#24 Study of Colloidal Gold Solution

Purpose: Visible spectroscopy and color changes are used to study a solution containing gold nanoparticles.

Background:

Nanotechnology deals with processes that take place on the nanometer scale, that is, from approximately 1 to 100 nm. In this experiment you will study colloidal gold solution which contains gold nanoparticles that are about 12-13 nm in diameter. Each of the Au nanoparticles contains about 49,000 Au atoms. Properties of metal nanoparticles are different from those of bulk materials made from the same atoms. For example, gold metal is yellowish, but nanoparticles of gold are wine-red.

Spectroscopy and Size of Nanoparticles

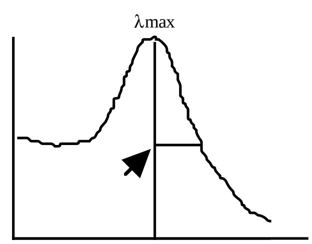
The visible spectrum of a colloidal gold solution provides information about the size and uniformity of its particles.

Particle size is related to the peak position, λ max. For the 12-13 nm Au nanoparticles, the maximum wavelength is 520 nm*. For smaller particles the maximum is less than 520, and for larger ones, more than 520. (See table below)

Distribution of sizes: The peak width at half maximum (PWHM) indicates distribution in particle size. The broader the peak the greater the spread in particle size. For the particles you will study, the range in size is ± 1.5 nm, and the peak width should be between 80 and 90 nm. If the range is greater, the peak width will be broader (more than 100 nm).

*Note that λ_{max} may vary somewhat from sample to sample. Your instructor will give you the value expected for the solution used in your class.

Particle Size nm	λ_{max} nm
< 12	< 520
12	520
>12	> 520



For PWHM, first find the half maximum point (see arrow), then find the length in nm of the horizontal line ---and double it.

Aggregation of Au nanoparticles

The Au particles in the colloidal solution are negatively charged, repel each other and stay in solution. Salts such as NaCl or KI shield the negative charges allowing the particles to clump together to form aggregates. The colloidal gold solution then turns a deep blue. To prevent aggregation the nanoparticles can be coated with a polymer such as polyethylene glycol (or PEG), a polymer with the repeat unit, ~CH_2CH_2O~ meaning that a segment of the polymer would look like:

~$CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2O$ ~

PEG inhibits aggregation and stabilizes the gold colloid even when salt is added.

Apparatus: You will be taking a spectrum of colloidal gold solution. Refer to the operating instructions. If you are using a Spectronic-20, record %T (easier to read) and convert to A.

A = log (100/%T), so if %T is 50, the value of A is log 100/50 = log 2.0 or 0.30

Safety and Waste Disposal: Safety glasses are always required in the laboratory. Gloves *must* be worn. A container will be made available for any waste colloidal gold.

Procedure: The colloidal gold solution will be prepared in advance for this experiment. Pour about 30 mL of the red solution into a 50-mL beaker, using the marks on the beaker. This should be enough for both parts of the experiment. The foil covering the container of colloidal gold protects the solution from light.

A. Taking the Spectrum of Colloidal Gold Solution

1. Pour about 2 mL into a cuvet. Dilute by adding an equal volume of distilled water, using the water wash bottle. The idea is to have a concentration such that the peak absorbance is somewhere between 0.3 and 1. Check this by taking the first measurement at 520 nm, which is near the absorbance maximum. Continue to dilute if needed, possibly as much as 5 to 1.

2. Measure the % transmittance every 10 nm between 400 nm and 700 nm. You can record %T every 5 nm in the region around the peak wavelength near 525 nm.
Note: When finished, pour the diluted colloidal Au solution into the marked waste bottle.

3. Convert % transmittance to absorbance. Make a plot of absorbance vs. wavelength, by drawing a smooth curve through the points.

4. Record the wavelength of the peak absorbance, λmax, and compare with tabulated values. Find the peak width in nanometers (nm) at half max (PWHM). Use *twice* the width of the right hand side of the peak at λmax. (See Figure on page 1 in the Background section.)
Note: See instructor if λ_{max} is not close to 520 nm or if the peak width is greater than 100 nm.

Part B. Aggregation and Stabilization of Colloidal Au

1. You will be given the following solutions: 1.5M NaCl, 0.020M NaOH, and PEG solution. The concentration of PEG is about 20μg/mL or 0.5 μg/drop.

2. Pour about 5 mL of undiluted Au colloid solution into five test tubes. Adjust the pH by adding 0.020 M NaOH dropwise until the pH is between 5.5 and 6. Use pH indicator strips. Add drops of polyethylene glycol (PEG) solution to each test tube as indicated.
CAUTION: pH meters cannot be used because the solution will ruin the electrodes.

	Drops PEG solution
Test tube 1	0
Test tube 2	0
Test tube 3	1
Test tube 4	2
Test tube 5	4

3. Add 1.5 M NaCl dropwise to test tube 2 while swirling the test tube vigorously until the solution turns blue. Record the number of drops. Add the same amount to test tubes 3-5 and observe any color changes. What is the minimum number of drops of PEG needed to prevent any color change.

Data and Results (Colloidal Au)

Name(s) ____

A. Taking the Spectrum of Colloidal Gold Solution

Colloidal gold solution			Colloidal gold solution		
λ nm	%T	A	λ nm	%T	A
400			545		
410			550		
420			555		
430			560		
440			565		
450			570		
460			580		
470			590		
480			600		
490			610		
500			620		
505			630		
510			640		
515			650		
520			660		
525			670		
530			680		
535			690		
540			700		

Comparing λmax and PWHM with known values for 12-13 nm gold nanoparticles:

Quantity	Your value (nm)	Known value (nm)
λ max		520
PWHM		80 – 90

Comment on the size and uniformity of the particles in the colloidal gold solution.

Part B. Aggregation and Stabilization of Colloidal Au

Samples	NaOH drops	PEG drops	NaCl drops	Color
Test Tube 1 (standard)				
Test Tube 2 Unprotected				
Test Tube 3				
Test Tube 4				
Test Tube 5				

Minimum Stabilizing amount of PEG: ________ drops

Question

1. In the background section it states that a 14 nm Au nanoparticle contains about 49,000 Au atoms. Show this, keeping in mind that this is a crude estimate. Assume that each gold atom is a cube with an edge of 0.3 nm. (Volume of a sphere = $4/3\ \pi\ r^3$)

2. Why is the PWHM, peak width at half maximum, measured by doubling the width of one half of the peak--- instead of simply measuring the entire peak width?

Instructor's Guide
(Colloidal Au)

Typical Results:

A. Taking the Spectrum of Colloidal Gold Solution

Colloidal gold solution			Colloidal gold solution		
λ nm	%T	A	λ nm	%T	A
400	*35*	0.46	545	*29*	0.54
410	*35*	0.46	550	*33*	0.49
420	*36*	0.45	555	*37*	0.44
430	*36*	0.45	560	*40*	0.40
440	*36*	0.45	565	*44*	0.36
450	*35*	0.46	570	*48*	0.32
460	*35*	0.46	580	*57*	0.25
470	*34*	0.47	590	*63*	0.20
480	*31*	0.51	600	*71*	0.15
490	*28*	0.55	610	*75*	0.125
500	*25*	0.60	620	*78*	0.105
505	*23*	0.64	630	*81*	0.085
510	*22*	0.66	640	*83*	0.075
515	*21*	0.68	650	*86*	0.065
520	*21*	0.68	660	*87*	0.060
525	*21*	0.68	670	*88*	0.052
530	*22*	0.66	680	*89.5*	0.045
535	*23*	0.64	690	*91*	0.040
540	*26*	0.58	700	*91*	0.040

Comparing λmax and PWHM with known values:

Quantity	Your value (nm)	Known value (nm)
λ max	*520*	around 520
PWHM	*90*	80 – 90

Part B Aggregation of colloidal gold

Samples	NaOH drops	PEG drops	NaCl drops	Color
Test Tube 1 (standard)	*2-3*	*0*	*0*	*red*
Test Tube 2 Unprotected	*2-3*	*0*	*5-7*	*turns blue*
Test Tube 3	*2-3*	*1*	*5-7*	*bluish-red*
Test Tube 4	*2-3*	*2*	*5-7*	*reddish-blue*
Test Tube 5	*2-3*	*4*	*5-7*	*stays red*

Minimum Stabilizing amount of PEG: ______*4*___ drops

Questions

1. In the background section it states that a 14 nm Au nanoparticle contains about 49,000 Au atoms. Show this, keeping in mind that this is a crude estimate. Assume that each gold atom is a cube with an edge of 0.3 nm. (Volume of a sphere = $4/3\ \pi\ r^3$)

Ans: Volume spherical nanoparticle = $4/3\ \pi\ 7^3\ nm^3$; Volume of a gold atom is about $0.3\ nm^3$

Number of atoms = $\frac{4/3\ \pi\ 7^3\ nm^3}{0.3^3\ nm^3}$ = 53,000 or about 50,000

(Note: The diameter of a gold atom is 0.288 nm)

2. Why is the PWHM, peak width at half maximum, measured by doubling the width of one half of the peak--- instead of simply measuring the entire peak width?

Ans: There is additional absorbance (that shouldn’t be included) on the left hand side of the peak

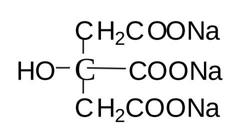
Equipment and Materials: per group

Time:

Items	**Amount**	**Comment**
50-mL beaker	1	To store the colloidal gold
Test tube rack	1	
Test tubes	5	
Wash bottles	1	Ordinary distilled water should be fine
Spectronic-20	1	
Cuvettes	2	1 for sample and 1 for blank
Colloidal gold solution	30 mL	Ready-made for students*
Pasteur pipets	3	For adding solutions
pH papers	1 pk	
PEG (aq) (polyethylene glycol)	100 mL	For the entire class (more than enough)
1.5 M NaCl (aq)	100 mL	For the entire class (more than enough)
0.02 M NaOH (aq)	100 mL	For the entire class (more than enough)
Marker / label	1	To label test tubes
Safety glasses	1/student	
Rubber gloves	1 box/class	

Ideas and Information

1. *Synthesis of Colloidal Gold solution*:

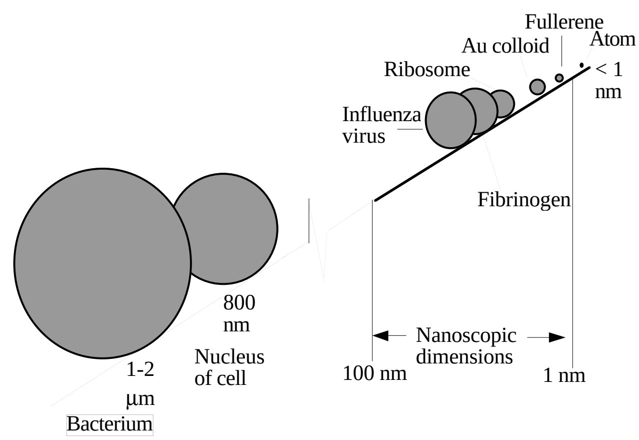


The procedure that was used to make the colloidal gold solutions required only wet chemistry techniques and simple equipment. In general, reducing agents are reacted with a metal compound to produce nanoparticles of the metal. For gold, the reducing agent is sodium citrate, $C_6H_5O_7Na_3$ (formula on the right) and the starting gold compound is hydrochloroauric acid , $HAuCl_4$. Once they form, the colloidal Au nanoparticles (NPs) are stabilized by a protective layer of citrate, chloride and sodium ions. Depending on exactly how the colloidal gold solutions are prepared, such as the choice of reducing agent, concentrations, etc, spherical NPs from 3 nm to 150 nm in diameter can be obtained. Particles in a given sample of colloidal gold are monodisperse, that is, they are all close to the same size. (In a polydisperse sample there would be a greater distribution in particle size.) Studying the brightly colored reddish colloidal gold is easily done with visible spectroscopy.

2. The method above produces a colloidal gold solution that is more concentrated than the commercially available solution, and can be used to produce large quantities of Au at a fraction of the cost.

3. The procedure for determining the minimum stabilizing concentration of adsorbate such as PEG is called a “flocculation assay”.

4. The material below, some of which is not likely to be in text books, seemed to be too much for the background section:
The figure shows sizes of “small” particles. The two larger ones are not drawn to scale---20% of actual size. The influence of nanoparticles on color has been known since antiquity. Colors of stained glass windows result from the presence of small metal clusters in the glass. Ruby glass contains finely divided gold colloid.



Particles of colloidal solutions range in size from 10 to 100 nm, compared to “true” solutions where the particle sizes are between 0.1 and 10 nm.

***Procedure for Preparing Colloidal Gold Solution (used in Part A)**

1. Glassware must be *very* clean. It should be soaked a few hours or overnight in alcoholic KOH: 1 L 95% ethanol + 120 mL water + 120 g KOH.
CAUTION: If you are doing the cleaning, wear gloves and handle carefully.

2. Two solutions are needed.
a) $HAuCl_4$(aq): Add 0.1 g $HAuCl_4$ to a 250-mL volumetric and dilute to the mark with distilled water. The solution will be roughly 0.001 M. The molar mass of $HAuCl_4$ is 393.
b) $C_6H_5O_7Na_3$ (aq): Add 2.5 g sodium citrate (or 3 g sodium citrate trihydrate) to a 250 mL volumetric and dilute to the mark with distilled water. The molar mass of anhydrous sodium citrate is 258 and for the trihydrate, it is 312. The solution is around 0.04 M

3. Add 250 mL 0.001M $HAuCl_4$ to a 500 mL Erlenmeyer with a large stir bar. Mark the 250 mL volume since some water will evaporate unless a condenser is used. Boil with vigorous stirring. Solution is yellow.
Note: If it is very convenient to use a condenser, water, ice, or air-cooled, do so. If not, you will be able to dilute back to the 250 mL mark.

4. Add 25 mL 0.04 M sodium citrate all at once with vigorous stirring. The yellow solution turns clear, dark blue, then a deep red-burgundy color within a few minutes.

Stir and boil for 10-15 min after red color appears.

5. Remove from heat, move to another stirring plate and continue stirring for 15 min.

6. Cool to room temperature . Add water as needed to make 250 mL. Store in a clean dark (or foil-covered) glass bottle. The shelf life of the solution is several weeks to months.

$HAuCl_4 \cdot 3H_2O$ (trihydrate) Aldrich Cat No: 24,459-7

Procedure for Preparing
1.5M NaCl, 0.020M NaOH, and PEG Solutions (used in Part B)

Solutions can be prepared by adding grams (*g*) of the compound to a volumetric flask and then diluting with distilled water to the mark on the flask.

Compound	Molarity (mol/L)	*g* compound for 1 L solution	*g* compound for 500 mL solution
NaCl	1.5	87.8	43.9
NaOH	0.020	0.80	0.40
Polyethylene glycol*		0.02	0.01

***PEG solution is polyethylene glycol (M_n = 8000) Aldrich Cat No: 20,245-2

Variation
A similar experiment in which gold is replaced by silver has been designed. The silver nitrate is much cheaper than the $HAuCl_4$ used to make colloidal gold. Students will be able to make the yellow colloidal silver. Making copper nanoparticles is also being explored.

References
1.. "Kinetics and Thermodynamics of Au Colloid Monolayer Self-Assembly", Keating, C., Musick, M., Keefe, M., Natan, M., *J. Chem. Educ*. **1999**, *76*, 950.
2. "Colloidal Gold: Principles, Methods, and Applications" Vol.1 ,Ch 2, by Dean a. Handley; "Methods for synthesis of colloidal gold", Academic Press, 1989.
3. "Introduction to Nanotechnology" by C.P. Poole and F.HJ. Owens, Wiley, 2003.