Spectrochemical Analysis

PART V

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Introduction to Spectrochemical Methods

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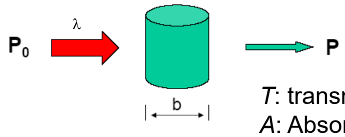
1

Definition and Overview

- Spectroscopy:

A general term for the science that deals with various types of ***<u>electromagnetic radiation</u>*** (EMR) with *mater*.



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

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

$= - \log T$

T: transmittance;
A: Absorbance

$A = f(b, C)_\lambda$ Absorption Spectroscopy

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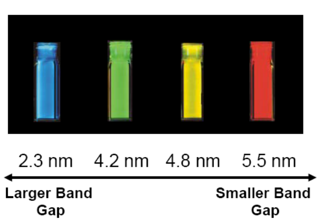
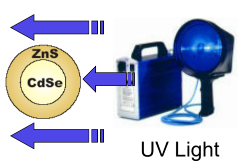
Optical Properties of Semiconductor Nanoparticles





Courtesy of Bawendi and Coworkers.

$I = f(C)$

Emission Spectroscopy

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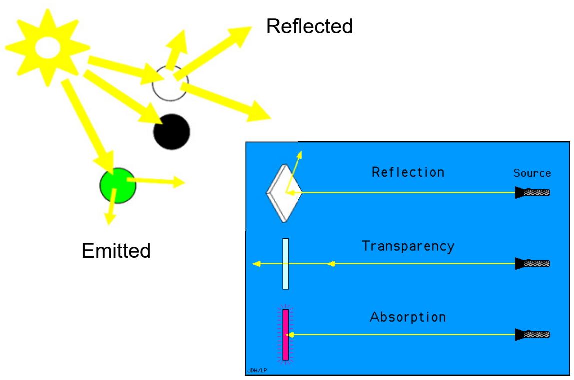
Examples of EMR Interaction with Mater



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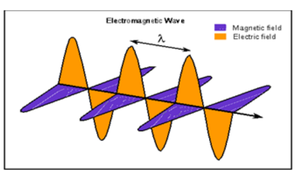
Properties of Electromagnetic Radiation (EMR)

- EMR—light—is a form of energy whose behavior is described by the properties of both waves and particles.
- **Waves:** an *oscillating* electric and magnetic field which travels through space



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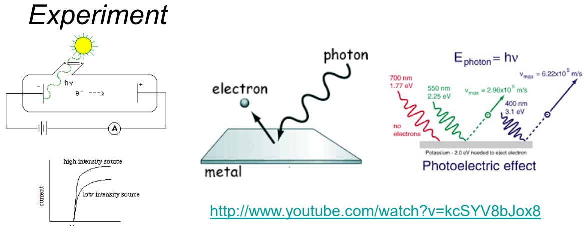
- **Particles:** a discrete series of "particles" that have a specific energy but have <u>*no mass*</u>
- Direct Evidence showing light is a stream of discrete particle — *Photoelectric Effect Experiment*



http://www.youtube.com/watch?v=kcSYV8bJox8

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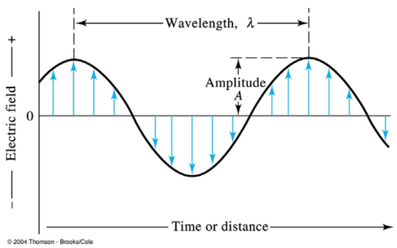
Wave Properties of EMR



Characterized by

λ: Wavelength

A: Amplitude

ν(nu): Frequency

Wave Equation for a single wave

y = *A* sin (2πν*t* + ϕ)

ϕ--phase angle: radian NOT degree

360° = 2π

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Wave Properties of EMR

The product of λ and ν is constant:

$\lambda \times \nu = c$

Since ν has units of sec^{-1}(hz) and λ has units of length, their product, *c*, is the *velocity* of the wave:

- **in a vacuum**, all EMR travels at a velocity of: **2.99792458 x 10^8 m/s** (= *c*) ("The Speed of Light")
- Wave number: $\bar{\nu} = 1/\lambda$ (unit: cm^{-1})

C =3×10^8 m/s = 3×10^{10} cm/s = 3×10^{17} nm/s = 3×10^{18} Å/s

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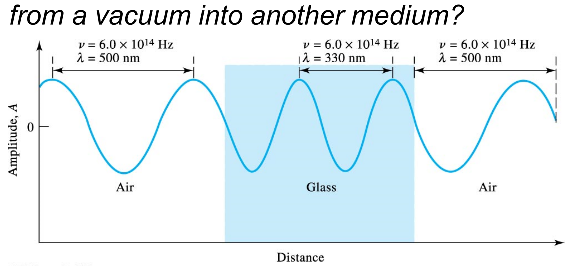
Propagation Velocity

- *What happens as an EMR wave propagates from a vacuum into another medium?*



ν ***unchanged***; λ *decreases*; velocity *decreases*.

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EMR Spectrum

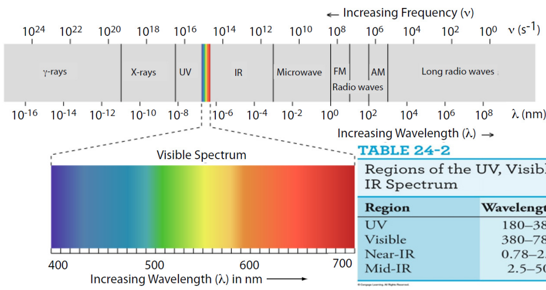

TABLE 24-2
Regions of the UV, Visible, and IR Spectrum

Region	Wavelength Range
UV	180–380 nm
Visible	380–780 nm
Near-IR	0.78–2.5 μm
Mid-IR	2.5–50 μm

EMR covers *a wide range* of wavelengths and frequencies.

Visible Light 380-780 nm

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Table 10.1 Examples of Spectroscopic Techniques That Involve an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique[a]
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	*UV/Vis spectroscopy* *atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectrosco nuclear magnetic resonance spectr
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy* *phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

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Particle Properties of EMR

- EMR: A beam of energetic particles ("photons").
- Photons are "destroyed" after absorption by a sample.
- Energy of a photon is related to its frequency.

$$\boxed{E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}}$$

h is Plank's constant (6.63×10^{-34} J·s)

What is the energy of a photon from the sodium D line at 589 nm?

Solution

The photon's energy is

$$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\text{Js})(3.00\times10^{8}\,\text{m/s})}{589\times10^{-9}\,\text{m}} = 3.37\times10^{-19}\,\text{J}$$

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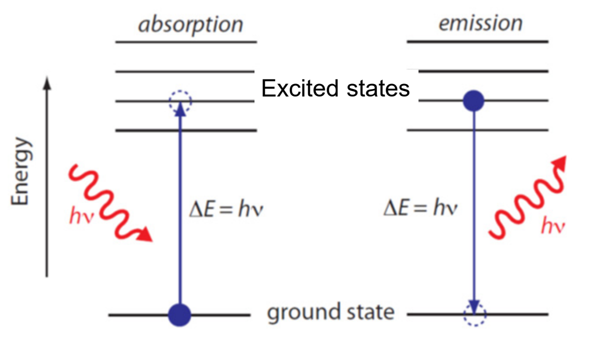
Absorption vs Emission



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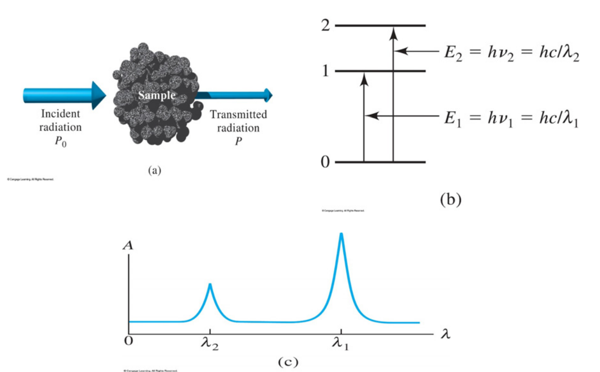
Absorption Spectra



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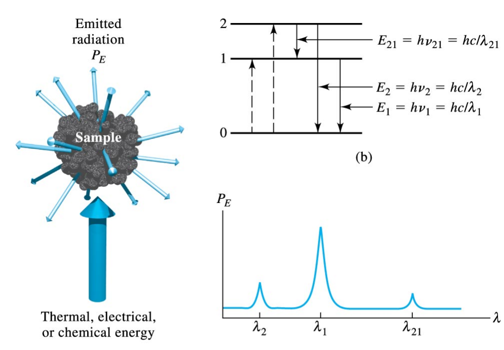
Emission/Luminescence Spectra



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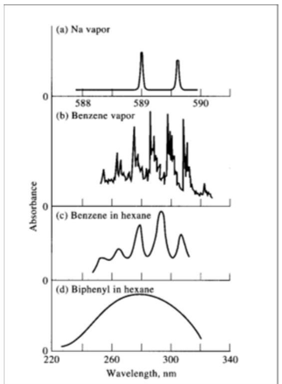
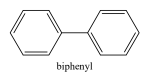
Absorption Spectra -Examples



Line Spectrum

Band Spectrum



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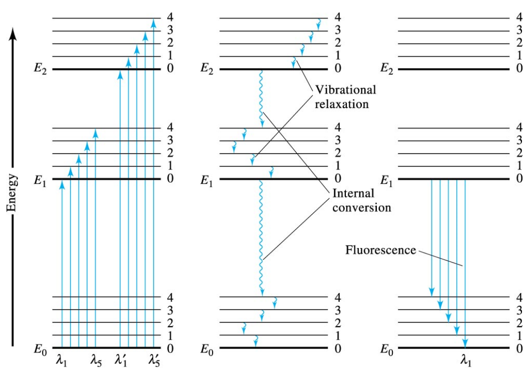
Transitions and Energy Levels



(a) Molecular absorption (b) Nonradiative relaxation (c) Fluorescence

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4 Basic Components of Instruments for Chemical Analysis

- signal generators
- detectors (input transducers)
- signal processors (circuits & electrical devices)
- readout devices

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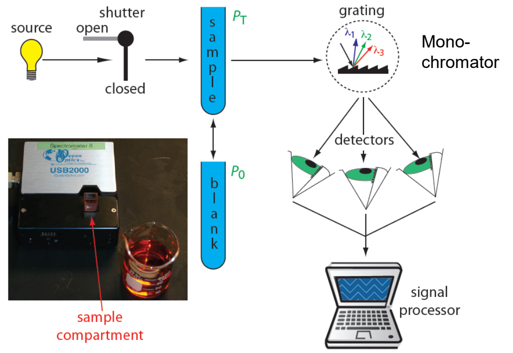

Schematic diagram of a diode array **UV-Vis spectrophotometer.** The photographic insert shows a typical instrument. Note that the 50-mL beaker provides a sense of scale. Because the spectrometer is small and compact, it is easy to transport into the field.

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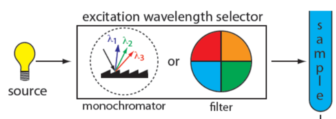
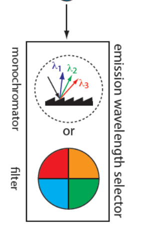
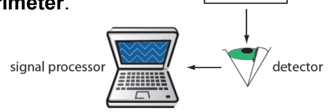


Schematic diagram for measuring **fluorescence** showing the placement of the wavelength selectors for excitation and emission. When a filter is used the instrument is called a **fluorimeter** and when a monochromator is used the instrument is called a **spectrofluorimeter**.





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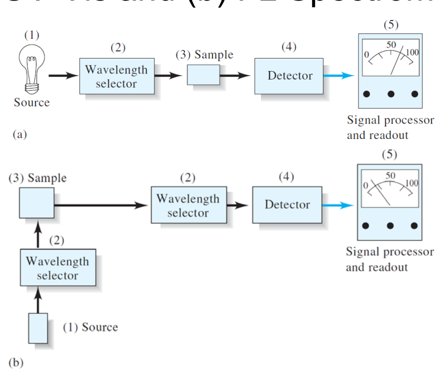
Typical Block Diagrams of (a) UV-Vis and (b) FL Spectrometers



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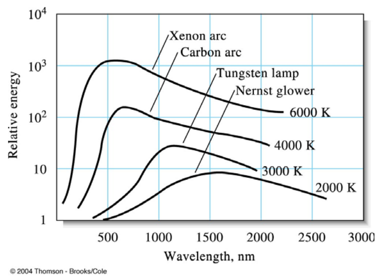
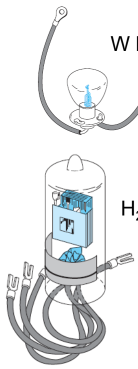
Light Sources: Thermal (Black body) Radiation





Heated to Incandescence

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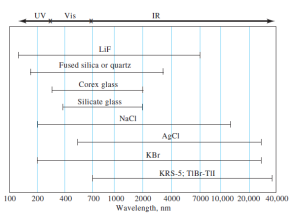
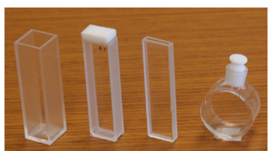
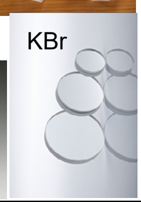
Transmittance Ranges for Various Optical Materials

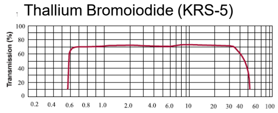


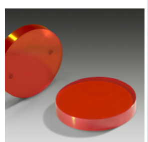


KBr



Thallium Bromoiodide (KRS-5)





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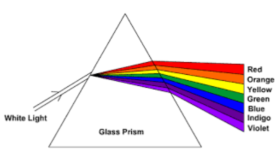
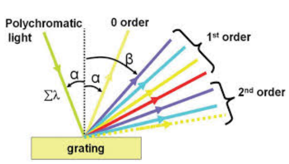
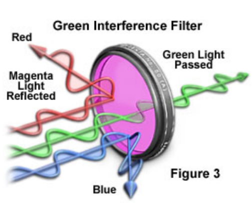
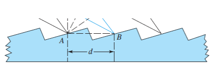
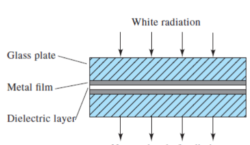
Wavelength Selectors











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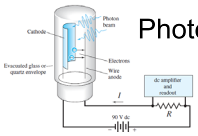
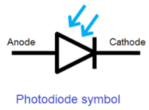
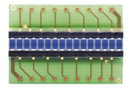
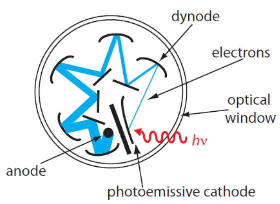
Detectors/Transducers

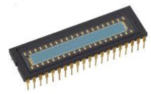


Phototube









Photodiode array 1024

Photomultiplier Tube (PMT)

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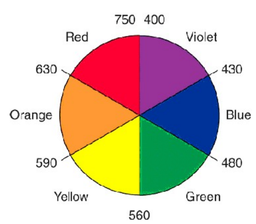
Color Wheel Complementary Colors



Roy G. Biv

R = Red (700 nm)

O = Orange (620 nm)

Y = Yellow (550 nm)

G = Green (510 nm)

B = Blue (450 nm)

~~I = Indigo (450-425 nm)~~

V = Violet (410 nm)

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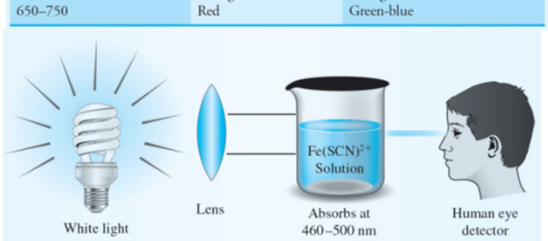
The Visible Spectrum

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



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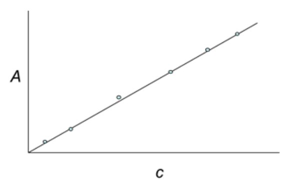
Beer's Law

$$A^{\lambda} = -\log T^{\lambda} = -\log[\frac{P}{P_0}]_{\lambda}$$

$$A^{\lambda} = a_{\lambda}bc = \varepsilon_{\lambda}bc$$

A = absorbance
a = absorptivity
b = thickness
c = concentration
ε = molar absorptivity

When *b* in cm, *c* in mol/L, *a* is called molar absorptivity and is given the special symbol ε (in L/(mol cm))



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Beer's Law for Mixture-Additive

At any given wavelength of EMR absorption:
$A^{\lambda} = \varepsilon^{\lambda}bc$, for a mixture with n components,
the total A^{λ}_{Total} :

$$A^{\lambda}_{Total} = A^{\lambda}_1 + A^{\lambda}_2 + ...A^{\lambda}_3 = \sum_{i=1}^{n} A^{\lambda}_i = \sum_{i=1}^{n} \varepsilon_i{}^{\lambda} bc_i$$

Example:
Mixture of Co(II), Cr(III), Ni(II), Cu(II)

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In Class Practice:

A mixture solution of Co(II) and Ni(II) shows an absorbance of 1.000 at 500 nm. What percentage of incident light is absorbed by the solution? Under the given conditions if 75.0% of the absorbance is ascribed to the contribution of Co(II), then what the absorbance of Ni(II) will be?

Key: 90.0%; 0.250

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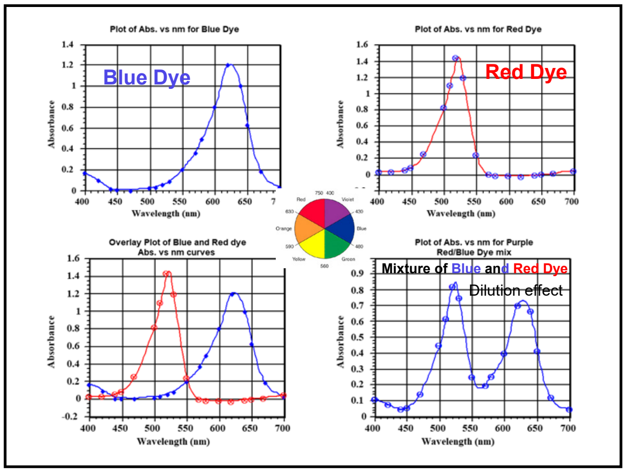

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Example:

The concentrations of Fe^{3+} and Cu^{2+} in a mixture are determined following their reaction with hexacyanoruthenate (II), $Ru(CN)_6^{4-}$, which forms a purple-blue complex with Fe^{3+} (λ_{max} = 550 nm) and a pale-green complex with Cu^{2+} (λ_{max} = 396 nm). The molar absorptivities (M^{-1} cm^{-1}) for the metal complexes at the two wavelengths are summarized in the following table.

	ε_{550}	ε_{396}
Fe^{3+}	9970	84
Cu^{2+}	34	856

When a sample that contains Fe^{3+} and Cu^{2+} is analyzed in a cell with a pathlength of 1.00 cm, the absorbance at 550 nm is 0.183 and the absorbance at 396 nm is 0.109. What are the molar concentrations of Fe^{3+} and Cu^{2+} in the sample?

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Solution:

$$A_{550} = 0.183 = 9970C_{Fe} + 34C_{Cu}$$

$$A_{396} = 0.109 = 84C_{Fe} + 856C_{Cu}$$

To determine C_{Fe} and C_{Cu} we solve the first equation for C_{Cu}

$$C_{Cu} = \frac{0.183 - 9970C_{Fe}}{34}$$

and substitute the result into the second equation.

$$0.109 = 84C_{Fe} + 856 \times \frac{0.183 - 9970C_{Fe}}{34}$$

$$= 4.607 - (2.51 \times 10^5)C_{Fe}$$

Solving for C_{Fe} gives the concentration of Fe^{3+} as 1.8×10^{-5} M. Substituting this concentration back into the equation for the mixture's absorbance at 396 nm gives the concentration of Cu^{2+} as 1.3×10^{-4} M.

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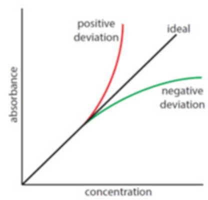
Limitations to Beer's law

1. **Concentration Limit: ≤ 0.10 M.**

(a) At higher *c* the individual particles of analyte no longer are independent of each other- changing the ε value.

(b) The ε value depends on the solution's refractive index that varies with the *c*.



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Limitations to Beer's law

2. Chemical limitations when chemical reactions occur.

Example: different *c* of a weak acid dissociation in water (acid-base indicators)

HIn (Color 1, in acid) = H^+ + In^- (Color 2)

Increase total $[HIn]_{total}$, [HIn] and $[In^-]$ increase non-linearly.

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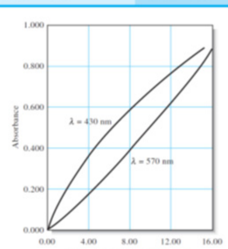
TABLE 24-4

Absorbance Data for Several Concentrations of the Indicator in Example 24-5

c_{HIn}, M	[HIn]	$[In^-]$	A_{430} (In^-)	A_{570} (HIn)
2.00×10^{-5}	0.88×10^{-5}	1.12×10^{-5}	0.236	0.073
4.00×10^{-5}	2.22×10^{-5}	1.78×10^{-5}	0.381	0.175
8.00×10^{-5}	5.27×10^{-5}	2.73×10^{-5}	0.596	0.401
12.0×10^{-5}	8.52×10^{-5}	3.48×10^{-5}	0.771	0.640
16.0×10^{-5}	11.9×10^{-5}	4.11×10^{-5}	0.922	0.887



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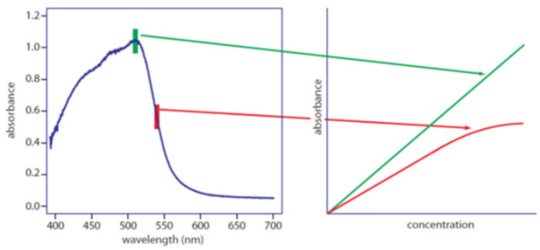
Limitations to Beer's law

3. Instrumental limitations.



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- Beer's Law Should be used Only for a Single Wavelength Incident Light.
- It is the basis of quantitative Analysis of Absorption Spectroscopy.

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Photometric Titrations

- A photometric titration curve is a plot of absorbance as a function of the volume of titrant.
- The spectrometer detects the color change of an indicator allowing the endpoint to be accurately determined.
- For example: titration of an acid and base using phenolphthalein clear ⇔ pink

$$A + T \xrightleftharpoons{\text{Indicator}} P$$

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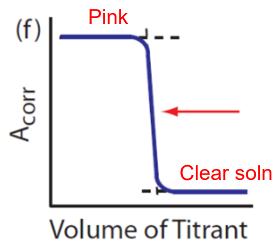

Only the indicator absorbs

Base (phenolphthalein) ←acid

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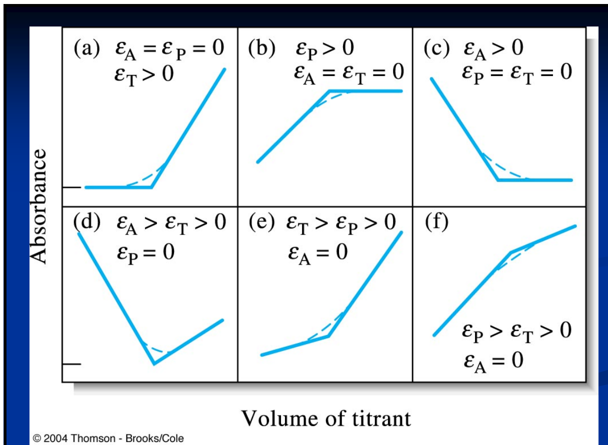

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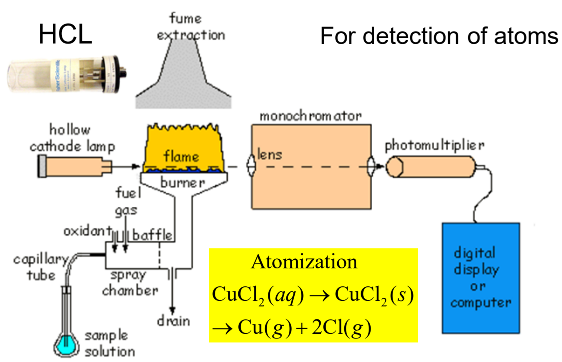
Atomic Absorption Spectrometer

For detection of atoms



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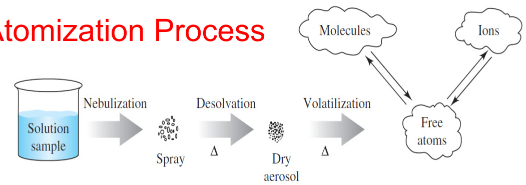
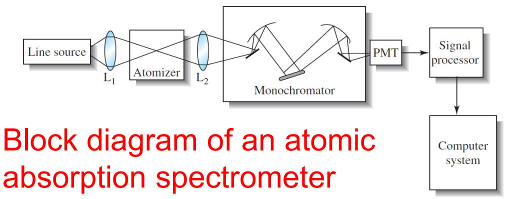
Atomization Process





Block diagram of an atomic absorption spectrometer

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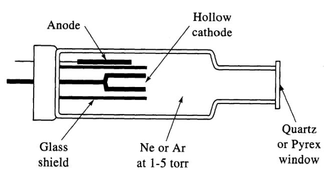
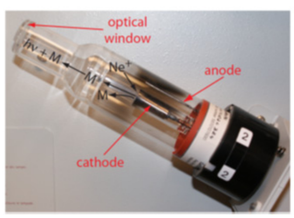
Hollow Cathode Lamps



Hamamatsu Produces ~186 HCL Lamps

Can be used to detect ~70 metals



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Chapters 24-28 Summary

- Electromagnetic radiation (EMR): waves and particles
- Spectroscopy vs spectra vs spectrometer
- Emission and absorption processes
- Beer's law and its consequences and uses
- Molecular/atomic absorption spectra
- Diagrams of electronic transitions and energy levels
- Deviations from Beer's law
- Atomic absorption spectrometer, HCLs

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Important Equations

$c = \nu \bullet \lambda \qquad \bar{\nu} = 1/\lambda$ (unit: cm^{-1})

$E = h\nu = h\dfrac{c}{\lambda} = hc\bar{\nu}$

$T = \dfrac{P}{P_0} = \dfrac{I}{I_0}$

$A = -\log(T) = abc = \varepsilon bc$

For a mixture with n components,

$A_{Total}^{\lambda} = A_1^{\lambda} + A_2^{\lambda} + \ldots\ldots A_3^{\lambda} = \sum_{i=1}^{n} A_i^{\lambda} = \sum_{i=1}^{n} \varepsilon_i^{\lambda} bc_i$

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