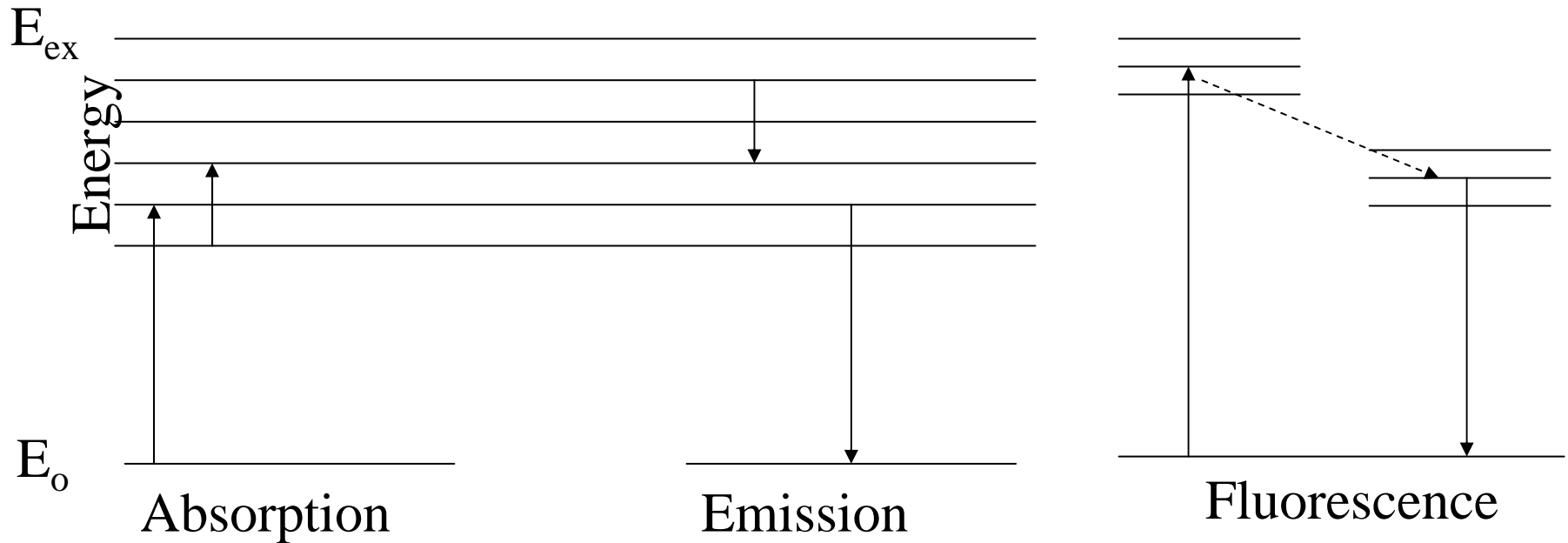


Review

Nine properties of electromagnetic radiation

- **Diffraction**
- **Refraction**
- **Dispersion**
- **Reflection**
- **Scattering**
- **Polarization**
- **Transmission**
- **Absorption**
- **Emission**

- **Absorption:** atom or molecule “absorbs” a photon of specific energy, goes to a higher energy state
- **Emission:** atom or molecule releases a photon of specific energy, goes to a lower energy state; nonradiative excitation
- **Fluorescence:** absorption followed by re-emission



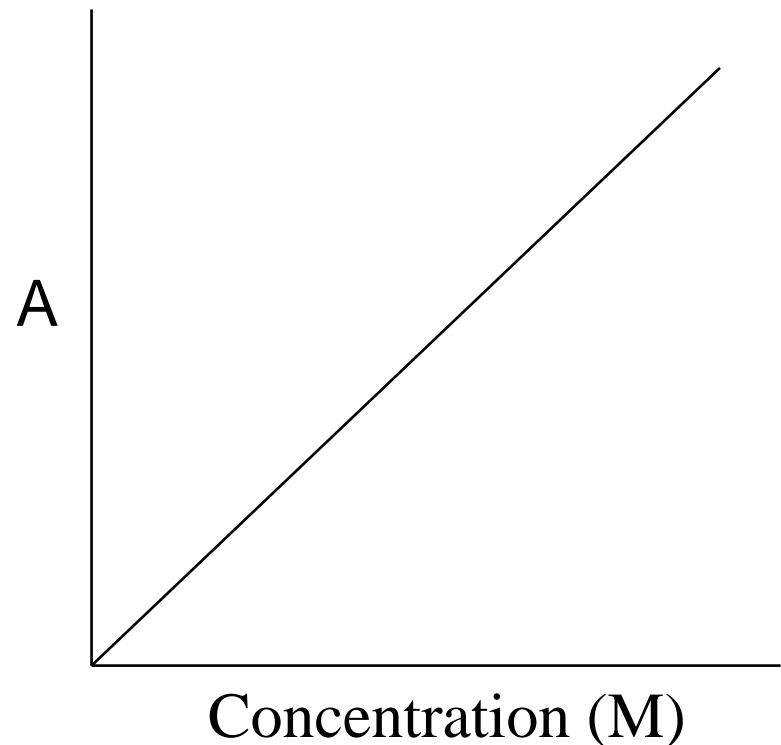
Absorption Methods, Beer's Law

$$A = \epsilon bc$$

$b \Rightarrow$ path length (cm)

$c \Rightarrow$ concentration (M)

$\epsilon \Rightarrow$ molar absorptivity
($M^{-1}cm^{-1}$)



Question 1.

Which of the following relationships between absorbance and % Transmittance is **incorrect** ?

- a) $A = -\log_{10} T$
- b) $A = 2 - \log_{10} T$
- c) $A = \log_{10} T$

Question 2.

In the equation, $A = \epsilon bc$, what quantity is represented by " ϵ " ?

- a) Absorbitivity
- b) Molar absorbitivity
- c) Path length

Question 3.

Why is it generally preferable to use absorbance as a measure of absorption rather than % Transmittance?

- a) Because %T cannot be measured as accurately as absorbance
- b) Because %T is dependant on the power of the incident radiation
- c) Because absorbance is proportional to the concentration of the analyte, whereas %T is not.

Question 4.

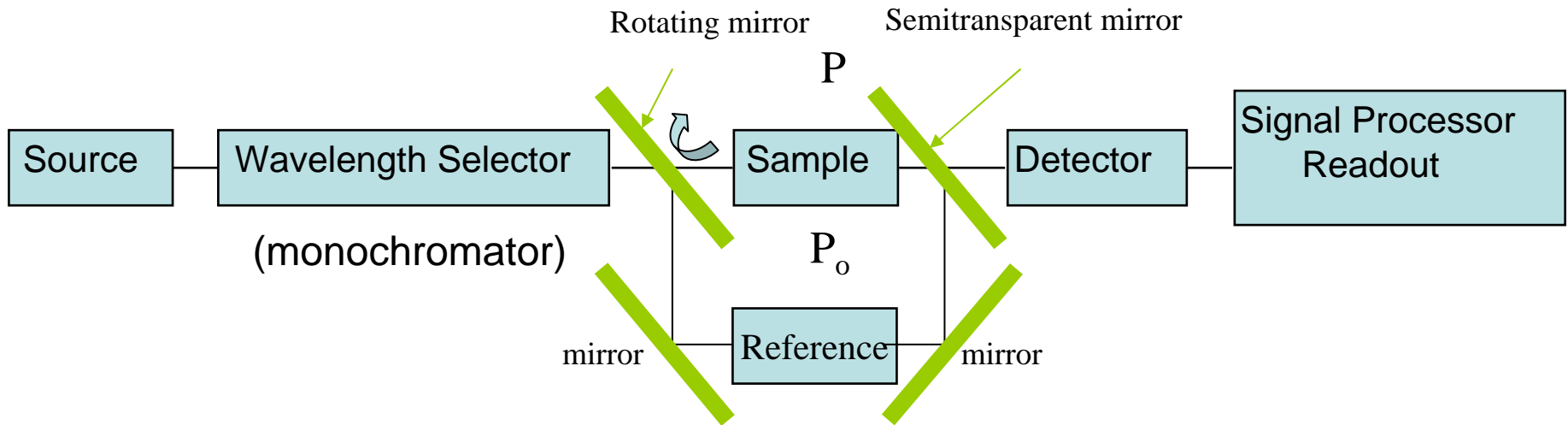
Does a compound with high molar absorbitivity have a higher or lower limit of detection than a compound with low molar absorbitivity?

Beer's law problem

A 3.96×10^{-4} M solution of compound A has an absorbance of 0.624 at 238 nm in a 1.0 cm cuvet. A blank solution containing only solvent had an absorbance of 0.029 at the same wavelength.

- a) What is the molar absorptivity of compound A?
- b) The absorbance of an unknown solution of compound A in the same solvent and cuvet was 0.375 at 238 nm. Find the concentration of A in the unknown solution.
- c) A concentrated solution of compound A in the same solvent was diluted from an initial volume of 2.0 mL to a final volume of 25.0 mL. The diluted solution had an absorbance of 0.733. What is the concentration of A in the concentrated solution?

Components of Optical Instruments



Noise

- Unwanted component of the measured signal that affects and limits measurements of the chemically relevant signal component
- The absolute magnitude of noise may not be important; however, the **signal-to-noise ratio (S/N)** is critical!
- Improving the S/N is critical in some measurements

$$S/N = (\textit{magnitude of signal}) / (\textit{magnitude of noise})$$

The **S/N** gets lower as one approaches the detection limit. Some methods of determining the LOD are based upon detection limit, e.g. **S/N = 2** at the detection limit.

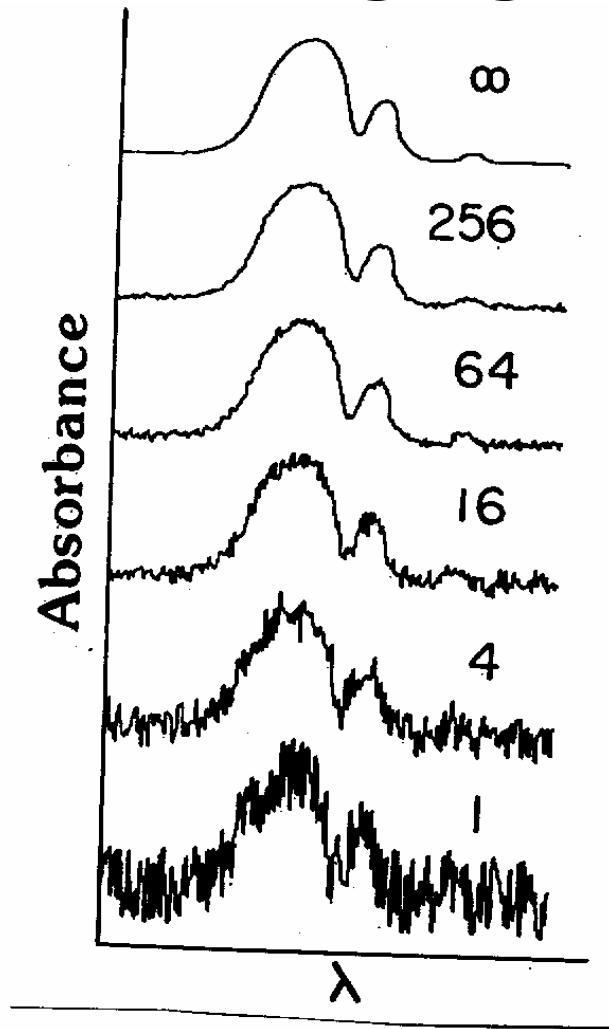
How to improve the S/N:

- Improve background (sample matrix, electronics, detector, etc.)
- Signal average multiple measurements

S/N improves as \sqrt{n}

(where n is the number of measurements)

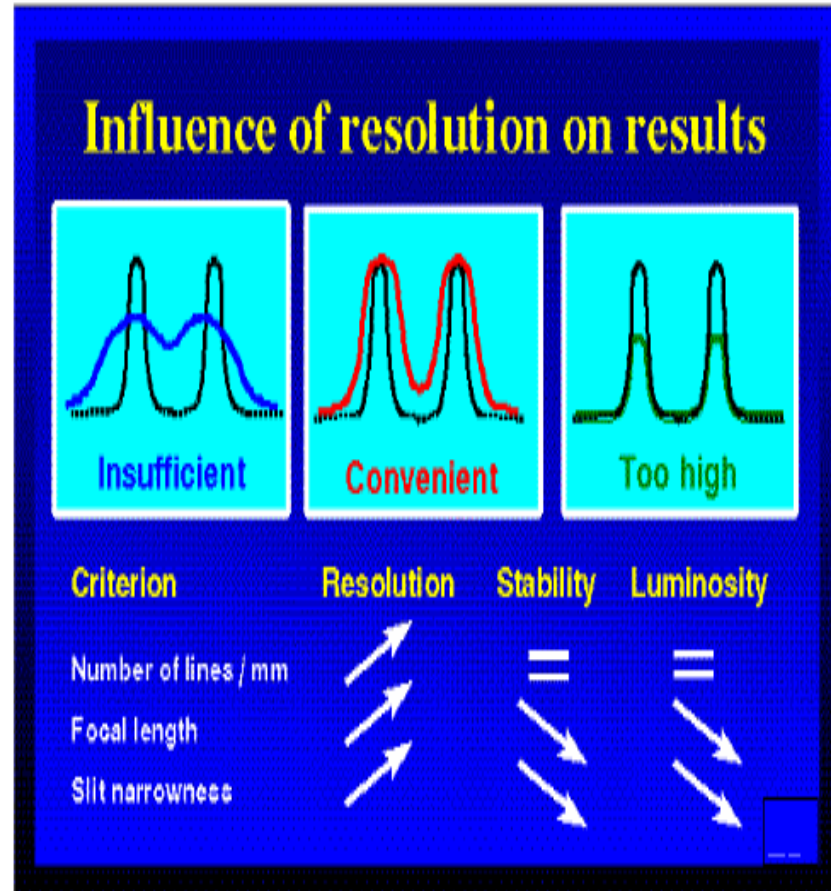
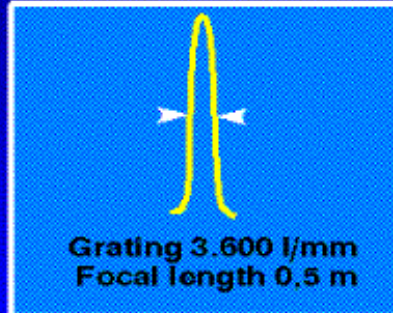
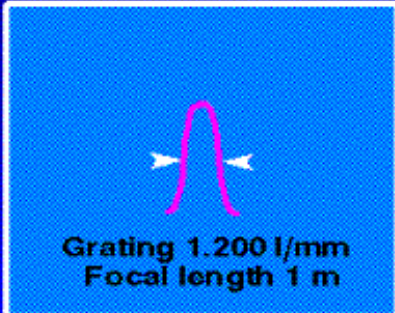
Example of S/N improvement by signal averaging



Resolution of the spectrum

Resolving power of the spectrometer

- Resolving power = $\lambda / \Delta \lambda$
- Resolving power is influenced by design - number of grooves/mm,



Oximetry – measurement of O₂ content

Small instrument based on the color difference of oxygenated blood (bright red) and deoxygenated blood (dark red, almost purple).

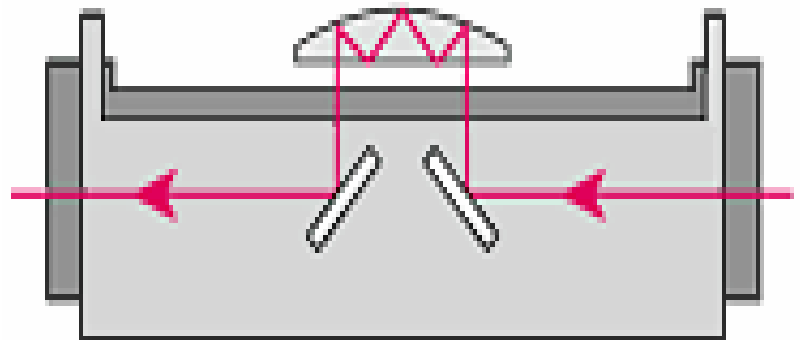
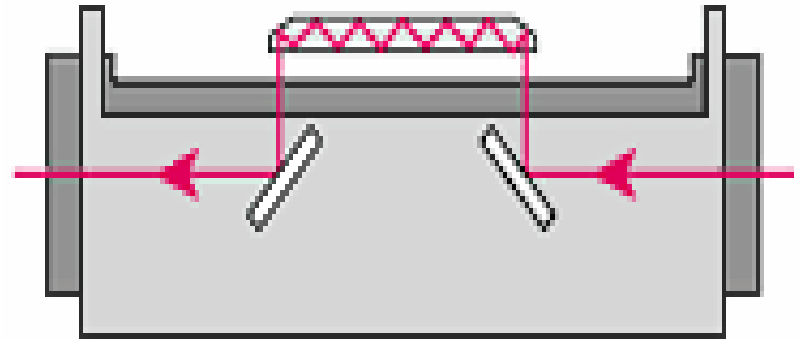
Absorption spectroscopy used to quantitatively determine O₂ in blood quickly.



<http://www.avweb.com/articles/oximeter.html>

Attenuated total reflectance IR Spectroscopy

- The beam is confined to an “ATR” crystal (ZnSe is common for IR).
- Sample is coated on the surface
- If the sample absorbs light, the transmitted light beam is attenuated
- Diamond ATR crystal allows for analysis of very “hard” samples



<http://www.nicolet.com/>

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