Gold Nanoparticles Synthesis

Purpose

To investigate principles of chemical reactions and colloids.

Learning Objectives

- Analyze the impact of excess reagents on the formation of gold nanoparticles.
- Construct scientific explanations about gold colloids and factors affecting their stability.
- Utilize a laser pointer to perform light scattering tests.

Introduction

Adapted from: OpenStax Chemistry: Atom First, Chemistry: Atoms First. OpenStax CNX. Nov 13, 2018. Download for free at http://cnx.org/contents/4539ae23-1ccc-421e-9b25-843acbb6c4b0@9.17.

Colloids

As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These suspensions are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing.

On the other hand, when we make a solution, we prepare a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing.

A group of mixtures called **colloids** (or **colloidal dispersions**) exhibit properties intermediate between those of suspensions and solutions (Figure 1). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.

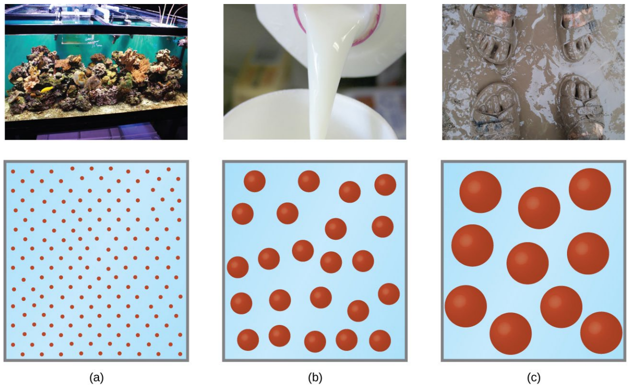

Figure 1. (a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

Tyndall Effect

The particles in a colloid are large enough to scatter light, a phenomenon called the **Tyndall effect**. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in Figure 2. Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.

Figure 2. The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: "Bahman"/Wikimedia Commons)

The term "colloid"—from the Greek words *kolla*, meaning "glue," and *eidos*, meaning "like"—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as "solute" and "solvent," the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the **dispersed phase** and the substance or solution throughout which the particulate is dispersed is called the **dispersion medium**. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in Table 1.

Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion
liquid	solid	jellies, gels, pearl, opal (H_2O in SiO_2)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

Table 1. Examples of colloidal systems

Preparation of Colloidal Systems

We can prepare a colloidal system by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

> *Dispersion methods*: that is, by breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
>
> *Condensation methods*: that is, growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Some atomizers produce colloidal dispersions of a liquid in air. Powdered milk particles of colloidal size are produced by dehydrating milk spray.

We can prepare an **emulsion** by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an **emulsifying agent**, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents. Sodium citrate, which will be used in this lab experiment, is often used as an emulsifying agent in foods like cheese sauces and macaroni and cheese.

Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions.

For example, we can prepare a red colloidal suspension of iron(III) hydroxide by mixing a concentrated solution of iron(III) chloride with hot water:

$$Fe^{3+}(aq) + 3Cl^{-}(aq) + 6H_2O(l) \longrightarrow Fe(OH)_3(s) + H_3O^{+}(aq) + 3Cl^{-}(aq)$$

A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

$$Au^{3+} + 3e^{-} \longrightarrow Au$$

Our chemical system of interest in lab focuses on the synthesis of gold nanoparticles, Au(s), by this method.

To prepare the gold nanoparticles in this lab, you will follow a synthesis in which solutions of chloroauric acid ($HAuCl_4$) and sodium citrate ($Na_3C_6H_5O_7$) are mixed. The **net ionic equation** for this synthesis is given below. In this case, citrate is the reducing agent being used to convert Au^{3+} (in the form of $HAuCl_4$) into metallic gold atoms. Excess citrate in the reaction serves a second purpose of controlling the structure of the nanoparticles formed.

$$\mathbf{4\ HAuCl_4(aq) + 3\ C_6H_5O_7^{3-}(aq) + 3\ H_2O(l) \rightarrow 4\ Au(s) + 6\ CO_2(g) + 3\ C_4H_6O_4(aq) + 7\ H^{+}(aq) + 16\ Cl^{-}(aq)}$$

Procedure

LASER POINTER SAFETY NOTE: Never look directly into the laser beam, and do not shine the laser pointer at other people. If you are observed violating these instructions and threatening the safety of others in your use of the laser pointer, you will be removed from lab and reported to student conduct.

Activity I – Initial Ideas

Review the introduction and chemical reaction being performed in this lab:

$$4\ HAuCl_4(aq) + 3\ C_6H_5O_7^{3-}(aq) + 3\ H_2O(l) \rightarrow 4\ Au(s) + 6\ CO_2(g) + 3\ C_4H_6O_4(aq) + 7\ H^+(aq) + 16\ Cl^-(aq)$$

You will be performing three separate reactions (mixtures A, B, and C labeled below) where different amounts of $HAuCl_4(aq)$ and $Na_3C_6H_5O_7(aq)$ are mixed at elevated temperature.

	Molarity of $HAuCl_4(aq)$	Volume of $HAuCl_4(aq)$	Moles (=MxV) of $HAuCl_4$	Molarity of $Na_3C_6H_5O_7(aq)$	Volume of $Na_3C_6H_5O_7(aq)$	Moles (=MxV) of $Na_3C_6H_5O_7$
A	0.00050 M	0.0500 L	0.000025 mol	0.00375 M	0.0050 L	0.000019 mol
B	0.00050 M	0.0500 L	0.000025 mol	0.00500 M	0.0050 L	0.000025 mol
C	0.00050 M	0.0500 L	0.000025 mol	0.0250 M	0.0050 L	0.00013 mol

Consider your own understanding of what is different in each reaction above (A, B, and C) and how that might impact the Au(s) product you form during each reaction.

Do not look up, reference, or copy someone else's ideas – all these responses should be your own original ideas.

Discuss ideas with your lab partner and answer the following in your lab notebook:

1. The gold nanoparticles you will prepare from these reactions will have diameters ranging from 10-100nm. These nanoparticles are basically small 'chunks' of metallic gold with varying sizes and shapes. Sketch a picture showing two different gold nanoparticles, one small nanoparticle and one larger. In your sketch, use basic circles to represent individual gold atoms. Don't add more than 10 atoms per nanoparticle to demonstrate the size.

    - *Take a picture of your hand-drawn sketch (showing both nanoparticles sizes) and save the image file to insert into your lab report submission. Be sure your photo is clear/in focus and appropriately sized so details will be easy to read.*

2. Describe what you expect to occur at the macroscopic level as you produce Au(s) according to the chemical reaction given. In other words, explain the observable changes you expect to see when $HAuCl_4(aq)$ is converted into Au(s).

3. On a single page in your lab notebook, sketch three molecular-level pictures representing mixtures A, B, and C after the reaction to synthesize Au(s) nanoparticles has occurred. Do not

draw more than 10 nanoparticles into each picture. The pictures should be representative of your given explanations.

- *Label everything in your pictures. You must include labeling or a key that identifies the chemical formula for what the symbols represent. You do not need to show water in your pictures.*
- *Take a picture of your hand-drawn sketches and save the image file to insert into your lab report submission. Be sure your photo is clear/in focus and appropriately sized so details will be easy to read.*

Activity II – Experiment

*****The use of a laser pointer can be considered a simplified version of a much more complex analytical technique for investigating the scattering of light through a solution. While only qualitative data can be determined here, this method can still be a valuable technique for evaluating solutions.*****

1. In your lab notebook, make an observation table that looks like the following (keep the table on one page of your notebook):

	General visual observations	**Laser pointer observations**
Vial (1)		
Vial (2)		
Vial (3)		
Vial (4)		
Vial (3) after shaking		
Vial (4) after shaking		
Vial (5)		
Vial (6)		
Vial (5) and (6) mixed		
Vial (7)		
Vial (8)		

2. Using the provided laser pointer (and without shaking or agitating the samples), shine the laser beam directly through the contents of the four vials at your bench (labeled **1-4**). The four vials contain:
   (1) aqueous solution of potassium permanganate, $KMnO_4$
   (2) aqueous solution of copper (II) sulfate, $CuSO_4$
   (3) finely ground charcoal, C(s), in air
   (4) finely ground charcoal, C(s), in water
   When shining the laser beam through the vials, record all your observations. Shine the beam both through the bottom of the vial (aiming the beam towards the cap) and through the side of each vial. Observe the laser beam carefully while shining it in both directions.
3. Shake vials **(3)** and **(4)** vigorously, then immediately use the laser pointer to check for differences in the light scattering through the contents of each vial. Record your observations.
4. Observe and record what happens when you shine the laser through vials **(5)** and **(6)**. These vials contain: **(5)** 0.0010 M aqueous silver nitrate ($AgNO_3$) and **(6)** 0.0010 M aqueous sodium chloride (NaCl).

5. Remove the caps from vials **(5)** and **(6)**, then pour one solution into the other vial. Place the cap on the vial that contains the mixture, shake the vial, and then shine the laser beam through the mixture. Record your observations. Repeat these observations after letting the mixture stand for at least 5 minutes.
6. Observe and record what happens when you shine the laser through vials **(7)** and **(8)**. These vials contain the reactant solutions for the synthesis of gold nanoparticles: **(7)** aqueous sodium citrate ($Na_3C_6H_5O_7$) and **(8)** aqueous chloroauric acid ($HAuCl_4$).
7. Empty the contents of vials **(5)** and **(6)** into the appropriate waste container. All other vials should be saved and kept unopened at your lab bench.

Activity III – Analysis

Consider the observations you made when shining the laser pointer through the different vial samples for the light scattering technique. Discuss and write responses to the following in your lab notebook:

1. What patterns/trends did you notice in the laser behavior among the samples? What was similar about the samples? Different?
2. Using a full lab notebook page, make a table with two columns like this:

	Molecular level sketch of vial contents	**Molecular basis for the laser pointer behavior observed for vial contents**
Vial (1)		
Vial (2)		
Vial (3) after shaking		
Vial (4) after shaking		
Vial (5)		
Vial (6)		
Vial (5) and (6) mixed		
Vial (7)		
Vial (8)		

- Fill in the table by sketching a molecular-level picture for the contents of each vial. Keep your pictures sized so that the entire remains on one lab notebook page.
- Provide a short description of what you think is happening at the molecular-level that accounts for the observations made with the laser pointer.

Take a picture of your lab notebook page with the table and save the image file to insert into your lab report submission. Be sure your photo is clear/in focus and appropriately sized so details will be easy to read.

Activity IV – Experiment

As described in the pre-lab, you will be synthesizing gold nanoparticles (GNPs) by mixing aqueous solutions of chloroauric acid ($HAuCl_4$) and sodium citrate ($Na_3C_6H_5O_7$) according to the equation:

$$4\ HAuCl_4(aq) + 3\ C_6H_5O_7^{3-}(aq) + 3\ H_2O(l) \rightarrow 4\ Au(s) + 6\ CO_2(g) + 3\ \underset{\text{succinic acid}}{C_4H_6O_4(aq)} + 7\ H^+(aq) + 16\ Cl^-(aq)$$

You will only perform one of the three experiments (A, B, or C) listed below. You will then share samples of mixtures A, B, and C so that everyone in the class can make their own observations of the resulting mixtures.

	Molarity of $HAuCl_4(aq)$	Volume of $HAuCl_4(aq)$	Moles (=MxV) of $HAuCl_4$	Molarity of $Na_3C_6H_5O_7(aq)$	Volume of $Na_3C_6H_5O_7(aq)$	Moles (=MxV) of $Na_3C_6H_5O_7$
A	0.00050 M	0.0500 L	0.000025 mol	0.00375 M	0.0050 L	0.000019 mol
B	0.00050 M	0.0500 L	0.000025 mol	0.00500 M	0.0050 L	0.000025 mol
C	0.00050 M	0.0500 L	0.000025 mol	0.0250 M	0.0050 L	0.00013 mol

1. Your TA will assign you one of the following experiments and provide you with a brown storage bottle with the appropriate label:

Experiment	1	2	3	4	5	6
Prepare Mixture	A	B	C	C	C	C

2. Once you know which experiment you are performing, identify the concentration of $Na_3C_6H_5O_7(aq)$ you should use based on the table above. Clearly record the assigned mixture and the concentration of $Na_3C_6H_5O_7(aq)$ in your lab notebook.
3. Using a graduated cylinder, measure out 50.0 mL of 5.0×10^{-4} M $HAuCl_4(aq)$ and pour it into a thoroughly cleaned and rinsed 100 mL beaker.
4. Add a magnetic stir bar to the beaker and mark the liquid level of the beaker with a Sharpie.
5. CAREFUL which knobs you turn on/off of the hotplate. There is a knob for heating and a separate knob for the magnetic stirring. DO NOT turn on the magnetic stirring! Turn on the heating knob only and begin heating the solution. Once the solution begins to boil, turn on the magnetic stirrer and continue heating until the solution comes to a **FULL ROLLING BOIL**! If you do not know what a full rolling boil looks like, check with your TA before moving on to the next step. *IMPORTANT: Do not try to shorten this step. The best synthesis will occur if you achieve a true full rolling boil before continuing. Students who try to cut time tend to produce poor nanoparticle results.*
6. **Add 5.0 mL of your assigned concentration of $Na_3C_6H_5O_7(aq)$** to the beaker on the hotplate.
7. After adding the $Na_3C_6H_5O_7(aq)$, allow the mixture to boil for an additional 10 minutes, then turn off the heat and magnetic stirrer.
8. Dilute the mixture in the beaker by adding DI H_2O until the bottom of the meniscus reaches the marked line (Sharpie). Once you have diluted the mixture, turn the magnetic stirrer back on at a low speed (DO NOT turn the heat back on).

9. **<u>If you were assigned to experiment 1, 2, or 3</u>**, label six glass vials with the letter corresponding to the mixture you have prepared (A, B, or C). **<u>If you were assigned to experiment 4, 5, or 6</u>**, you do not need to prepare glass vials.
10. Follow the instructions for handling your prepared mixture:

    a. *If you are performing experiments 1, 2, or 3…*
        i. After the mixture has cooled, use a plastic pipette to carefully transfer enough solution to fill the six labeled glass vials until they are approximately ¾ of the way full. As you fill each vial, try to obtain a representative sample of the mixture so that all the vials have similar contents.
        ii. Transfer any mixture remaining in your 100 mL beaker into the empty brown storage bottle labeled with your mixture letter (A, B, or C). Double check your storage bottle so that you ***<u>DO NOT ACCIDENTALLY MIX A, B, and C!!</u>*** **These mixtures will be used by all students (including you) next week**.

    b. *If you are performing experiments 4, 5, or 6…*
        i. After the mixture has cooled, transfer your entire mixture from the 100 mL beaker into an empty brown storage bottle labeled with your mixture letter (A, B, or C). Double check your storage bottle so that you ***<u>DO NOT ACCIDENTALLY MIX A, B, and C!!</u>*** **These mixtures will be used by all students (including you) next week.**

11. Obtain sample vials from experiments 1, 2, and 3 so that you have a vial of each mixture (A, B, and C).
12. In your lab notebook, make an observation table that looks like the following (keep the table on one page of your notebook):

	General mixture visual observations	**Laser pointer observations**
Mixture A		
Mixture B		
Mixture C		

13. Observe the mixtures in the three vials and record all your observations. While observing, perform the same light scattering experiment used earlier on each mixture, and hold each mixture up to an overhead light source (to observe its opacity and color under fluorescent lighting).
14. When you are done observing the mixtures, return the vials to those that originally prepared and distributed them. Then, place the contents of your vials into the appropriate brown storage bottle (A, B, or C) for your mixture. Double check your vials and storage bottle so that you ***<u>DO NOT ACCIDENTALLY MIX A, B, and C!!</u>***
15. Once your vials have been completely transferred to a storage bottle and are empty, thoroughly clean the vials and beakers used in this experiment with brushes, soap, and water. *Note - do not add wash rinse or soapy water into the hazardous waste container. Also, a small amount of isopropanol may be used for removing Sharpie labels.*
16. Place your brown storage bottle in the appropriate spot designated by your TA.

Activity V – Analysis

Consider the observations you made while synthesizing and observing the mixtures prepared in A, B, and C. Discuss and write responses to the following in your lab notebook:

1. What similarities and differences did you observe for the prepared mixtures A, B, and C? How do these observations compare to your pre-lab predictions?
2. Consider the stoichiometry of the balanced chemical reaction and the amounts of each reagent used in producing the different mixtures. The reaction ratio of $Na_3C_6H_5O_7$ to $HAuCl_4$ is 3:4 which could be reported as a mole ratio of 0.75 (3 mol $Na_3C_6H_5O_7$ / 4 mol $HAuCl_4$ = 0.75). Based on this, make a table like this one in your lab notebook and fill in the table completely:

	Mole ratio of $Na_3C_6H_5O_7$ / $HAuCl_4$	**Which is the limiting reagent?**	**Amount of excess reagent (in moles)?**
Mixture A			
Mixture B			
Mixture C			

Take a picture of your lab notebook page with the table and save the image file to insert into your lab report submission. Be sure your photo is clear/in focus and appropriately sized so details will be easy to read.

3. The excess reagent is not acting as an innocent spectator ion. Rather, the excess citrate is directly changing the properties of the nanoparticles being formed during synthesis. What is your initial molecular-level hypothesis for how the excess citrate may be impacting the nanoparticle synthesis? This does not need to be an accurate hypothesis, but it should be your own ideas and it should be scientifically reasoned based on general chemistry principles
4. The light scattering experiment is providing evidence about what was produced in this reaction between chloroauric acid and sodium citrate. Explain how the laser pointer provides evidence that can differentiate between the reactants and products of this chemical reaction.

Before Leaving Lab

- Properly dispose of all lab waste
- Thoroughly clean your workspace area
- Sanitize all equipment as directed
- Check to make sure you have the necessary data and files for your lab report submission. In addition to the observations and written responses collected in your notebook, for this lab you should have:
  - Two pictures of your lab notebook page containing the original sketches from Activity I
  - Picture of your lab notebook page containing the table from Activity III
  - Picture of your lab notebook page containing the table from Activity V

Post-Lab Additional Questions (16 pts)

Do not look up, reference, or copy ideas from any other sources besides your own thinking.
All responses given on these questions should be your own original ideas.

1. Summarize what you did in this lab experiment by responding to the questions below. Your responses should be written CONCISELY and in proper sentence/paragraph form. Provide responses that look like what you would put into a formal lab report. Also, assume the audience/reader has never previously seen this experiment, but has a general knowledge of science/chemistry. In other words, write 'to your peers, not the TA.'

    a. (2 pts) Concisely explain (~2-3 sentences) the scientific purpose of what you did in Activity II.

    b. (2 pts) Provide a concise description (~2-3 sentences) of the scientific data and conclusions that can be drawn from the laser pointer test used in this lab.

    c. (2 pts) Provide a concise description (~2-3 sentences) of which variables were held fixed and which were varied in the experiments performed in Activity IV.

2. Consider how you think nanoparticles are similar and/or different from other chemical systems you have studied in previous lab experiments (such as NaCl, sugar, dyes, or metal salts in water). Based on your own thinking about these systems, answer these questions:

    a. (4 pts) Sketch two molecular-level pictures depicting gold nanoparticles in comparison to at least one of the other chemical systems studied this semester. One picture should be for the gold nanoparticles, and the second picture should be for the comparison system you have chosen.
        - *Label everything in your pictures. You must include labeling or a key that identifies the chemical formula for what the symbols represent. You do not need to show water (as solvent) in your pictures.*
        - *Take a picture of your hand-drawn sketches and save the image file to insert into your lab report submission. Be sure your photo is clear/in focus and appropriately sized so details will be easy to read.*

    b. (4 pts) Provide a thorough molecular-level explanation that distinguishes gold nanoparticles from your comparison system. Clearly provide both similarities and differences in your comparison.

3. (2 pts) In these reactions, the amount and role of excess sodium citrate is very important. In fact, the sodium citrate is normally referred to as a capping agent. Based only on the wording of that term, what do you think a 'capping agent' does when interacting with a gold nanoparticle? What would it mean at the molecular-level to "cap" the particle? Your response does not need to be accurate, however, it does need to be a scientifically logical idea and based on general chemistry principles.