CHEM*3440

Chemical Instrumentation

Topic 7

Spectrometry

Spectrum of Electromagnetic Radiation

Electromagnetic radiation is light. Different energy light interacts with different motions in molecules.

Radiofrequency	MHz	Nuclear Spin	NMR
Microwave	GHz	Electron Spin Molecular Rotation	ESR (EPR) Microwave Spec.
Infrared	THz	Molecular Vibrations	I.R. Spectroscopy
UV–Visible	PHz	Valence Electron Transitions	UV/Vis Spectroscopy
Far UV – X-ray	PHz	Core Electron Transitions	XUV – X-ray Spectroscopy
Gamma Ray	EHz	Nuclear Transitions	Mössbauer Spectroscopy

Photon Energy Units

Different units for light quanta energy are used for different experiments.

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

1 eV = 8065.6 cm^{-1}

1 eV = 1.602 x 10^{-19} J

1 eV = 241.8 THz

1 eV = 1239 nm

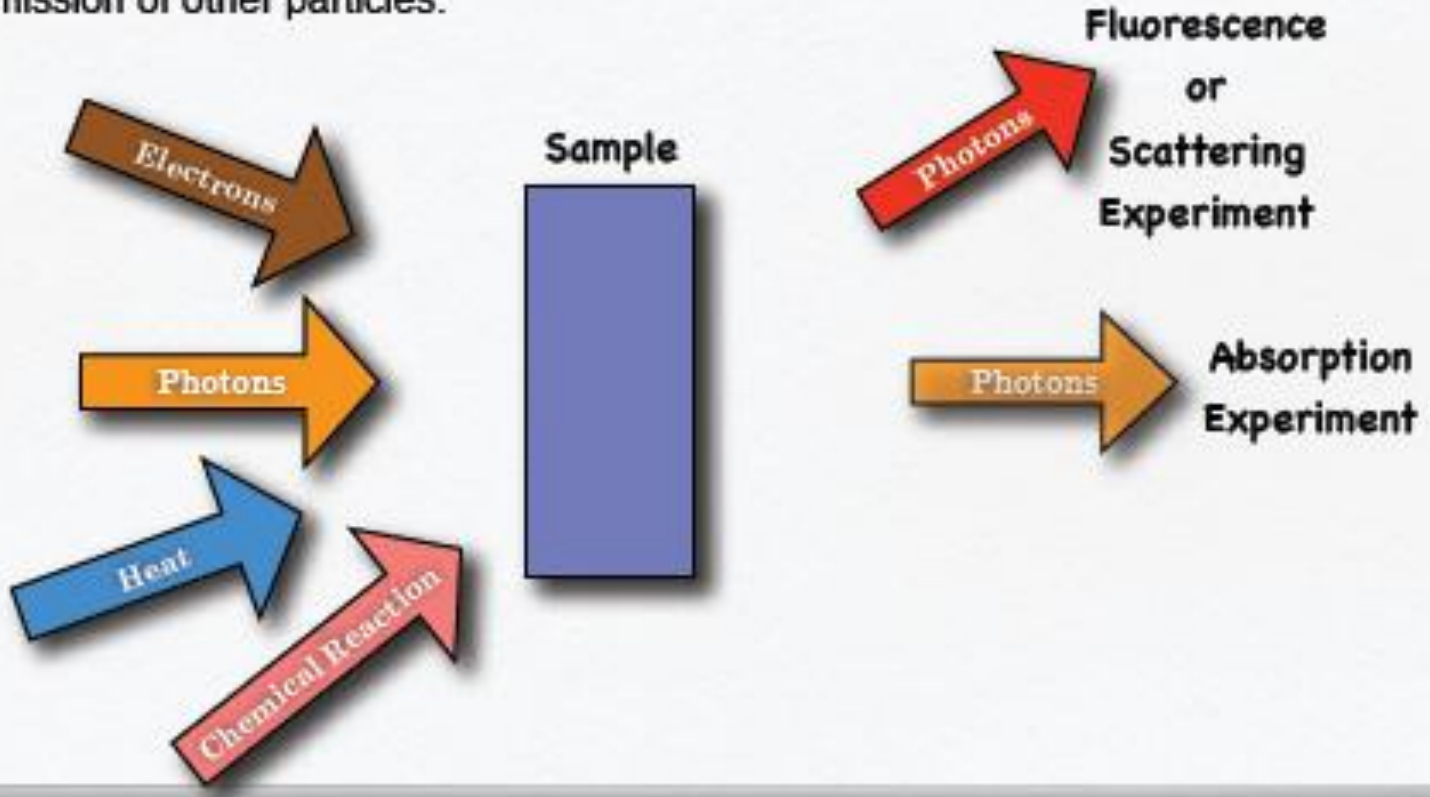
Correspondence between different units used in spectroscopy.

MHz	NMR
GHz	ESR
cm^{-1}	IR
eV, nm	UV-Visible
eV, Å	Far UV/X-ray

Units used in different spectroscopic experiments or regions.

Spectroscopic Experimental Concept

Spectroscopic experiments involve probing a system with some particles so as to disturb its equilibrium and then monitor its response by observing the emission of other particles.

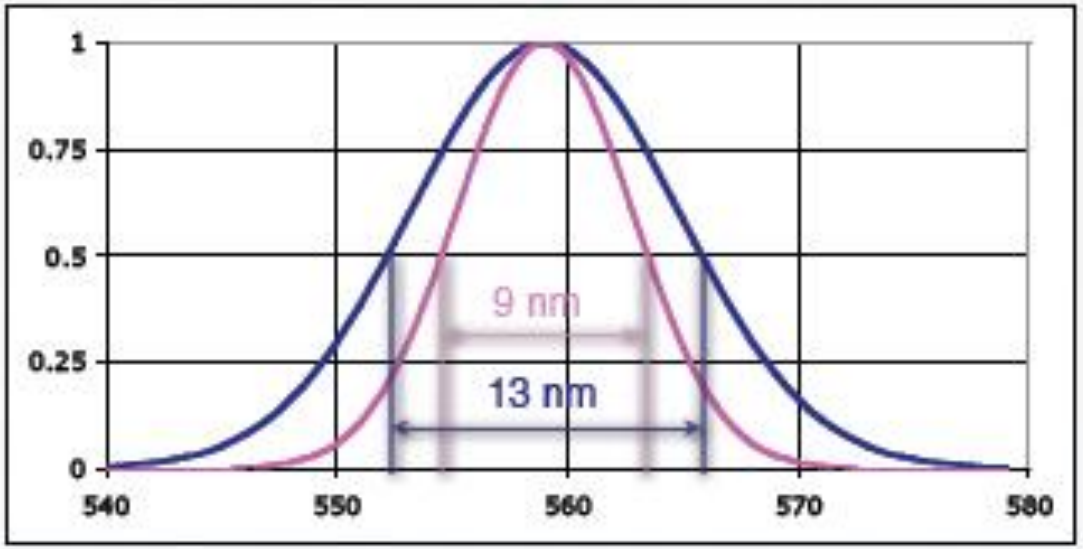


Spectral Bandwidth

Radiation emission is distributed over a certain wavelength range in a close-to-gaussian manner. Two defining parameters:

- Peak position
- Full Width at Half-Maximum (FWHM)

Peak at 559 nm for both curves.



The Spectrometer

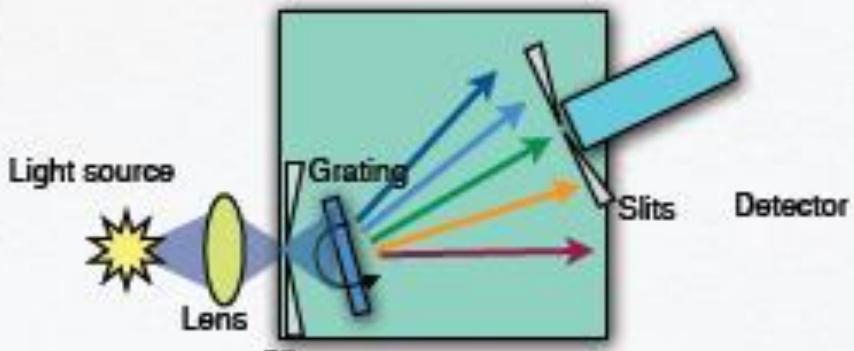
Spectroscopy infers the analysis of the distribution of radiant power by wavelength. Spectrometers separate the various spectral components into the spectrum.

Generally we can categorize different spectrometers based upon the way they deal with the spectrum.

- Broadband radiation from which one selects a monochromatic band
  - Dispersive spectrometers (diffraction gratings, prisms)
  - Non-Dispersive spectrometers (filters, Fourier transform)
- Narrow emission lines
  - Coherent sources (lasers, synchrotrons)
  - Incoherent sources (atomic lamps)

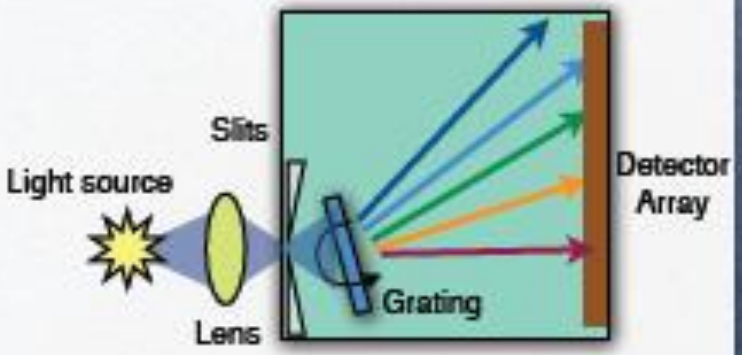
Dispersive Spectrometers

Measure one wavelength at a time. A serial detection scheme.



Monochromators.

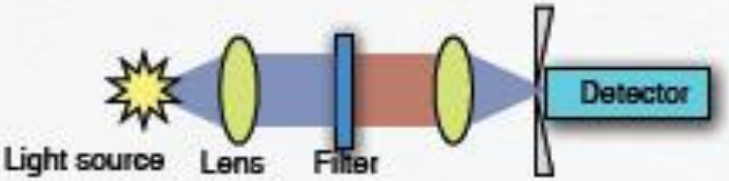
Array Detectors



Measure a large range of wavelengths simultaneously. A parallel detection scheme.

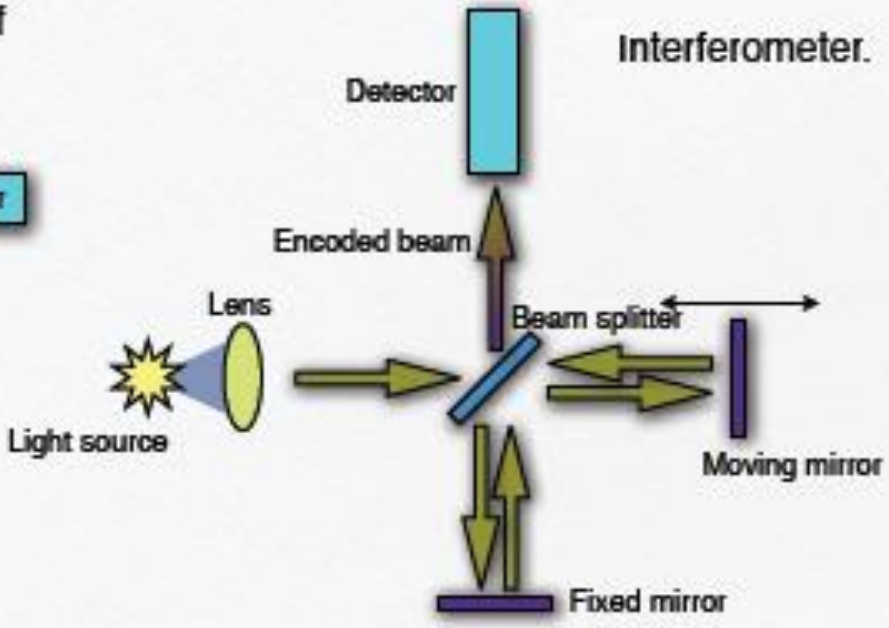
Non-dispersive Spectrometers

Good to detect a single band of wavelengths.



Filter-selecting spectrometer

Interferometer.



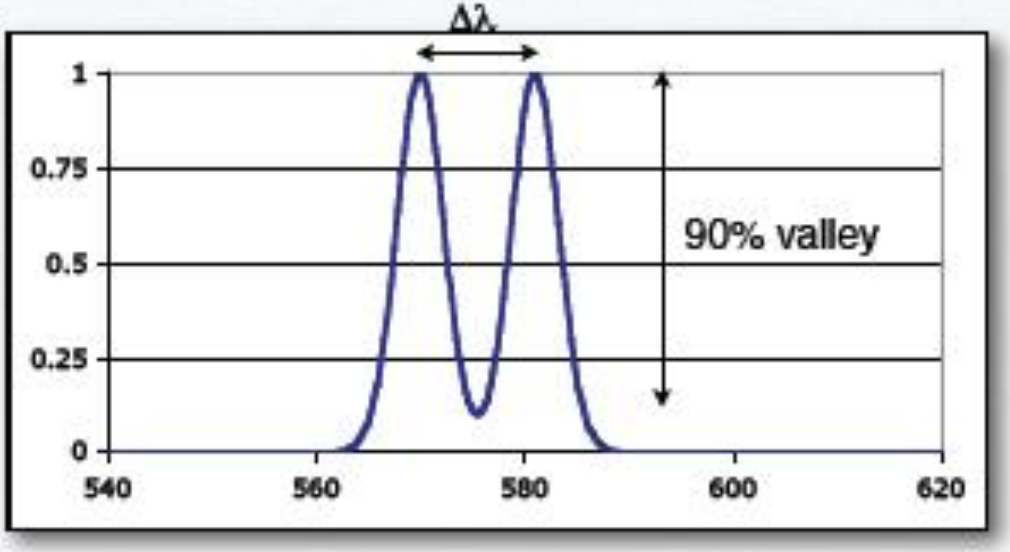
Encodes spectral data into time domain. Many advantages.

Spectral Resolution

When are two different colours really "different?

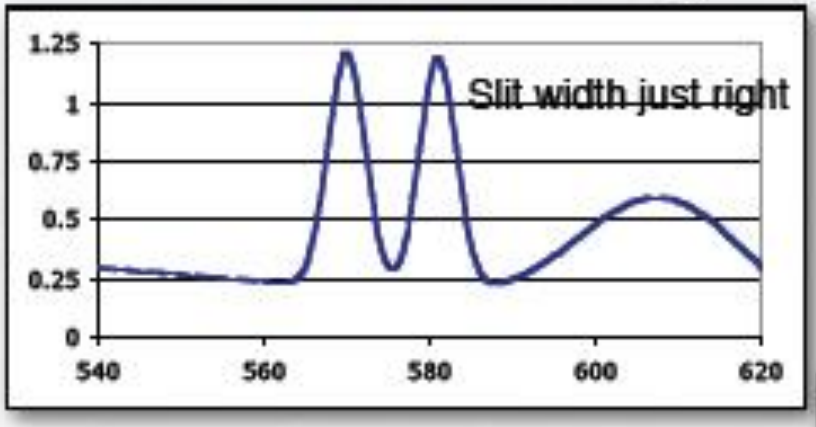
The resolution if any spectral feature can be quantified by the peak separation and the valley depth.

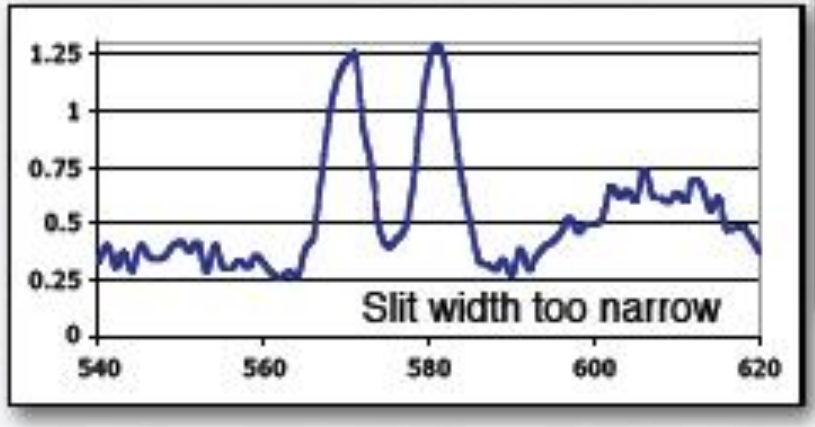
Two peaks are commonly said to have been resolved if the valley between them is 20%.

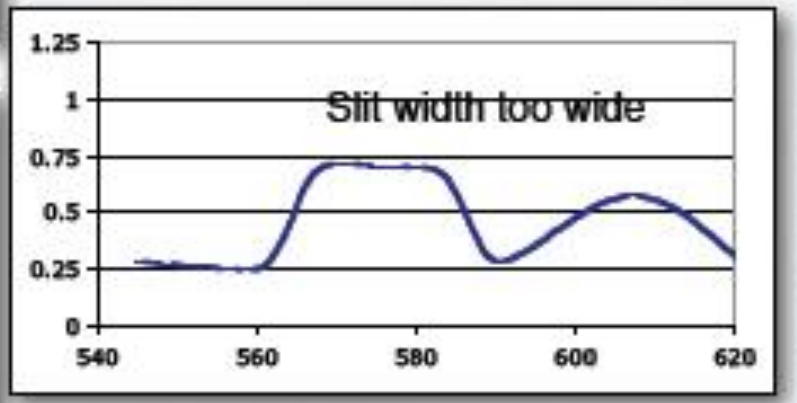


Resolving power is an instrument-specific measure: report as $\lambda/\Delta\lambda$.

Measuring a Spectrum







Spectrometric Experiments

Three general classes of spectrometric experiments:

- Light Scattering
  - photon momentum not conserved
  - measure particles size
  - identify molecules
- Emission
  - photons generated by sample
  - quantify through atomic
- Absorption
  - photons absorbed by sample
  - identify and quantity molecules

Scattering Experiments

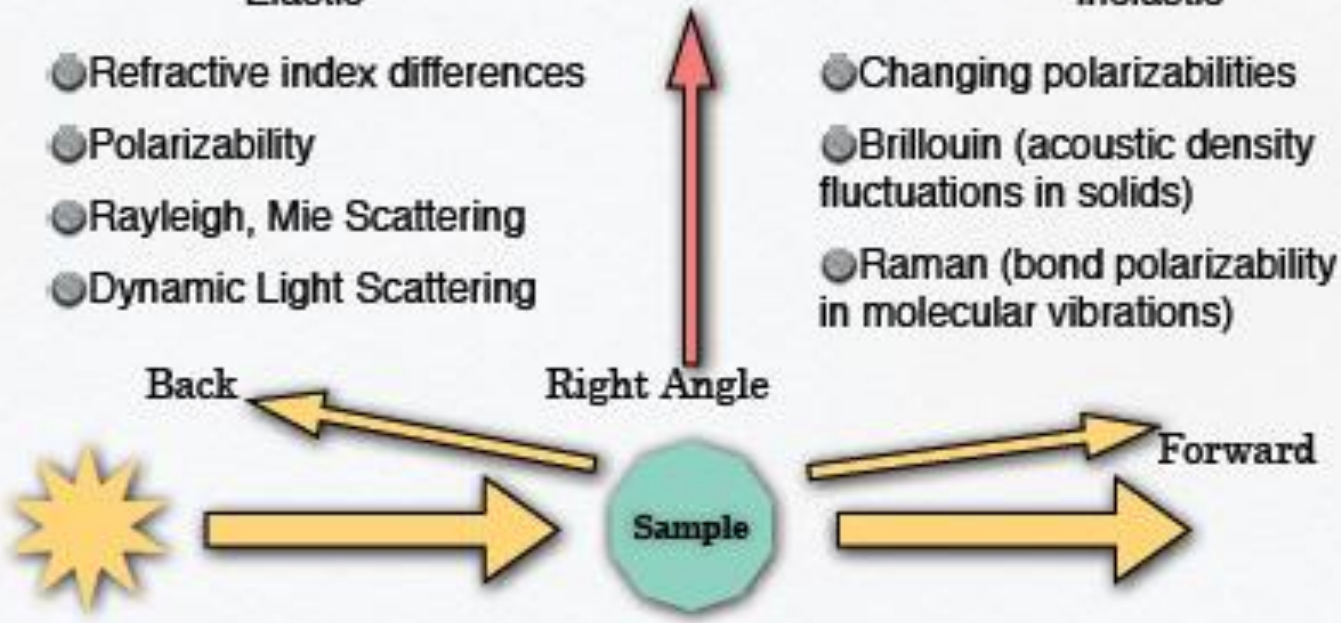
There are two types of light scattering experiments: Elastic, in which the energy of the photon does not change but its direction or momentum does, and Inelastic, in which the photon energy changes.

Elastic

- Refractive index differences
- Polarizability
- Rayleigh, Mie Scattering
- Dynamic Light Scattering

Inelastic

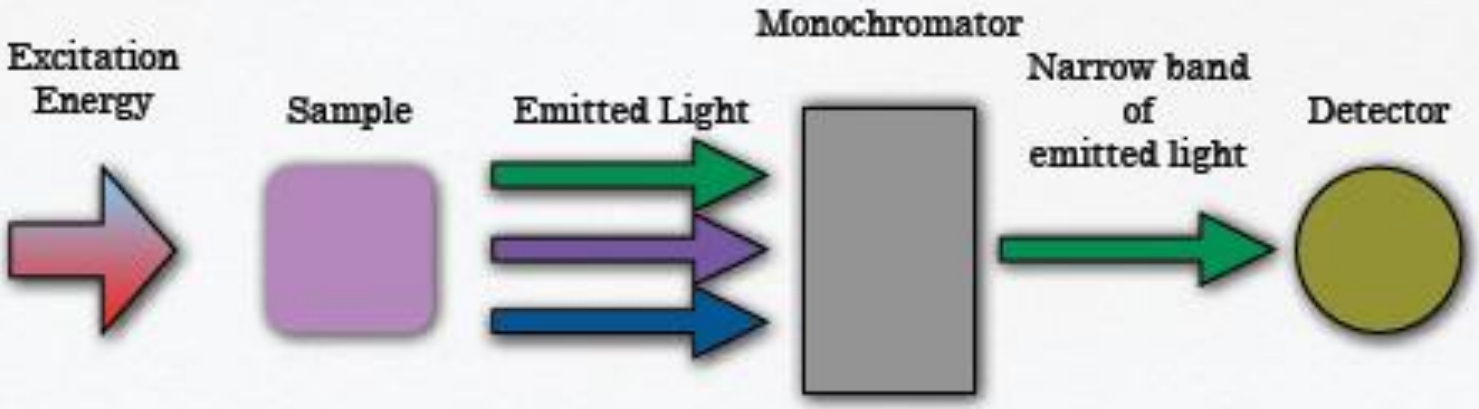
- Changing polarizabilities
- Brillouin (acoustic density fluctuations in solids)
- Raman (bond polarizability changes in molecular vibrations)



Emission Experiments

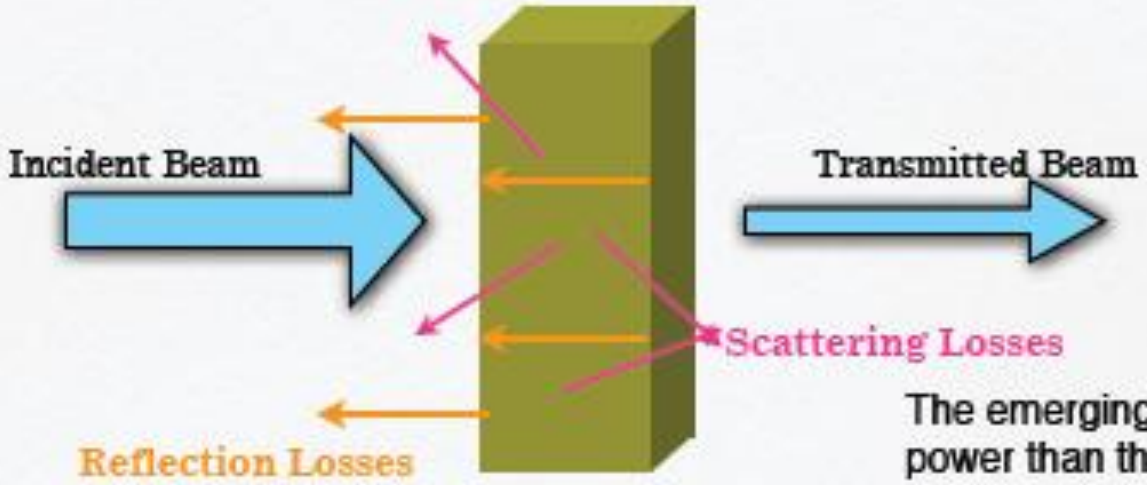
In these experiments, a sample is excited by injecting energy (heat, light, electrons, etc.). The sample relaxes by the emission of light and this light is analyzed.

- Arc Discharge
- Inductively Coupled Plasma (ICP)
- Fluorescence and Phosphorescence
- Energy-Dispersive (EDX) and Wavelength Dispersive (WDX) X-Ray Spectroscopy



Absorption Experiments

In this case, an incident beam impinges upon a sample and the light passes through it is monitored for its decrease in power due to absorption by the sample. Widely used for sample analysis.



The emerging beam has less power than the incident beam because of the absorption process of interest and also due to various loss mechanisms, such as scattering and reflection.

Absorbance or Transmittance

The absorption process is measured in one of two ways:

- Transmittance: $T = P/P_0$
- Absorbance: $A = -\log_{10} T = \log_{10} [P_0/P]$

In order to account for the numerous losses other than absorption, an experimental approximation to the above definitions is to measure P0 with a cell containing everything (solvent) except the analyte of interest. The expectation is that the losses will be the same in both sample and reference cells, thereby canceling the effect in both. This approximation is acceptable and constitutes our working definition for A and T.

- Transmittance: $T = P_{sample}/P_{reference}$
- Absorbance: $A = \log_{10} [P_{reference}/P_{sample}]$

Note that the sample and reference switch places in the definitions. THis makes T a number between 0 and 1 (the transmitted beam is always weaker than the incident beam) and A a positive number.

Beer's Law

Model the absorption process by assuming each absorbing molecule has a a cross-section within which a photon will absorbed if it reaches it. The proportion of the power absorbed from the beam is equal to the proportion of the absorbing cross-section to the total cross-section of the beam. When this relation is solved, it leads to the well-known Beer's Law or more completely the Beer-Lambert Law.

$$A = \log_{10}[P_0/P] = \varepsilon bc$$

concentration

path length

molar absorptivity (molar extinction coefficient)

A spectroscopic experiment because ε depends upon wavelength and so the absorbance is wavelength dependent too.

Absorbance adds in a multicomponent system (assuming no interaction between the components).

Transmittance is the property measured in an experiment but absorbance is the property directly related to concentration.

Limitation's to Beer's Law

Is the absorbance *really* linear with respect to the variables?

Path length (b): Essentially this is always found to be linear.

Concentration (c): Nonlinearity can arise from

- Intermolecular interactions
- Shifting chemical equilibria

Molar absorptivity (ε): Non-linearity can arise from the solution's index of refraction.

The instrument itself can skew the behaviour away from linearity in a number of ways.

Intermolecular Interactions

Beer's Law is strictly a limiting law for dilute solutions.

At high concentrations (=> 0.01 M) the average distance between analyte molecules is small enough that the charge distributions around one affects that around another.

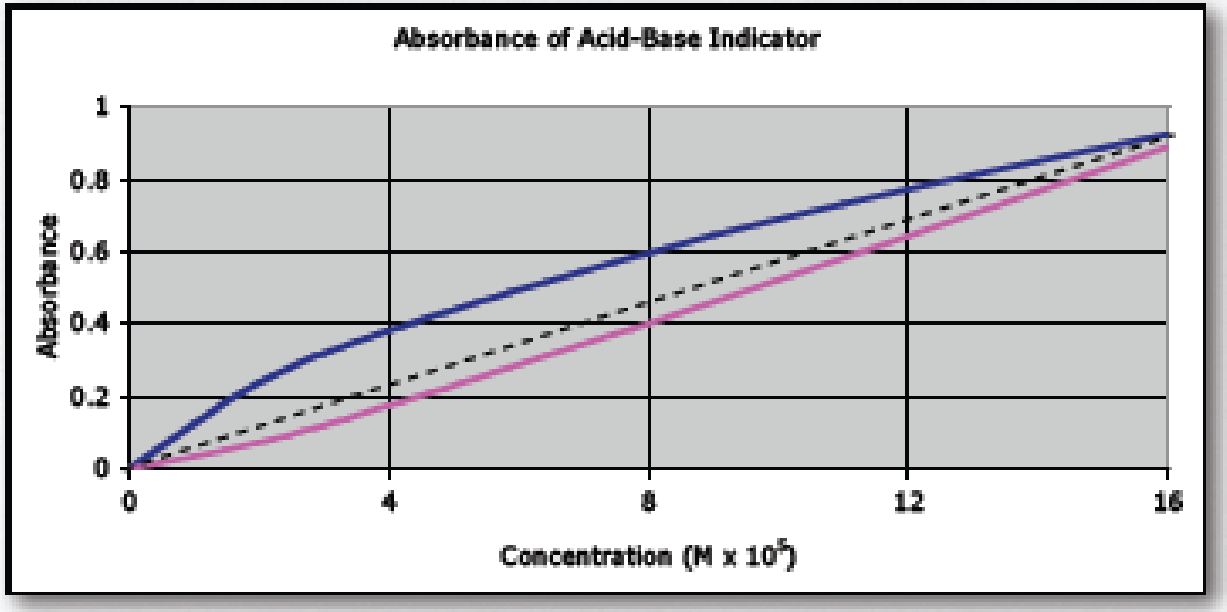
Sometimes high concentrations of inert electrolytes can themselves alter the absorptivity of a species present even at low concentrations.

Some organic molecules can show deviations even at 10^{-6} M concentrations

Need to be aware of concentration linearity and confirm its validity in a given experiment.

Chemical Equilibrium

When a substance is involved in a chemical reaction, the extent of that reaction is concentration dependent. If the alternate form of the molecule has a different absorption spectrum, there will be non-linear distortion away from Beer's Law.



Example: An indicator dye with $K_a = 1.42 \times 10^{-5}$. Absorbance is measured at two wavelengths (430 and 570 nm), Note the curvature in the plots.

Index of Refraction

The molar absorptivity depends upon the index of refraction of the solution. In some cases, the index of refraction can change with concentration.

Use an expression for molar absorptivity ε which is dependent upon the index of refraction. Often this is approximated by the expression

$$\varepsilon(n) = \varepsilon[n/(n^2 + 2)^2]$$

When a concentration change causes a significant change in the refractive index, then this can cause a deviation in Beer's Law away from linearity. In practice, this correction is never very large and is rarely significant at concentrations below 0.01 M.

Polychromatic Radiation

Beer's Law is strictly applicable only for monochromatic radiation.

All excitation sources have a non-zero bandwidth.

Analyte will have a different absorptivity at each wavelength. If variation is large, then the non-linearity can be observed.

Remedy:

- Choose a spectral range where the absorptivity changes slowly with wavelength.
- Select an excitation radiation bandwidth that is <0.1 of the analyte's spectral FWHM.

Photometric Accuracy

Experimental noise leads to an uncertainty in determining absorbance.

Partial differentiation leads to a relationship between error in T and error in A.

$$\Delta A = -\left(\log_{10} e\right)\frac{1}{T}\,\Delta T$$

This error in absorbance naturally is connected to an error in concentration.

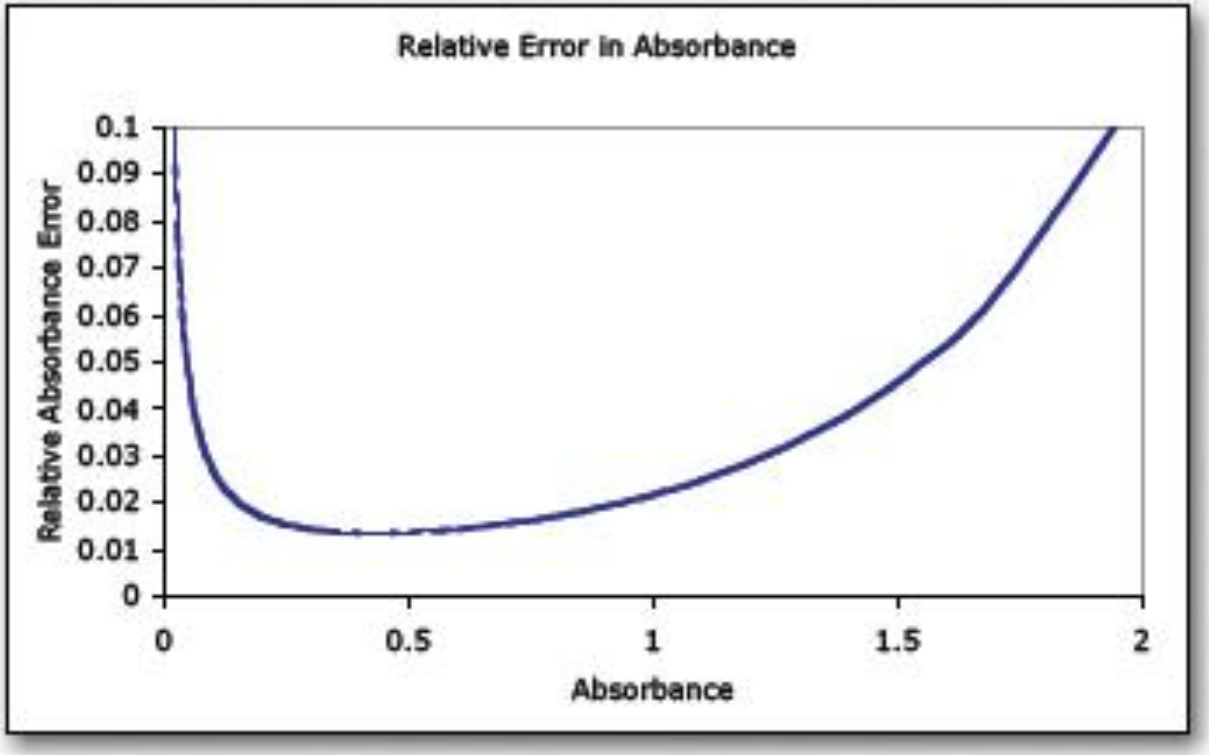
Partial differentiation of Beer's Law leads to the relationship

$$\Delta c = \frac{1}{\varepsilon b}\,\Delta A = -\left(\log_{10} e\right)\frac{1}{\varepsilon b T}\,\Delta T$$

Error in A

Assume a fixed relative T error of 0.5% (0.005).

Absorbance measurements between A = 0.05 and A = 1.55 keeps the A error <5%.



T Error Depends Upon T

A careful analysis of the problem shows that different noise sources will contribute differently to T error. Three general cases have been identified:

(1) T error is constant

- Limited readout resolution. Thermal detector (Johnson noise). Dark current and amplifier noise.

(2) T error varies as $(T^2 + T)^{1/2}$

- Shot noise

(3) T error varies as T

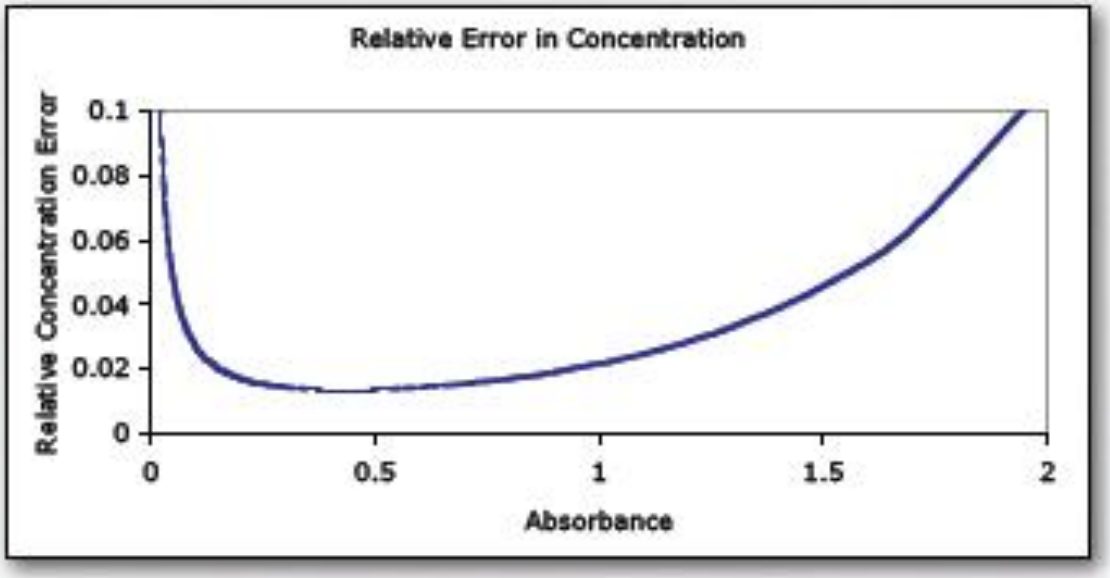
- Cell positioning uncertainty
- Source 1/f noise

Constant Error in T

Arises in inexpensive spectrometers which suffer from limited readout resolution.

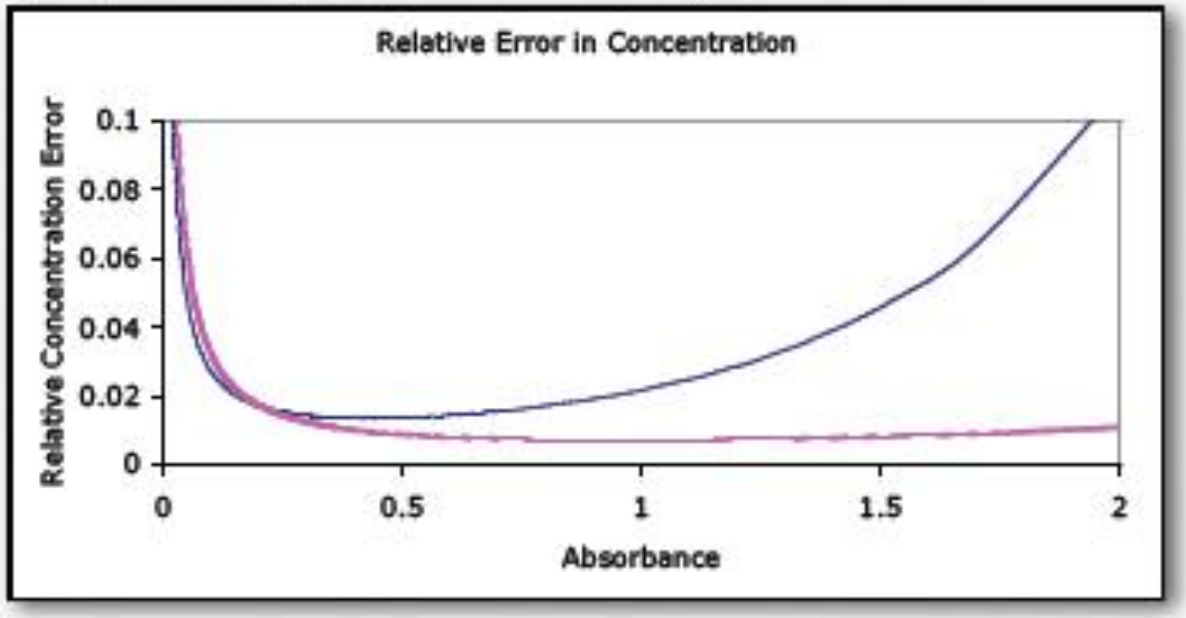
IR spectrometers will be subject to Johnson noise.

Experiments where source intensity is low or detector sensitivity is low will be limited by dark current and amplifier noise.



$\text{Error} \propto (T^2 + T)^{1/2}$

High quality UV/Vis spectrometers are susceptible to this case.

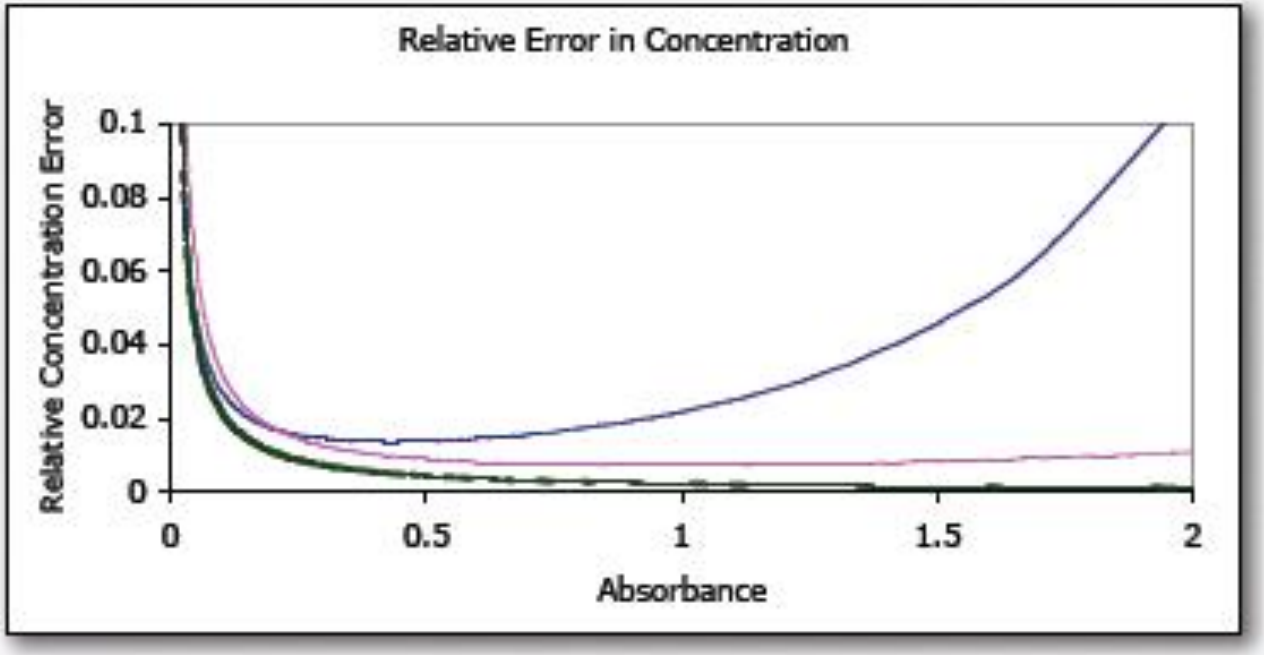


Note how this process allows us to make measurements out to much higher absorbances. This can be done with high quality instruments. Need to be careful, however, that another error source doesn't start to dominate.

Error ∝ T

High quality UV/Vis and IR spectrometers will be subject to cell positioning errors.

Inexpensive IR spectrometers will be subject to flicker noise.



Choose Absorbance Range Carefully

The take-home message here is that just because a machine gives you a number, doesn't mean you have to believe it. When making spectrometric measurements, you need to adjust the concentration of the sample so that the absorbance range covered falls in the region which will minimize the instrumental error.

Absorbance range between $A = 0.1$ and $A = 1$ should give reliable results with almost all instruments.

Good spectrometers can make absorbance measurements down to $A = 2$.

Only the very best can make measurements beyond $A = 3$.

Slit Width Affects Absorbance Measurements

If a significant variation in absorptivity occurs over the spectral bandwidth admitted by the slot, a non-linear variation (non-Beer's Law) with concentration will be observed.

This arises because the spectrometer measures the average transmissivity over the spectral bandwidth, but transmissivity and concentration are not linearly related.

Keep slit width large to increase S/N ratio but must keep it small enough to maintain a linear relationship with concentration changes.

This effect is minimized if the absorptivity changes slowly with wavelength. Select a wavelength near a peak maximum. Use a slit width to provide a bandwidth that is about 1/10 of the spectral feature's width.

Other Problems

Stray Light: it is a problem when working at the limits of a spectrometer's range.

Cells and Solvents: everything besides the analyte should be as transparent as possible.

Sample Preparation: if two samples are prepared so that one carries along a greater concentration of insoluble particulates, then additional scattering will lead to an apparent greater absorption.