

Size Determination of Gold Nanoparticles using Mie Theory and Extinction Spectra

OUTLINE OF THE PROCEDURE

- A) Measure the extinction spectra of each of your samples.
- B) Model the extinction spectrum of your particles using MiePlot
- C) Plot both data in Excel and report the best estimates of the particle size.

Lab Report Check List

Your lab report should include:

- 1. 50pts)** Graphs of experimentally measured extinction spectra and your best fit spectra. Graphs must be clearly labeled.
- 2. 55pts)** A table summarizing the results of your measurements and modeling (see example table).
- 3. 35pts)** Sample calculations for each of the questions showing the equations (algebra) and substitutions into the equations with the units clearly shown.
- 4. 10pts)** The yellow pages or photocopy from your notebook.

Total 150pts.

Assigned Sols _____

PART A Measure the extinction spectra of each of your samples.

Step 0) log on the the Cary 50 computer. The user name and password are taped to the monitor.

Step 1) Start the program by selecting `scan` from the program menu, or from `programs/CaryWinUV/scan`.

- When the program starts, you should hear the Cary 50 start up (high pitched sound). A window opens with two big buttons at top center `start` and `stop`.
- If instead you see two buttons `connect` and `stop` (and text at the lower left `cary 50 off line`). Click on the `connect` button, you should hear the Cary 50 start up (high pitched sound). Then the buttons will change to `start` and `stop`.

Step 2) Set up the scan. There are 3 buttons on the left, `set up`, `zero`, and `baseline`. Click `set up`. Select the `cary` tab. Use the following settings.

- x mode: start 1000nm; stop 400 nm
- y mode: mode: abs; Y min -0.05; Y max 2
- cycle mode: not checked
- beam mode: dual beam
- scan control: simple; medium
- display options: overlay

Step 3) Perform baseline and zero corrections.

3A) Setup the corrections. In the `setup` window, click on the `baseline` tab (the same window as in step 2). Use the following settings.

- correction: zero/baseline

3B) Baseline measurement. Prepare the blank sample for the baseline measurement (100% transmittance, 0 absorbance reference). The blank should include all of the components except to one you want to measure. In our experiment this is a cuvette filled with deionized water. The cuvette should be about $\frac{3}{4}$ full. Be sure that there are not air bubbles on the windows of the cuvette. Insert the sample in the cuvette holder, close the cover, and click `baseline`. The Cary 50 will scan and acquire the *baseline* spectrum.

3C) Zero measurement. Remove the blank and replace it with the black plastic beam block. Click on `zero`. The Cary 50 will scan and acquire the *zero* spectrum.

Step 4) Sample measurement. Empty the distilled water from the blank and replace it with a sample of one of your gold nanoparticle preparations. Use the waste container provided. Be sure that it is about $\frac{3}{4}$ full and that there are no air bubbles on the windows. Click on the `Start` button at the top center of the main window. You will be prompted for a file name. Create your own directory in the following path

C:\Cary 50 user data\Nano Lab 2007

The Cary 50 will now scan and acquire the *absorption* spectrum of your sample. Note that the y axis is absorbance units. The x axis is wavelength in nanometers.

step 5) Export your data as CSV. Your spectrum is automatically saved, but this is in a format that can only be read by the CaryWinUV program. Because you need to import the data into excel later, save the file in CSV format. To do this, go to the file drop down menu, select `save as`, then from the file type drop down list select `spreadsheet ascii (*.csv)`, save.

Step 6) Measure any other samples. Measure your other sample by repeating step 4. You do not need to repeat steps 1-3 unless you have shut down the instrument.

Step 7) Shut down the Cary 50 and clean up. Remove your cuvette from the Cary 50. Rinse the cuvette with deionized water from the wash bottle. dry the outside of the cuvette with a Kimwipes, then invert it over the filter paper and cover it with the beaker. Clean up all pipettes, Kimwipes, and other debris. Close the cover of the Cary. Close the program, copy your files (or email them to yourself). Log off the computer.

Step 8) Import your results into Excel. Import the CSV file into Excel. Plot your data using unsmoothed lines with lines connecting the data points, and no symbols. Your y axis should be 'absorbance'. The x axis should be 'wavelength (nm)'. Make one graph for each of your gold nanoparticle preparations. From you graph measure the wavelength of the absorption peak. We are only interested in the peaks that occur at wavelengths longer than 500 nm. You will use these values as you model the extinction spectrum in MiePlot

Part B) Model your results in MiePlot.

Step 0) Download Mieplot from the NanoLab [www site](#). Install this on your computer. It is a small program and should not present any difficulty.

Step 1) Start MiePlot and set it up to model the extinction spectra of gold nanoparticles.

1A) Set up for Gold spheres in water. From the Advanced drop down menu select refractive index, sphere, gold. Then again from the Advanced drop down menu select refractive index, surrounding medium, water, Segelstein, then a box will pop up, check complex.

1B) Set up to calculate and to plot the extinction, scattering, and absorption cross sections versus wavelength. On the top right from the drop down box (initially: intensity v. scattering angle) select $C_{ext}/C_{sca}/C_{abs}$ v. wavelength.

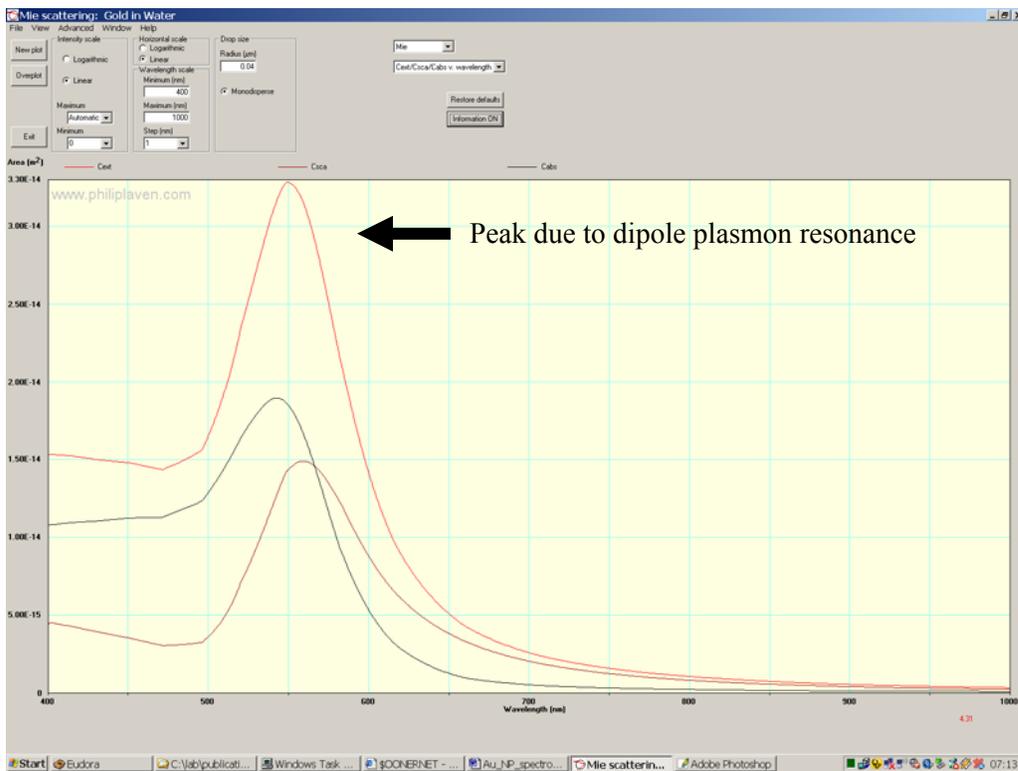
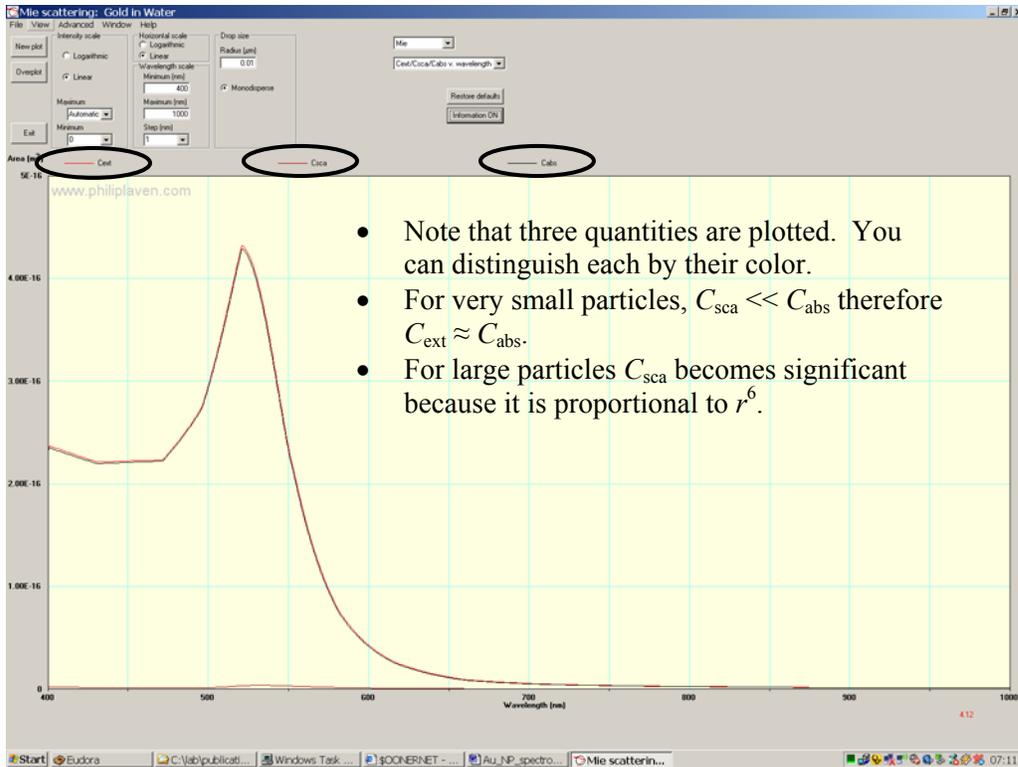
1C) Set up the wavelength range to correspond to the 400 nm to 1000 nm range that you measured with the Cary 50.

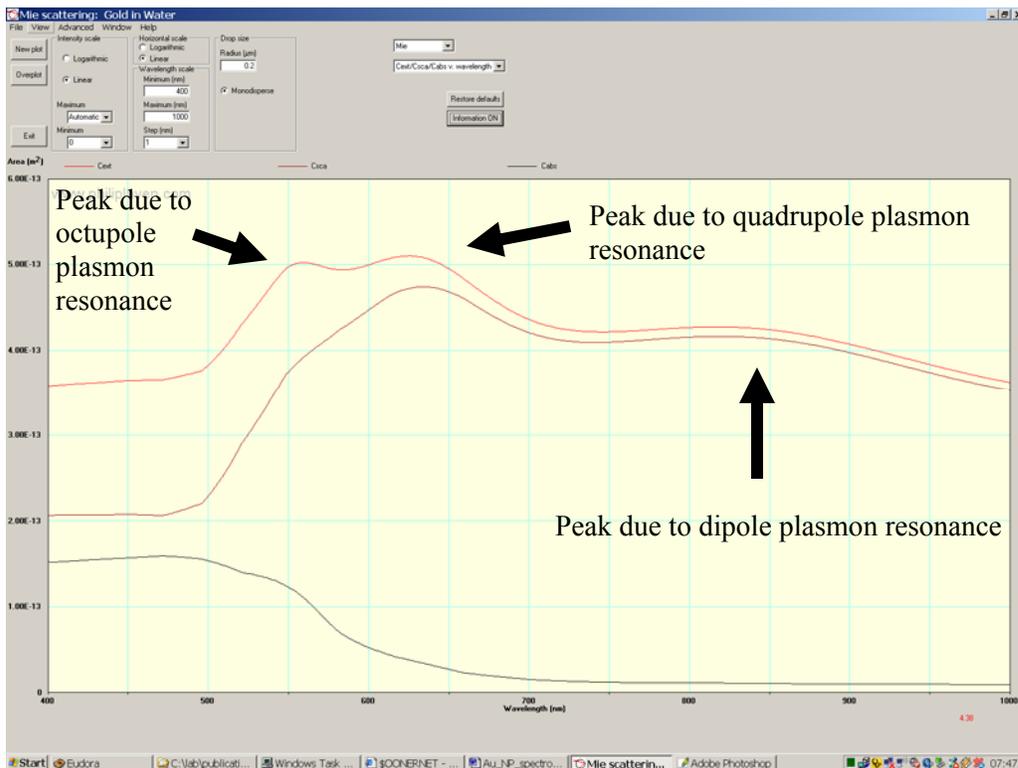
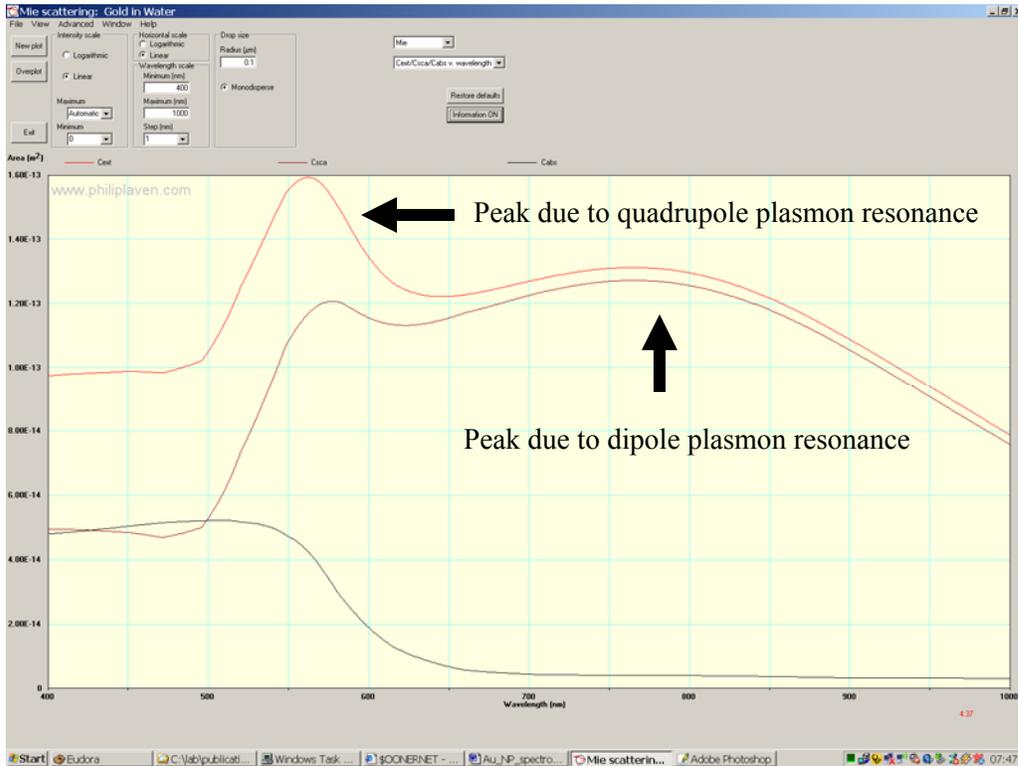
1D) Select the size of the sphere. NOTE MiePlot uses RADIUS in units of MICROMETERS. Start with a radius of 0.005 μm .

1E) Calculate the values and make the plot. Click New Plot. A progress bar will appear on the upper right. When it is finished your plot will be displayed. Note the three cross sections are displayed in different colors. We are specifically interested in C_{ext} .

Step 2) Perform the modeling. Mie theory calculations are a complex. They can be used to calculate the spectra of nanoparticles give their size and refractive index. However the mathematics cannot be easily inverted. You cannot put a spectrum into the calculation and get a particle out! To determine the particle size we perform several calculations and then compare then to our experimental data. The particle size of the best-fit spectrum will be the particle size we determine from Mie Theory

See the examples that follow. Note that as you increase the particle size, the peak moves to longer wavelengths and becomes broader. This peak is the dipole plasmon resonance. *Dipole* means that the wave set up on the surface of the particles has *one node*. On further increase in particle size, a second peak begins to emerge where the dipole resonance occurred for small particles. This is the quadrupole plasmon resonance. *Quadrupole* means that the wave set up on the surface of the particles has *two nodes*.





Exporting and working with data from Mieplot.

From the file menu, select save numerical results as text file.

This file can be imported into excel as a **TAB** delimited text file.

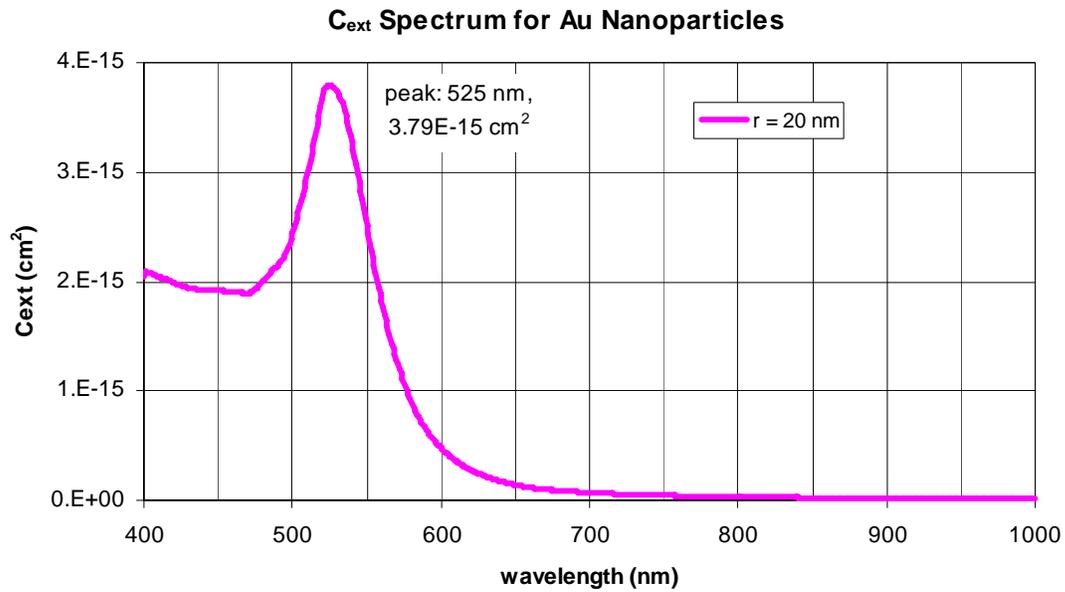
From the file drop down menu select open. From the open window, select files of type: text files (*.prn, *.txt, *.csv). Now navigate to your file and select open. The text import wizard will start. Note that tab delimited text is the default, so pressing finish on this screen often will give you the desired result.

In detail:

- step 1) under delimited, click next;
- step 2) in the delimiters box select tab, click next;
- step 3) in the column data format box select general, now click finish.

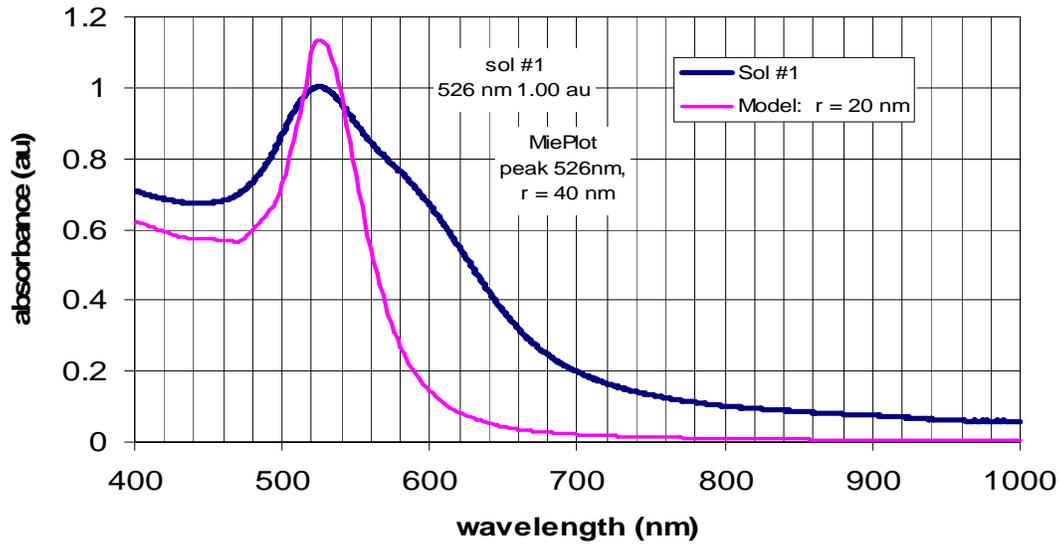
MiePlot v3.4.10					
Date & Time: 2005-03-10 08:07:20					
Calculation Method: Mie (plane wave)					
Sphere:		Gold			
Medium:		Water			
Graph type:		Cext/Csca/Cabs v. wavelength			
Scattering angle = 0					
Wavelength	Ref Index (real)	Ref Index (imaginary)	Cext	Csca	Cabs
400	1.087871431	1.446879408	2.04E-15	1.23E-16	1.92E-15
401	1.087514072	1.447303652	2.09E-15	1.33E-16	1.96E-15
402	1.087156632	1.447727993	2.09E-15	1.31E-16	1.95E-15
403	1.08679913	1.448152407	2.08E-15	1.30E-16	1.95E-15
404	1.086441546	1.448576918	2.07E-15	1.29E-16	1.95E-15
405	1.086083131	1.449000474	2.07E-15	1.28E-16	1.94E-15
406	1.085723491	1.449422573	2.06E-15	1.27E-16	1.94E-15
407	1.085363769	1.449844767	2.06E-15	1.26E-16	1.93E-15
408	1.085003987	1.450267031	2.05E-15	1.24E-16	1.93E-15
409	1.084644123	1.450689391	2.05E-15	1.23E-16	1.93E-15

We are interested only on C_{ext} . Graphing C_{ext} versus wavelength give us the calculated extinction spectrum of the Au nanoparticles.



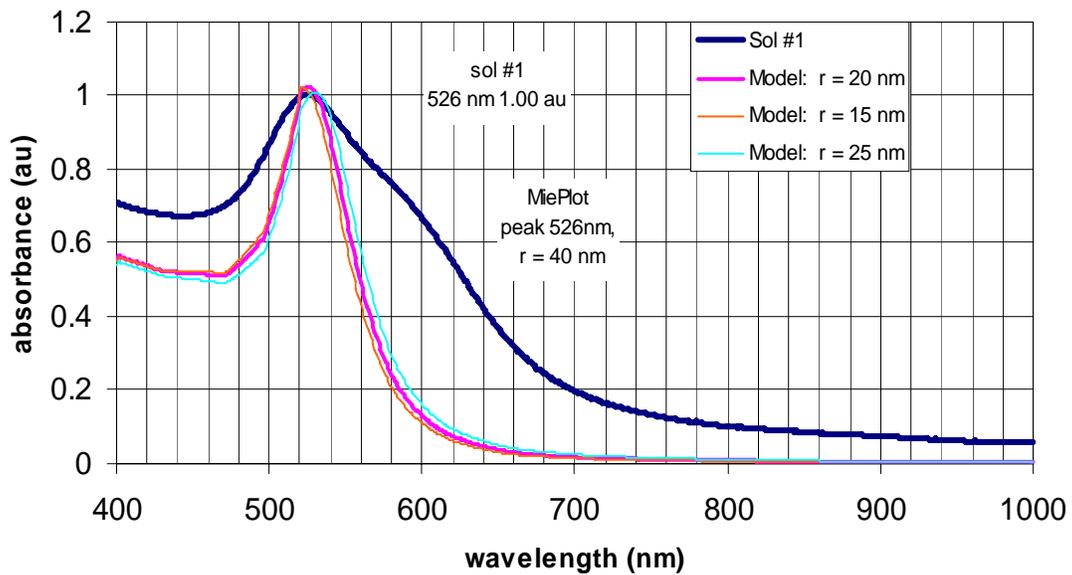
Example Graph showing your experimental data with the extinction spectrum from the best fit particle size.

Au Sol #1 Extinction Spectrum with Model Calculations



Example Graph showing your experimental data with the extinction spectrum from the best fit particle size with sizes above and below the best fit radius.

Au Sol #1 Extinction Spectrum with Model Calculations



Prepare a table of your results. The following is a guide.

sol	Measured		Best Fit		Calculated values				
	$\lambda @ A_{\max}$ (nm)	A_{\max}	$\lambda @$ max C_{ext} (nm)	max C_{ext} (cm^2)	N (cm^{-3})	m_{Au} available (g)	$c_{\text{Au}} m_{\text{Au}}$ available (M^{-1})	$c_{\text{Au}} m_{\text{Au}}$ from extinction (M^{-1})	fraction available Au present as nanoparticles

Using the best fit particle size that you found.

SHOW YOUR WORK, EQUATIONS, SUBSTITUTIONS IN TO THE EQUATIONS AND THE ANSWERS TO GET CREDIT.

$$[N_{\text{A}} = 6.02 \times 10^{23}; V = (4/3)\pi r^3; A = 4\pi r^2; \rho_{\text{Au}} = 19.3 \text{ g/cm}^3; m_{\text{Au}} = 197 \text{ g/mole}]$$

The spectrophotometry lecture contains concepts and equations that will be useful.

Your gold sols were made using the following procedure:

- Bring to a boil with 50 mL of 2.5×10^{-3} M hydrogen tetrachloroaurate(III) (HAuCl_4) solution.
- With vigorous stirring, add 0.1–2.0 mL of 34 mM sodium citrate solution.
- Continue stirring and allow to boil for 5–10 min while the nanoparticle growth completes.
- Remove from hotplate and cool to room temperature. Store in refrigerator.

For the purpose of your calculations below, assume the final volume of the sol is 50 mL.

- 1. 10pts)** Calculate the concentration of nanoparticles N (number of nanoparticles per cm^3) using the absorbance you measured experimentally and the calculated C_{ext} . The path length of your cuvette was 1 cm.
- 2. 10pts)** Using your results above, calculate the total mass of gold in the 50 ml of your Au sol.
- 3. 15pts)** Continuing this line analysis, we will compare the number of moles of Au we started with in the preparation of the Au nanoparticle to that in our final sol. a) How many moles of Au (atom) are present the original 50 ml of solution. b) How many moles are present in the final sol (assume 50ml). c) What is the fraction of gold converted into nanoparticles?