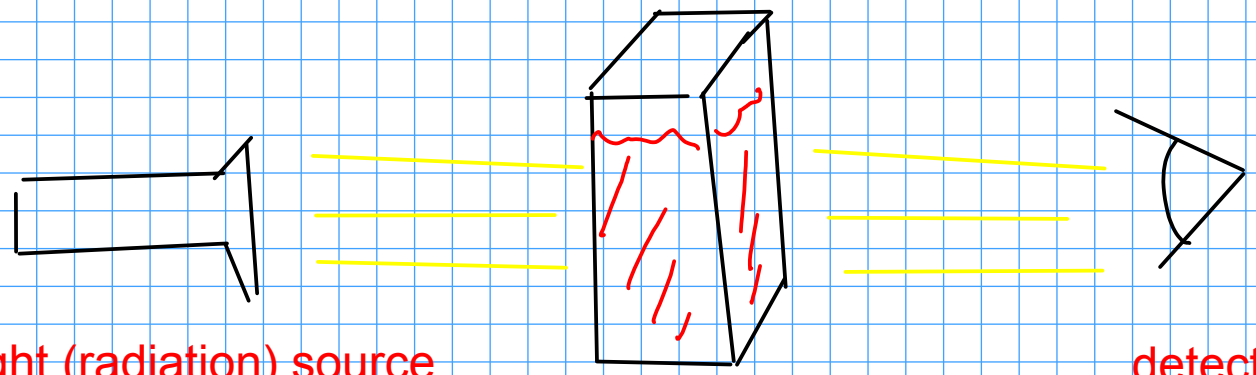
SPECTROSCOPY

- SPECTROSCOPY - analysis of a sample by way of interaction with electromagnetic radiation

- SPECTROMETRY - quantitative determination of a sample by way of interaction with electromagnetic radiation



light (radiation) source
flashlight

sample
red Kool-Aid

detector
eye

So what happens?

White light interacts with the Kool-Aid and you get a different color and intensity of light out of the other side (and into the eye)

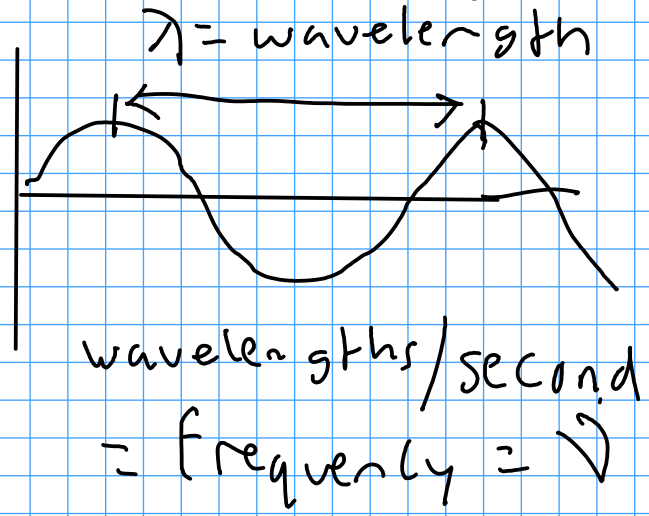
- How does light interact with the Kool-Aid (or any other matter)

Light / EM radiation is composed of particles we call "photons", which are essentially packets of energy

$$E = h\nu$$

FREQUENCY

PLANCK'S CONSTANT



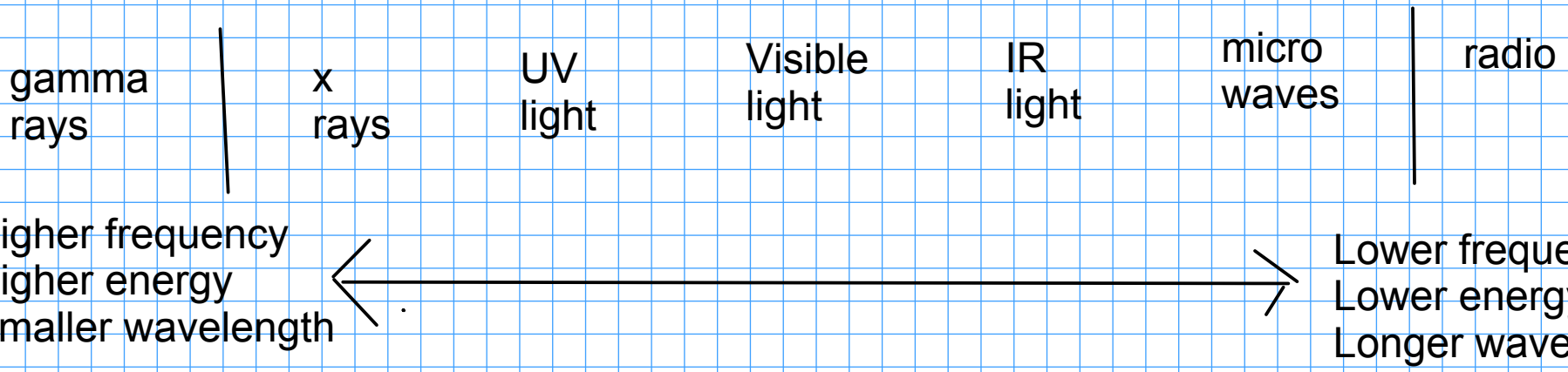
Different colors of light have different energy content. This energy can interact with atoms and molecules.

EM Spectrum

gamma rays | x rays | UV light | Visible light | IR light | micro waves | radio

Higher frequency
Higher energy
Smaller wavelength

Lower frequency
Lower energy
Longer wavelength



X-rays: Cause ionization

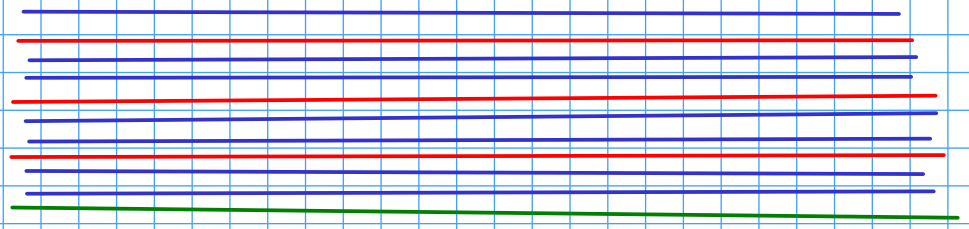
UV: Causes "electronic transitions" - electrons changing energy levels

Visible: Causes "electronic transitions" -electrons changing energy levels

IR: Causes molecular VIBRATION

Microwaves: Cause molecular ROTATIONS

Most ANALYTICAL (quantitative) spectrometry is of the UV/Visible (UV/VIS)



E1, excited state

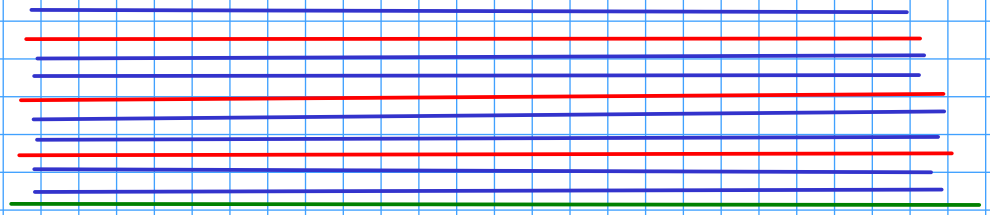
Rotational states

V3

V2

V1

V0



E0, "ground state"

Vibrational "ground state"

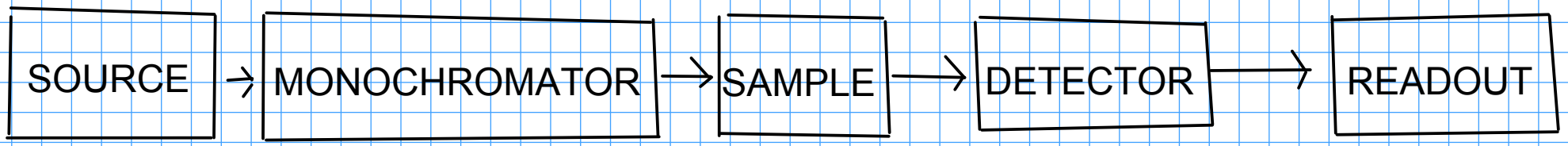
Electronic transitions - highest energy requirement. Involve UV/VIS light

Vibrational transitions - lower energy requirement. Involve IR light

Rotational transitions - lowest enegy requirement. Involve microwaves

How do we use these transitions to our benefit?

INSTRUMENTATION



Sources:

- depends on the type of radiation needed

VISIBLE: Tungsten filament incandescent bulb

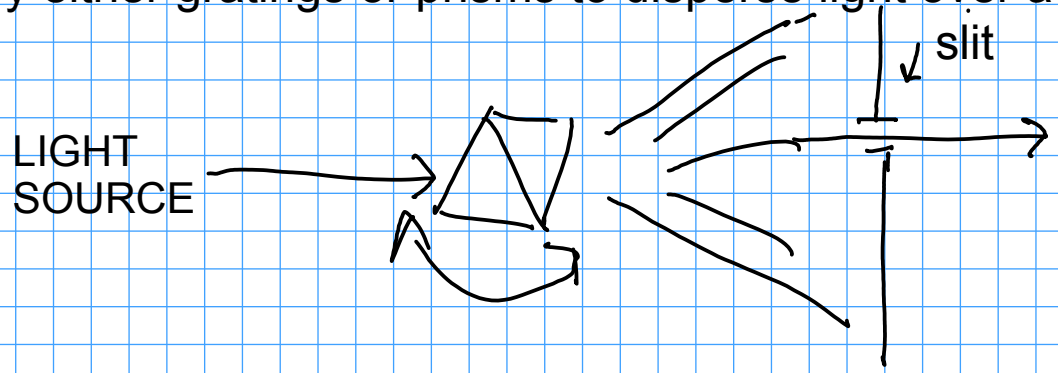
UV: Hydrogen or deuterium lamp

IR: "Globar". Essentially, a heated filament.

Monochromator

-device that allows only radiation of a certain frequency to pass

- employ either gratings or prisms to disperse light over a slit, which blocks most of the dispersed light



Adjust the frequency of light by rotating prism or grating.

Samples:

- generally held in CELLS (usually samples are in liquid form)

- CELLS must be transparent to the kind of radiation used for the analysis

- Different techniques require different materials

    VIS: Glass or quartz

    UV: Quartz (but not glass)

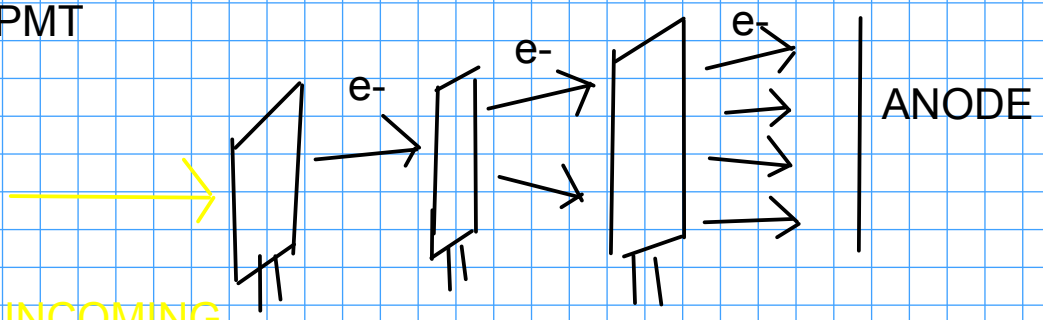
    IR salt plates (various configurations) - NaCl, KBr

Detectors

- Type of detector depends on the region of the EM spectrum we need to see!

- UV/VIS: Uses either PHOTOMULTIPLIER TUBES(PMTs) or PHOTODIODES

PMT



Incoming light causes electrons to be emitted from the cathode of the photomultiplier tube, leading to a cascade of electron emission in the tube, Each photon ends up causing the release of many electrons, giving the PMT high sensitivity!

Photodiodes are sometimes used in an ARRAY, since they are much smaller than PMTs. This array can contain many sensors to detect many different wavelengths of light at once. However, they are less sensitive than PMTs.

- IR

- Uses detectors that are more sensitive to heat than light, like THERMOCOUPLES or THERMISTORS, which change their electrical characteristics with temperature

TYPICAL SPECTROMETERS

1. Single beam (Examples: The "classic" Spec-20, and the Nicolet instrument in our lab)

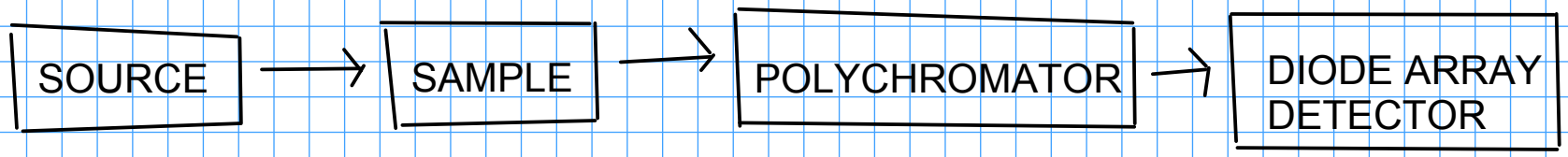
- Can contain only one cuvette at a time, either sample OR blank
- Relatively inexpensive
- May require re-zeroing at wavelength changes

2. Double-beam

- Can contain two cuvettes at once, since the light from the source is split into two beams
- Expensive and more difficult to maintain than a single-beam instrument
- Can leave the blank in during a series of analyses - saving time

3. Diode-Array

- Different in construction from the other two kinds. This allows the instrument to measure many wavelengths at once:

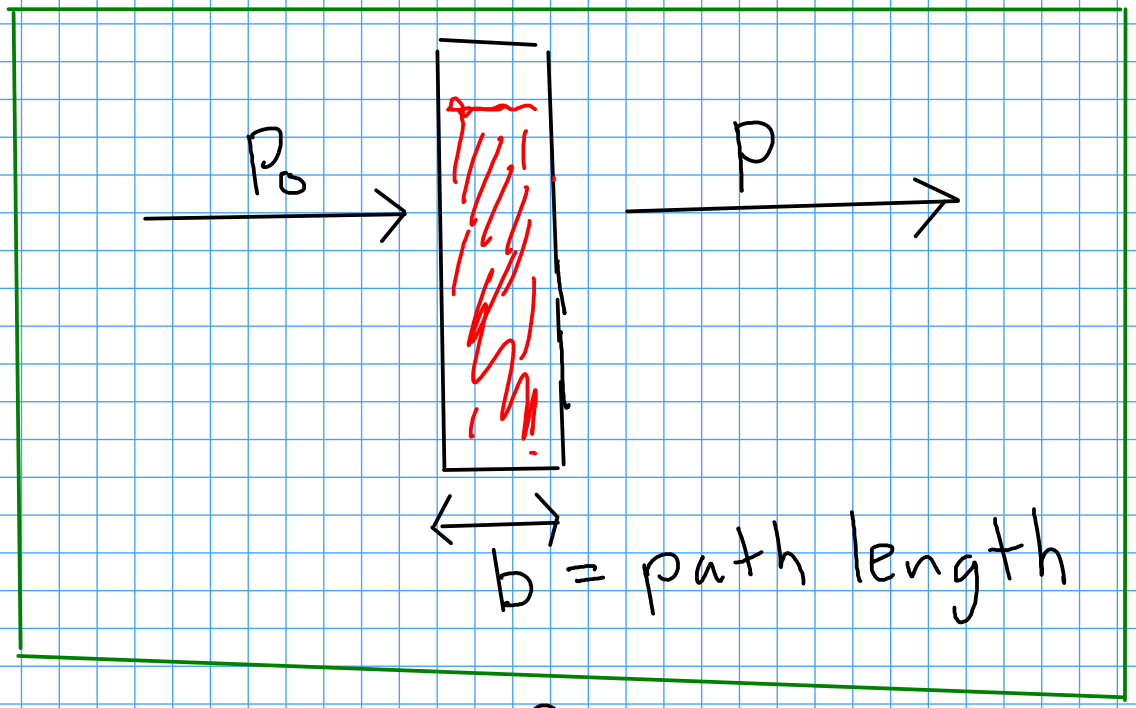


- Always computer-controlled. Good for complex analyses (ex: many-component mixtures)

SPECTROSCOPY CALCULATIONS

- Absorbance

$$A = \log\left(\frac{\text{Power of incident radiation}}{\text{Power of transmitted radiation}}\right) = \log\left(\frac{P_0}{P}\right)$$



- Transmittance

$$\%T = \frac{P}{P_0} \times 100\%$$

... the percent of light that makes it through the sample

... so why do people use ABSORBANCE instead of the seemingly simpler TRANSMITTANCE in spectrometric analysis?

BEER'S LAW

- The relationship between the CONCENTRATION and the ABSORBANCE (for dilute solutions) is LINEAR. (Transmittance is NOT linearly related to concentration!)

$$A = \varepsilon b c$$

A = Absorbance

ε = molar absorptivity ($M^{-1} cm^{-1}$ units)

b = path length (cm)

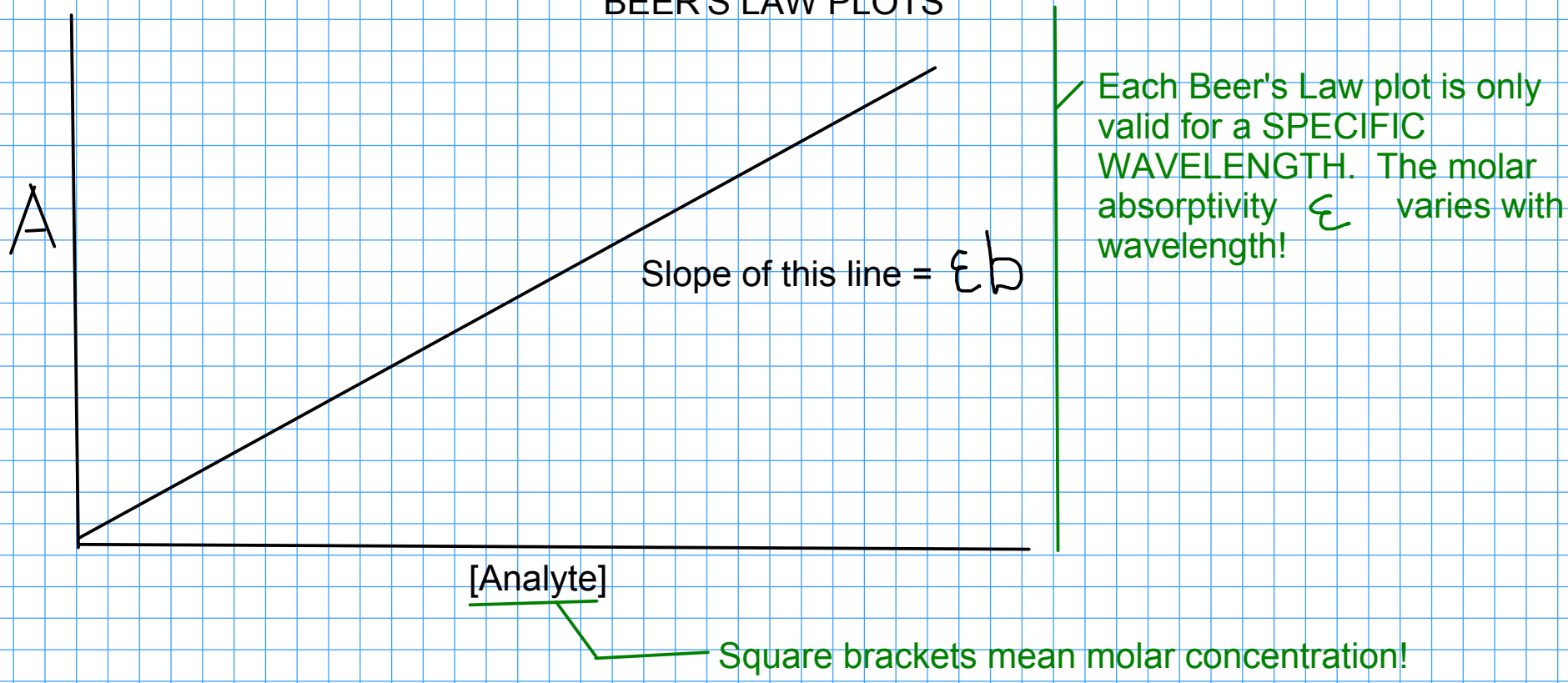
c = molar concentration (M)

(In the past, we've called εb the "Beer's Law Constant", k)

- In a typical UV/VIS spectrometer, the path length (b) is 1.0 cm, but this may vary with the size of the cuvette used.

- In short, Beer's Law predicts that a plot of ABSORBANCE (y axis) vs CONCENTRATION (x axis) will be a straight line!

BEER'S LAW PLOTS



Each Beer's Law plot is only valid for a SPECIFIC WAVELENGTH. The molar absorptivity ε varies with wavelength!

Square brackets mean molar concentration!

Basic procedure for spectrometry:

1. - Pick a wavelength, usually by scanning over a range of wavelengths to find out where your analyte absorbs the most radiation
2. - Calibrate the instrument at the selected wavelength, using prepared standards. Record ABSORBANCE for each
3. - Plot ABSORBANCE vs CONCENTRATION. Find the molar absorptivity at the selected wavelength.
4. - Run unnown, then use the plot or the molar absorptivity to determine the concentration based on the absorbance of the unknown.

MULTICOMPONENT MIXTURES

- If you have more than one component absorbing, their absorbances at the same wavelength ADD:

$$A_T = A_x + A_y + \ldots$$

- For a two component micture, we can separate the two absorbances if we measure at TWO wavelengths!

$$A_1 = A_{x_1} + A_{y_1}$$

$$A_2 = A_{x_2} + A_{y_2}$$

Components are X and Y
Wavelengths are 1 and 2

$$A_1 = \varepsilon_{1x} b C_x + \varepsilon_{1y} b C_y$$

$$A_2 = \varepsilon_{2x} b C_x + \varepsilon_{2y} b C_y$$

$\varepsilon_{1x}, \varepsilon_{2x}, \varepsilon_{1y}, \varepsilon_{2y}$ can be measured by analyzing the components separately!

b is a constant (width of cuvette)

A_1, A_2 are measured, so there are two variables and two equations. Solvable!

ERRORS IN SPECTROMETRY

- For small values of absorbance or large values of transmittance, the amount of relative error is large!

- For very large absorbances (very small transmittances), the relative error is also large

- Theoretically, the MINIMUM amount of relative error occurs at an absorbance of about 0.43 for a diode instrument, and about 0.87 for a PMT isntrument!

... but A depends on concentration, so how is that useful? We can DILUTE or CONCENTRATE our solutions to make their absorbances closer to a desired value.

- It's not practical to try to make every sample come out to an absorbance of 0.43 or 0.87, but we can try to minimize error by keeping our absorbances CLOSE to a desired range:

DESIRED ABSORBANCE RANGE FOR MINIMUM ERROR

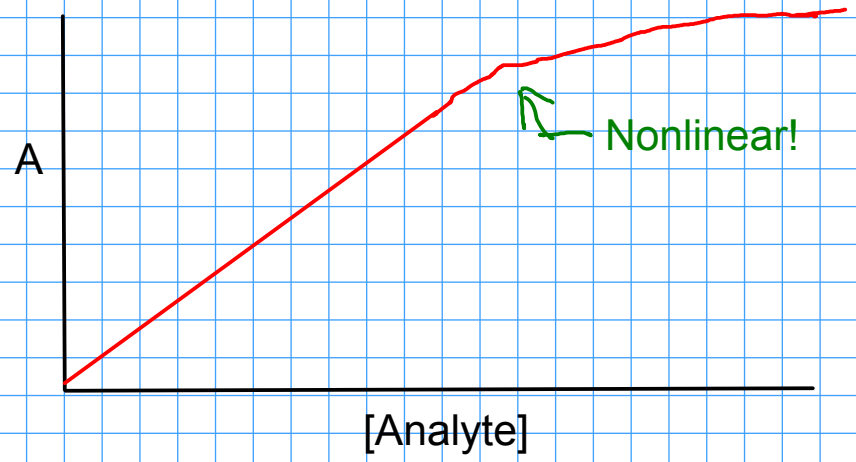
0.1 to 1.0 .... diode-based instruments

0.1 to 1.5 ... PMT-based instruments

DEVIATIONS FROM BEER'S LAW

- Sometimes, A does not appear to be linearly related to concentration. Why not?

1. High concentrations (high values for absorbance): Beer's Law is not valid for these situations. Absorbance begins to level out at high concentration!



2. Substantial differences between samples and blank. (Other species in the sanple but not the blank may absorb!). it's best to keep the blank as much like the sample as possible!

3. Monochromator passing too many wavelengths of light. Beer's Law is strictly true only for monochromatic light.

4. Other chemical or instrumental interferences (stray light, other absorbing species, etc.)

Atomic Spectrometry

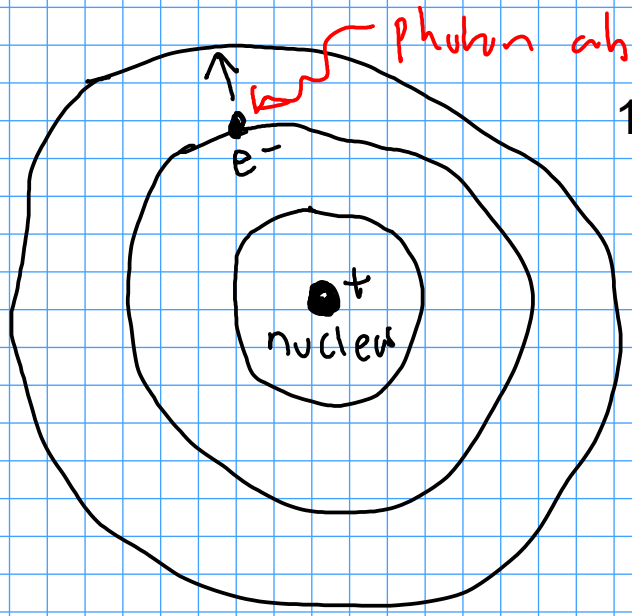
BASIC THEORY

-uses the phenomenon of the interaction of electromagnetic radiation with the ELECTRONS of an atom.

- involves the UV/VIS region of the spectrum

Bohr model of the atom

- Admittedly, the Bohr model isn't accurate for atoms other than H, but it is sufficient to get an idea of how atomic spectrometry works. (Real model: quantum mechanics)



1) Electrons exist in ENERGY LEVELS

2) Electrons may TRANSITION (jump) directly from one energy level to another by either absorbing (to go up) or emitting (to go down) a photon with the required energy

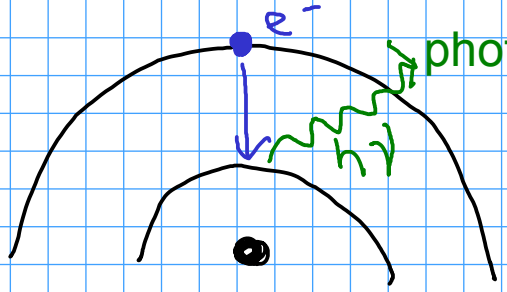
- To move from one energy level to another, a FIXED amount of energy is involved.

$$E = h\nu$$

Equation for energy of a photon

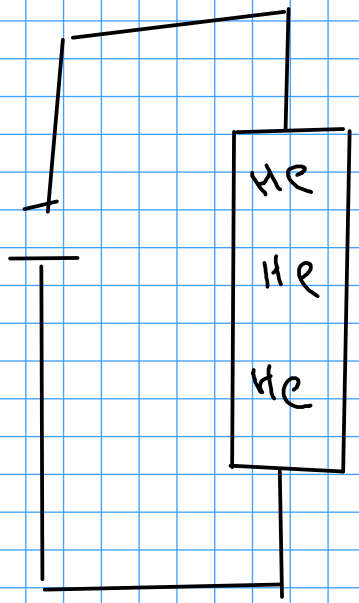
ν = frequency

h = Planck's constant



- The atom returns to "ground state" (not excited) by releasing a PHOTON of a certain energy ... light at a certain wavelength or frequency.

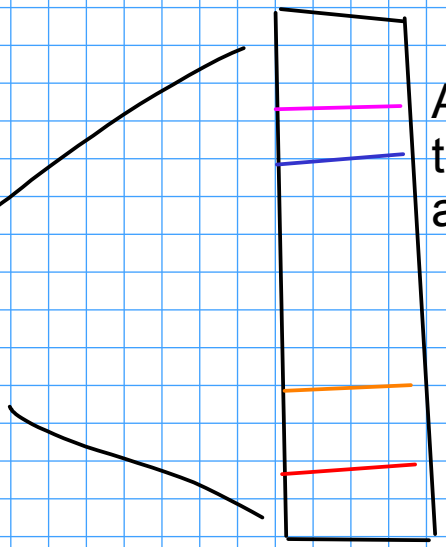
- Since these transitions are at fixed energies for each kind of atom, each element has a fixed pattern of emitted light (a "fingerprint")



Apply electricity to "excite" atoms: promote electrons to higher energy levels

light is emitted as atoms return to GROUND STATE

Prism separates light



Atomic line spectrum: the "fingerprint" of an element

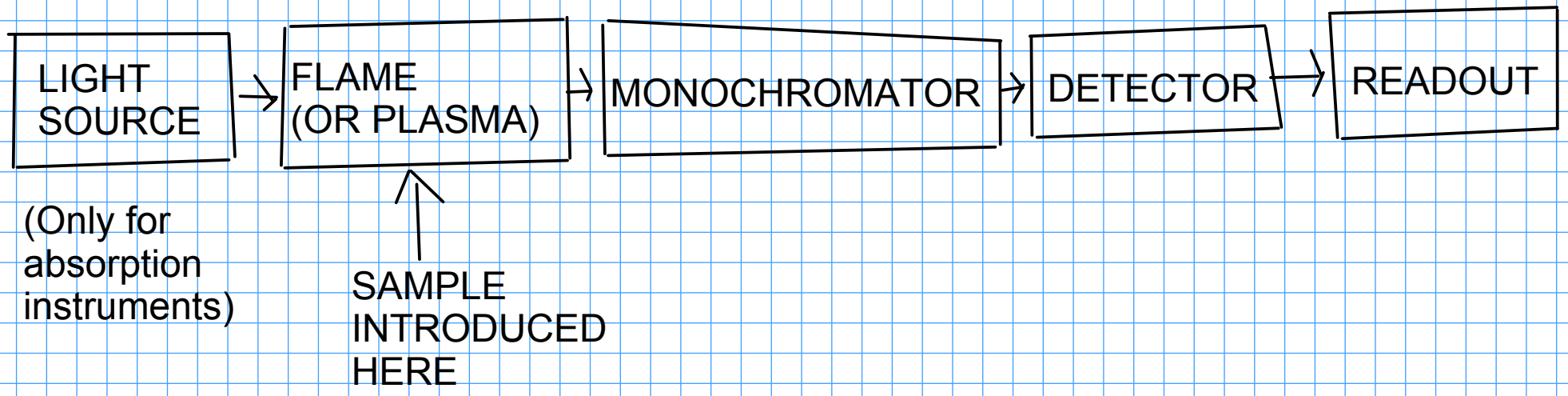
Each element emits a pattern of fixed wavelengths.

- You can identify an element (in the gas state, anyway) by its emission pattern

- Atoms ABSORB the same wavelengths that they EMI

- Either emission or absorption can be used for spectrometry. Atomic spectrometry is often used for trace metal analysis, particularly in aqueous streams.

INSTRUMENTS



SOURCE: "hollow cathode lamp" - lamp whose cathode is made of the element(s) that we want to analyze. These atoms produce light of the desired wavelengths. This light is perfectly suited to use for the analysis.

FLAME:

1) To reduce COMPOUNDS in the flame to ATOMS. Molecules interfere with atomic spectrometry because they absorb in BANDS not in LINES.

2) In emission spectrometry, the flame (or plasma) also excites atoms and causes them to emit

MONOCHROMATOR and DETECTOR: Same hardware as for UV/VIS spectrometry

ABSORPTION TECHNIQUES

Flame AAS (Atomic Absorption Spectrometry)

- uses a burner to ATOMIZE the sample (reduce sample to gaseous ATOMS)
- Typical samples: Dilute aqueous solutions, sucked in by the burning flame
- Used for metal analysis
- Flame is typically acetylene / air (just like welding): 2700K
- Hotter flames use acetylene / nitrous oxide
- Fuel / oxidant mixtures are optimized for specific analyses

Furnace AAS

- uses a FURNACE to atomize the sample instead of a flame
- Temperatures usually about 2800K
- uses much less sample than flame AAS!
- much more sensitive than flame AAS
- harder to use, and less reproducible than flame AAS

EMISSION TECHNIQUES

Flame AES (Atomic Emission Spectrometry)

- As in flame AAS, uses a flame to atomize the sample.

- Flame is ALSO used to excite atoms and cause EMISSION

- Useful for a limited range of analytes, since a flame is not energetic enough to excite most atoms

- Alkali metals (Group IA on the periodic table) are the most common analytes in flame AES

- Flame AES is available as a dedicated instrument to measure levels of sodium, potassium, etc. in urine samples.

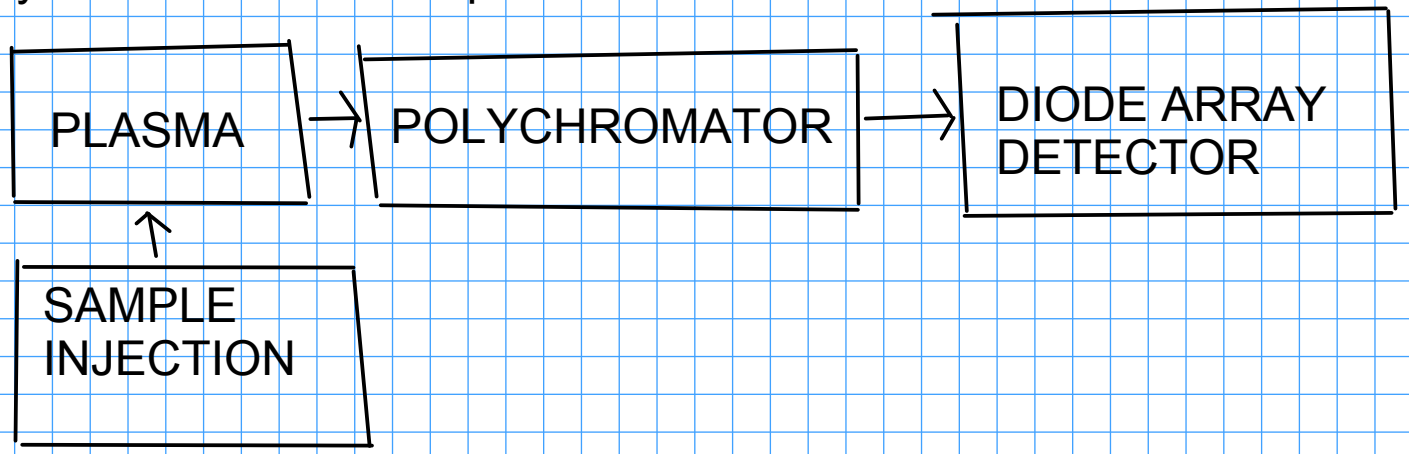
Plasma AES

- uses a PLASMA instead of a flame to atomize and excite atoms

- The plasma is hot, ionized ARGON gas at a temperature of 6000K - 10000K, much hotter than flame techniques.

- Plasma AES instruments use a lot of argon gas, meaning that they are costly to operate- much more so than a flame instrument.

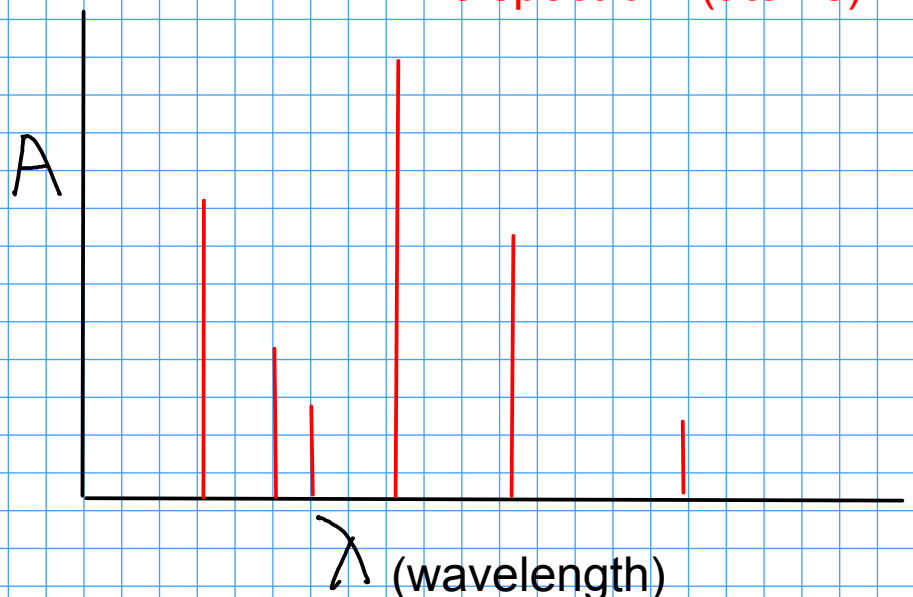
- Plasma can excite most elements, and can be used (with a diode-array detector) for the simultaneous analysis of MANY elements, without using many hollow-cathode lamps.



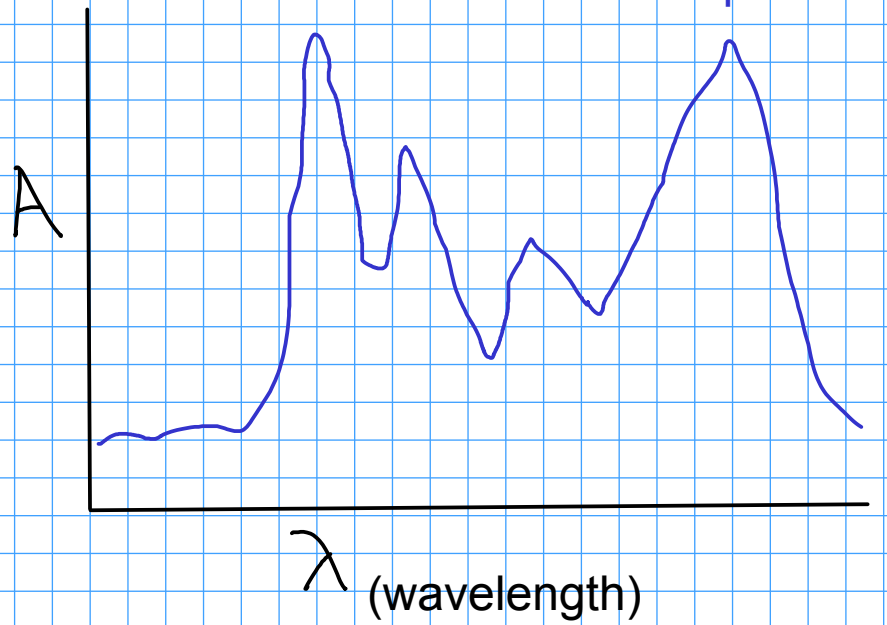
INTERFERENCES IN ATOMIC SPECTROMETRY

- As in all analytical techniques, the presence of certain things in a sample can cause error in atomic spectrometry. But, theoretically, atomic spectrometry should be almost error-free!

Line spectrum (atoms)



Molecular UV/VIS spectrum



- Individual atoms emit and absorb only at specific wavelengths, giving rise to LINE SPECTRA.

- Molecules emit and absorb over wide ranges of wavelengths!

- Why the difference? Molecules have more ways to distribute energy than atoms do. Bonds can also interact with EM radiation, and atoms close to one another can transfer energy to each other without emitting photons.

- So the presence of MOLECULES in the flame whose absorption overlaps the atomic line we are trying to measure may reduce sensitivity by creating a high background absorption.

Interferences other than absorbing molecules?

IONIZATION

- Flame AES and AAS generally use the line spectra of the ATOMS for analysis. Individual ions also produce spectra, but their lines are different than the atoms. Ionization of analyte, therefore, can REDUCE SENSITIVITY.

- The hotter the flame, the more energetic it is - and the more likely it is that we will ionize analyte.

- Trade -off: We need to have a flame that is hot enough to atomize (and for AES, excite) analyte, but not so hot as to ionize the analyte!

CHEMICAL REACTIONS

- It is possible for some analyte atoms to react in the flame, forming stable compounds (like oxides), which do not absorb light at the right wavelenghts.

- Formation of compounds in the flame REDUCES SENSITIVITY

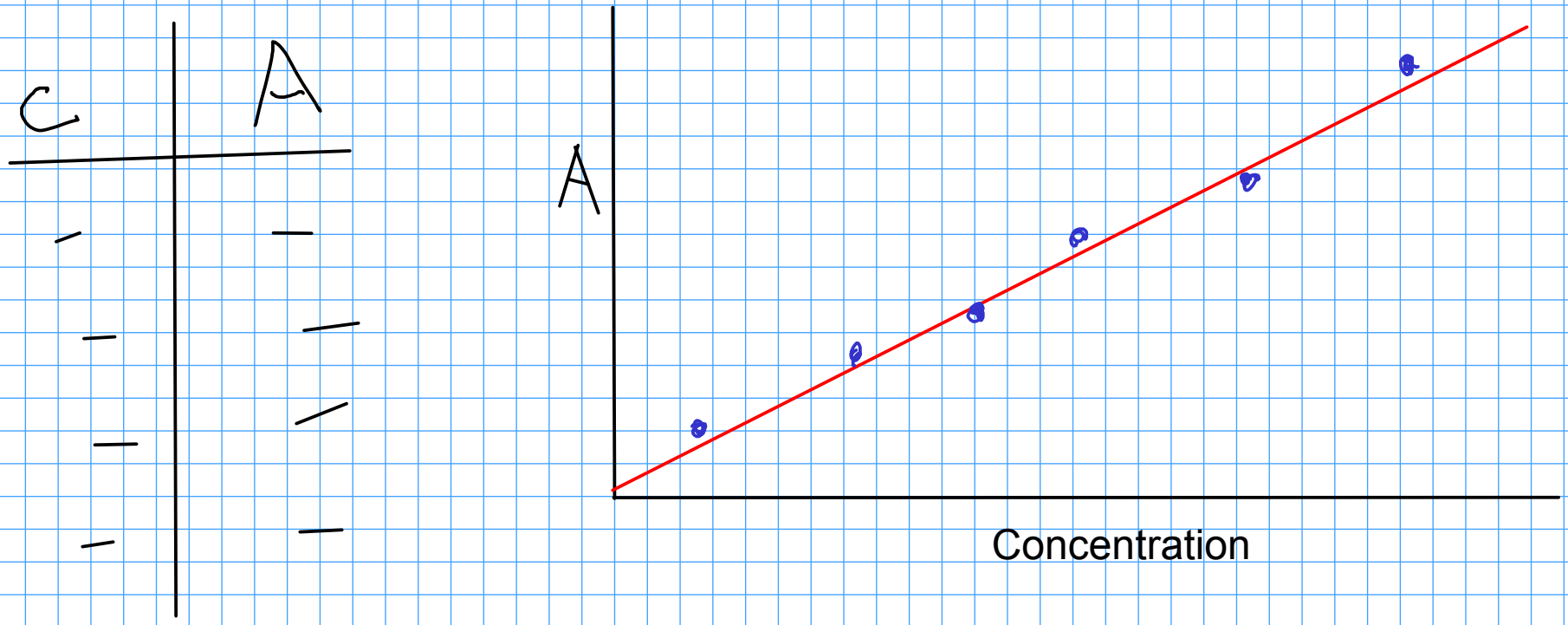
CHANGES IN INSTRUMENT CONDITIONS

- Irregular fuel or oxidant flow may change the characteristics of the flame, making the flame hotter or cooler

- Why? A hotter flame might ionize analyte. A cooler flame might not be able to atomize the sample.

CALCULATIONS IN ATOMIC SPECTROMETRY

- As for UV/VIS spectrometry, a calibration curve is prepared using absorbance or emission of light versus concentration.



- Make standard solutions, read absorbance or emission at the wavelength of an absorption/emission line, and plot absorbance or emission vs. concentration.

- For AAS, this is like making a Beer's Law plot: $A = \varepsilon b c$

Final Exam: Thursday December 6, 9:30 AM, Room 5422