

Size and Concentration Analysis of Gold Nanoparticles With Ultraviolet-Visible Spectroscopy

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Abstract. Spherical gold nanoparticles (GNPs) are synthesized by Turkevich Method and PEL 35 UV-VIS spectrophotometer recorded the wavelength and absorption of the Surface Plasmon Resonance (SPR) peak. The diameter and concentration of solute GNPs are calculated. The concentration of GNPs is done with Beer's law. The average diameter of GNPs is done via the ratio of SPR peak to the absorbance at 450 nm. The diameters are compared to SEM scan of synthesized GNPs and Sigma-Aldrich values.

Keywords. gold nanoparticles, Beer-Lambert Law, Mie Theory

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PROBLEM STATEMENT

The Turkevich Method, one of the most widely accepted protocols for gold nanoparticle (GNP) synthesis, produces polydisperse gold nanoparticles (Turkevich, Stevenson and Hillier). Due to the range of sizes, it may be difficult to determine the average size of these synthesized nanoparticles. Although there are set protocols to obtain a certain average size, the synthesis is extremely sensitive which makes a characterization of the produced nanoparticles a necessity. Another issue is that the theoretical concentration of gold nanoparticles suspended in solution may not be accurately depicted depending on whether the reaction is fully complete.

A possible method to characterize these gold nanoparticles is by observing their light-scattering properties. According to the Mie Theory, different-sized gold nanoparticles exhibit unique light-scattering properties (Mie). By observing these trends by collecting their absorption at their Surface Plasmon Resonance (SPR) and at a wavelength of 450 nm, the average size of the gold nanoparticles can be estimated. With Beer-Lambert's law, the concentration of gold nanoparticles in solution was calculated.

MOTIVATION

With the emergence of nanomedicine in the past decades, the utilization of GNPs has been recognized due to its optical, electrochemical, and physical properties. Particularly, GNPs within the size range of 1-100 nanometers feature significant promise in biotechnology with applications in cellular imaging, cochlear implants, drug delivery etc. However, each size nanoparticle presents its own unique set of properties, therefore, making it crucial to know the size of the GNPs. More complications can arise when producing GNPs by the Turkevich method.

Through this method it is nearly impossible to create exact monodispersed nanoparticles, therefore, a variety of different size will exist in the solution.

The most common forms of determining the size of GNPs is through utilization of a Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), or Dynamic Light Scattering (DLS) Instrument. However, these instruments may be out of reach or unaffordable to use. A UV-VIS Spectroscopy can be an alternative for any of the instruments to obtain data about the produced GNPs. Through the application of Calculus, one can make low error estimates about the concentration and average size of the GNPs produced.

MATHEMATICAL DESCRIPTION AND SOLUTION APPROACH

Using the data collected through the UV-Vis Spectrophotometer, determine the wavelength and absorption where the SPR peak occurs.

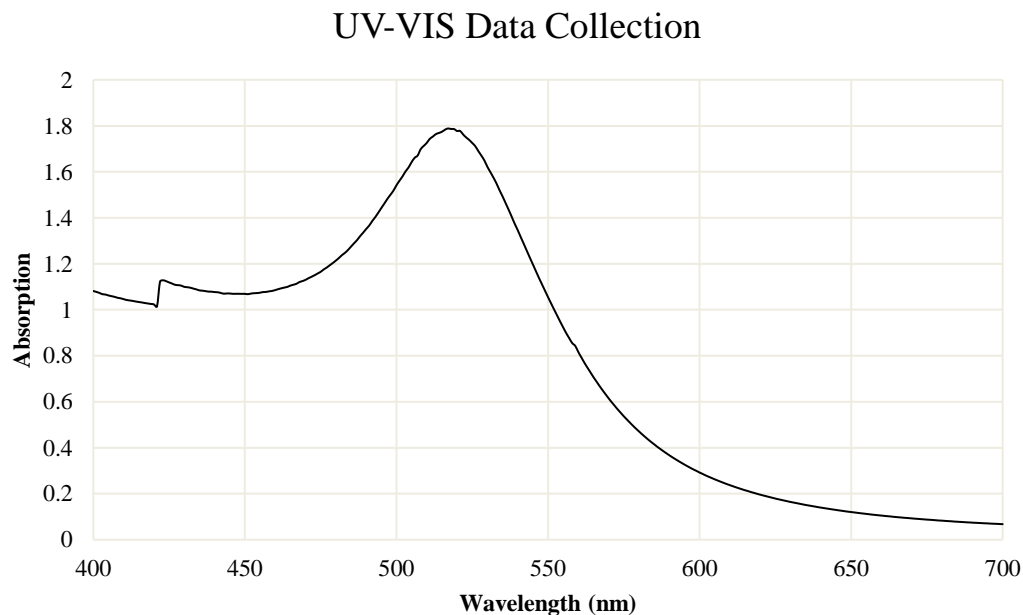


Figure 1: Above represents a UV-VIS analysis of a GNP sample from the Perkin Elmer Lambda 35 UV/Vis spectrophotometer. The absorption has been recorded from a wavelength of 400 to 700. SPR

Peaks occurs at (517, 1.788574)

In order to calculate the concentration of gold nanoparticles in solution, refer to Beer Lambert's Law (Swineheart, D. F.).

$$A = \epsilon c f \quad (1)$$

Where the product of molar concentration (c), molar absorptivity (ϵ), and the path length (b) equals to absorbance.

Through the Turkevich method involving the manipulations provided by Dr. Kumar (Kumar, Dhiraj; Meenan J., Brian; Mutreja, Isha; D'sa, Raechelle; Dixon Dorian), two attenuating species will exist in the solution (trisodium citrate dihydrate and gold (III) chloride trihydrate). Therefore, the absorbance of the GNP (A_{GNP}) would be represented as:

$$A_{GNP} = A_1 + A_2 = \epsilon_1 c_1 f + \epsilon_2 c_2 f \quad (2)$$

Where the sum of the absorbance of trisodium citrate dihydrate (A_1) and the absorbance of gold (III) chloride trihydrate (A_2) in the solution is equal to the absorbance of the GNPs. Then solve for the concentration of gold (III) trihydrate in the solution.

Solve for the amount of moles gold in the solution and then multiply by Avogadro's number to determine how many particles were produced in the synthesis.

The amount of atoms to form a nanoparticle (N) with diameter (d) would be defined as (Lu, Yan; Wang, Lixia; Chen, Dejun; Wang, Gongke):

$$N = \frac{\pi \rho d^3}{6M} \quad (3)$$

Where one must consider both density of gold (ρ), molar mass of gold (M), and the diameter in nanometers (d).

By knowing how many gold atoms consist of a single GNP, one can determine how many GNPs are formed in the solution by taking the quotient of GNPs in solution by number gold atoms to produce a single atom.

One then can calculate the concentration of the solution by dividing the number of nanoparticles by the volume of the solution.

Another approach to determining the concentration of GNPs in solution would to assume that the entire reducing agent has been used up and only one attenuating species exist in solution, the GNPs. The absorbance of the GNPs would be represented as:

$$A_{GNP} = \epsilon_{GNP} c_{GNP} f \quad (4)$$

Where ϵ_{GNP} would be represented as the molar absorptivity of the GNPs and c_{GNP} represents the concentration of the GNPs.

Referring to Figure 1, use the absorption at the SPR for the absorption of the GNPs to solve for the concentration of gold nanoparticles. The extinction coefficient for GNPs have an SPR peak at a wavelength of 515-520 was obtained from Sigma-Aldrich (Appendix, Table [2]). To determine the path length (f), the path length of the cuvette was used in the Perkin Elmer Lambda 35 UV/Vis spectrophotometer.

Using Equation (4), solve for the concentration of GNPs in the solution. With the molarity and volume of the sample, the moles of the GNPs can be calculated. With the moles of GNPs, multiply it by Avogadro's number to get the total number of GNPs in the solution. With the total number of GNPs in solution, find the concentration by dividing it by the volume of solution.

In order to determine the average diameter, the diameter of a GNP (d) can be represented as (Haiss, Wolfgang; Nguyen T. K., Thanh; Aveyard, Jenny; Fernig G., David):

$$d = e^{(B_1 \frac{A_{spr}}{A_{450}} - B_2)} \quad (5)$$

By knowing the absorption at the SPR peak and 450 nm, an estimate of the GNPS can be determined if the particles are between 5 to 80nm. Variables B_1 and B_2 are calculated values based on one's own produced data. B_1 is represented as the inverse of the slope of the plotted values in Figure 2 and B_2 is represented as the y-axis intercept divided by the slope.

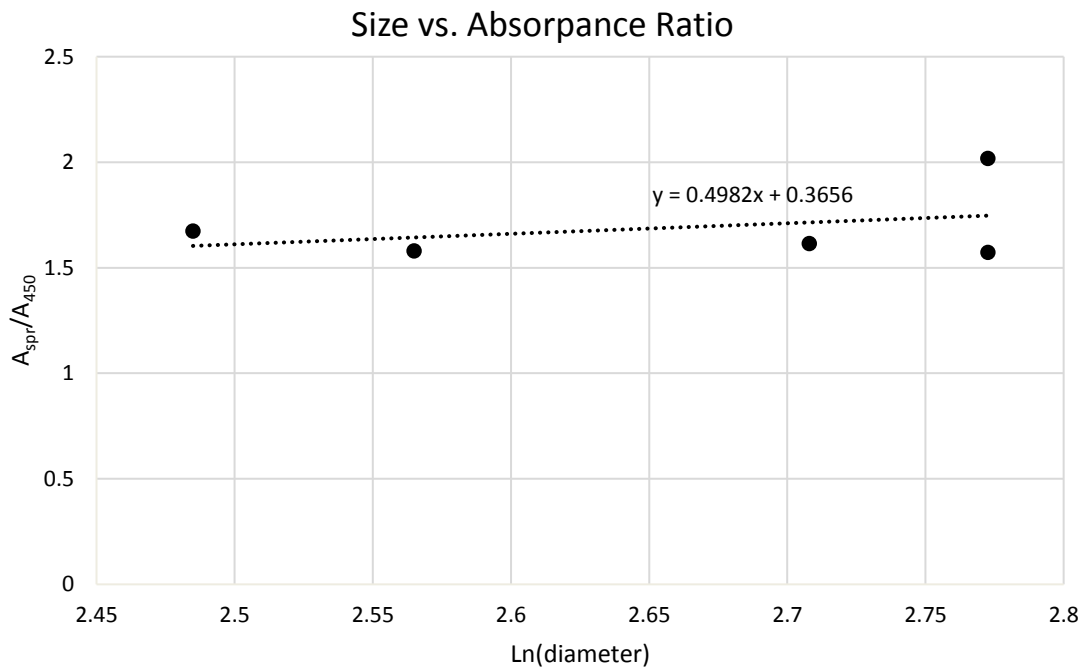


Figure 2: Above are five different GNPs sample. The ratio of the absorption at the SPR to the absorption at 450 nanometers was recorded over the natural log of the diameter of a GNP.

After collecting numerous data points, the function of the fitted line ($f(x_i)$), solved through the Method of Least Squares, is represented as:

$$\hat{y}_i = f(x_i) = \hat{b}x_i + \hat{b}_0 \quad (6)$$

Where the equation fits the experimental set of data in Figure (2). \hat{b} represents the slope of the line. x_i represents the natural log value of the diameter of a single gold nanoparticle, and \widehat{b}_0 represents the ratio of the absorbance of the GNP at the SPR and at 450 nanometers.

After developing the best fit line, B_1 and B_2 can be represented as:

$$B_1 = \frac{1}{\hat{b}} \quad (7)$$

$$B_2 = \frac{\widehat{b}_0}{\hat{b}} \quad (8)$$

Where B_1 is represented as the reciprocal of the slope of the best-fit line and B_2 is the ratio of the y-intercept of the best-fit line to the slope.

With these fit parameters, one can now determine the average size of a sample of GNPs with their own experimental values.

DISCUSSION

By using Beer's Law, the concentration of the solution fell into the range of theoretical values presented in Sigma-Aldrich. The calculated concentration is expected to have some inaccuracy due to the polydispersity of GNPs. The calculated concentration is under the assumption that the GNPs are monodispersed. As presented in the SEM scan in Figure 3, different size GNPs exist in the solution which would cause some discrepancy between the actual and theoretical calculation. Another issue presented is if the reducing agent, trisodium citrate dihydrate, was not fully used up in the reaction. If so, then floating particles of trisodium citrate dihydrate would exist in the

solution, therefore, Equation (6) would be appropriate to use. By using Equation (6), the amount of error would be reduced since the assumption that two attenuating species exist in solution.

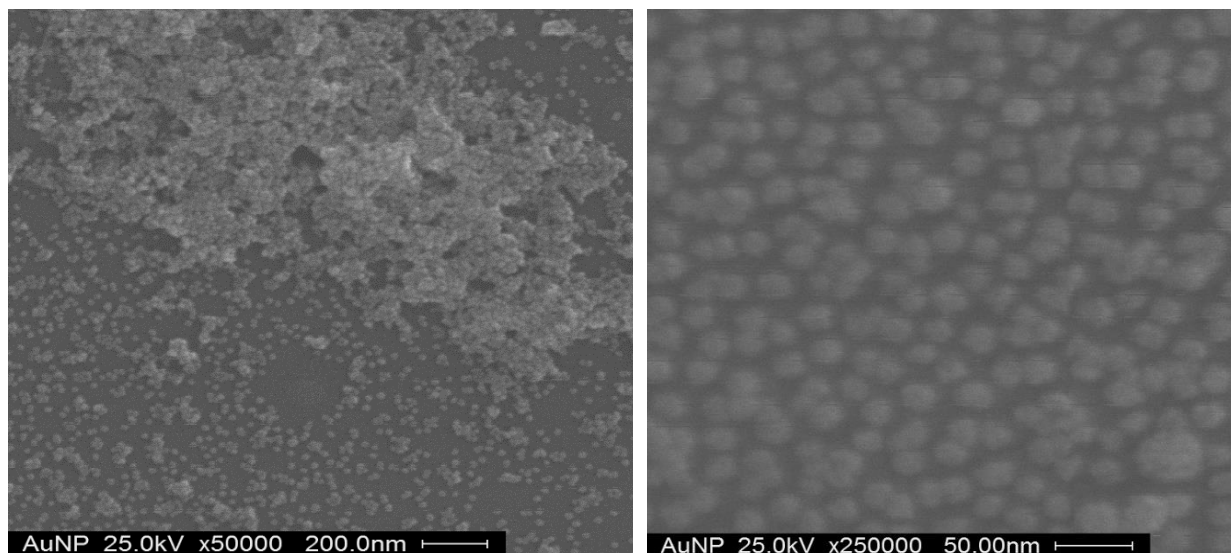


Figure 3: The images are SEM scans of the GNPs at various strengths. The imaged nanoparticles are the same as the ones that were characterized in Figure 1.

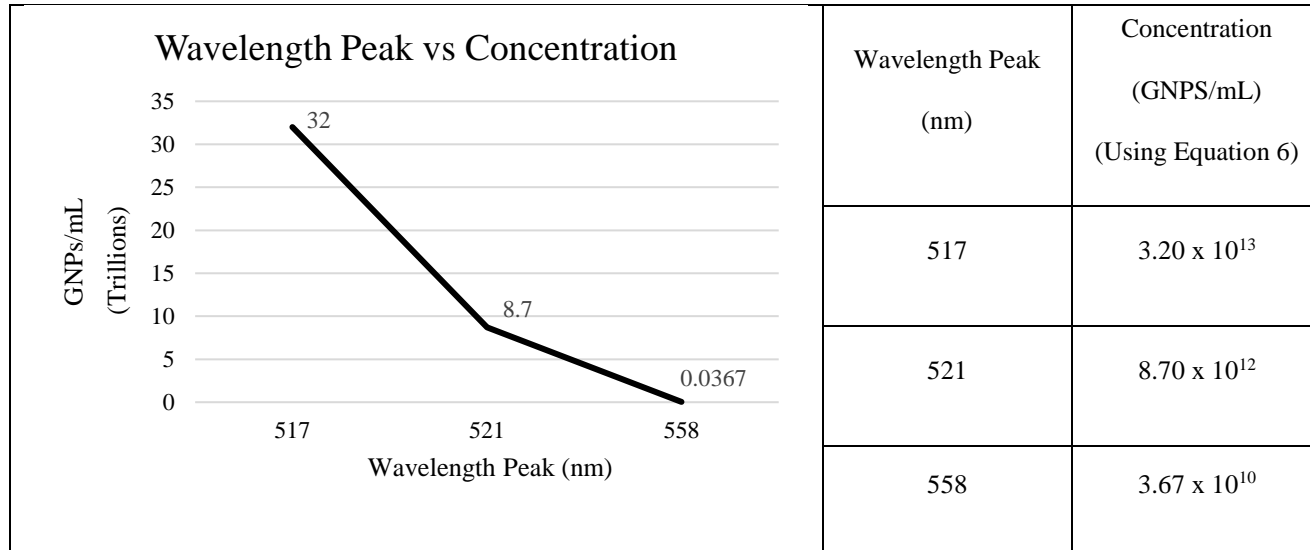
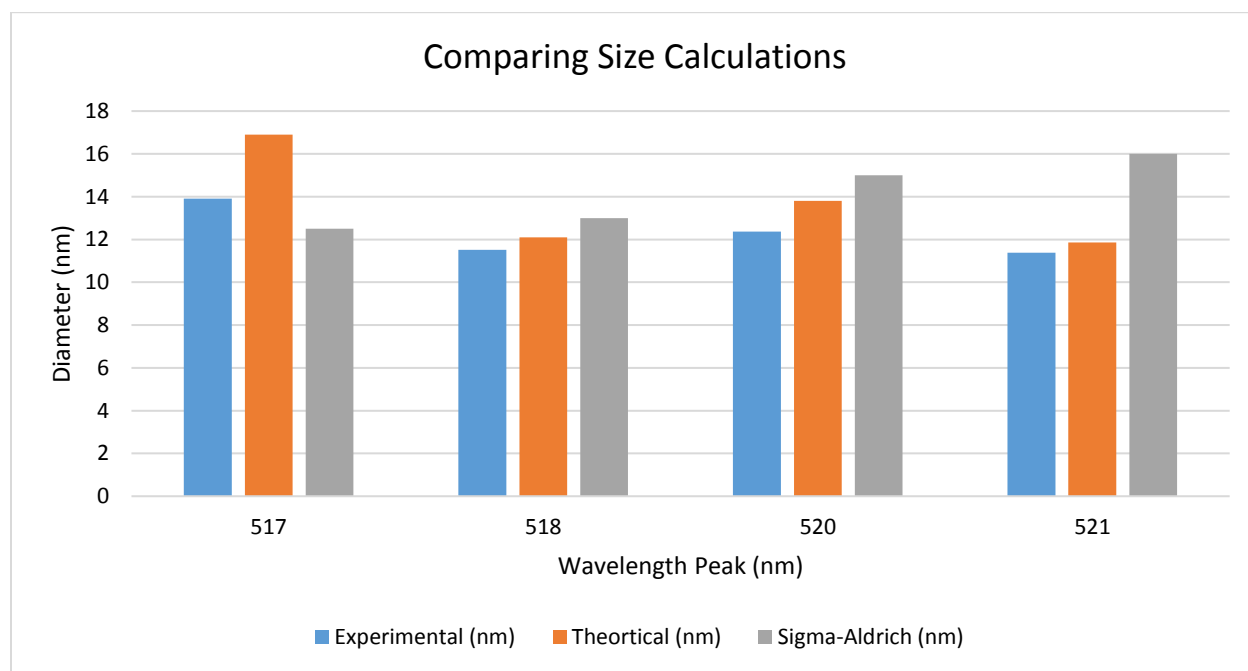


Figure 4: The graph and table present the concentration of GNPs that was solved over various wavelengths recorded through UV-VIS

In Figure 4, a logical correlation between wavelength peak and concentration exists showing validity in using Beer-Lambert’s law. As the wavelength of the SPR peak shifts further

to the right, the larger is the diameter of the GNPs. If the particle size increases, then the concentration of GNP should decrease since the GNPs will be taking up a larger volume of the solution.

By using the data collected from the UV-VIS spectrophotometer in Figure 1, the λ , A_{spr} , and A_{450} were calculated. When using Equation (1), both theoretical that were developed in the literature ($B_1 = 3.55$ and $B_2 = 3.11$) and experimental values ($B_1 = 2.01$ and $B_2 = 3.11$) of B_1 and B_2 was used. The diameters that were received were then compared to the average diameter recorded by Sigma Aldrich.



Peak (nm)	Experimental Fit Diameter (NM)	Theoretical Fit Diameter (NM)	Sigma-Aldrich reported values (NM)
517	13.9	16.9	10-15
518	11.5	12.1	10-15
520	12.4	13.8	15
521	11.4	11.9	15-20

Figure 5: The graph and table present the GNP diameter calculated from the experimental fit parameters, theoretical fit parameters, and from Sigma-Aldrich.

CONCLUSION AND RECOMMENDATIONS

By utilizing Beer-Lambert's law to determine the concentration of GNP in solution a fairly accurate estimate can be drawn if one assumes that no excess trisodium citrate dihydrate remains in the solution and that the size is monodispersed. To improve the accuracy of the data, one should use a DLS instrument to determine the average diameter of the GNP and use the corresponding extinction coefficient. Another improvement that could be made is to filter out any particles of trisodium citrate dihydrate which would allow one to use Equation (4) with high precision.

By using the ratio of the absorbance of the SPR peak to the absorbance at 450 nanometers, a fair approximation of the average diameter of the GNPs suspended in solution can be made. However, higher accuracy may be obtained if one uses their own fit parameters based on their previous GNP samples. By using the equation to determine the size, it cannot be assumed that all the particles are monodispersed. Therefore, the equation does not consider the polydispersity of the GNPs which will result in error. An improvement that can be made is to use

a wider set of values when plotting the best fit line. Having a larger spread of data points can allow one to use their own experimental values for a wider range of GNP sizes. Using the absorbance peak should not be used as the main determinant of finding the average diameter of the GNPs. The best accuracy may be obtained by using an SEM, TEM, or DLS instrument.

NOMENCLATURE

Symbol	Description	Value/Unit
ϵ	Extinction Coefficient	$M^{-1}cm^{-1}$
c	Concentration	M
f	Length of Light Path	cm
M	Atomic Weight of Gold	197.0 g
ρ	Density of Gold	$19.3 g/cm^3$
d	Diameter of GNP	nm
A	Absorbance	-
N	Number of Atoms in GNP	-
B_1	Fit Parameter 1	-
B_2	Fit Parameter 2	-
A_{spr}	Absorbance at SPR peak	-
A_{450}	Absorbance at 450 nanometers	-
\hat{B}	Slope of Best-Fit Line	-
\hat{B}_0	Y-Intercept of Best-Fit Line	-

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APPENDIX

Sigma-Aldrich Reported Values:

Diameter (nm)	SPR Peak Wavelength (nm)	Extinction Coefficient ($M^{-1}cm^{-1}$)
5	515-520	1.10×10^7
10	515-520	1.01×10^8
15	520	3.67×10^8
20	524	9.21×10^8
30	526	3.36×10^9
40	530	8.42×10^9
50	535	1.72×10^{10}
60	540	3.07×10^{10}
80	553	7.70×10^{10}
100	572	1.57×10^{11}

UV-VIS Data:

SPR Peak (nm)	Absorbance at SPR Peak	Absorbance at 450 nm
517	1.788574	1.069299
518	1.666837	1.055632
520	1.830586	1.133888
521	1.766482	1.123132