Introduction to Spectroscopy

Introduction

Spectroscopy

Spectroscopy is the study of matter interacting with electromagnetic radiation (e.g., light). There are many subfields of spectroscopy that vary in the type of electromagnetic radiation, particularly the frequency (or equivalently the energy or wavelength) but also the polarization, intensity and fate of the radiation. In this course we will be primarily concerned with absorption spectroscopy in which the radiation (photons) is simply absorbed by the matter (molecules) and its energy is deposited into the molecule. The frequency (or wavelength) of the radiation determines where that energy goes, for example, absorption of visible or ultraviolet light excites the electrons, infrared radiation absorption puts energy into the vibrations of the molecule, microwaves excite the rotations of the molecule.

An absorption spectrum is obtained by scanning the frequency (or wavelength) of radiation over a range and measuring the amount (intensity) absorbed as a function of this frequency; this is usually plotted in terms of the absorbance or the transmittance. Quantum mechanics governs the process with the most important result being that light can only be absorbed if its energy equals the energy difference between two allowed energy levels of the molecule. Thus, the spectrum
tells us about the allowed energy levels of the molecule. Since these are unique characteristics of molecules, a spectrum is like a molecular fingerprint and can be used to identify molecules or provide detailed information about a known molecule.

In this laboratory we will focus on visible absorption spectroscopy, which is sensitive to the electronic character of molecules. Human vision is based on this very property as the color we see is determined by the allowed energies of the electrons in the molecules at which we look.

**Solution Preparation (Accuracy and Precision)**

Making accurate and meaningful scientific measurements requires an understanding of basic laboratory techniques and the proper use of common laboratory equipment and instrumentation. Over the course of the semester, you will be using many different types of glassware to measure volumes and prepare solutions. The glassware that is used when making a solution ultimately determines the uncertainty in the solution’s concentration. Most of the glassware you will need, including beakers, flasks, and graduated cylinders, is located in your glassware drawer. Occasionally, you will be provided with additional types of glassware (e.g., burets, volumetric pipettes, graduated pipettes, and volumetric flasks), especially when you are asked to perform a titration or when extremely accurate volume measurements are needed. Each type of laboratory glassware has a specific task for which it is best-suited. For example, beakers should only be used when rough estimates of volume are required (e.g., 50 mL). When increased accuracy and precision are needed (e.g., 50.0 mL or 50.00 mL), then a graduated cylinder, a pipette, or a volumetric flask might prove more useful. The precision of a given type of glassware can be determined by the divisions printed on it or estimated from repeated laboratory measurements. Alternatively, outside resources (including your TA, the textbook, or the Internet) may be consulted for this information. It is important that you learn how to use laboratory glassware, when to use a certain type of glassware, and how to properly record the measurements made with them. In that aim, you will be asked to investigate the precision of several types of glassware in Part 2 of this exercise. This analysis will help you determine which glassware should be used when preparing a series of copper(II) nitrate solutions.

**Pre-lab**

Familiarize yourself with the electromagnetic spectrum, including the energies and wavelengths of radio, microwave, infrared, visible, ultraviolet, and x-ray radiation. Pay particular attention to the visible spectrum and the wavelengths associated with various colors.

Read the instructions for the operation of the Ocean Optics Spectrophotometer. This instrument will be used during this and many future laboratory exercises, so it is important to become familiar with its operation.

Review the instructions for maintaining your laboratory notebook and properly completing the pre-lab assignment.

**Pre-lab Assignment:** Please answer the following questions in your lab notebook. This assignment is due at the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and submitted to your TA.
1) What is the frequency (in Hz) of the laser used in CD players that has a wavelength of 780 nm? What type of radiation is this (i.e., in which region of the electromagnetic spectrum is this wavelength found)?

2) What is the difference between accuracy and precision? Which would you expect to provide a more precise measurement of a 100 mL sample of water: a 1 L beaker, a 100 mL graduated cylinder, or a 100 mL volumetric flask?

3) Describe how you would prepare 50 mL of an aqueous 0.10 M Cu(NO₃)₂ solution. Mention amounts of chemicals as well as glassware.

4) A 10.0 mL sample of 0.1 M K₂CrO₄ stock solution is added to 50.0 mL of water. What is the concentration (in M) of the dilute solution?

5) What do you expect the absorption spectrum to look like for a red-colored solution? Provide a simple sketch.

Procedure

Safety: Goggles must be worn at all times. Please do not uncap or discard the solutions in the pre-filled cuvettes. The other solutions that you work with in this lab may be rinsed down the drain.

Part 1 – Assessing the Impact of Color in Spectrophotometry

Visible light spectrophotometers like the Ocean Optics 2000 measure visible absorption spectra. In one sense, this means they are capable of "seeing" the same colors that the human eye sees. In this exercise, you will see how information from the spectrophotometer can be correlated with the observed color of aqueous solutions.

Open the LoggerPro software and prepare the Ocean Optics spectrophotometer (Click here for instructions.) Prepare a spectrometer calibration blank simply by filling a rinsed cuvette approximately two-thirds full with distilled water. Calibrate the spectrophotometer as described in the instructions.

Obtain a pre-filled cuvette of each of the following solutions: 0.10 M Co(NO₃)₂, Cu(NO₃)₂, Ni(NO₃)₂, and K₂CrO₄. (Please do not uncap or discard the solutions in the pre-filled cuvettes.) Record the color of each solution. Now place one of the colored solution cuvettes into the spectrometer and view its transmittance spectrum (viewable by selecting Experiment → Change Units → Spectrophotometer → %Transmittance). Determine the wavelength range for which transmittance is at its maximum. Repeat this process for the other three colored solutions. Talk with your group members about the wavelength ranges for the colors of the visible spectrum. Does the color of a given solution relate to the range of wavelengths transmitted by that solution?

Now view the absorbance (viewable by selecting Experiment → Change Units → Spectrophotometer → Absorbance) spectrum for each of the four colored solutions listed above. At what wavelength does the absorbance exhibit a maximum (this wavelength is denoted as λ_max)? What is the relationship between the color transmitted and the color absorbed for each solution? For help, you may wish to refer to the visible spectrum.

Note: If you copy and paste any spectra into a Word document to refer to them later, do not forget to delete these spectra files from the computer before you leave.
Part 2 – Preparing and Diluting a Colored Solution

Dilute solutions of copper(II) nitrate prepared from a 0.1 M stock solution will be used to investigate the effect of concentration on absorbance. Work with your group members to develop a scheme for combining measured volumes of 0.10 M Cu(NO₃)₂ solution with distilled water to generate four additional solutions: 0.050 M, 0.025 M, 0.015 M, and 0.010 M Cu(NO₃)₂. As your group decides how these solutions should be prepared, keep in mind that you will need enough of each solution to fill a cuvette about two-thirds full. Show your plan to your TA before preparing any solutions. Fill cuvettes with each of the four dilute solutions; also fill one cuvette with the undiluted, 0.10 M stock solution. Before you analyze this series of solutions with the spectrophotometer, note any systematic difference in the appearance of the five Cu(NO₃)₂ solutions.

Finally, place each cuvette into the spectrophotometer and note the absorbance reading at the wavelength of maximum absorbance for Cu(NO₃)₂. This wavelength should already be recorded in your notes from Part 1. Use Excel to generate a graph of absorbance vs. Cu(NO₃)₂ concentration. Does your plot show a trend? Use mathematics to help you answer this question by adding a trend-line to your Excel data, i.e., fit the data to a line.

Part 3 – Analyzing a Cu(NO₃)₂ Solution of Unknown Concentration

Often, quantitative analytical studies employ absorbance vs. concentration plots similar to the one prepared above to determine the concentration of an unknown. Such a plot is known as a calibration curve. The solutions of known concentration used to acquire the data for the curve are referred to as standards. To use the curve, measure the absorbance of a sample of unknown concentration and then, using graphical interpolation, determine its concentration. (Hint: The process of interpolation will be easiest if your group uses Excel to display the equation associated with the trend line.) Employ this approach to determine the concentration of the Unknown Cu(NO₃)₂ solution provided to you.

Part 4 – Solution Spectra Before and After Mixing

Fill a cuvette approximately two-thirds full with 1.0 x 10⁻³ M Fe(NO₃)₃ solution. Fill a second cuvette approximately two-thirds full with 5.0 x 10⁻³ M KSCN. Based on their appearance, what do you expect the absorbance spectrum of each of these solutions to look like? Try it and find out! Now mix the contents of these two cuvettes in a small container. Is the absorbance spectrum remarkably different for the mixture? Note that when an acidic solution of Fe(NO₃)₃ is added to a solution of KSCN, the following net reaction occurs: Fe³⁺ (aq) + SCN⁻ (aq) ⇌ [Fe(SCN)]²⁺ (aq). How does this influence the spectrum of the mixture?

Report

Your lab report should be a formal, individual report that addresses all the questions posed in this write-up in the context of the spectroscopy used in these experiments. It should be prepared according to the “Guidelines for Laboratory Reports” on the lab website.
Glossary

absorbance
a measure of the amount of electromagnetic radiation absorbed as defined by $A = \log(1/T)$ where $T$ is the transmittance defined below

absorption spectrum
the absorbance as a function of the incident electromagnetic radiation; effectively the amount of light absorbed by a material as a function of the wavelength

color wheel
a diagram that displays the components of the visible region and their respective wavelengths

cuvette
a transparent container used for spectroscopic measurements

electromagnetic radiation
radiation composed of electric and magnetic fields oscillating perpendicular to one another and perpendicular to the direction of propagation; examples include radio waves, microwaves, infrared, visible, ultraviolet, x-rays, and gamma rays; comes in quantum mechanical units called photons

frequency
the number of oscillations per unit time undergone by the electric (or magnetic) field amplitude of electromagnetic radiation; denoted $\nu$; inversely related to the radiation wavelength, $\lambda = c/\nu$, and proportional to the energy, $E = h\nu$

spectrophotometer
an apparatus used to obtain a spectrum by measuring the intensity of light transmitted through a sample relative to the intensity of the incident light

stock solution
a concentrated solution of known molarity often used for making dilute solutions

transmittance
the fraction of incident radiation (as measured by the intensity) that passes through a material; depends on the radiation wavelength

wavelength
the spatial distance between two peaks in the electric (or magnetic) field magnitude of electromagnetic radiation; denoted $\lambda$; inversely related to the radiation frequency, $\nu = c/\lambda$, and energy, $E = h\nu = hc/\lambda$, where $c$ is the speed of light