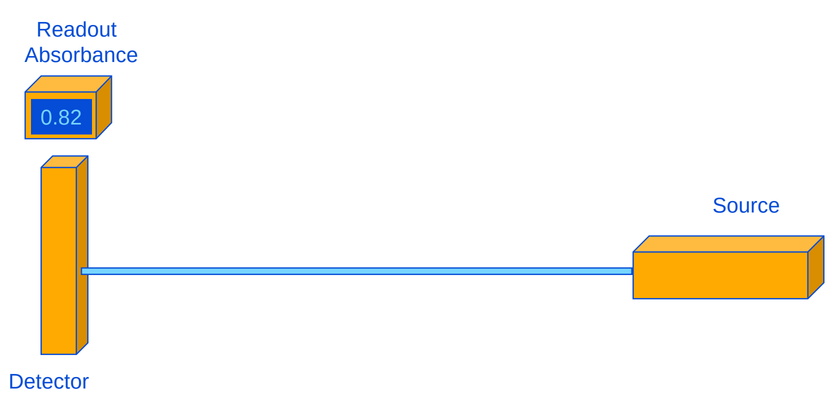
Attenuation of Light





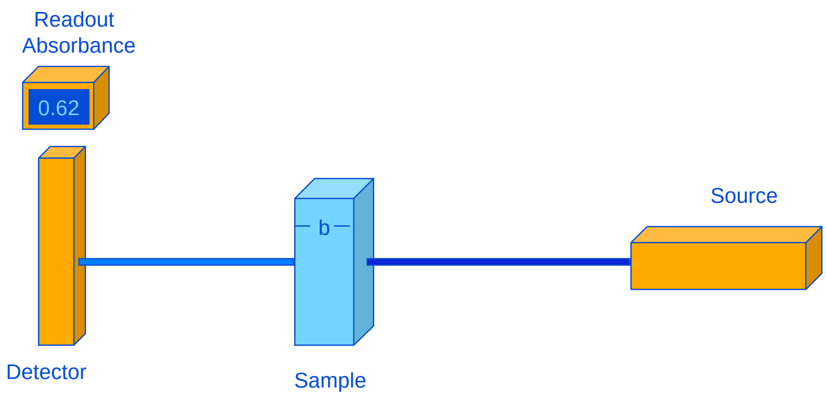
Beer’s Law A = a*b*c

Path Length Dependence, b



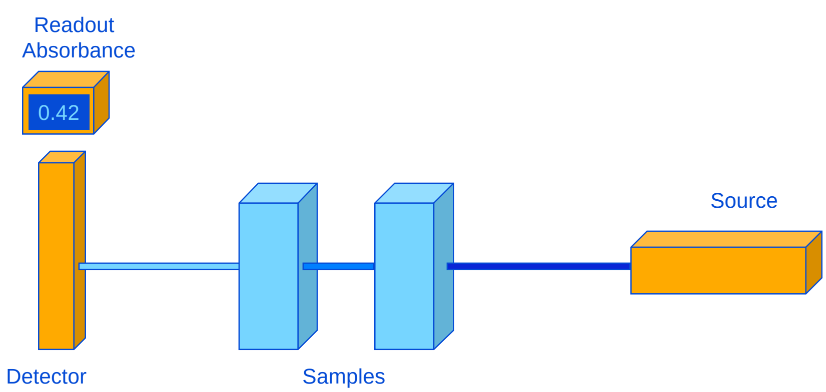
Beer’s Law A = a*b*c

Path Length Dependence, b



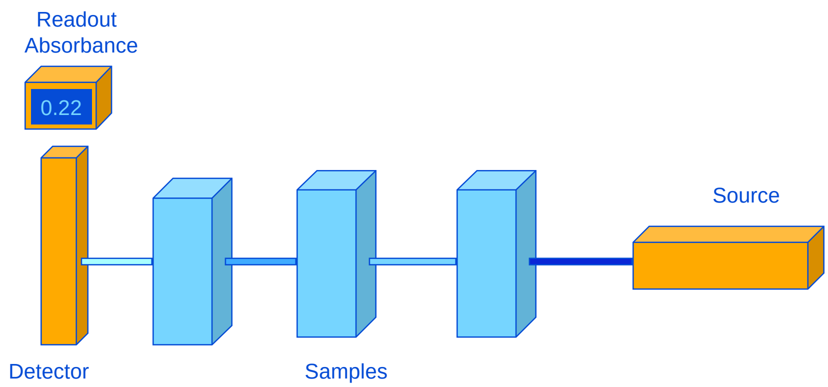
Beer’s Law A = a*b*c

Path Length Dependence, b



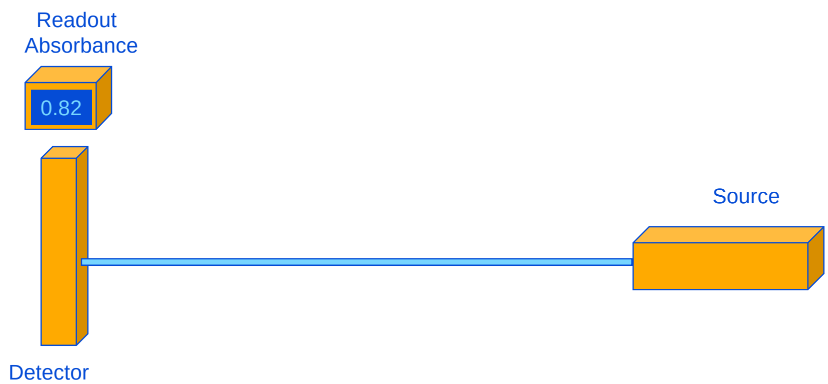
Beer's Law A = a*b*c

Path Length Dependence, b



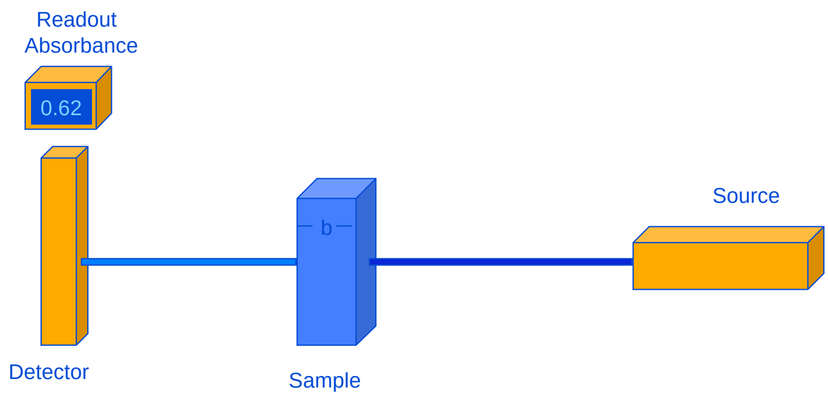
Beer's Law A = ab*c*

Concentration Dependence, c



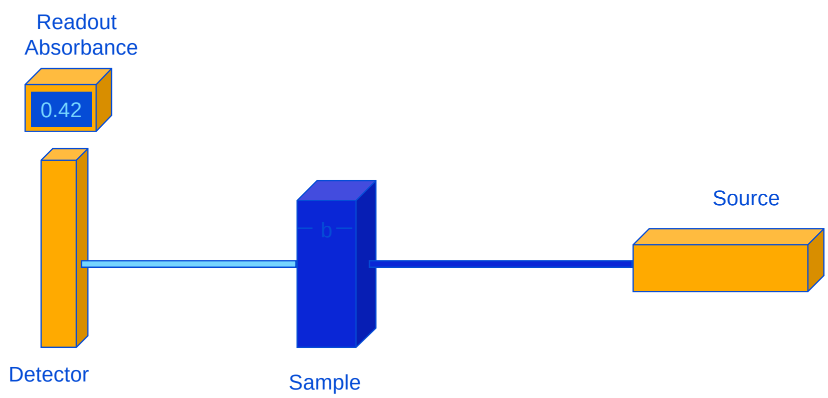
Beer's Law A = ab*c*

Concentration Dependence, c



Beer's Law A = ab*c*

Concentration Dependence, c

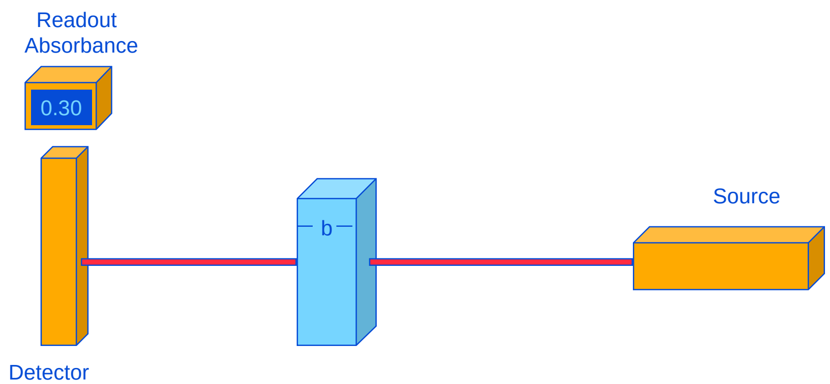


Beer’s Law A = *a*bc

Wavelength Dependence, a

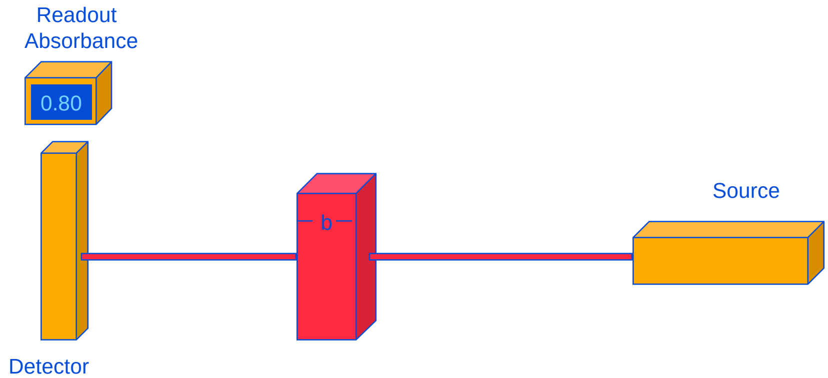
Beer’s Law A = *a*bc

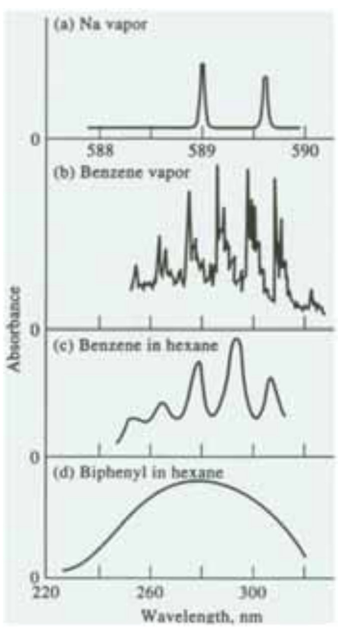
Wavelength Dependence, a



Beer's Law A = *<u>a</u>*bc

Wavelength Dependence, a



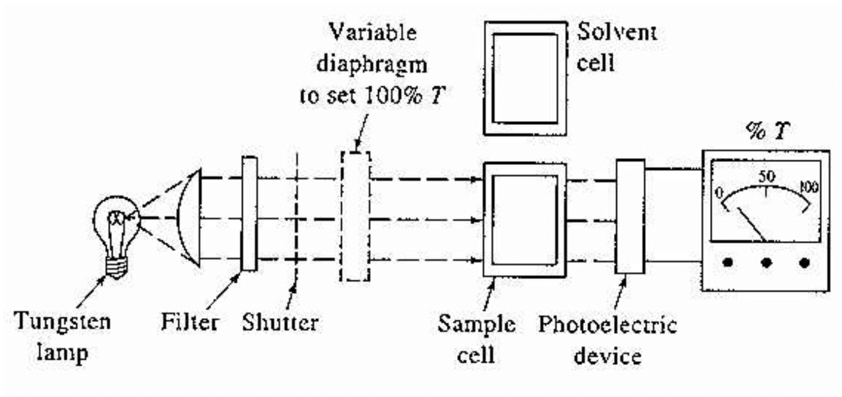


The relative simplicity of atomic spectra is due to the small number of possible energy states for the absorbing particles.

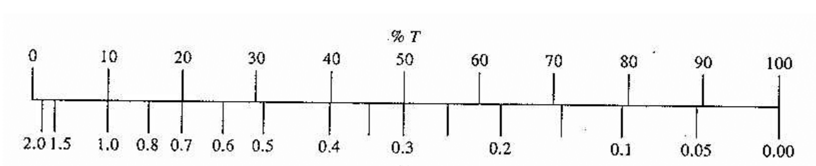
Only electronic transitions are encountered

The absorption spectra fro polyatomic Molecules are considerably more complex Because the number of energy states is Enormous. Here the vibrational and rotational States are involved.

Simple Spectrometer



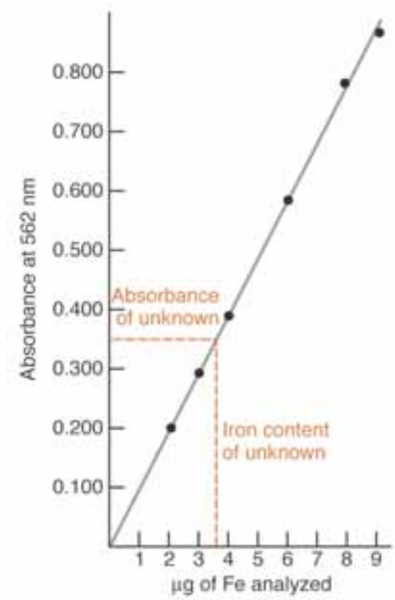
Relationship of Transmittance and Absorbance

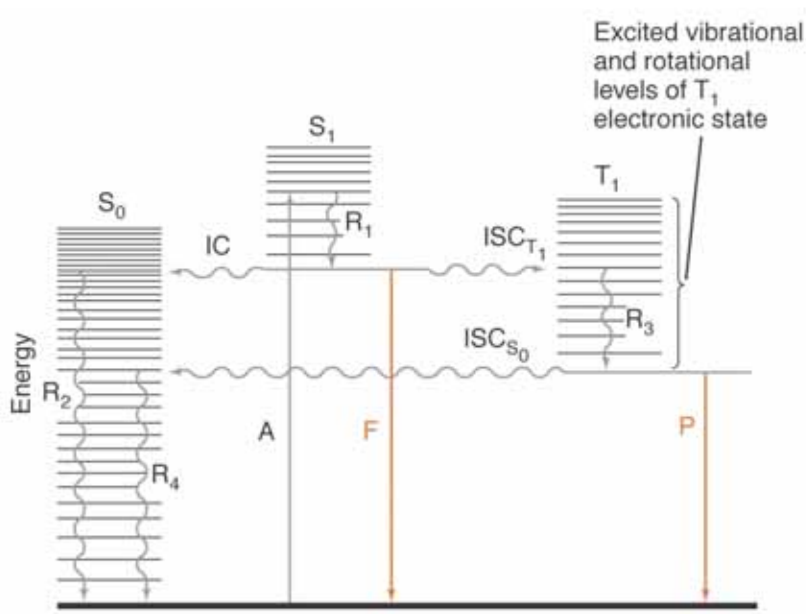


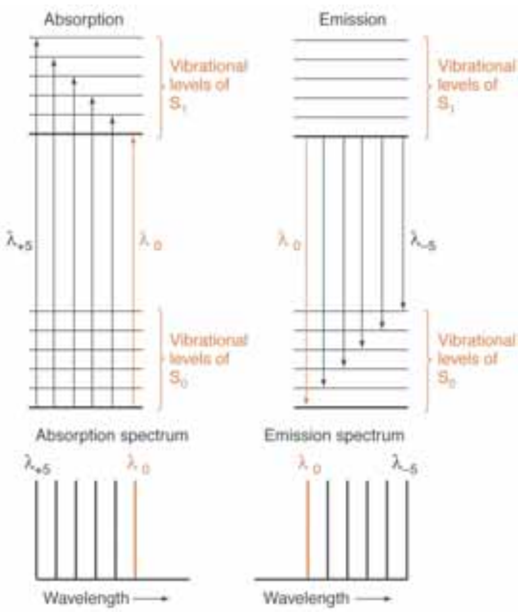
transmittance scale is linear

absorbance scale is exponential

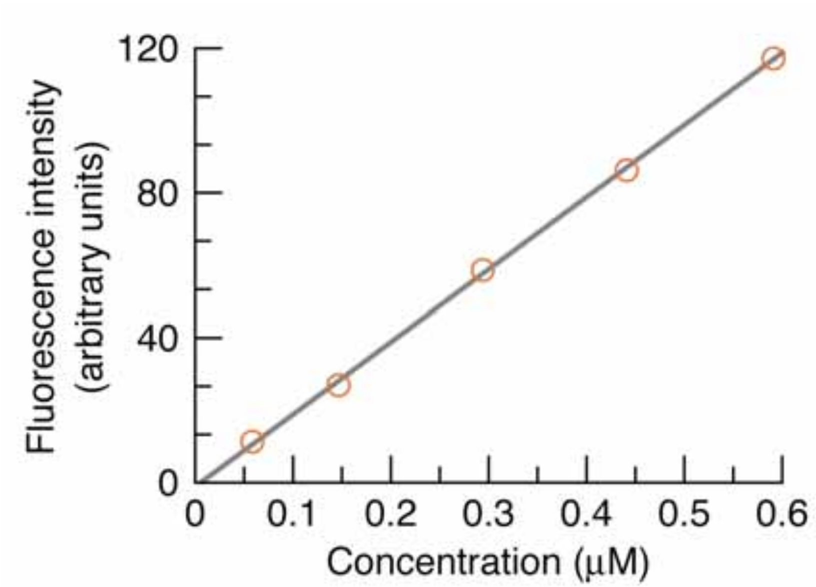
thus, read transmittance, then calculate absorbance


Absorbance at 562 nm
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
Absorbance
of unknown
Iron content
of unknown
1 2 3 4 5 6 7 8 9
µg of Fe analyzed

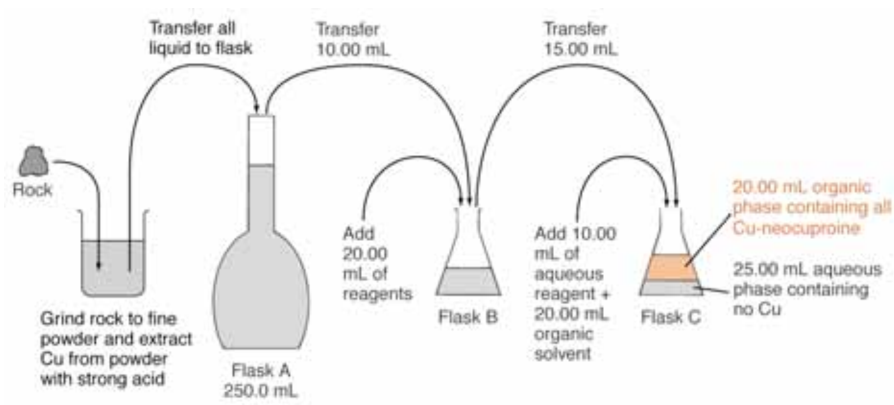

Excited vibrational
and rotational
levels of T_1
electronic state
S_1
T_1
S_0
IC
R_1
ISC_{T_1}
R_3
ISC_{S_0}
Energy
R_2
R_4
A
F
P

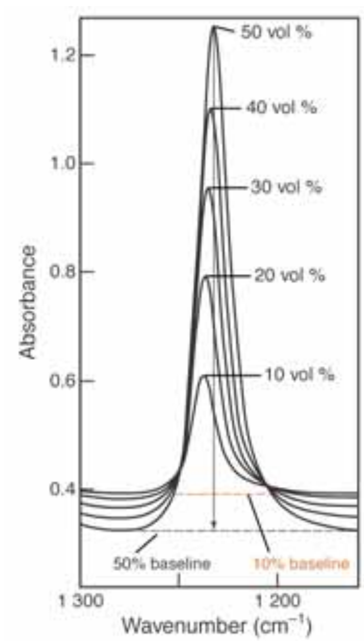


Absorption
Emission
Vibrational levels of S_1
Vibrational levels of S_1
λ_{+5}
λ_0
λ_0
λ_{-5}
Vibrational levels of S_0
Vibrational levels of S_0
Absorption spectrum
Emission spectrum
λ_{+5}
λ_0
λ_0
λ_{-5}
Wavelength →
Wavelength →



Fluorescence intensity (arbitrary units)
120
80
40
0
0
0.1
0.2
0.3
0.4
0.5
0.6
Concentration (μM)


Transfer all liquid to flask
Transfer 10.00 mL
Transfer 15.00 mL
Rock
Grind rock to fine powder and extract Cu from powder with strong acid
Flask A 250.0 mL
Add 20.00 mL of reagents
Flask B
Add 10.00 mL of aqueous reagent + 20.00 mL organic solvent
Flask C
20.00 mL organic phase containing all Cu-neocuproine
25.00 mL aqueous phase containing no Cu


50 vol %
40 vol %
30 vol %
20 vol %
10 vol %
1.2
1.0
0.8
0.6
0.4
Absorbance
50% baseline
10% baseline
1 300
1 200
Wavenumber (cm^{-1})