Lab Documentation

Silver Nanoparticles: Synthesis and Spectroscopy

PA State Standards:

3.7.12.A	Apply advanced tools, materials, and techniques to answer complex questions. • Demonstrate the safe use of complex tools and machines within their specifications.
3.4.10. A	Explain concepts about the structure and properties of matter.
3.1.10.D	Apply scale as a way of relating concepts and ideas to one another by some measure. • Convert one scale to another.
2.5.8.B	Verify and interpret results using precise mathematical language, notation and representations, including numerical tables and equations, simple algebraic equations and formulas, charts, graphs, and diagrams.
1.2.11.A	Read and understand the central content of informational texts and documents in all academic areas.

Introduction:

Silver nanoparticles (AgNPs), or colloidal silver, will be synthesized in the presence of starch according to the following redox reaction:

$$2AgNO_{3\,(aq)} + C_6H_{12}O_{6(aq)} + H_2O_{(l)} \longrightarrow 2Ag_{(s)} + 2HNO_{3(aq)} + C_6H_{12}O_{7(aq)}$$

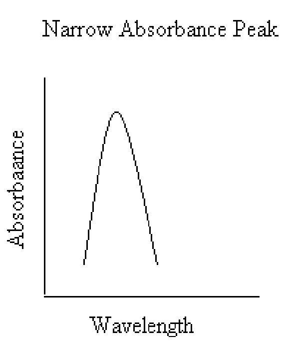
In this reaction, glucose ($C_6H_{12}O_6$) reduces the silver cations from the silver nitrate. As the silver metal forms, starch coats the outsides of the particles, preventing them from aggregating and forming larger particles.

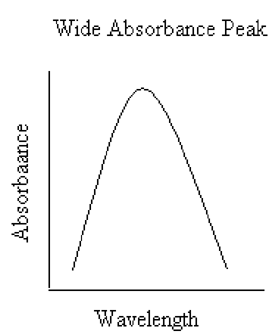
Nano-sized materials often have different properties than the bulk materials; for example, silver nanoparticles appear yellow. A visible spectrum of AgNP solution will be determined.

Guiding Question:

Please answer the following question before beginning the lab.

Sometimes the sizes of the particles synthesized are fairly uniform; other times, their sizes are more varied. What effect might a large variance in particle size have on the width of the absorbance peak in the visible spectrum?





Equipment / Materials for Synthesis:
0.1M $AgNO_3$ ($AgNO_3$ CAS 7761-88-8)
0.1M α-D-glucose (α-D-glucose CAS 50-99-7)
0.2% wt. soluble starch (soluble starch CAS 9005-84-9)
200 µL pipet
1000 µL pipet
10 mL pipet or graduated cylinder
Hot plate
Small Erlenmeyer flask or beaker
Glass vials

Equipment / Materials for Spectroscopy:
Droppers
Spectrophotometer
Cuvettes
Kimwipes
0.2% wt. soluble starch for blank

Safety:
- Always wear safety glasses in the lab.

Procedure:
Part I: Synthesis of Silver Nanoparticles
1. Place 200 µL of 0.1M $AgNO_3$ into a small Erlenmeyer flask or beaker.

2. Add 500 µL of 0.1M glucose, making sure that it comes into contact with the $AgNO_3$.

3. Invert the starch solution several times. Add 10mL of the starch solution.

4. Heat the solution on a hot plate on a high setting until it is boiling vigorously. **Do not stir the solution!**

5. Boil the solution for 10 minutes. The solution should turn yellow.

6. Remove the sample from the hot plate, and let it cool.

Part II: Spectrophotometric Analysis of the Silver Nanoparticles
1. Turn on the spectrophotometer and allow it to warm up for the recommended length of time.

2. Put the instrument in Transmittance mode. With the sample compartment empty, set the dark current to zero.

3. Invert the starch solution several times. Fill a clean cuvette with the starch solution. Wipe the outside with a Kimwipe, then insert it into the sample compartment.

4. Set the wavelength at 350nm and zero the absorbance.

5. Insert a clean cuvette filled with the AgNP solution, and record the absorbance in the data section in Table 1.

6. Repeat steps 4 and 5 for different wavelengths; increasing the wavelength by 25nm each time until a reading is obtained for 650nm. Remember to zero the machine each time you change the wavelength. Record the data in **Table 1** of the data section.

7. Identify the wavelength from Table 1 with the highest absorbance. Use the spectrophotometer to collect additional absorbance readings by varying the wavelengths in that specific area of the spectrum to determine which gives the wavelength of maximum absorbance (λ_{max}). Record these observations in **Table 2** of the data section. (For example, if the maximum absorbance in Table 1 is at 500 nm, then test the absorbance of the AgNPs at 490, 495, 500, 505, and 510 nm, looking for the wavelength that gives the maximum absorbance).

8. Divide the absorbance at the λ_{max} by 2 and record in **Table 3** of the data section as absorbance at ½ max.

9. Graph the data from Table 2 on a separate sheet of graph paper or in Excel.

10. Using the graph created in step 9, mark the maximum absorbance on the y-axis. Mark the ½ max. absorbance on the y-axis and find the corresponding wavelength on the x-axis.

11. Zero the spectrophotometer at the interpolated $\lambda_{1/2max}$ from step 10. Compare the absorbance of the AgNPs at the interpolated $\lambda_{1/2max}$ to the absorbance calculated in step 8. Adjust the wavelength on the spectrophotometer and record the absorbance of the AgNPs until a value close to the calculated value of the absorbance at $\lambda_{1/2max}$ from step 8 is obtained. Record this wavelength in **Table 3** as wavelength at ½ max.

Data:

Table 1

Wavelength (λ) (nm)	Absorbance
350	
375	
400	
425	
450	
475	
500	
525	
550	
575	
600	
625	
650	

Table 2

Wavelength (λ) (nm)	Absorbance

Table 3

	Wavelength (nm)	Absorbance
max		
½ max		

Calculations:

1. To determine the Peak Width at Half Max (PWHM), first subtract the λ_{max} from the $\lambda_{1/2max}$. The difference is half the peak width. Multiply by 2 to get the PWHM.

2. How many silver atoms are in one nanoparticle?
Determine the average number of atoms per nanoparticle using the following formula:

$$N = \frac{\pi \rho D^3}{6 \ M} N_A$$

N = number of atoms per nanoparticle
ρ = density of face centered cubic (fcc) silver = 10.5g/cm^3 (convert to g/nm^3)
D = average diameter of nanoparticles = 11nm
M = atomic mass of silver
N_A = number of atoms per mole
Note: This equation is taken from Liu, Atwater, Wang, and Huo (see References.) It assumes that the nanoparticles have a spherical shape and a uniform fcc crystaline structure.

Be sure your units are consistent!

3. What is the concentration of your silver nanoparticle solution?
Determine the molar concentration of the nanoparticle solution using the following formula:

$$C = \frac{N_T}{NVN_A}$$

C = molar concentration of nanoparticle solution
N_T = Total number of silver atoms added in $AgNO_3$
N = number of atoms per nanoparticle (determined in Calculation 2)
V = volume of the reaction solution in L
N_A = number of nanoparticles per mole
Note: This equation is also taken from Liu, Atwater, Wang, and Huo (see References.) It assumes that the reduction of Ag^+ to Ag^0 was complete.

Questions:

1. Look at your PWHM calculation. What effect might a large variance in particle size have on the width of the absorbance peak in the visible spectrum?

2. Name a physical property of silver that changes at the nanoscale.

Acknowledgements:

National Nanotechnology Infrastructure Network
For more information, visit www.nnin.org.

Penn State Center for Nanotechnology Education and Utilization
For more information, visit www.cneu.psu.edu or contact Amy Brunner at abrunner@engr.psu.edu.

Penn State Center for Science and the Schools
For more information, contact Bill Carlson at wsc10@psu.edu.

Science in Motion at Juniata College
For more information, contact Tara Fitzsimmons at fitzsit@juniata.edu.

References:

Kalaugher, L. (2004, January 12). *Green Technique Makes Silver Nanoparticles.* Retrieved July 3, 2007, from Nanotechweb.org: http://nanotechweb.org/articles/news/3/1/1/1

Liu, X., Atwater, M., Wang, J., & Huo, Q. (2006). Extinction coefficient of gold nanoparticles with different sizes and different capping ligands. *Colloids and Surfaces B: Biointerfaces*.

Raveendran, P. F. (2006). A Simple and "Green" Method for the Synthesis of Au, Ag, and Au-Ag Alloy Nanoparticles. *Green Chemistry* , 34-38.

Raveendran, P., Fu, J., & Wallen, S. L. (2003). Completely "Green" Synthesis and Stabilization of Metal Nanoparticles. *J. Am. Chem. Soc.* , 13040-13041.

Silver Nanoparticles S-MITE. (n.d.). Retrieved July 31, 2007, from American Elements: Silver Nanoparticles Supplier & Tech Info: www. americanelements.com/agnp.html#MSDS

Solomon, S. D., Bahadory, M., Jeyarajasingam, A. V., Rutkowsky, S. A., Boritz, C., & Mulfinger, L. (2007). Synthesis and Study of Silver Nanoparticles. *Journal of Chemical Education* , 322-325.

Silver Nanoparticles: Synthesis and Spectroscopy
Teacher Notes

Time for Completion:
Part I can easily be completed in a 40 minute period. An additional 40 minute period will be necessary for Part II.

Target Grade Level:
This lab is designed for an advanced chemistry class, but may also be done with first year students. Prior experience with spectroscopy is recommended.

Objectives:
1. The students will demonstrate the appropriate use of a spectrophotometer.
2. The students will obeserve differences in physical properties at the nanoscale.
3. The students will convert between different units of measurement.

Major Concepts:
- Differences in physical properties at the nano-scale
- Scale/Unit Conversions
- Visible spectroscopy
- Relationship between standard deviation of particle size and the PWHM

Preparation of Solutions:
To prepare 0.1M $AgNO_3$, dilute 1.6988g $AgNO_3$ (CAS 7761-88-8) to 100mL with deionized water.

To prepare 0.1M glucose, dilute 1.8016g of glucose (CAS 50-99-7) to 100mL with deionized water.

To prepare 0.2%wt. soluble starch, dissolve 0.4g soluble starch (9005-84-9) in 200mL deionized water.

Sample Data:

Table 1

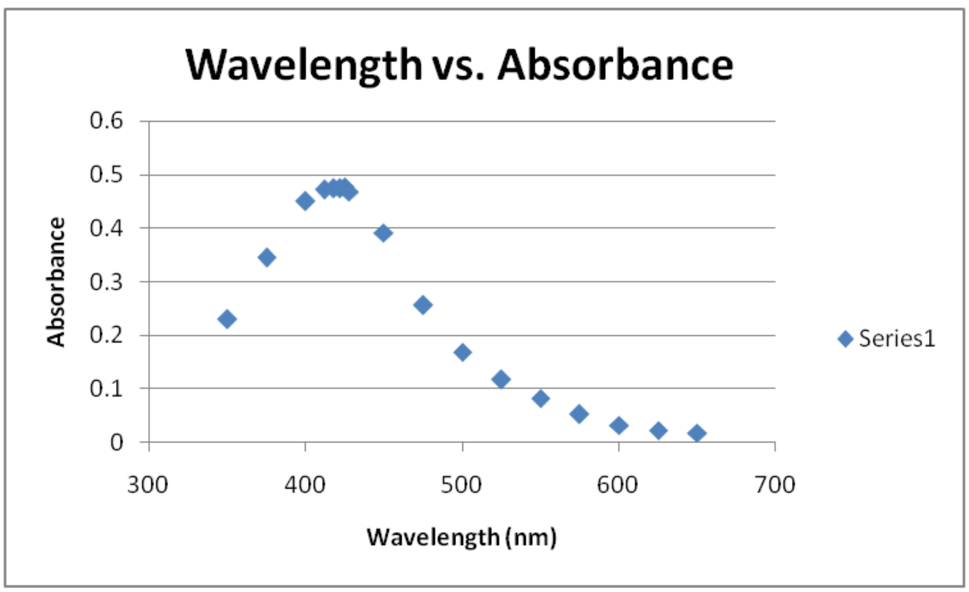
Wavelength (λ) (nm)	Absorbance
350	0.230
375	0.345
400	0.450
425	0.478
450	0.392
475	0.257
500	0.169
525	0.118
550	0.083
575	0.053
600	0.033
625	0.023
650	0.018

Table 2

Wavelength (λ) (nm)	Absorbance
412	0.472
418	0.474
422	0.474
428	0.468
480	0.243
483	0.232
481	0.236

Table 3

	Wavelength (nm)	Absorbance
λ_{max}	425	0.478
$\lambda_{1/2max}$	480	0.239



The wavelength at half the maximum absorbance appears to be approximately 480nm. Wavelengths around this value were tested in the above data table.

Sample Calculations:

1. To determine the Peak Width at Half Max (PWHM), first subtract the λ_{max} from the $\lambda_{1/2max}$. The difference is half the peak width. Multiply by 2 to get the PWHM.

$$PWHM = (\lambda_{1/2max} - \lambda_{max})*2$$
$$PWHM = (480nm-425nm)*2$$
$$PWHM = 110nm$$

2. Determine the average number of atoms per nanoparticle using the following formula:

$$N = \frac{\pi \rho D^3}{6 \ M} N_A$$

N = number of atoms per nanoparticle
ρ = density of face centered cubic (fcc) silver = 10.5g/cm^3
D = average diameter of nanoparticles = 11nm
M = atomic mass of silver
N_A = number of atoms per mole
Note: This equation is taken from Liu, Atwater, Wang, and Huo (see References.) It assumes that the nanoparticles have a spherical shape and a uniform fcc crystaline structure.

Be sure your units are consistant!

ρ must be converted to g/nm^3; $\rho = 1.05x10^{-20}$g/nm^3
D = 11nm
M = 108g/mol
$N_A = 6.022x10^{23}$ atoms/mol

$$N = \frac{\pi \rho D^3}{6 \ M} N_A$$

$$N = \frac{\pi(1.05x10^{-20})(11)^3}{6(108)} 6.022x10^{23}$$

$$N = 4.08x10^4 \ atoms/NP$$

3. Determine the molar concentration of the nanoparticle solution using the following formula:

$$C = \frac{N_T}{NVN_A}$$

C = molar concentration of nanoparticle solution
N_T = Total number of silver atoms added as salt
N = number of atoms per nanoparticle
V = volume of the reaction solution in L
N_A = number of nanoparticles per mole
Note: This equation is also taken from Liu, Atwater, Wang, and Huo (see References.) It assumes that the reduction of Ag^+ to Ag^0 was complete.

$$N_T = 200\mu L AgNO_3 \left(\frac{1x10^{-6} L\ AgNO_3}{1\mu L\ AgNO_3}\right)\left(\frac{0.1 mol\ AgNO_3}{1L\ AgNO_3}\right)\left(\frac{1 mol\ Ag}{1 mol\ AgNO_3}\right)\left(\frac{6.022x10^{23} atoms\ Ag}{1 mol\ Ag}\right)$$

$$N_T = 1.20x10^{19} atoms\ Ag$$

$$N = 4.08x10^4 \frac{atoms}{NP}\ from\ Calculation\ 3$$

V = 0.010L (This volume is approximate; 10.7mL was the initial volume, but some water evaporated during boiling. For increased precision, measure the volume of the final solution.)
N_A = $6.022x10^{23}$ NP/mol

$$C = \frac{N_T}{NVN_A}$$

$$C = \frac{1.20x10^{19}}{(4.08x10^4)(0.010)(6.022x10^{23})}$$

$$C = 4.88x10^{-8} M\ AgNP\ or\ 48.8nM\ AgNP$$

Answers to Questions:

1. What effect might a large variance in particle size have on the width of the absorbance peak in the visible spectrum?
   Different sized nanoparticles will absorb different wavelengths of light. A large variance in particle size will result in a wider absorbance peak. A Peak Width at Half Max (PWHM) of 100 or less would indicate a fairly uniform distribution of particle sizes.

2. Name a physical property of silver that changes at the nanoscale.
   The color of silver changes; this procedure produces yellow silver nanoparticles (AgNPs). The melting point of silver also drops at the nanoscale.

Extensions:
Add 1M NaOH dropwise to aggregate the particles, if desired. The synthesized silver nanoparticles may be used to do experiments on *E. coli* inhibition. Students may also research practical uses of silver nanoparticles; they are currently used for their antimicrobial properties in products such as socks, food containers, and washing machines.