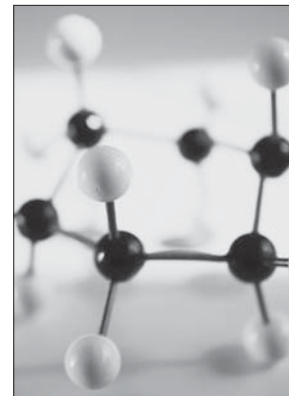


Experiment 5



Preparation and Optical Properties of Silver Nanoparticles

Learning Outcomes

This experiment will introduce the concept of nanomaterials, spectrophotometry and Beer's Law. Solutions of silver nanoprisms of various sizes will be prepared. The solutions will be used to obtain absorption spectra. Serial dilutions of one nanoprism solution will be performed to run a Beer's Law experiment and determine the molar absorptivity of blue nanoprisms.

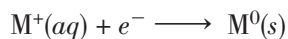
Introduction

Nanomaterials are of great interest to current scientific exploration and are becoming increasingly important in emerging technologies of electronics, medicine, and energy, among others. Drug delivery, tuning of optical properties and catalysis are examples of how nanotechnology is put to use. In this experiment, we will focus on the optical properties of silver nanoprisms.

The prefix “nano” denotes a factor of 10^{-9} , so one nanometer is equal to one billionth of a meter. Nanotechnology usually includes structures ranging from 1 to 100 nm in size. At this scale, quantum mechanical effects play an important role in the properties of the material. In some cases, the properties of a nanomaterial depend more on quantum size effects than on the elemental composition of the material itself. In this experiment, we will exploit the size effects of silver nanoprisms to tune the absorption of visible light via a mechanism called surface plasmon resonance. The specifics of this mechanism are beyond the scope of this lab, but the size effects are quite evident, as the different sized silver nanoprisms display vastly different colors in solution.

Control of size and shape is essential to obtain the desired properties of nanoparticles. To discuss nanoparticle synthesis, it's helpful to define the various stages through which nanoparticles go as they grow. The process begins with **nucleation**, in which the sub-nanometer-sized particle grows from a few bonded atoms to the point where the atomic arrangement begins to resemble, as more atoms are added, the arrangement (i.e., structure) they will take in the final nanoparticle (and, usually, the structure they adopt in the bulk material involved). After the nucleation phase, nanoparticles enter the **growth** phase—wherein the particles grow to their final size. In most nanoparticle synthetic procedures, the growth phase ends when a “capping reagent” covers the surface of the nanoparticles to prevent the addition of more atoms *and* to prevent the nanoparticles from aggregating together to form a bulk solid. In practice, because it can affect the rate at which atoms are added to different surfaces of the growing nanoparticle, the capping reagent can influence the shape of the nanoparticles.

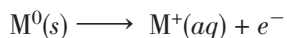
Most metal nanoparticles are synthesized in a reduction reaction in which dissolved metal ions react with a **reducing agent** to form elemental metal nanoparticles,



Preparation and Optical Properties of Silver Nanoparticles

Reduction step: The reducing agent used is sodium borohydride, NaBH_4 .

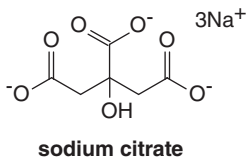
If one does not use a capping reagent or uses a reducing agent that is too strong, a bulk-metal “mirror” or macroscopic metal particles will result. An etching agent is often included to remove more reactive, undesired atoms at the surface of the growing nanoparticle so that the most stable shape is predominant. For metal nanoparticles, a suitable oxidizing agent is often used as an etching agent. The etching agent reoxidizes M^0 on less stable surfaces to M^+ , so that the metal ion can be deposited on more stable particle shapes/sizes.



Oxidation or “etching” step: The oxidizing agent used is hydrogen peroxide, H_2O_2 .

The oxidation and reduction reactions reach equilibrium and ensure that only the most stable shape and size of nanoparticles survives.

Metal complexing agents are added to the reaction to slow the rate of reduction and to stabilize particles of certain shapes and sizes. In this experiment, sodium citrate acts to charge-stabilize the silver nanoprisms; it tunes the reduction rate and stabilizes crystal growth directions. The structure of sodium citrate (chemical formula: $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) is shown below. Sodium bromide is added to control the size of the nanoprisms. Bromide binds to the silver, and at higher concentrations limits the growth of the nanoparticle, inhibiting the growth of the nanoparticle so that smaller nanoprisms are formed.

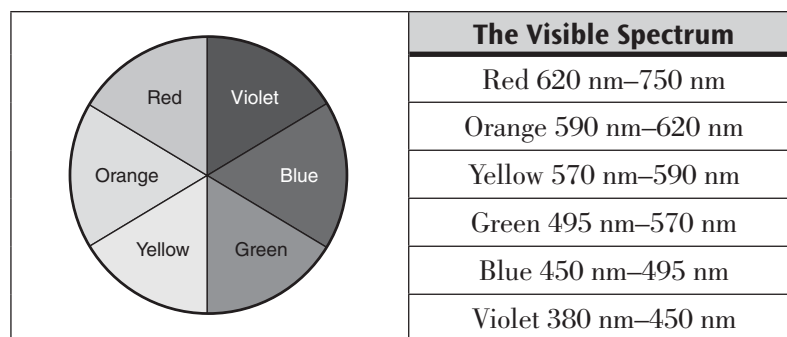


The procedure followed in this experiment is known to produce a high yield of silver nanoprisms. Other shapes of silver nanoparticles can be formed under different experimental conditions.

Spectrophotometry

The nanoparticle solutions will display vastly different colors than bulk silver metal. The colors we see are a result of the way that the solutions interact with visible light. In this experiment, you will examine the cause of these colors by obtaining a visible spectrum of each solution.

Visible light is just a small component of the electromagnetic spectrum, which spans wavelengths from short wavelength (high energy) X-rays to long wavelength (low energy) radio waves. The wavelengths of visible light range between 400 nm (violet) and 700 nm (red). When white light, which spans all visible wavelengths, shines on colored molecules or solutions, the molecules absorb some wavelengths of light, while other wavelength photons are transmitted (or reflected). What we see are the wavelengths of light not absorbed. The combination of transmitted light wavelengths generates the complimentary color that we perceive. For instance, objects that absorb red light reflect blue and yellow light, which makes them appear green. The following color wheel has the complementary pairs of colors across from each other.



When light passes through a light-absorbing solution, a portion of the light is absorbed by the solute and another portion is scattered by particles in solution and by the sample holder or cuvette (Figure 1).

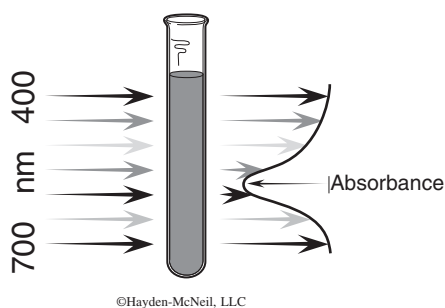


Figure 1. A solution will absorb light of specific wavelengths.

A spectrophotometer is used to measure the amount of light at a given wavelength, λ , that passes through a sample. **Transmittance** is defined as the ratio of the light intensity, I , that passes through the solution to the light intensity that passes through a *blank* sample, I_0 . The blank sample usually contains the solvent used to prepare the solution so that any light scattering or absorption by the solvent and the cuvette is accounted for. Transmittance is generally reported as percent transmittance, %T.

$$\%T = \frac{I}{I_0} \times 100$$

Absorbance is simply defined as the negative logarithm of the transmittance, T ,

$$A = -\log T = -\log \frac{I}{I_0} = \log \frac{I_0}{I}$$

The absorbance and transmittance of light for a solution depend on the wavelength of light used and the concentration of the absorbing solute. The spectrophotometer we will use is a SpectroVis Plus. Light (from the LED and tungsten bulb light sources) passes through the sample. Emerging light goes through a good-quality diffraction grating, and then the diffracted light is collected and sorted by the CCD array detector and sent to the computer (Figure 2).

Preparation and Optical Properties of Silver Nanoparticles

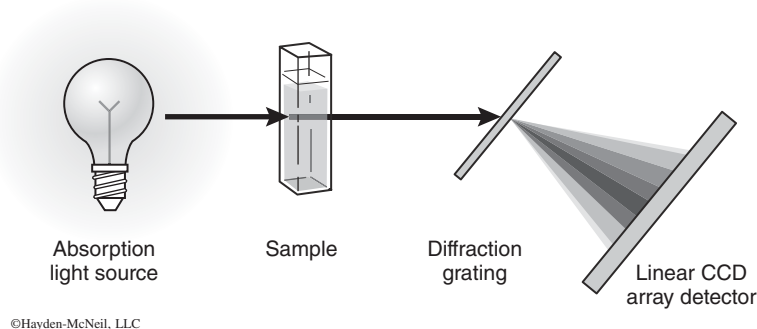


Figure 2. Schematic diagram of a SpectroVis Plus.

Beer's Law

The absorbance of a sample is directly proportional to the sample concentration, c (in mol/L), and the distance traveled by the light through the sample, or path length, b (in cm). An equation relating the Absorbance to the product of b and c is completed by including a wavelength-dependent proportionality constant that depends on the properties of the solute called **molar absorptivity**, ϵ (in L/mol•cm). The resulting expression is known as Beer's Law.

$$A = \epsilon bc$$

When determining the absorbance of a particular solute in solution, a correction (the subtraction of the absorbance of the solvent) is typically applied. This step is achieved by obtaining a “background” spectrum of a *blank* solution containing the solvent and any other solutes excluding the analyte or compound being studied. The background level absorbance becomes the “zero” absorbance. When the blank is replaced with the sample, any additional absorbance is due to the analyte. The spectrophotometers we will use only need to have this background spectrum obtained once when the spectrophotometer is initially started.

If the solutions of nanoparticles obey Beer's Law, a plot of absorbance versus concentration for a series of samples with different but known concentrations will produce a straight line with a positive slope passing through the origin (a sample with $c = 0$ will not have any absorbance). The slope of this line is equal to the quantity ϵb . For most spectrophotometers the path length b is a constant, usually 1.0 cm.

The Experiment

In this experiment, four different solutions of silver nanoparticles will be prepared. The only variable that will be changed for the solutions is the amount of added sodium bromide. If successful, each of the final solutions will exhibit a different color. An absorption spectrum will be obtained for each of the four solutions, and the wavelength of maximum absorbance, λ_{\max} , for each solution will be identified. Dilutions of one of the four solutions of nanoparticles will then be performed, and the absorption of each solution at the different concentrations will be measured to determine if these solutions obey Beer's Law. If Beer's Law is followed, the molar absorptivity of the nanoparticles will be determined.

Safety Considerations

Sodium citrate may cause irritation to the skin, eyes, and respiratory tract. Silver nitrate is poisonous, corrosive, and a strong oxidizer. Solutions of silver nitrate are light sensitive and will be stored in amber-colored glass bottles. Silver nitrate solutions can also stain clothing, skin, and jewelry. As a strong oxidizer, hydrogen peroxide is corrosive, causing burns to the eyes, skin, and respiratory tract. Sodium bromide is harmful if swallowed or inhaled. Sodium borohydride is a corrosive, flammable solid that is dangerous when wet and may release hydrogen gas. Solutions of sodium borohydride should not be kept in tightly sealed vials to avoid possible explosions. The vials with the freshly synthesized nanoprisms should not be capped due to possible gas release from unreacted borohydride and hydrogen peroxide.

This experiment uses dilute solutions, which minimizes most of the risks associated with handling these chemicals. However, if any of these solutions are spilled on your skin, clothing or get into your eyes, immediately and thoroughly wash the affected area with water for at least 15 minutes and notify your instructor of the incident. Approved chemical splash goggles must be worn at times when chemicals and/or glassware are in use anywhere in the lab.

All waste solutions should be discarded in the inorganic waste container in the hood.

Chemicals

Millipore grade purity ($>18\text{ M}\Omega$) water
 $1.25 \times 10^{-2}\text{ M}$ sodium citrate
 $3.75 \times 10^{-4}\text{ M}$ silver nitrate
 $5.00 \times 10^{-2}\text{ M}$ hydrogen peroxide
 $1.00 \times 10^{-3}\text{ M}$ sodium bromide
 $5.00 \times 10^{-3}\text{ M}$ sodium borohydride

Equipment

$4 \times 20\text{ mL}$ (or larger) glass vials
 $3 \times 50\text{ mL}$ beakers
 200 mL beaker (*for waste collection*)
 10 mL graduated cylinder
Microliter syringe (two per lab)
 5 mL volumetric pipet
Labeling tape
Spectrophotometer (four per lab)
 4 cuvettes
Kimwipes or other lint-free tissues

Experimental Procedure

Part A: Solution Preparation

The success of this experiment depends on controlling the number of ions in solution. For this reason, Millipore grade water is used to prepare all of the solutions. Furthermore, although all of the glassware in the lab should be cleaned and thoroughly rinsed, all glassware must have a final rinse performed with Millipore water before beginning this experiment.

1. Carefully and thoroughly rinse all glassware three times with a small amount of Millipore grade water. **Do not use tap water. Do not use distilled water.**
2. Label the vials 1–4.

Preparation and Optical Properties of Silver Nanoparticles

- Using the calibrated dispensing pumps, add the indicated volumes of the solutions listed below to **each** of the four vials. Be careful while using the dispensing pumps. They dispense precise volumes, but they cannot dispense quickly. Do not apply excessive pressure to the pumps.
 - 2 mL of 1.25×10^{-2} M sodium citrate to all four vials
 - 5 mL of 3.75×10^{-4} M silver nitrate to all four vials
 - 5 mL of 5.00×10^{-2} M hydrogen peroxide to all four vials
- Using a microsyringe, add the following amounts of 1.00×10^{-3} M sodium bromide solution to each of the indicated vials. **Note:** Carefully controlling the amount of this reagent is critical to producing solutions with four different colors. Make sure that there are no air bubbles in the syringe, as having bubbles will introduce error into the volumes of NaBr solution added.

Vial 1: 0 μ L

Vial 2: 20 μ L

Vial 3: 25 μ L

Vial 4: 40 μ L

- Rinse a 50 mL beaker with a small amount (~1–2 mL) of 5.0×10^{-3} M sodium borohydride solution and then discard this into your designated waste beaker. Collect slightly more than 10 mL of the sodium borohydride solution in the beaker.
- Rinse your clean graduated cylinder or a graduated pipet with a small amount (< 0.5 mL) of the sodium borohydride solution and discard the solution into your designated waste beaker. Add 2.5 mL of 5.00×10^{-3} M sodium borohydride to each vial. Gently swirl each vial to mix the reactants. Record any observations regarding color changes in your lab notebook; these should begin almost immediately. Once a stable prism size is obtained (as judged by a constant solution color), the visible spectrum of the resulting silver nanoprism dispersion can be determined. This should take about 5 minutes.
- Discard any excess reagents in your designated waste beaker.

Part B: Obtain Absorption Spectra



The spectrophotometer will obtain an absorption spectrum from 380–900 nm, which extends into the infrared region of the electromagnetic spectrum. This will allow you to see the full absorption curve for all of the samples. When you obtain an absorption spectrum, it is important to have an unobstructed path for the light to pass through a sample. If the light is somehow blocked (by debris or air bubbles in the sample, or by fingerprints or water droplets on the outside of the cuvette) then your data will be unreliable. If the nanoparticle solutions are left sitting in the cuvettes for too long, tiny air bubbles will accumulate in the solution. Therefore, ***wait until right before you measure your absorption spectra to fill the cuvettes with each nanoparticle solution.***

If you are the first person to use your spectrometer:

Connect the spectrometer to the computer by attaching the cord to the spectrometer and plugging the other end into the USB port on the computer (***do NOT plug it in to the Vernier Box***). The computer will recognize the spectrometer. Start LoggerPro and open the experiment file “Silver Nanoparticles” from the lab drive in the usual manner.

Under the “Experiment” heading in the toolbar, select “Calibrate” and then “Spectrometer 1.” This will turn on the light source; wait 90 seconds for the bulb to warm up. Then fill a cuvette about 3/4 of the way full with Millipore water and insert the cuvette in the instrument, orienting the cuvette so the clear sides line up with the white arrow on the top of the spectrophotometer. Then click on “Finish Calibration.” The spectrometer will acquire the background. Click on “OK.”

To obtain your absorption spectra:






1. Obtain four clean cuvettes and rinse them three times with a small amount of Millipore grade water.
2. Use a small amount (< 0.5 mL) of the nanoparticle solution in vial 1 to rinse the first cuvette, and then discard this solution into your waste beaker. Do the same with the remaining cuvettes and nanoparticle solutions, using a new cuvette for each new nanoparticle solution. Note the color of each solution so you do not confuse your cuvette and sample pairings.
3. Take your four nanoparticle solutions and four cuvettes to the spectrophotometer.
4. Take the cuvette for the vial 1 solution and carefully fill it 3/4 of the way full with the nanoparticle solution from vial 1. Inspect the solution to make sure there are no debris or air bubbles in the cuvette. Using a lint-free tissue, wipe off the sides of the cuvette to remove any fingerprints or water droplets and place it in the SpectroVis Plus. Be sure to orient the cuvette so that the clear sides (those without ridges) are lined up with the white markings on the spectrophotometer. With the cuvette in place, click on “Collect”  in the LoggerPro software to begin collecting your spectrum. After about 3 seconds, the spectrum of the solution in vial 1 should appear on the computer screen. Click on stop  to stop the data collection. Note the general size and shape of the spectrum in your lab notebook.
5. Repeat the process in step 4 with your samples from solutions 2–4. This time, after you press “Collect,” a dialogue box will appear to ask if you want to erase the data from your previous collection; **click on “Store Latest Run.”** When you are finished, you will have four different spectra on the same plot.
6. Save your file (do **not** export as a CSV file yet) and transfer the data file to the computer at your workstation. When you are done collecting data for this experiment, you will need to re-open this file to format your graph and collect data for the experiment analysis.
7. Keep the cuvette with the solution from vial 1; you will use this solution again in the final part of this experiment. **Note:** *If your solution in vial 1 did not produce a blue-colored solution, you should use the solution from vial 2 for Part C of this experiment, so keep this solution instead. Solutions in the remaining cuvettes can be poured into your waste beaker and the cuvettes cleaned for the next step.*

Part C: Beer’s Law Experiment

You will now perform dilutions of your nanoparticle solution from vial 1 to determine if this solution follows Beer’s law. First you will dilute a known volume to half of its initial concentration. Then, you will take a portion of this “half” concentration solution and dilute the concentration in half again. After measuring the absorbance of each solution, you will generate a plot of absorbance vs. concentration for this solution.



1. Rinse three 50 mL beakers, two cuvettes and a 5 mL volumetric pipet three times with a small amount of Millipore grade water. Two of the beakers need to be dried. Label the beakers A and B. The third should be filled with 15–20 mL of Millipore water.

Preparation and Optical Properties of Silver Nanoparticles

- Using the volumetric pipet, add 5 mL of Millipore grade water to beakers A and B.
- Using the 5 mL volumetric pipet, pull up a small amount (< 0.5 mL) of the silver nanoprisim solution from vial 1. Wet the inside of the pipet with this solution by turning the pipet horizontally and rolling the pipet carefully along the bench top. **DO NOT fill the pipet all of the way to the mark to rinse it; you will not have enough solution.** Drain this solution from the pipet into your waste beaker. Then, using the same volumetric pipet, take 5 mL of the silver nanoprisim solution from vial 1 and place it into beaker A. The resulting solution has a concentration of 0.5 times the solution in vial 1. Pour a small amount of this solution into the previously rinsed cuvette. Discard the solution from the cuvette into your waste beaker and fill this cuvette about 3/4 of the way full with the diluted solution.
- Rinse the 5 mL volumetric pipet with a small amount (< 0.5 mL) of the silver nanoprisim solution in beaker A as you did in the previous step. Then, using the same volumetric pipet, take 5 mL of the silver nanoprisim solution from beaker A and place it into beaker B. The resulting solution in beaker B has a concentration of 0.25 times concentration of the solution in vial 1. Pour a small amount of this solution into a second previously rinsed cuvette. Discard the solution from the cuvette into your waste beaker and fill this cuvette about 3/4 of the way full with the diluted solution. You now have three solutions to use for your Beer's law measurements.
- Take your three cuvettes back to the spectrophotometer and acquire a spectrum of the most concentrated sample, the original solution, as you have done before. After the acquisition is complete, click on the Configure Spectrometer Data-Collection icon  in the toolbar menu. A dialogue menu will appear. In the left most column under "collection mode" make sure the option "Absorbance vs. Concentration" is selected. The wavelength for λ_{\max} will automatically be selected. Record this value in your lab notebook. Click on "OK" to continue.
- Your most concentrated (original) sample should still be in the sample holder. Click on Collect  and then Keep . Enter the concentration of the sample. As this is the most concentrated sample, enter "1" for the concentration and click OK. Record the absorbance of this solution in your lab notebook. During your data analysis, you will adjust the concentration by multiplying this value by the concentration of silver in solution.
- Wipe the sides of the cuvette containing your second sample (from Beaker A, with a concentration of 0.5 times the original solution) with a lint-free cloth and place the cuvette in the spectrophotometer. After the reading stabilizes, click Keep . Enter the concentration of the sample. As this solution has half of the concentration of the original sample, enter "0.5" and click "OK." Record the absorbance of this solution in your lab notebook.
- Repeat the previous step for the most dilute sample from Beaker B, entering "0.25" for the concentration. Record the absorbance in your lab notebook. After you are done, click on Stop  to stop the data collection. Then, export your data as a CSV file and transfer the data to your computer.
- Empty the cuvettes, beakers with the diluted solutions, and any remaining nanoparticle solutions or reagents into your designated waste beaker. Pour all of your collected waste into the designated waste bottle in the hood. Thoroughly wash all glassware and the cuvettes with soap and water, and then rinse them with distilled water before returning it to the storage area. *Do not use the brushes to clean the cuvettes*; this could scratch the cuvettes. Wipe down your work area with a damp paper towel before you leave lab.

In-Lab Data Analysis

For the visible spectrum obtained for each of the nanoparticle solutions: Open the LoggerPro file with the absorption data for your 4 nanoparticle solutions.

1. **Determine λ_{\max} :** With your spectral data open in LoggerPro, click the “Stat” button  in the toolbar menu. This will bring up a dialogue box asking you to select the columns for statistics. You may select them all at once or one at a time. Here, run 1 will be the first solution you analyzed, run 2 will be the second, and so on. The “Latest” option will be the data for the final solution you analyzed. After clicking on “OK,” a text box will appear. In the second line of each text box is both the minimum and maximum absorbance data. Record both the value for λ_{\max} and the absorbance for each nanoparticle solution (from vials 1–4) in your notebook. **Note:** If you do not see these statistics, right click in the textbox and select “Statistics Options.” Add a checkmark in the box that says “Use Entire Range” and click on “OK.”
2. **Format your graph:** You will need to print a copy of this plot and turn it in with your Data Reduction and Analysis sheets for this experiment. Most of you will find it easier to format the graph in LoggerPro, rather than replot the data in Excel. After formatting, you can capture an image of the graph in LoggerPro by pressing the “Print Screen” button on the keyboard and pasting the image into Paint or Word, but first make sure that the following formatting criteria are in place.
 - Make sure that you can see the top most part (highest absorbance) of each peak. If you cannot see the peaks, click on the Autoscale  button in the toolbar.
 - Right click in the plot area and select “Graph options.” Start in the “Graph Options Tab.”
 - Type in a title for your graph in the “Title” box.
 - Under the “Examine” menu, click in the box beside legend to add a legend to the graph.
 - Go to the “Axis options” tab and make sure that the y-axis label is “Absorbance.”
 - Click on “Done” to save these changes.
 - You can revise the labels for the legend by right clicking on the plot area and selecting the “Column Options” menu. Select the data column, under the “Column Definition” tab, enter a new name for the label.
3. Capture an image of your graph and paste it into Paint or Word. Save your work and export your LoggerPro data as a CSV document for any future analysis you may need to perform.

Postlab Analysis

1. Calculate the number of moles (per single nanoparticle solution) of each reagent used in this experiment. All of the solutions have the same number of moles of sodium citrate, silver nitrate, hydrogen peroxide, and sodium borohydride. The number of moles of sodium bromide varies per preparation.
2. Calculate the concentration of each reagent in your nanoprism preparations. The volume introduced for any NaBr that may have been added can be ignored; it does not significantly change your concentrations.

Preparation and Optical Properties of Silver Nanoparticles

- Determine the ratio of moles of NaBr to moles of silver (added as silver nitrate) for each of the four nanoprism preparations. Plot a graph of the molar ratio of Br⁻/Ag (independent variable) to λ_{\max} (dependent variable) for each solution.
- Determine the concentration of silver nanoprisms in your blue solution. (The solution without any bromide added.) To make the calculation simpler, you should make two assumptions: All of the silver atoms in solution are in blue nanoprisms, and no other colored species is present in solution.
 - It is known that silver nanoprisms that display a blue color in solution have an average volume of 9,400 nm³ and the density of silver is 10.5 g/cm³. Using this information, calculate the number of silver atoms per nanoprism.
 - Use the number of silver atoms per prism and the number of moles of silver added to the solution to calculate the number (“moles”) of silver nanoprisms in the blue solution.
 - Convert the number of moles of silver nanoprisms in solution to the concentration of silver nanoprisms in the blue solution.
- Taking the concentration calculated in the previous step, determine the concentration of silver nanoprisms in your diluted samples for the Beer’s Law experiment. Then, using graphing software such as Excel, plot a graph of absorbance vs. concentration for vial 1 silver nanoprisms at λ_{\max} . Use the calculated concentrations of silver nanoprisms in this graph; **do not use the relative concentrations**. Fit a linear regression line to your data. Solutions that follow Beer’s Law have no absorbance at 0 concentration, therefore you need to force the trendline to go through the origin. Do this by selecting “Set Intercept = 0.0” when you add a trendline in Excel.
- Use the equation for this regression line of the graph (of the form $y = mx + b$) and Beer’s law, $A = \epsilon bc$, to determine the molar absorptivity (ϵ) of the nanoprism solution. The slope of the fit line (m) is equal to

$$\epsilon b$$

Postlab Assignment

Refer to the course syllabus to determine whether you will write a full report or if you will submit the Data Reduction and Analysis (DRA) worksheet for this experiment. If this experiment requires a report, then in addition to the required components listed in the report guidelines, answer the following questions in the discussion section of your report:

- Write three paragraphs in which you discuss the results of this experiment. In the first paragraph, address the synthesis of the nanoprism solutions. Answer the following questions:
 - What is happening chemically during the reduction step?
 - What are the roles of each reagent in the preparation? Which reagent seems to control the size of the nanoparticle solutions being prepared?
 - The preparation of nanoparticle solutions adds a reducing reagent, sodium borohydride, to an oxidizing agent, hydrogen peroxide. Is it conceivable that these two reagents would react with each other? What experimental evidence do you have to support your answer?

2. In the second paragraph, discuss the results from the absorption spectra that were obtained for your solutions and answer the following questions:
 - Summarize the appearance and absorption spectra data for each of the nanoparticle solutions you prepared.
 - What effect does increasing the amount of bromide ion have on λ_{max} for the solutions? Refer to your plot of the molar ratio of Br^-/Ag to λ_{max} for each solution.
3. In the third paragraph, discuss the results from the Beer's Law experiment and answer the following questions:
 - Do the nanoparticle solutions appear to follow Beer's Law? Why or why not?
 - Why is it important to force the regression line in the Beer's Law plot of absorbance vs. concentration to go through the origin? Would adding the point (0,0) to your data set have the same effect? Why or why not?
 - What is the molar absorptivity of the blue nanoprisms?

Be sure to use your experimental results to support your conclusions. Discuss the confidence you have in your conclusion while citing examples from your data. In each case, explain what is happening on a *molecular* level.

Reference

The procedure followed in this experiment is derived from an article by Frank, A. J. *et. al. J. Chem. Ed.* **2010**, 87, 1098–1101.

Preparation and Optical Properties of Silver Nanoparticles

Preparation and Optical Properties of Silver Nanoparticles

Name _____

Lab Partner _____

TA Name _____

Section _____

Score _____

____ Plot of absorbance for nanoparticle solutions stapled to back of DRA

____ Plot of moles of Br⁻/Ag vs λ_{max} stapled next

____ Plot of Beer's law experiment next

____ Data sheet stapled to back of plots

Part A: Nanoparticle Solution Preparation

1. Show a sample calculation for determining *both* the number of moles and the molar concentration of sodium citrate in the nanoparticle solution preparations. Then, calculate the same values for each of the reagents in the nanoparticle solutions.

General Equations	
Moles:	Concentration:

Chemical	Moles	Concentration
Sodium citrate		
Silver nitrate		
Hydrogen peroxide		
Sodium borohydride		
Sodium bromide (Vial 1)		
Sodium bromide (Vial 2)		
Sodium bromide (Vial 3)		
Sodium bromide (Vial 4)		

Preparation and Optical Properties of Silver Nanoparticles

- Write a chemical equation for the reduction step in the formation of silver nanoparticles.
- What is the role of sodium borohydride?

Part B: Absorption Spectra

- Summarize the appearance and absorption spectra data for each of the nanoparticle solutions you prepared.

Solution	Color (appearance)	λ_{\max} (nm)	Absorbance	Color of Light Absorbed
1. 0 μL NaBr				
2. 20 μL NaBr				
3. 25 μL NaBr				
4. 40 μL NaBr				

- Calculate the percent transmittance at λ_{\max} for the silver nanoparticles in vial 1. (The following equation can be used to find the percent transmittance: $A = 2 - [\log (\%T)]$)

General Equation

3. Give the ratio of moles of Br^- (added as NaBr) to moles of silver (added as silver nitrate) for each of the four nanoprism preparations. Show your work in the space provided.

Vial 1: _____

Vial 2: _____

Vial 3: _____

Vial 4: _____

General Equation

4. What effect does increasing the amount of bromide ion have on λ_{max} for the solutions? Refer to your plot of the molar ratio of Br^-/Ag to λ_{max} for each solution.

Part C: Beer's Law Experiment

1. Give the wavelength at which the absorptions were measured for the Beer's Law experiment.
2. Do the silver nanoprisms from vial 1 obey Beer's Law? Why or why not?