Introduction to Natural Science (2006/07)

Winter 2007 Quarter

Chemistry Lab III: “Absorption & Emission Spectroscopy”

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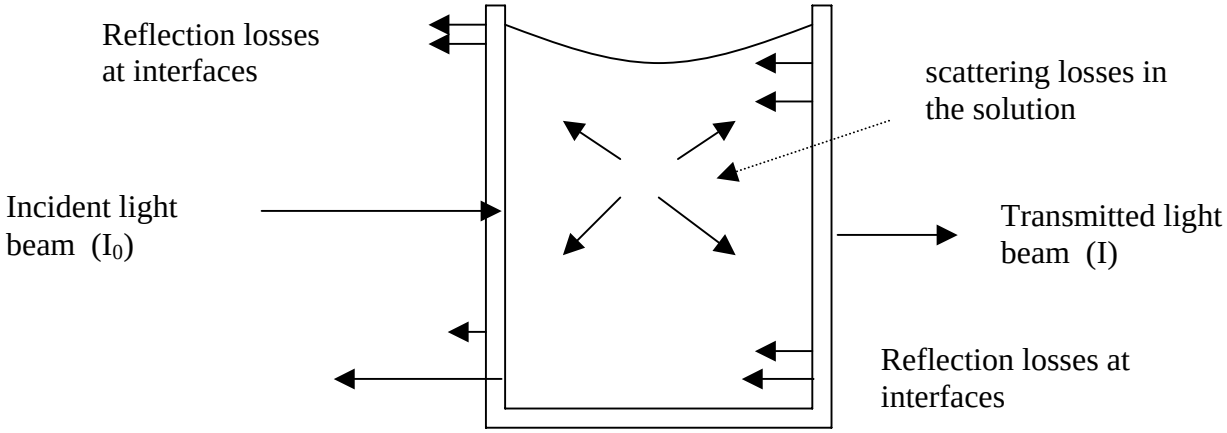
Experiment 1: Absorption Spectroscopy

Do this lab in pairs. Read the following carefully, at least 4 times, before coming to lab.
In this lab we will record absorption spectra of several food dye solutions and "unknown solutions" using a diode array spectrometer.

Light, when passing through a solution, can be absorbed, transmitted, reflected and scattered. These processes are shown in the following diagram.



The diode array spectrometer is based on Beer-Lambert's law. Beer-Lambert's law relates the absorbance of light passing through a medium (a solution, in this case) to the path length and concentration as follows.

$$A = -\log\left[\frac{I}{I_0}\right] = \varepsilon_\lambda C L$$

where
A = absorbance
ε_λ = molar absorptivity coefficient (or molar extinction coefficient) which is wavelength dependant
C = concentration of the sample (a solution, in this case)
L = path length through which light travels
I = intensity of the transmitted radiation
I_0 = intensity of the incident radiation

Transmittance is defined as $T = I/I_0$

Notice from the equation: $A = \varepsilon_\lambda C L$ that absorbance is:

- directly proportional to concentration (C)
- directly proportional to path length (L)

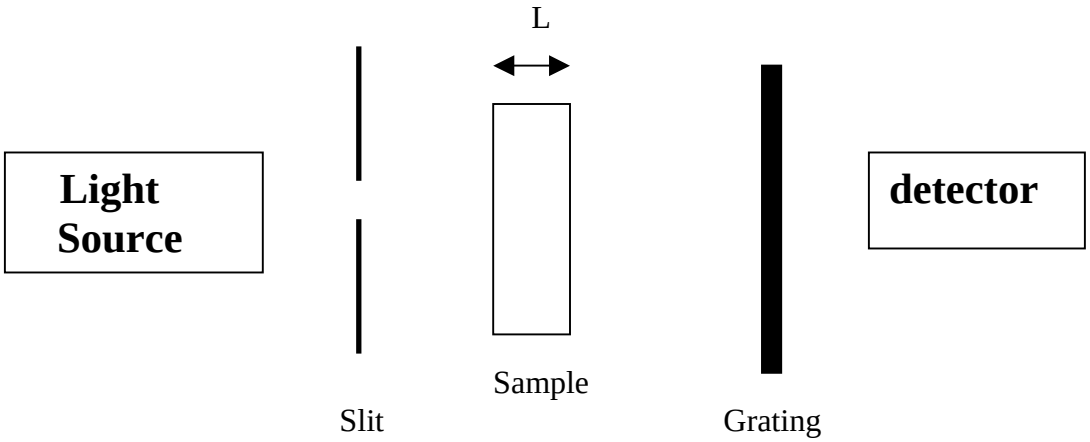
Therefore we can increase the absorbance by either increasing the concentration of the sample or by increasing the path length (since molar absorptivity coefficient is an inherent property of matter and we have no way of changing it).

At high concentrations of the sample however deviations from the direct proportionality between absorbance and concentration occur frequently. Therefore when recording absorption spectra we use samples of low concentration so that absorbance stays below 1.

Pre-Lab Assignment:

1. What is Beer-Lambert's Law (mathematical expression, with terms defined)?
2. Derive the relationship between absorbance (A) and transmittance (T).
3. The absorbance of a solution of 0.354 M concentration of a red dye is 0.250 at a given wavelength λ. If the concentration of the dye is increased to 0.935 M without changing the path length, what is the absorbance of the concentrated dye solution at the same wavelength?

Block Diagram of a Diode Array Spectrometer



- The diode array spectrometer has a UV/visible light source.
- The liquid sample is contained in a plastic cuvette, of 1 cm width.
- The detector is a diode array.
- The grating performs the same function as a prism (i.e. it separates light into different wavelengths).
- The resolution of the instrument is 2 nm.

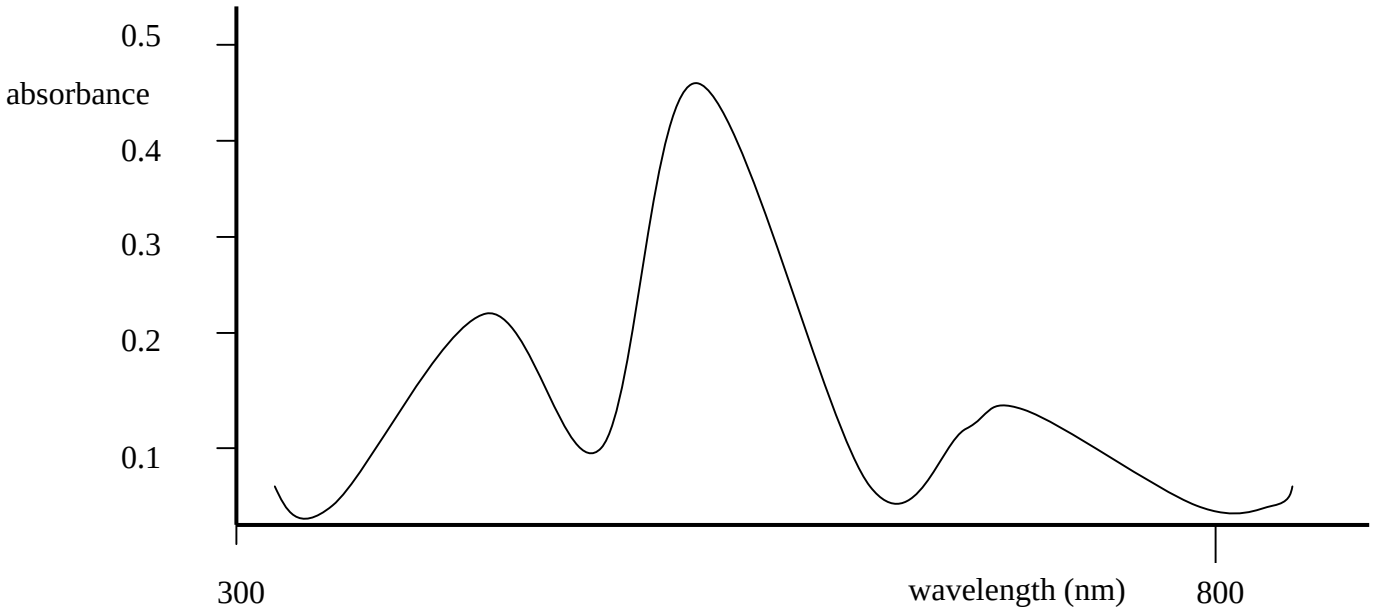
Although we are using a UV/visible diode array spectrometer, we will only use it in the visible region. We can do that by selecting the wavelength we want to work in (350-800 nm work well).

In this lab we will record absorption spectra, which are graphs of absorbance versus wavelength. The spectrum tells us what wavelengths of light are absorbed by a given sample.
Note that

$$A = -\log\left[\frac{I}{I_0}\right]$$

The spectrometer records I and I_0. Then it computes the value of absorbance (A) using the above mathematical relationship.

For the food dye sample: Record the intensity of the incident beam by using DI water in the cuvette. This is called a **blank spectrum** (I_0). Intensity of the transmitted beam is recorded by putting the food dye sample in the cuvette. This is called the **sample spectrum** (I). The instrument uses the **sample spectrum** and the **blank spectrum** to generate the **absorption spectrum of the sample**. The absorption spectrum is then displayed on the screen.



Once you have obtained a spectrum you need to save it to your INS network folder. Instead of saving the spectrum (or the graph) we will save the data points as a table, so we can later export it into Microsoft Excel and print the spectrum.

Wavelength (nm)	Absorbance
300	
302	
304	
306	
308	
310	
312	
314 etc.	

Record the spectrum of one dye sample first. Then save the data to your network folder with an appropriate name. Then move on to the next dye solution. Continue in this manner until you are done with all of the dye solutions. **Always remember to record a blank spectrum (I_0) before starting on a dye solution (I).** Also remember to record the colors (naked eye observations) of the dye solutions. Each student must have their own data saved to their network folders before leaving lab. **Write down the concentrations of the "known dye solutions" before leaving the lab.**

Post Lab:

1. Using Microsoft Excel, plot the absorption spectra of the "known dye solutions", one spectrum for each dye, on separate sheets (not on the worksheet but as a chart). Add your name and the name of the solution to the title of the spectrum.
2. Create the following table for **each** "known" dye solution.

   Food dye color: _____(as seen by naked eye)

Peak wavelength	Peak absorbance	Relative intensity of peak

(Relative intensity means "strong", "medium" or "weak" for a given peak).

3. Based on your observations, decide which wavelengths are transmitted and which wavelengths are absorbed for each of the "known dye solutions".
4. Correlate the wavelengths that are transmitted with the color (naked eye observation) of each of the "known dye solutions".
5. For the **primary colors only (red, blue and yellow dyes)**, determine the molar extinction coefficients for each of the "known dye solutions" at each of the wavelengths were light is absorbed. What are the units of the molar extinction coefficient? Show all work.
6. Plot the spectra of the "unknown dye solutions" on **one graph** (i.e. all spectra should be **overlaid**).
7. The "unknown dye solutions" were prepared by mixing up the "known dye solutions". Using the naked eye observations for the "unknown dye solutions", the overlaid plot of the spectra, and the spectra of the "known dye solutions", determine how the "unknown solutions" were made (i.e. determine which of the "known dye solutions" were mixed in order to make the "unknown dye solutions").
8. Use the molar extinction coefficients you calculated above, to determine the exact concentrations of the "known dye solutions" that are present in the "unknown solutions".

[For example: Unknown solution A contains 0.234 M of Red #3 dye and 0.156 M of Green #3 dye]

9. Express the above as a percentage.

[For example: Unknown solution A contains 45% of Red #3 dye and 55% of Green #3 dye]

10. Experiment 2: Emission Spectroscopy - Flame Tests

Do this lab in pairs.

- Light the Bunsen burner, adjust the amount of air to get a blue flame and use it for all flame tests.
- Clean the nichrome wire by
    - Dip in conc. HCl
    - Burn in the blue flame
    - Dip in alcohol
    - Burn in the blue flame
- Take a small amount of the known ionic compound to the clean nichrome wire and hold it to the blue flame of the Bunsen burner. Record the color of the flame (naked eye observation) as descriptively as possible. It often helps to have your wire wet with conc. HCl to get a good flame test.
- Continue in this manner until you are done with all the ionic compounds. **Clean the nichrome wire each time you start a new compound.**

Tabulate your data as follows.

name	**formula**	**cation**	**anion**	**color of flame**	**inference**

Ionic compounds for flame testing:

copper (II) nitrate
sodium chloride
potassium nitrate
lithium chloride
strontium chloride
calcium chloride
copper (II) chloride
potassium chloride
strontium nitrate
magnesium chloride
calcium nitrate
iron (II) chloride
iron (II) sulfate
barium chloride
sodium bicarbonate
barium nitrate
magnesium sulfate
lithium nitrate

Post Lab: If you were to test the following ionic compounds using flame tests, what color flames do you expect to observe and why?
sodium fluoride, copper (II) sulfate, iron (II) nitrate, strontium carbonate

Experiment 3: Application of Emission Spectroscopy - Making Sparklers

(Keeney A., Walters C., Cornelius R.D., *Journal of Chemical Education*, **1995**, *72*, 652-653)

Background information about sparklers

Oxidation/reduction reactions are one of many topics discussed in general chemistry. They are unique in that their consequences are readily and sometimes dramatically observable. Anyone who has watched a rocket being launched or has seen a fireworks show has witnessed the results of an oxidation/reduction reaction. Sparklers provide another excellent example for these reactions. Also unlike rocket fuels, sparklers are relatively safe to create and test in the laboratory. We will be using barium nitrate as one of the ingredients in sparklers. At high temperatures, such as in a flame, barium nitrate decomposes to form oxides, nitrogen and oxygen. Potassium chlorate, another ingredient in sparklers, also decomposes into potassium chloride and oxygen gas. These gases help eject other burning materials on the sparkler, providing the "sparkler effect". Some of the metallic ingredients are used because they provide spectacular colors to the sparklers. Magnesium, aluminum and iron are the powdered metals we will be using in this laboratory to make the sparklers. Therefore, the sparks themselves are actually bits of reactive metals, which ignite in air to produce oxides. The burning of magnesium in particular is impressive, and is responsible for the bright white sparks in non-colored sparklers.

Work in pairs. Wear gloves. Use a **top-loading balance** for weighing.

Weighing the Ingredients

Handle metal powders with care. Weigh the following **inorganic ingredients** using a clean, dry weighing boat. When the correct amount is weighed, transfer it into a single, labeled, 150 ml (small) beaker and cover it with a parafilm before moving to the lab bench.

Inorganic ingredients

10. grams iron powder
0.5 grams magnesium powder
2.0 grams aluminum powder
6.0 grams potassium chlorate
25.0 grams barium nitrate

Preparing the starch mixture

1. Weigh 6.0 grams of soluble starch into a clean 150 ml beaker.
2. Using a graduated cylinder, add 15 ml of de-ionized water to the beaker.
3. Place beaker on a hot plate, that is also equipped with a magnetic stirring mechanism. Add a magnetic stir bar to the mixture.
4. Begin stirring and heating the starch mixture gently. You will need to experiment with the heat settings on your hot plate. Some steam should eventually come off as the water evaporates, but do not let the mixture boil and splatter.
5. Remove the beaker from the hot plate when it becomes a thick paste. (**This may happen quite suddenly, so keep a close eye on it**). The consistency should be that of tomato paste.
6. Remove the stir bar using a clean spatula. Wash and return your clean stir bar to the lab staff.

Preparing the sparkler

Make two sparklers per person. The amounts used are sufficient for four sparklers. Keep some hot water available to add to the mixture if it thickens over time.

1. Slowly add the inorganic ingredients to the starch solution while stirring with a wooden rod (Popsicle stick). With the addition of the solids, the mixture will be dense. If there are dry, chunky areas add a few drops of hot water.

2. Scrape the mixture onto a spatula and smear the mixture on to the iron wire (approximately 20-cm in length and 2-mm in diameter). To burn consistently, the wire must be completely coated. **Thicker the sparkler, the better it will light!** Be sure to leave room for a handle so that you can hold the sparkler when you are done!

3. Label your sparkler with your name. Leave in the hood to dry overnight. At this point, the water has evaporated out, and the starch is holding the ingredients together.

Igniting your sparklers

We will do this once the sparklers are dry. **Caution:** When dealing with pyrotechnics, (particularly self-produced), it is important to take safety precautions. Always ignite sparklers in the fume hood or outside. If outside, be sure that there are no plants, lawns, etc. nearby which may catch on fire. **Wear safety glasses and lab coats. Do not hold the sparkler in your hand during/after lighting it.** Lighters work better than matches to light these sparklers. Enjoy chemistry in action!