

Why are things colored?

Electromagnetic radiation is characterized by its wavelength and its intensity. The range of wavelengths humans can perceive, approximately from 390 nm to 750 nm, is known as "visible light".

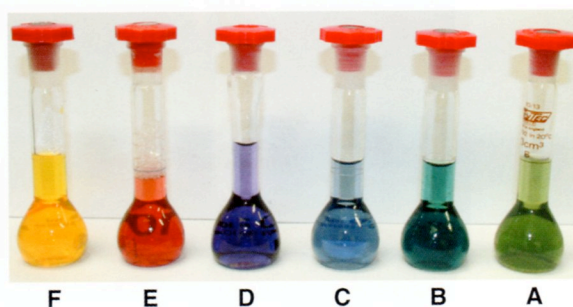
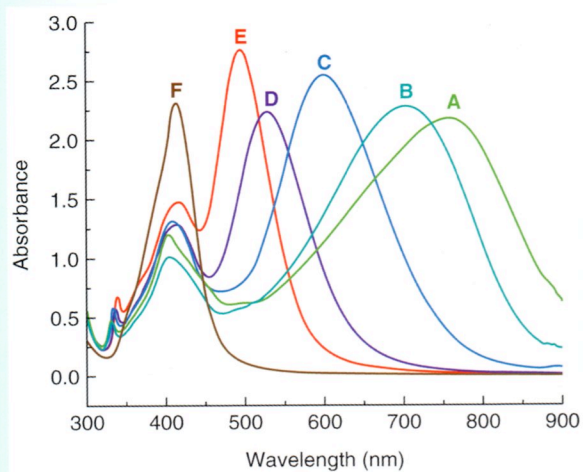
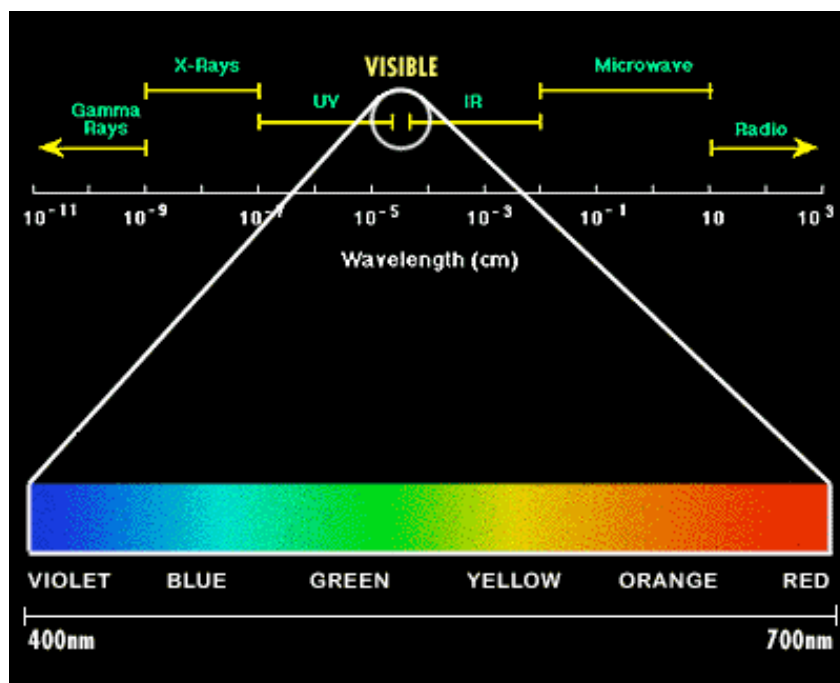
color	wavelength interval
red	~ 700–635 nm
orange	~ 635–590 nm
yellow	~ 590–560 nm
green	~ 560–490 nm
blue	~ 490–450 nm
violet	~ 450–400 nm

Color of objects

Light arriving at a surface is either reflected/scattered or absorbed.

White - reflected/scattered all wavelengths across the visible spectrum

Black - absorbed all of wavelengths across the visible spectrum

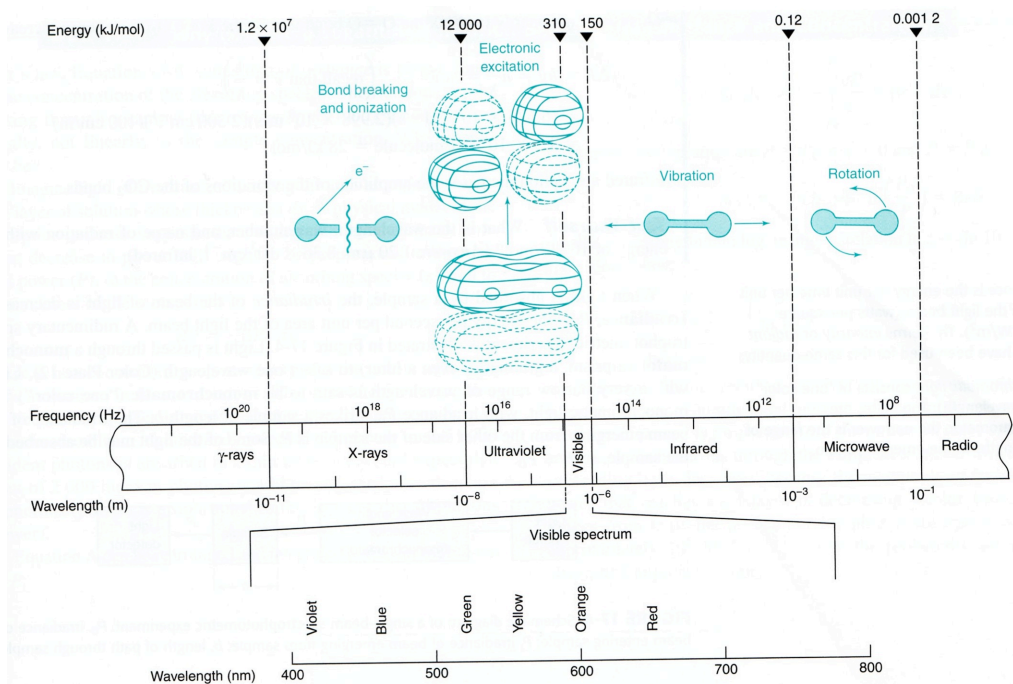


Color Plate 15 Absorption Spectra and Color (Section 17-2 and Problem 17-9) Flasks contain suspensions of silver nanoparticles whose color depends on the size and shape of the particles, which are approximately triangular plates with edge lengths of ~50–100 nm. The visible absorption spectrum of each suspension is shown in the graph. Stable suspensions of nanoparticles are called *colloids* (Demonstration 26-1). [From D. M. Ledwith, A. M. Whelan, and J. M. Kelly, *J. Mater. Chem.* **2007**, *17*, 2459. Courtesy J. M. Kelly and D. Ledwith, Trinity College, University of Dublin.]

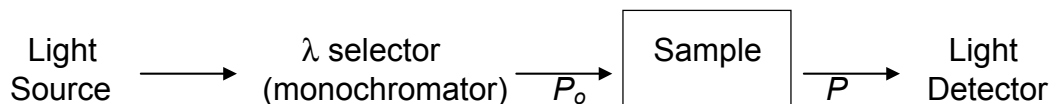
What happens what molecules absorb light? (Sec. 17-2, 17-6)

Absorption of photo leads to promotion to an excited state. The change in energy must match of the photo being absorbed:

$$\Delta E = h\nu = h \cdot c / \lambda$$



Obtaining Absorption Spectra (Figure 17-4):



Transmittance, T

$$T = P / P_o$$

- ratio of light intensity after/before passing through sample (0 - 100 %)

Absorbance, A

$$A = \log (P_o / P) \quad \text{or} \quad -\log T$$

Concentration of analyte is related to A

$$A = a b c \quad \text{(Beer's Law)}$$

a = molar absorptivity - how much does the analyte absorb at a given λ ?

b = path length

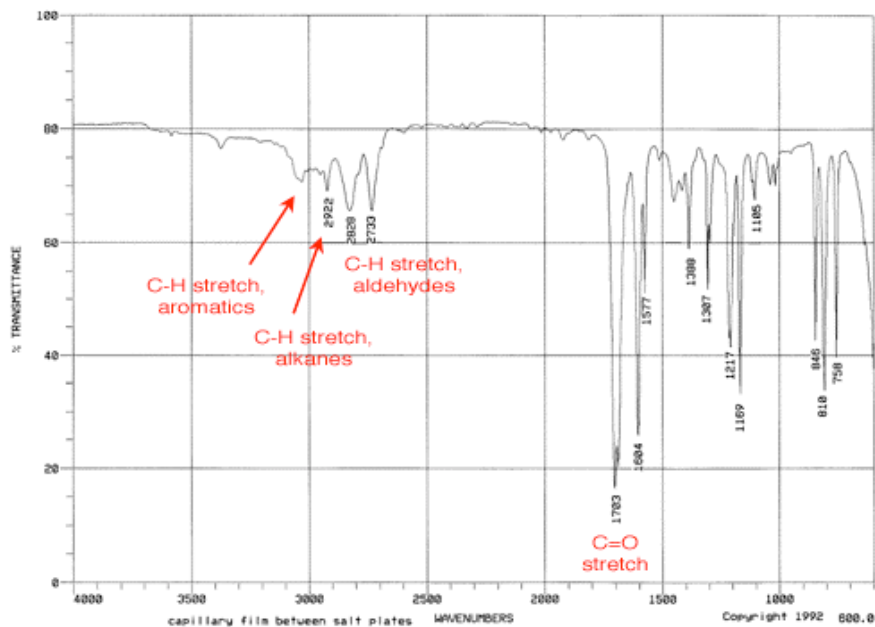
c = concentration

What can we learn from the *Beer's Law*:

1. absorptivity (a) is wavelength dependent, and it may be used for analyte identification
2. one can determine analyte concentration by measuring A (linear calibration plot); but A has to be measured one wavelength at a time.
3. A is proportional to the size (width) of curvet (sample holder)



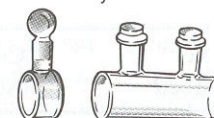
COLOR PLATE 13 Beer's Law (Section 19-2) $\text{Fe}(\text{phenanthroline})_3^{2+}$ standards for spectrophotometric analysis. Volumetric flasks contain $\text{Fe}(\text{phenanthroline})_3^{2+}$ with Fe concentrations ranging from 1 mg/L (left) to 10 mg/L (right). The absorbance, as evidenced by the intensity of the color, is proportional to the iron concentration.



Standard
1-cm path



Cylindrical



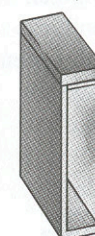
5-mm
path



1-mm
path



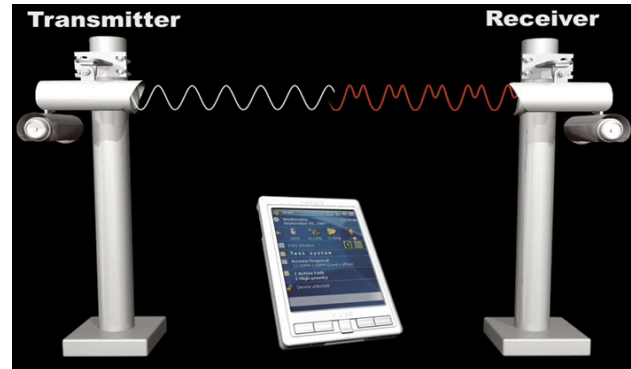
20-mm path



Taking advantage of long absorption path for enhanced sensitivity

Example:

Open path gas detectors with Enhanced Laser Diode Spectroscopy (ELDSTM) technology



At the heart of the ELDS technique is harmonic fingerprinting and real-time multiple wavelength signal integration. ELDS will detect low ppm level hydrocarbon gases.

Source:

<http://www.ngoilgasmerna.com/article/Innovations-in-line-of-site-gas-detection/>

Detectors (Sec. 19-3)

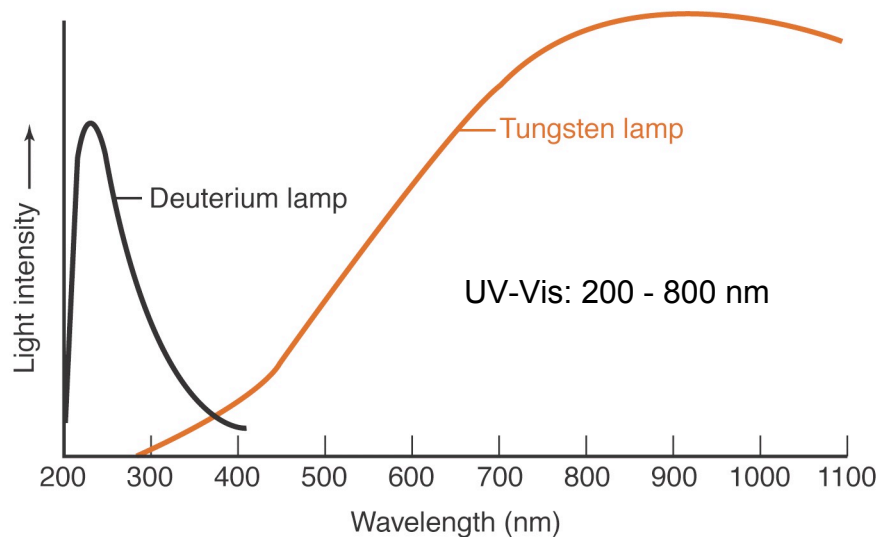
Detectors - produces electric signal when struck by photons.

Ideal Characteristics:

- electric signal linearly proportional to light intensity (dynamic range)
- constant response over a wide range of wavelength
- produces reliable signal at very low amount of light (sensitivity)
- signal is stable over time, and wavelength

UV-Visible Absorption Spectrometry

Sec. 19-1 Lamps: Sources of Light



Ideal characteristics:

- broad emission (all wavelength)
- strong intense
- constant intensity (time)
- constant intensity (over wavelength)

Sec. 17-3: Sample Holder

Cuvette – constant pathlength (b),
flat, optically transparent windows



UV/visible

1 mm – 5 cm, 1.0 cm typical
glass (visible), quartz (UV/vis)

IR
KBr

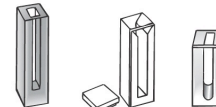
Standard
1-cm path



Cylindrical



Micro cells



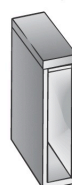
5-mm
path



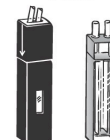
1-mm
path



20-mm path



Flow

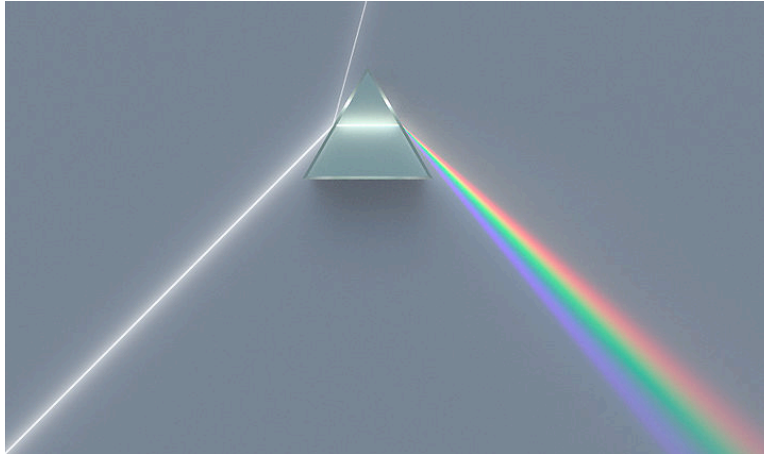


Thermal



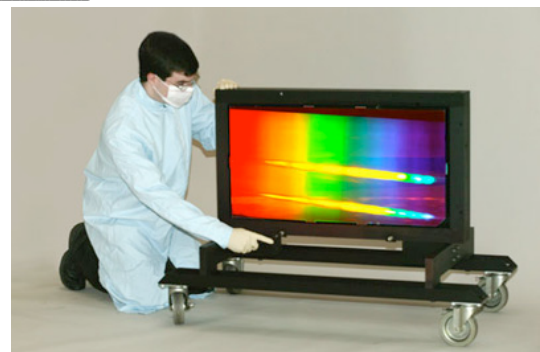
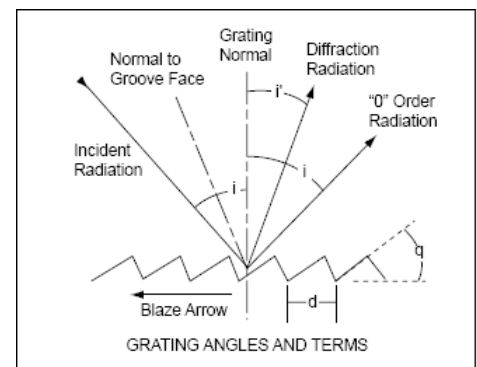
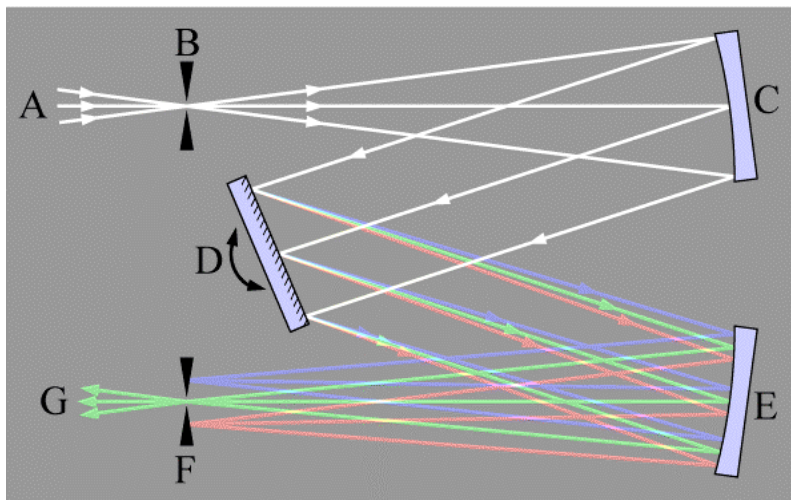
Monochromators (Sec. 19-2)

A monochromator is an optical device that transmits a mechanically selectable narrow band of wavelengths of light or other radiation chosen from a wider range of wavelengths available at the input.

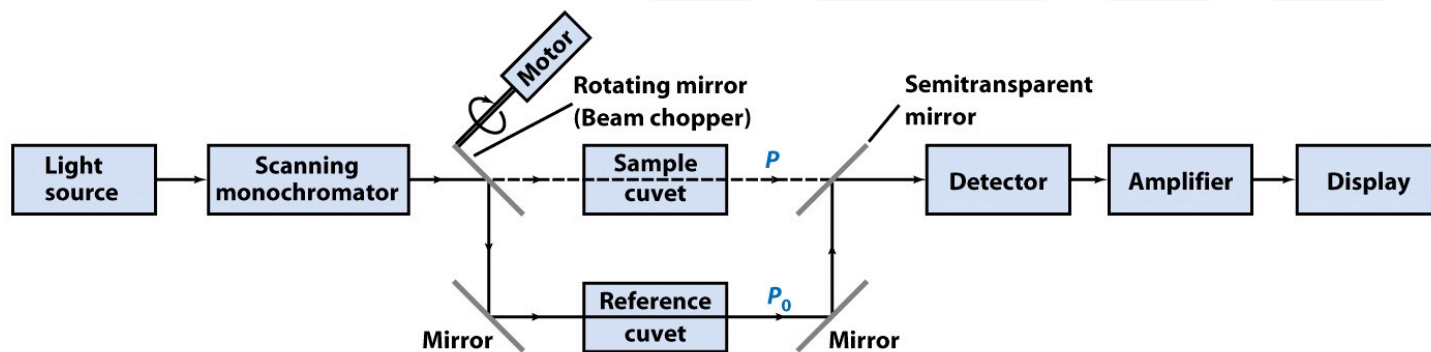
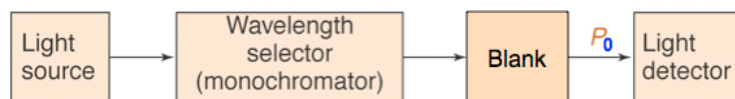
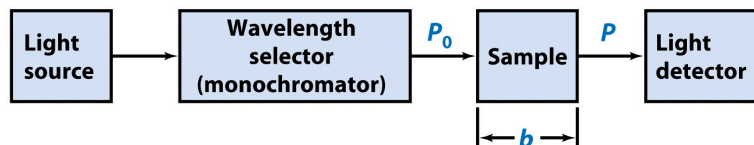


e.g., a prism is an example of monochromator (not used in modern instruments)

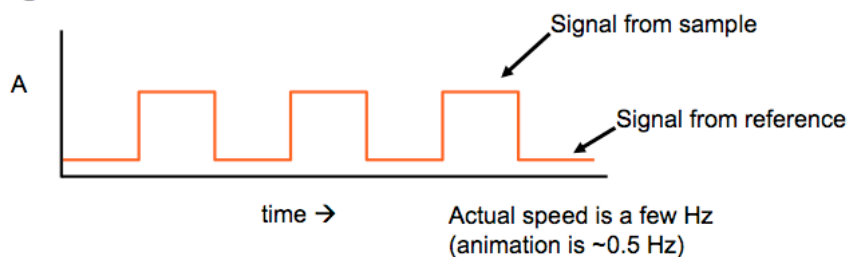
A modern monochromator based on *diffraction gratings* (D)



Single beam vs. double beam spectrophotometers (Ch. 19, p 445-447)



Signal at detector looks like:



Double Beam allows simultaneous measurement of sample and reference (blank).

Advantages:

- correct for slow instrument drift related to light intensity (time-lapsed measurement)
- minimize cell positioning imprecision (variable reflection condition can lower precision)

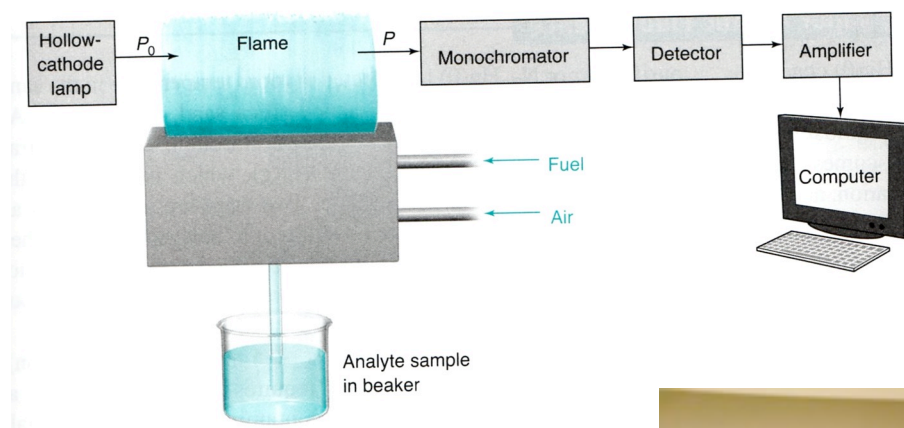
A good summary of spectrophotometry components:

http://www.chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Electronic_Spectroscopy/Electronic_Spectroscopy:_Application

Spectrophotometry: absorption, by molecules, UV-Vis, IR

Spectroscopy: not limited to absorption (emission, fluorescence), not limited to molecules (atoms), not limited to UV-Vis, IR (UV, x-ray)

Atomic Absorption Spectroscopy (Ch. 20)



Beer's Law applies for quantitative measurement:

$$A = a b c$$

Absorbance:

$$A = \log (P_0 / P)$$

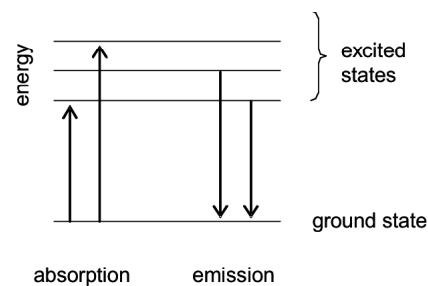
Analysis -

1. Blank measurement
2. Standardization with known concentration (Calibration)
3. Unknown measurement



Hollow cathode lamp (Sec. 20-4):

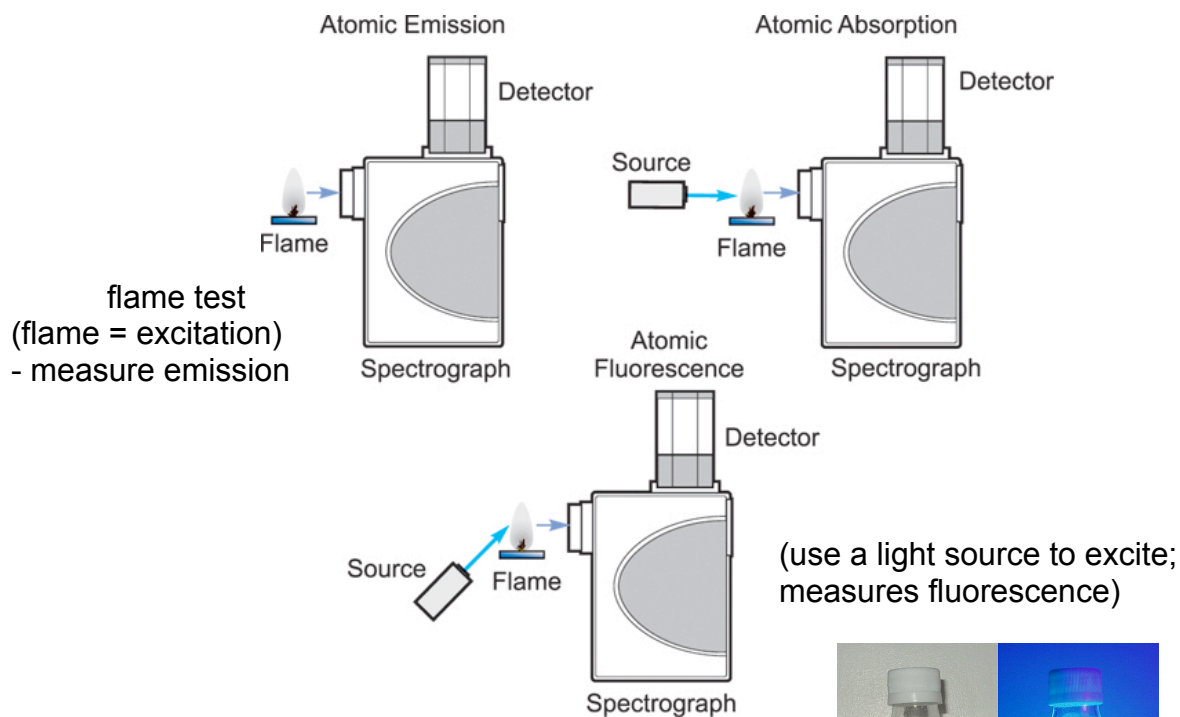
- contains the metal analyte
- match the HCL with metal analytes
- provides the exact λ required for atomic absorption



ΔE is characteristic of the metal atoms

Flame, atomization and burner (Sec. 20-2)

- the flame is a sample holder, analyte as gaseous atoms

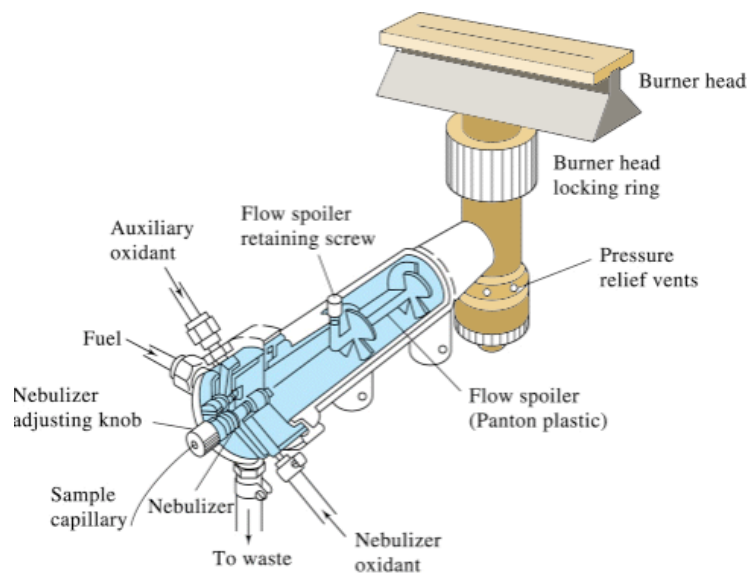


flame test
(flame = excitation)
- measure emission

(use a light source to excite;
measures fluorescence)



fluorescence



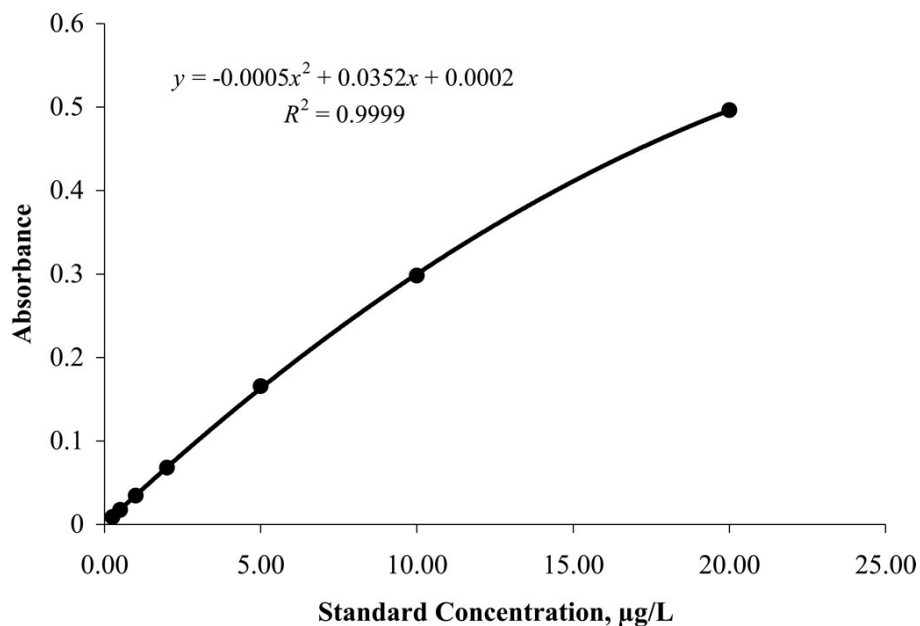
emission

Inside the burner:

solution → aerosol → evaporation → gaseous compound → gaseous metal atoms

Typical AAS Calibration Data:

Standard Solution μg/L	Absorbance
0.25	0.0088
0.50	0.0173
1.0	0.0344
2.0	0.0681
5.0	0.1658
10.0	0.2982
20.0	0.4964



- curvature is typically observed, caused by "stray light" (covered in Chem 3372)
- can be approximated as a straight line when limited to lower concentration range
- may require dilution of unknown solutions

More in Chem 3372:

- other sources of interferences in AAS
- emission spectroscopy
- other molecular spectroscopy techniques