Analyzing Ancient Nanotechnology

Subject Area(s) Chemistry, Physics,

Associated Unit

Lesson Title Analyzing Ancient Nanotechnology

Grade Level (11-12)

Time Required
4 – 6 50-minute class periods

Day 1: Pre-lab discussion, introduction to nanoparticles
Day 2: Synthesis of silver and gold nanoparticles
Day 3-4: Spectroscopic characterization of nanoparticles
Day 4-5: Recreating the Lycurgus cup

Summary

In this project-based learning activity, students explore the properties of noble metal nanoparticles and the technology used to characterize them. Students start by synthesizing silver and gold nanoparticles. After synthesis, students build their own spectrophotometer using low cost materials and smartphones to analyze their nanoparticles. Once they've analyzed their nanoparticles, students are tasked with recreating the ancient optical effects of the Lycurgus cup by creating a nanoparticle infused "stained glass" project.

Engineering Connection

In this activity students are presented with multiple engineering challenges to solve. On day two, students will need to master sensitive laboratory techniques that require a particular attention to detail and cleanliness to succeed. On day three, students will need to design a working spectrophotometer to analyze their nanoparticles. This process encompasses engineering and problem solving by asking the students to design a working circuit to power an LED light source, selecting the correct resistors and batteries to do so, and to devise a way of limiting light contamination to analyze their sample and construct an apparatus for their mobile phone camera to be used as a sensor. On day 4, students are tasked with creating a nanocomposite material that mimics the properties of the Lycurgus cup as closely as possible. Students will need to devise a methodology based on evidence to recreate the effect, conducting trials with their nanoparticles without using them all up.

Engineering Category =

1. Relating science and/or math concept(s) to engineering
2. Engineering design process

Keywords

nanotechnology, nanoparticles, spectroscopy, project based learning

Educational Standards

Florida State Standards:

SC.912.P.10.14: Differentiate among conductors, semiconductors, and insulators.

SC.912.P.10.15: Investigate and explain the relationships among current, voltage, resistance, and power.

SC.912.P.10.19: Explain that all objects emit and absorb electromagnetic radiation and distinguish between objects that are blackbody radiators and those that are not.

SC.912.P.8.10: Describe oxidation-reduction reactions in living and non-living systems.

LAFS.910.RST.1: Cite specific textual evidence to support analysis of science and technical texts, attending to the precise details of explanations or descriptions.

LAFS.1112.RST.1.3: Follow precisely a complex multistep procedure when carrying out experiments, taking measurements, or performing technical tasks; analyze the specific results based on explanations in the text.

ITEEA Standard

Design:

Standard 10. Students will develop an understanding of the role of troubleshooting, research and development, invention and innovation, and experimentation in problem solving. (K-12)

Abilities for a Technological World:

Standard 11. Students will develop abilities to apply the design process. (K-12)

NGSS Standard

HS-PS1-2. Construct and revise an explanation for the outcome of a simple chemical reaction based on the outermost electron states of atoms, trends in the periodic table, and knowledge of the patterns of chemical properties

HS-PS1-7. Use mathematical representations to support the claim that atoms, and therefore mass, are conserved during a chemical reaction.

HS-PS3-5. Develop and use a model of two objects interacting through electric or magnetic fields to illustrate the forces between objects and the changes in energy of the objects due to the interaction.

CCSS Standard

CCSS.ELA-LITERACY.RST.11-12.1: Cite specific textual evidence to support analysis of science and technical texts, attending to important distinctions the author makes and to any gaps or inconsistencies in the account.

CCSS.ELA-LITERACY.RST.11-12.3: Follow precisely a complex multistep procedure when carrying out experiments, taking measurements, or performing technical tasks; analyze the specific results based on explanations in the text.

Pre-Requisite Knowledge

Students should have completed a first year high school chemistry course. Knowledge of electron structures, metallic bonding, ion formation, intermolecular forces, colloids, and aqueous reactions will all help the student make sense of the activities herein, but may not be required. Students should have a basic knowledge of chemistry laboratory techniques.

Learning Objectives

After this lesson, students should be able to:

- Use laboratory techniques to synthesize gold and silver nanoparticles
- Describe the process and steps associated with nanoparticle synthesis
- Design a working spectrophotometer and describe how it functions
- Use ohm's law to determine a circuit that will correctly power an LED
- State several unique properties and uses for noble metal nanoparticles
- Use evidence from reading to design a process to recreate the effect of the Lycurgus cup

Introduction / Motivation (5E – Engage)

Nanotechnology has to do with the use of materials that are so small that they exist on the scale of nanometers. To give you some idea of how small that is, here are some examples:

1. Look at the meter stick in front of the room: If you were to cut that meter stick into 1 million equal pieces, the length of one of those piece would still be 1000 times bigger than a nanometer.
2. The width of an average human hair is 100,000 nanometers wide.
3. A gold atom is about 1/3 of a nanometer wide.

Do you think that microscopes can be used to view materials at the nanoscale? To put this into perspective, consider this: The Scale of the Universe.

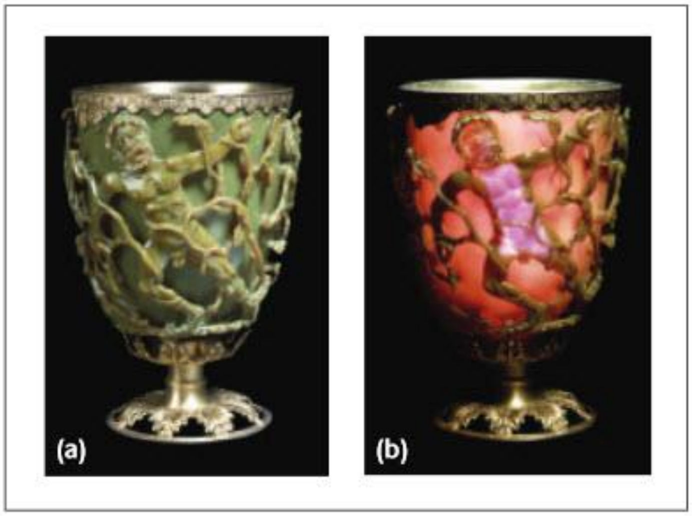


Figure 1 (a and b)

The Lycurgus Cup *1958,1202.1 in reflected (a) and transmitted (b) light. Scene showing Lycurgus being enmeshed by Ambrosia, now transformed into a vine-shoot. Department of Prehistory and Europe, The British Museum. Height: 16.5 cm (with modern metal mounts), diameter: 13.2 cm. © The Trustees of the British Museum*

Nanotechnology is currently at the cutting edge of science. It has enabled the creation of powerful electronics and sensors, alternative energy sources such as solar power, and even better sunblock and cosmetics. Scientists all over the world are studying nanotechnology and it's applications to make our lives better and you can thank them for the smartphone in your pocket.

Even though nanotechnology is a relatively new field of study for scientists, it was recently discovered that ancient Roman glassmakers may have been the first nanotechnologists. When the British Museum acquired an ancient Roman chalice known as the

Lycurgus Cup in the 1950's, curators and scientists noticed something very odd about it, other than its exquisite carvings. The cup appeared to be made out of some kind of glass that would change color, depending on whether or not light was being transmitted through it. From the outside, the cup appears green. When lit from the inside, the cup appears red. Scientists suspect that it changed color depending on the liquid that was inside of it.

This phenomenon escaped explanation until the 1980's, when scientists were able to analyze pieces of the glass from the original base and found that it contained gold and silver nanoparticles, along with traces of sodium chloride. That is, the glass contains particles of silver and gold that are between 50-100nm in diameter.

Here is a video showing the Lycurgus Cup changing colors:

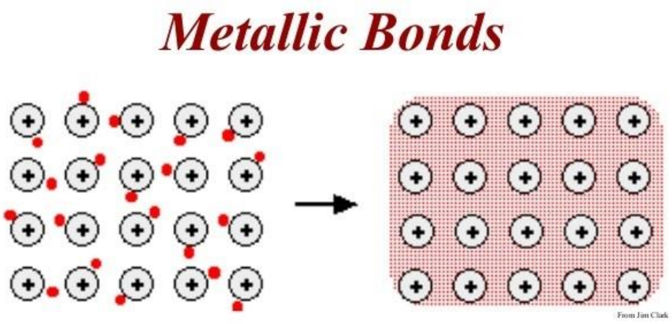
The Lycurgus Cup

In modern times, silver and gold nanoparticles are used for everything from antibacterial coatings to biosensors to detect disease, and even cutting edge treatments for cancer. Many of our modern applications for the nanoparticles are based on the same properties that the Roman glassmakers were exploiting when they used them in their glass for the Lycurgus cup. Over the course of the next few days you will make your own silver and gold nanoparticles and explore their properties using some of the same tools that professional scientists use in an effort to recreate the effect of the Lycurgus cup.

Lesson Background & Concepts for Teachers (5E – Explain)

Day 1 and 2: Intro and Synthesis

The interesting properties seen in the Lycurgus cup arise from a phenomenon observed in metals known as surface plasmon resonance. In order to understand surface plason resonance, it's first important to understand metallic bonding. The force responsible for holding metallic substances together is called metallic bonding, which students are likely familiar with if they have taken a first year chemistry course. In metallic bonding, metal nuclei are held together through their collective attraction to loosely held, delocalized valence electrons. On one hand, metals hold their valence electrons loosely because of their effective nuclear charge being low, but on the other hand they are extremely electron deficient in terms of a full valence shell,



A metallic bond is produced when electron orbitals overlap and all electrons are shared between atoms. This is often referred to as a "sea of electrons," and is responsible for the high conductivity, reflectivity, malleability, and ductility of metals. Metallic bonding is restricted to atoms of a single element.

Figure 2: "Sea of Electrons"

and so form strong attractions to other metal valence electrons. This results in a sharing of electrons that are free to move between metal atoms as they occupy empty electron positions.

The model usually used for discussing metallic bonding is called the “sea of electrons” model. This model essentially has the positive nuclei bobbing around and attracted to an ocean of negative charge formed by the delocalized electrons. This model is useful for understanding surface plasmon resonance. A surface plasmon is essentially the extension of the electron cloud on the surface of the metal out into space. Thinking of the electron cloud as an electromagnetic wave, it’s easy to visualize then, that if you strike it with other electromagnetic waves of the right wavelength, then the plasmons might resonate with the wave.

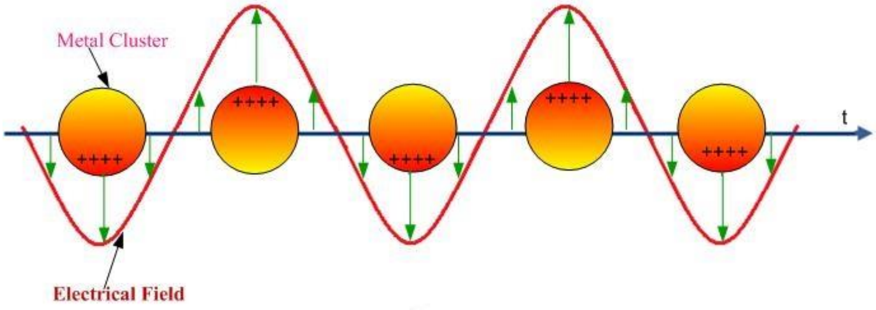


Figure 3: Surface Plasmons

In metals, this resonance usually results in the characteristic luster of the metal as light is reflected out after traveling along the surface plasmons and exciting them. In nanometals, the plasmons resonate differently because they do not have a long surface to travel across. This is called localized surface plasmon resonance (LSPR) and it is responsible for the effects seen in the Lycurgus cup. Two unique properties result:

1.) Strong absorption of light at a frequency that resonates well with the LSPR. This changes the color of the metal as it absorbs the light.
2.) Scattering of light as a result of excitation of the LSPR. This can result in an interesting change of color of the light and almost fluorescent look to the particles when in solution.

Day 3:

Spectrophotometer Design and Theory

Spectroscopy is the field of science that analyzes electromagnetic radiation in order to gain information about the matter that it interacts with. There are many types of spectroscopy, each concerned with a different type of interaction or type of electromagnetic radiation. In this part of the project, students will build a spectrometer capable of analyzing the wavelengths and intensity of visible light.

The spectrometer works by analyzing the intensity (brightness) and the wavelength of light that it detects. With the right software, freely available, a cell phone camera can do both of these things. If you want to detect the optical properties of a solution or sol, you can pass a light through the solution and analyze the light that comes out for wavelength and intensity. If you compare it to light that would come out of just the solvent alone, you can determine several properties of the solution, includes the wavelengths of light that it absorbs and the relative concentration of the solution based on the decrease of intensity of the transmitted light.

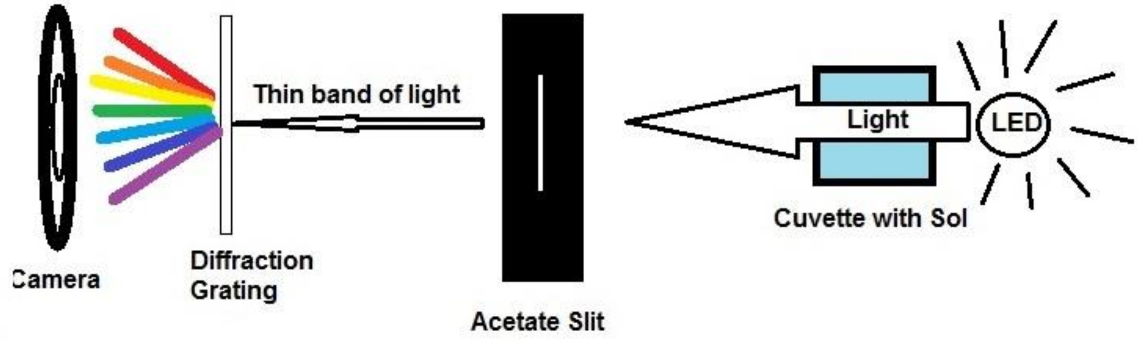


Figure 4: Spectrometer Operation

For instance, if you pass white light through a blue solution and then analyze the light that comes out with a spectrometer, you will not likely see much red light, because the blue solution absorbs it. It appears blue to your eyes because that's the predominant wavelength that it lets through. You can also determine the concentration of the solution by how MUCH red light it absorbs. Darker solutions appear darker because they absorb more light, which could be because of concentration or the length that the light has to travel through the solution. This relation is called Beer's law:

$$A=\epsilon l c$$

A=Absorbance

ϵ= Molar Extinction Coefficient

l= Length the light must travel through

c= Concentration of the sample

In the case of nanoparticles, their localized surface plasmon resonance leads to deep extinction in specific bands in the visible and UV regions of light, with the wavelength of extinction dependent on their size. This is caused by a combination of two reasons: absorbance of the light, and scattering of the light. The size of the nanoparticles can be determined based on the wavelength of light where the greatest extinction occurs.

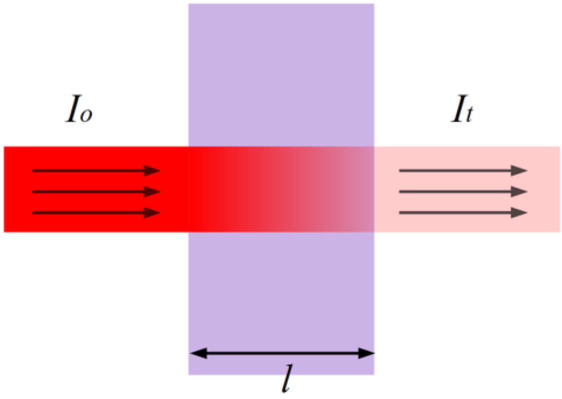


Figure 5: Transmittance of Light

LED’s, semiconductors and circuits

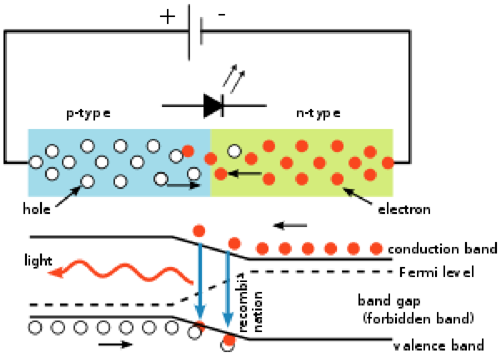


Figure 7: LED p-n Junction

The light source for this spectrometer is a light emitting diode (LED). This technology is a simple. A semiconductor is a material that will conduct electricity under certain circumstances but not others. Recall that metals can conduct electricity easily because they have delocalized, easily mobile electrons. This occurs because they are electron deficient in terms of valence shells, and also have a loose hold on their valence electrons. This is in contrast to nonmetals, which hold their electrons tightly because of high effective nuclear charge, and bond to complete their valence shell. Semimetals are in-between.

Another model for visualizing metallic bonding would be the molecular orbital model. In this model, atomic orbitals in bonded atoms merge to create whole molecule orbitals of different energy levels. The energy levels that the valence electrons naturally occupy make up what’s called the “valence band” of energy levels. The energy levels made up of empty molecular orbitals are called the “conduction band”. The amount of energy between the valence band and the conduction band is called the “band gap”. In metals, the band gap is nonexistent, and so electrons freely conduct. In semiconductors there is a small bandgap, which means electrons need to be excited to conduct. In nonmetals and insulators the bandgap is too high to conduct.

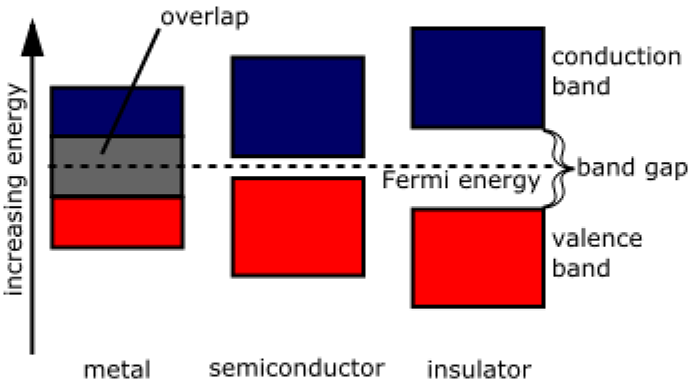


Figure 6: Band Gaps

Most semiconductors do not emit light when electrons drop from the conduction to the valence band, but LED’s have been engineered to emit light when this happens. The wavelength of the light is determined bit the size of the bandgap. The bandgap is manipulated by creating a p-n junction. In this case, “p” and “n” are referring to how the semiconductor has been doped. In the case of a “p” doped semiconductor, the semiconductor have been doped with some material that is electron deficient compared to itself. This creates positive “holes” in the valence band. In the case of an “n” type, the semiconductors has been doped with something that is electron rich compared to itself, placing electrons in the conduction band. A p-n junction is where these two doped material meet.

When a current is applied to the p-n junction, electrons from the n-type are pushed into the p-type, essentially “falling into” the p-type holes in the valence band. The distance they fall is the bandgap and determines the wavelength of light emitted.

The bandgap will also determine the amount of voltage needed to run the LED, with red LED’s having the smallest bandgap and white or blue ones having the highest. **You must control the current running through the LED, or you will burn it out.** Every LED will come with its own specs for current, but a typical current will be 20mA. In order to create the appropriate current in your circuit to power your LED, you will need to use Ohm's Law to select the proper resistor:

I=V/R

I= Current in amps

V= Voltage of circuit

R=Resistance in ohms

You will need to make one modification to Ohm's law, and that is that you cannot just use the voltage of whatever battery you are using to power your LED, because the LED actually subtracts voltage from the circuit itself as it runs. This is called the "voltage drop" or "forward voltage" of the LED. So the voltage you would use when plugging values into Ohm's law would be the Voltage drop of your LED subtracted from the voltage of your battery. ($V_{Supplied}$ - V_{LED}).

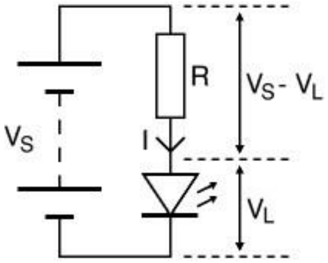


Figure 8: LED Circuit

Day 4: Nanoparticle Stained Glass

This activity deals with the idea of composite materials. That is, materials composed of more than one substance with the goal of yielding a new materials with properties different than either of the substances alone. Nanocomposites are composite materials in which one of the substances added maintained a grain size in the scale of nanometers.

Vocabulary / Definitions

Word	Definition
Band Gap	The energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band
Beer's Law	States that the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution.
Conduction band	The lowest range of vacant electronic states that electrons can be excited into.
Light Emitting Diode	A two-lead semiconductor light source. It is a p–n junction diode, which emits light when electrons are excited into the conduction band and fall back to the valence band.
Nanotechnology	The branch of technology that deals with dimensions and tolerances of less than 100 nanometers, especially the manipulation of individual atoms and molecules.
Nanocomposite Material	A material made by combination of one material with another material that has grain sizes measured in nanometers.
Semiconductor	A solid substance that has a conductivity between that of an insulator and that of most metals.
Surface Plasmon Resonance	The oscillation of electrons on the surface of a metal in resonance with an electromagnetic wave.
Sol	A fluid suspension of a colloidal solid in a liquid.
Spectroscopy	The branch of science concerned with the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation.

Spectrophotometer	An apparatus for measuring the intensity of light in a part of the spectrum, especially as transmitted or emitted by particular substances.
Ohm’s Law	States that the current through a conductor between two points is directly proportional to the potential difference across the two points
Valence Band	The highest range of electron energies in which electrons are normally present

Associated Activities (5E – Explore)

Day 2 Teacher Notes: Synthesis of Silver and Gold Nanoparticles (See handout for student instructions)

In order to get good results, all glassware should be soaked in an alcohol base bath prepared according to the following formula: 1 L 95% ethanol + 120 mL water + 120 g KOH. This should be done in advance by the teacher. Be sure that the piece of glassware is completely filled with the solution and is sitting upright. After several minutes of soaking, carefully remove the item (it will be slippery), and rinse thoroughly. **Always use an apron, eye protection, and thick black butyl gloves when manipulating glassware around the base bath! Rinse gloves after use to prevent spreading caustic all over your work area.**

The solutions for this section need to be prepared fresh with high quality distilled water. Both syntheses are highly sensitive to technique, cleanliness and accurate solution concentrations. The silver synthesis is more sensitive and challenging. Give less proficient students the gold synthesis. If you pre-chill the sodium borohydride you can reduce the time needed for the silver synthesis and put it more on par with the gold synthesis.

The silver nanoparticle synthesis chemicals can be prepared as follows:

The synthesis procedure for this section is from Soloman, S. D., Bahadory, M., Jeyarajasingam, A. V., Rutkowsky, S. A., Boritz, C., & Mulfinger, L. (2007). ”Synthesis and Study of Silver Nanoparticles.” J. Chem. Educ., 84(2), 322-325.

0.0010 M $AgNO_3$: Add 0.170 g $AgNO_3$ to a 1-L volumetric and dilute to the mark with distilled water. (Molar mass of $AgNO_3$ is 170).

0.0020 M $NaBH_4$: Add 0.0378 g sodium borohydride* to a 500 mL volumetric and dilute to the mark with distilled water. (Molar mass of $NaBH_4$ is 37.8).

*$NaBH_4$ is available in 99% purity and 99.95% purity. 99.95% purity will yield the best results, but costs almost twice as much. Researchers have reports hit or miss results with 99% purity. It is recommended to purchase the higher purity if possible

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0.3% PVP: PVP is available in different molar weights. Choose 10,000 to use for this lab.

The gold nanoparticle synthesis chemicals can be prepared as follows:

The synthesis procedure for this section is from A. D. McFarland, C. L. Haynes, C. A. Mirkin, R. P. Van Duyne and H. A. Godwin, "Color My Nanoworld," J. Chem. Educ. (2004) 81, 544A.

1.0 mM HAuCl4: The solid is hygroscopic so purchase HAuCl4.3H2O in 1.0 g quantities and use the entire bottle. Dissolve 1.0 g HAuCl4.3H2O in 250 mL distilled water to make a 10.0 mM stock solution of gold(III) ions that can be kept for years if stored in a brown bottle. This creates enough solution to do the experiment 250 times. Dilute 25 mL of stock to 250 mL to make the 1.0 mM concentration for this experiment.

38.8 mM $Na_3C_6H_5O_7$ (sodium citrate): Dissolve 0.5 g of the solid (dihydrate form) in a 50 mL volumetric and dilute to the mark with distilled water.

Unused Au nanoparticle solution made by the students can be stored for several years in a brown bottle. 1.0 mM $HAuCl_4$ solution is unstable and will last only a few days.

Day 3 Teacher Notes: Construction of a Spectrophotometer to Characterize Nanoparticles (See handout for student instructions)

Design ideas and diagrams for this section come from Asheim, J., Kvittingen, E. V., Kvittingen, L., & Verley, R. (2014). A Simple, Small-Scale Lego Colorimeter with a Light-Emitting Diode (LED) Used as Detector. J. Chem. Educ. 91(7), 1037-1039.

And from http://publiclab.org/wiki/spectrometer

The PhET simulation guide was created by Joel Barthel and it freely available on the PhET website at: https://phet.colorado.edu/en/contributions/view/3632

The creation of a reliable and working spectrophotometer is likely to be the most challenging and time consuming aspect of this project. While there is a substantial amount of benefit to students creating their own, teachers who need to cut down on time might be wise to skip this section in favor of using commercial spectrometers like the PASCO Spectrometer or Vernier SpectroVis to analyze the nanoparticle samples.

It's probably best to have the students do the LED calculations, power source selection and resistor selection in class, and then have them practice creating the circuit to power it. Students can use class time to discuss ideas with peers for creating an apparatus and come up with a basic idea. Actual creation of the spectrometer can happen at home.

It will be important to give students sufficient freedom to engineer a design that works. You should provide students with the data sheets that include the voltage drop for the LED they are using, and leave it up to them to determine the proper resistor and battery to use to gain the best light without burning it out. The diagrams provided are to get the students off on the right start, but it will be up to them to engineer a custom apparatus for their smartphone that can give sufficient reliability and hold everything in place. If available, students can compare results from their homemade spectrometer to one of the commercial ones.

Show students this short video on how to use the spectral workbench software with their spectrometer: Spectral Workbench

Students can also use their spectrometer or commercial ones to watch the change in extinction that happens as their particles coalesce up adding NaCl.

Day 4 Teacher Notes: Recreating the Lycurgus Cup: A "Stained Glass" Study

This procedure is adapted from "Nanoparticle Stained Glass" at http://www.nisenet.org/catalog/programs/nanoparticle_stained_glass_cart_demo

Students will want to keep their gold and silver sols, but the reductant and stabilizers in them, although not particularly hazardous, are still not chemicals that you want to allow students to leave with in solution. By immobilizing the nanoparticles into a polymer nanocomposite it gives the students a safe means to take home their end project with silver and gold in it.

It may or may not be possible to recreate the Lycurgus effect. Let me know if you do! That doesn't prevent students from learning a considerable amount in the process.

Advanced students can use the calculated nanoparticle size to estimate the concentration of nanoparticles in the sol and to do ppm calculations for addition to the PVA.

A faster drying technique would be to place the "stained glass" in the oven at 225F for 2 hours. It's unknown if the plexiglass will soften considerably at that temperature. Be careful if you try it. Silicone bake molds can also be used instead of trying to simulate stained glass.

View this video for a better idea of how this works: https://vimeo.com/channels/nisenet/11048874

Assessment (5E – Evaluate)

See Handouts for assessment questions. A formal report is suggested following the lab to enable students to write a complete narrative of their learning.

Lesson Extension Activities (5E – Extension)

See Day 4

References

Asheim, J., Kvittingen, E. V., Kvittingen, L., & Verley, R. (2014). A Simple, Small-Scale Lego Colorimeter with a Light-Emitting Diode (LED) Used as Detector. *Journal Of Chemical Education*, *91*(7), 1037-1039.

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Attachments

Synthesis of Gold and Silver Nanoparticles Day 2

Spectroscopic Characterization of Nanoparticles Day 3

8.5x11mini-spec3.8

Recreating the Lycurgus Cup Day 4

Lycurgus reading

Contributors

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Supporting Program

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Acknowledgements

Classroom Testing Information

This procedure in its entirety is untested. Derivations of each activity have been tested in various classrooms. (See references)

Attachments

Synthesis of Gold and Silver Nanoparticles

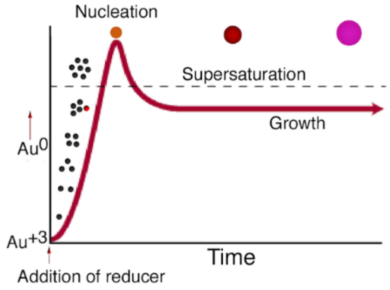
Background

Nanoparticles are particles so small that they are measured in nanometers (10^{-9}m), or billionths of a meter. Because of their small size, nanoparticles of materials have different properties than they would if they were larger. For instance, metal nanoparticles tend to strongly absorb specific wavelengths of light and scatter back others, giving them characteristic colors, depending on their material, shape, and size.

In this lab your teacher will assign you to either make silver or gold nanoparticles. Depending on which one you are assigned, your procedure will be different, but the principles behind what you are doing will be the same. In both methods you will be using a reducing agent to reduce the metal ions while they are in solution. You will also control their growth by using a stabilizer to ensure that the nanoparticles cannot agglomerate into larger metal particles. The steps are the same either way:

1.) Nucleation: This is where the nanoparticles are first reduced into a single metal atom. We call that first few metal atoms the nucleation site. How many nucleation sites there are depends on the concentration of ions and reducing agent used. The more simultaneous nucleation sites you create, the smaller the nanoparticles you get will be. ***If your glassware is even a little dirty, or you use low quality distilled water, your nucleation sites will be drastically affected because of interactions.**

2.) Growth: Provided you were able to achieve a clean nucleation step, your solution will become supersaturated with metal atoms. At this point, new nucleation sites will not form and remaining metal ions will be reduced onto your existing atoms, causing them to grow into **seeds** of multiple atoms.



3.) Ripening: As your nanoparticle seeds grow, they will take whatever shape is the easiest to form. Absent some kind of “shaping agent” that determines its shape, the particles will ripen into spherical shapes.

4.) Termination: At some point the growth will stop because you will run out of ions to reduce or because it will require too much energy to add more atoms to the particles. Your particles must be stabilized for prevent them from coalescing into larger metal particles. The chemical used to do this is called the **capping agent**.

Silver Nanoparticle Synthesis

Equipment and Materials (assuming that students work in groups of 2)

1 250mL Erlenmeyer Flask
1 50ml Buret, clamped to a stand
1 50mL Graduated Cylinder
1 Stirplate and Bar
10mL 0.0010M $AgNO_3$

30mL 0.0020M $NaBH_4$
Ice and distilled water
6 Test tubes in a test tube rack
0.3% PVP
1.5M NaCl

Procedure:
Glassware was cleaned by soaking in an alcoholic KOH bath, and is ready to use.

1. Two solutions will be available. Rinse all glassware with pure water before starting.
0.0010 M $AgNO_3$(aq) and 0.0020 M $NaBH_4$ (aq)

2. Using a graduated cylinder, pour 30 mL 0.0020 M sodium borohydride into the 250mL Erlenmeyer. Place the Erlenmeyer into an ice bath. Allow to cool for about 20 minutes. Note: The borohydride solution must be freshly prepared.

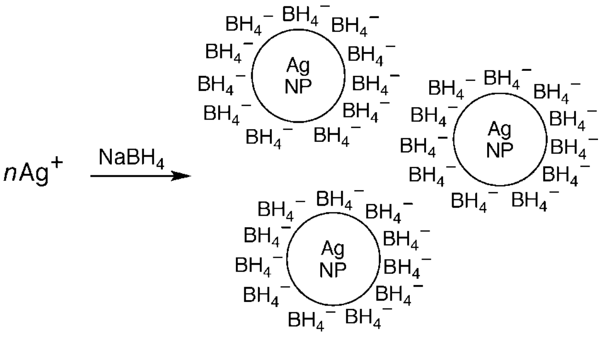
3. Place a stir bar in the Erlenmeyer, center the assembly on the stir plate and begin the stirring.

4. Pour 10 mL 0.0010 M $AgNO_3$ in a buret supported with a clamp and a ring stand. Add the solution dropwise, about 1 drop/second, until it is all used up. This should take around 3 minutes. After 2 mL has been added, the solution should turn light yellow. When all of the silver nitrate has been added, the solution should be a darker yellow.

5. *Stop the stirring as soon as all of the silver nitrate solution is added* and remove the stir bar. **CAUTION**: If the stirring is continued once all the silver nitrate has been added, aggregation is likely to occur; the yellow darkens, turns violet, then grayish as the particles settle out.

6. The product should be clear yellow once the reaction is completed and should remain yellow, although it may darken somewhat. Record the appearance of your product as soon as the stirring is stopped and after waiting for about 5 minutes. Note: Clear yellow colloidal silver will keep for weeks, even months, when stored in a transparent vial.

Note: The sodium borohydride reduces the Ag ions to nanoparticles of Ag metal. Excess borohydride ions in solution stick to the Ag metal surface, acting as your capping agent and giving an overall negative charge to each Ag nanoparticle.



Gold Nanoparticle Synthesis

Equipment and Materials (assuming that students work in groups of 2)

1 50mL Erlenmeyer flask or beaker
1 stirring hotplate and stir bar
1 10mL Graduated cylinder
20mL 1.0 mM HAuCl4
2mL 38.8 mM $Na_3C_6H_5O_7$
Distilled water
6 Test tubes in a test tube rack
1.5M NaCl

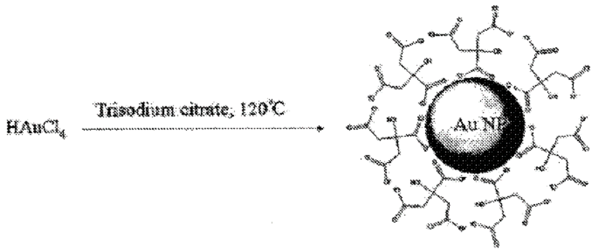
Procedure:

Glassware was cleaned by soaking in an alcoholic KOH bath, and is ready to use.

1. Rinse all glassware with pure water before starting. Add 20 mL of 1.0 mM HAuCl4 to a 50 mL beaker or Erlenmeyer flask on a stirring hot plate. Add a magnetic stir bar and bring the solution to a rolling boil.

2. To the rapidly-stirred boiling solution, quickly add 2 mL of a 1% solution of trisodium citrate dihydrate, $Na_3C_6H_5O_7.2H_2O$. The gold sol gradually forms as the citrate reduces the gold (III). Remove from heat when the solution has turned deep red or 10 minutes has elapsed. As the solution boils, add distilled water as needed to keep the total solution volume near 22 mL. Be sure to note how the solution visibly changes and when.

Note: The sodium citrate reduces the Au ions to nanoparticles of Au metal. Excess citrate anions in solution stick to the Au metal surface, acting as your capping agent and giving an overall negative charge to each Au nanoparticle.



Both Gold and Silver Nanoparticles

Stabilized metal nanoparticles can be used as sensors to detect the presence of electrolytes. Upon addition of positive ions to the Sol, your nanoparticles will destabilize and aggregate. Try it:

1. Place a 3mL of your Sol into a two small test tubes.
2. Add 3mL of distilled water to each tube to dilute the Sol.
3. Add saturated NaCl solution to one test tube dropwise. Record changes that you observe.
4. Add sugar solution to the other test tube dropwise. Record any changes you observe.
5. SILVER ONLY: Add 1 drop of 0.3% PVP to your sample to stabilize it further for long term storage when finished. PVP is a better capping agent than borohydride and will prevent aggregation.

Questions (Both silver and gold)

1.) Use your knowledge from class lectures and from this handout to discuss why you observed what you did when adding salt and sugar to your nanoparticle Sol. Write 1-2 paragraphs and be sure to discuss the role of the capping agent, and the reason for the differences in adding salt vs. sugar. Do this on another sheet of paper.

2.) Estimate the number of silver or gold atoms in a 12-nm nanoparticle. Use the value for the atomic radius of silver or gold to calculate its volume. (Volume of a sphere = $4/3\ \pi r^3$)

3.) Assuming all of your silver or gold ions are reduced, estimate the number of 12nm nanoparticles produced in your synthesis.

4.) Despite the fact that it is a simpler procedure, the mechanism of action for the gold nanoparticle synthesis is more complex than silver. Silver is a relatively straightforward redox reaction that takes the form:

$$AgNO_3 + NaBH_4 \rightarrow Ag + 1/2H_2 + 1/2B_2H_6 + NaNO_3$$

Show the oxidation and reduction half reactions for this equation.

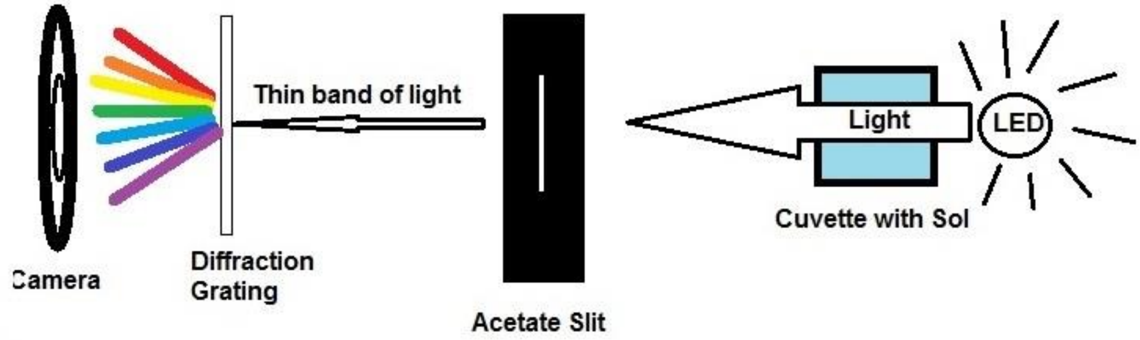
Spectroscopic Characterization of Nanoparticles

Background

Nanoparticles are far too small to see, even with a microscope, so scientists can use other instruments to determine the size and shape of nanoparticles. One instrument might be an electron microscope, which uses beams of electrons to image something, instead of light waves. Electron microscopes are very expensive and difficult to use, so a much better option would be to use an instrument called a spectrometer.

Think about this, how can you tell that there are nanoparticles in your sol, even though they are too small to see? Because of the color. Nanoparticles interact with light by absorbing or scattering it, giving them their color. As is turn out, the size of the nanoparticle determines the type of light that it absorbs, and scientists can determine the size and shape of nanoparticles just by the wavelength of light that they absorb.

In this project you will be building your own spectrometer and using it to analyze your nanoparticle sol. It works by passing light through your sample and the analyzing the light that emerges to see which wavelengths were absorbed by the particles, and how much. You will be using a white LED as your light source, and your mobile phone camera as the detector. First you will pass light through your sol, then block out all but a narrow slit of it to make it easier to analyze, and pass it through diffraction grating, which acts like a prism and separates it out into its parts. The colors that emerge are the ones that your sol let through. You can also tell information about concentrated your sol is by how much light it absorbs.



Understanding Solution Spectroscopy: Beer’s Law

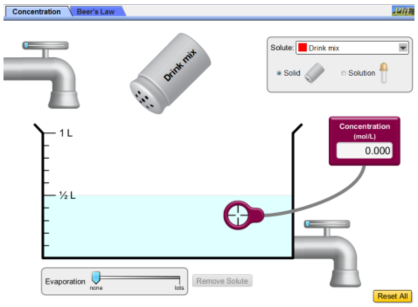
Every solution or sol will absorb light differently. If you can determine that exact relationship, called the “extinction coefficient” or “molar absorbance”, then you can make determinations about solution concentration from spectroscopy data. Complete the following online simulation to gain a better understanding of Beer’s Law before proceeding:

PhET Simulation - Beer's Law

Go to: http://phet.colorado.edu/en/simulation/beers-law-lab

Warm up -- collecting and maintaining a sample:

Start with the *Concentration* tab, as shown at the right.
Drag the concentration meter into the solution and complete the table:



Solute: Drink mix

● Solid ○ Solution

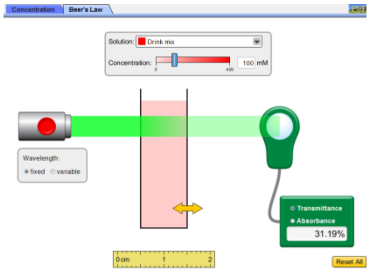
Concentration (mol/L) 0.000

Evaporation: none

What impact does each variable have on the concentration of a solution?					
Variable:	Adding a solid "pollutant"	Adding a liquid "pollutant	Adding more tap water	Draining off some water	Allowing water to evaporate.
Impact on concentration: (increase, decrease, unchanged)					

Once a sample has been collected from the environment, it is important to preserve the concentration and get an accurate measurement later in the lab. Does the size of the sample matter? What steps should the researcher take to ensure the concentration measurement doesn't change?

Part 1 – Transmittance and Absorbance.



Solution: Drink mix

Concentration: 100 mM

Wavelength: ● fixed ○ variable

○ Transmittance ● Absorbance 31.19%

Now click on the Beers Law tab, as shown at the right.
Reset all and turn on the light source.

The % of light that is transmitted through a sample depends upon four variables. First, just play around a bit. Manipulate these variables to see what their impact on % transmittance is.

The % of light transmitted will simultaneously tell us the amount of light absorbed. For example, what is the absorbance when the transmittance is "1", 100%? _______________

For this investigation we will examine all measurements of light in terms of Absorbance. Their relationship is mathematically expressed according to $A = -\log10\ T$

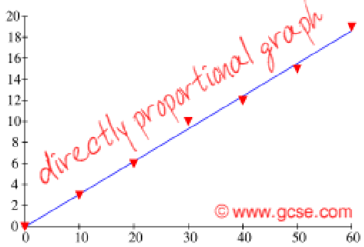
Remember: if you are testing/manipulating a variable and want to see the change it causes, then you must keep the other variables unchanged.

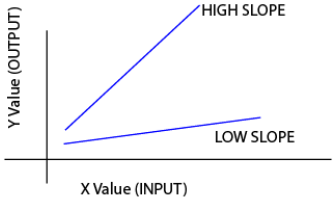
What impact does each variable have on the *measured concentration* of a solution, as given by *Absorbance*?				
Variable:	Concentration, **c** (maintain the same "pollutant" and the same Length of sample to go through)	Length of Sample to go through, **l** (maintain the same "pollutant" and the same Concentration)	Type of "Pollutant" examined, ε. (maintain the same concentration and length of sample)	Wavelength of light used? (maintain all other variables)
	For all of these tests maintain the default *fixed* wavelength of light!			
Relationship of this variable to Absorbance: (**direct** "both go up/down" OR **indirect** "one moves in the opposite direction as the other" OR … **Random** "unique to each"				

Part 2 – Beer's Law.

According to your observations, the measured absorbance will *increase* if you *increase* either the actual concentration or the sample cell length.

In fact, these measurements are *directly proportional* and should produce a straight line when graphed!





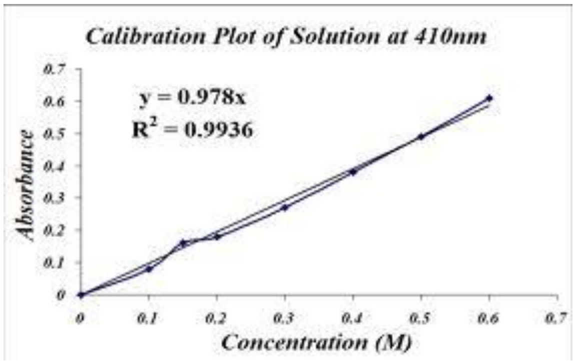
The rate of absorbance also depends upon the slope (type of pollutant examined), which is described by the "Molar Absorbance", ε .

A substance that "absorbs a lot of light" will result in a steeper slope when graphed because of the greater "Molar Absorbance", ε.

This also means that if you are looking at a particular(unchanging) type of pollutant, **ε**, using a particular(unchanging) sample length, **l**, the slope, **εl,** is constant.

Following the equation for a linear line, **y = m x** we get **A = εl c.** This is "Beer's law".

This equation can be applied to determine the concentration of almost any pollutant through its absorbance.



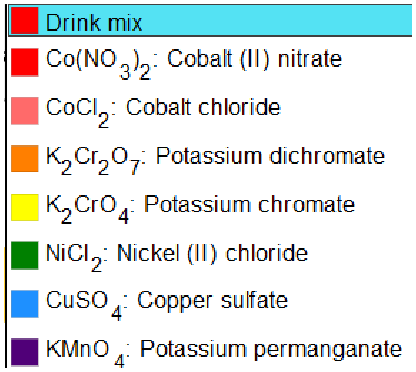
For example: if the following plot and equation of **A *vs* c** was obtained, then what would be the concentration of "pollution" for an unknown sample that has an absorbance of .55? ________

(hint: plug in .55 for the Absorbance value in the equation shown →)

Based on your earlier observations, it shouldn't surprise you that the graph above only applies to a particular wavelength of light, 410 nm. Although patterns of wavelength vs absorbance can be useful in identifying the substance, the pattern is so unique and random it is impractical for Beer's Law.

Although Beer's law can only applied to a "fixed" unchanging wavelength, it is a good idea to first determine which wavelength will be most suitable and then to conduct a Beer's Law analysis with that wavelength.

Which wavelength would be the best to apply if you were to graph the A vs c for each of these substances?



🟥 Drink mix
🟥 $Co(NO_3)_2$: Cobalt (II) nitrate
🟥 $CoCl_2$: Cobalt chloride
🟧 $K_2Cr_2O_7$: Potassium dichromate
🟨 K_2CrO_4: Potassium chromate
🟩 $NiCl_2$: Nickel (II) chloride
🟦 $CuSO_4$: Copper sulfate
🟪 $KMnO_4$: Potassium permanganate

Building Your Spectrometer

Equipment and materials (minimum)

High Intensity White LED
Wires and alligator clips
Various battery types (9V, AA, Coin Etc…)
Various resistors
Cuvettes
DVD-R
Black Card Stock
Android smartphone
6x16 Lego Plate (Optional)
2x2 Lego Bricks (2) (Optional)
2x1 Lego Brick with hole (Optional)

Your task is to build a spectrometer to analyze the absorption of your sol. It must meet the following criteria:

1.) The LED light source must be powered reliably in a way that can be turned off and on easily
2.) The cuvette needs to be in the path of the light, with the acetate slit and detectors on the other side to analyze the light that travels through the solution.
3.) Nothing on the apparatus is allowed to be held in place by your hands. Everything must be secure except for your mobile phone.
4.) The apparatus must prevent light contamination from sources other than the cuvette from reaching the camera. This includes unfiltered light from the LED as well as outside light.

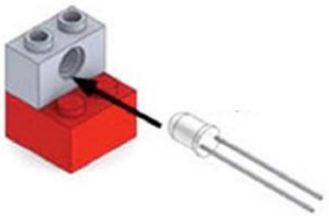
You can use the basic plans from http://publiclab.org/wiki/spectrometer as inspiration. The "Foldable Spectrometer" is probably most useful to you. Your teacher will provide blank DVD-R's for diffraction grating, LED's, resistors, batteries, acetate slits, and cardstock.

One suggestion for holding your LED and cuvette in place is to use Lego's. There are Lego blocks that can hold both nicely:

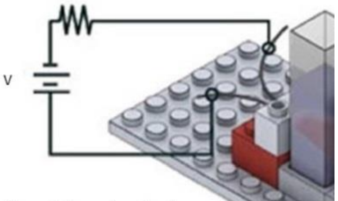
CAUTION Do not hold the block with your hand when sawing the top off! Secure it with a clamp!

2x2 Lego blocks hold cuvettes well if their top is cut off

LED light source



2x1 Bricks with holes hold LED's in place



A sample lego setup showing an LED passing light through a cuvette.

You will need to engineer how to wire your spectrometer, block out light pollution, hold the battery, hold your smartphone in place etc…

Wiring your LED

LED's operate at different voltages. Check the LED you have for the "forward voltage" or "voltage drop". This is the optimal voltage required to light your LED, and the amount that the voltage in your circuit will drop because of the LED. Choose a power source that supplies at least that voltage.

When wiring your LED to a power source, you must adjust the current so that the LED doesn't get burned out. Check the LED specs for the max forward current and calculate the resistor that you need based on your voltage using Ohm's law:

I=V/R
I= Current in amps
V= Voltage of circuit
R=Resistance in ohms

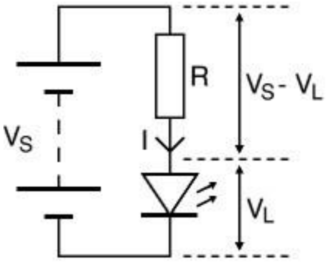
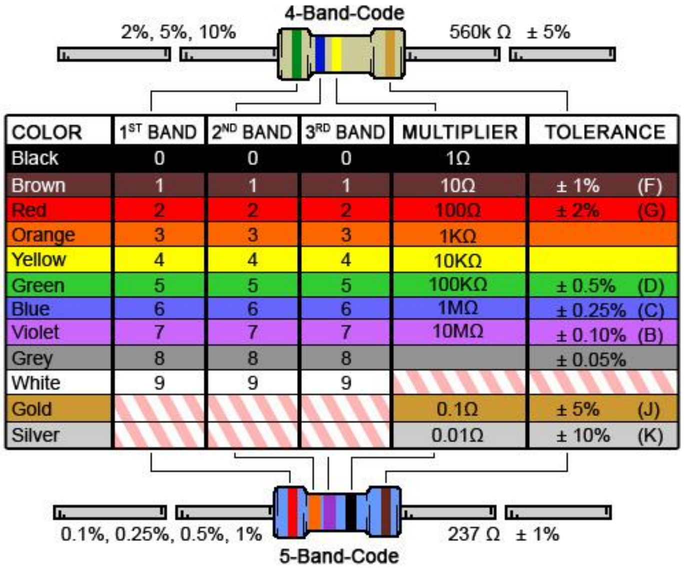


Figure 8: LED Circuit

You will need to make one modification to Ohm's law, and that is that you cannot just use the voltage of whatever battery you are using to power your LED, because the LED actually subtracts voltage from the circuit itself as it runs. This is called the "voltage drop" or "forward voltage" of the LED. So the voltage you would use when plugging values into Ohm's law would be the Voltage drop of your LED subtracted from the voltage of your battery. ($V_{Supplied}$ - V_{LED}).

Here are some tips for wiring your LED:

1. The longer prong is the positive terminal on the LED.
2. Choose a battery with a voltage higher that the forward voltage of your LED
3. After calculating the required resistance for your resistor, choose the closest resistor without going over. For instance, if you need a 380, but you only have 360 and 400, choose 400.
4. You can create higher voltage by wiring batteries together. The effect is additive, so 2 1.5V batteries would give you a 3V power supply.
5. You might notice the resistors aren't labeled. You can tell the resistance of a resistor in ohms by interpreting the colored bands on the resistor. Use the following chart:



COLOR	1ST BAND	2ND BAND	3RD BAND	MULTIPLIER	TOLERANCE
Black	0	0	0	1Ω	
Brown	1	1	1	10Ω	± 1% (F)
Red	2	2	2	100Ω	± 2% (G)
Orange	3	3	3	1KΩ	
Yellow	4	4	4	10KΩ	
Green	5	5	5	100KΩ	± 0.5% (D)
Blue	6	6	6	1MΩ	± 0.25% (C)
Violet	7	7	7	10MΩ	± 0.10% (B)
Grey	8	8	8		± 0.05%
White	9	9	9		
Gold				0.1Ω	± 5% (J)
Silver				0.01Ω	± 10% (K)

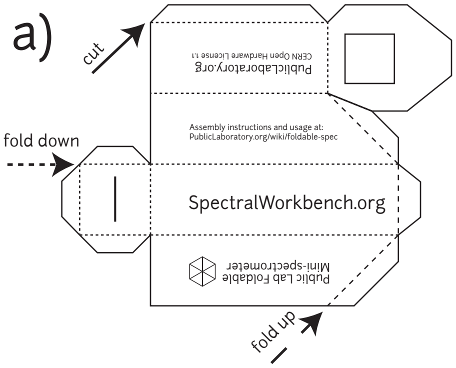
Analyzing Your Nanoparticle Sample

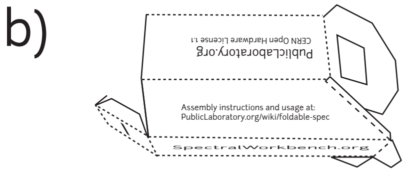
1. LED’s take time to warm up. Give your LED 5 minutes to warm up before using in order to get consistent readings. Use the free “Spectral Workbench” software at http://spectralworkbench.org/ to record your absorbance spectrum in the following steps.
2. Place a cuvette with just distilled water in your spectrometer and record the spectrum as your baseline to perform a calibration.
3. As it is now, your sample has too many nanoparticles in it to get a good reading from your spectrometer because it will absorb too much light. Fill a cuvette ¼ full with your sol, and dilute with distilled water to fill it.
4. Place your sample cuvette in your spectrometer and record the spectrum. Use the spectral workbench software to subtract your baseline and determine your absorbance’s. Dilute your sample more if necessary.
5. Determine the wavelength that give you the maximum absorption to determine the average size of your nanoparticles using the following chart:

Diameter (nm)	Peak Abs. Ag	Peak Abs. Au
10	390-405	515-520
20	390-410	524
30	400-410	526
40	405-425	530

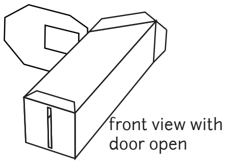
1. cut and fold

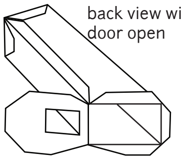
Cut along the outer edge. Fold up or down as indicated by the dotted and dashed lines. All labels should stay on the outside.





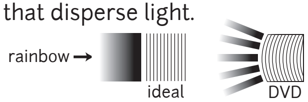
Except for the diffraction grating door, glue or tape all flaps down onto the outside.



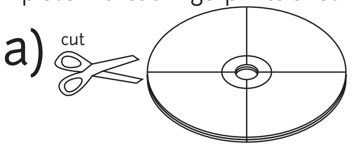


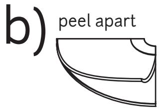
2. make a diffraction grating from a DVD-R

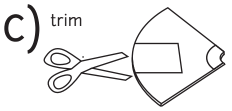
A diffraction grating is a series of close slits that disperse light.



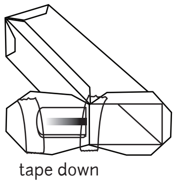
To make one from a DVD-R, split it into quarters, peel off the reflective layer and trim a small clean square out of the transparent layer. Try to pick a clean piece without fingerprints or scratches.

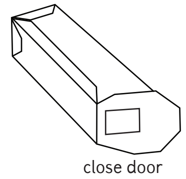






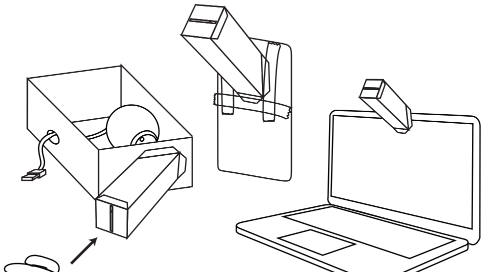
To work as a diffraction grating the DVD-R must be placed so that its grating is vertical, making a horizontal spectral rainbow. Tape your DVD piece to the inside of the spectrometer's door, then tape or glue the door closed.

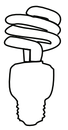




3. attach to a webcam, phone, or laptop

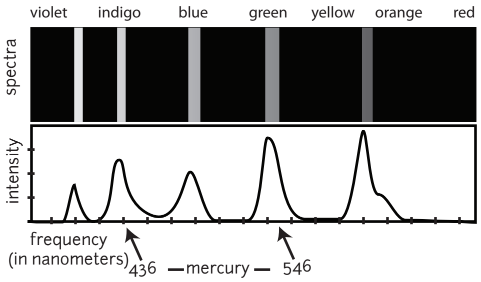
The spectrometer can be mounted on a camera phone, laptop, or with the help of a box, attached to a webcam. Line up carefully so that the rainbow is in the middle of the image, and tape down firmly so that the spectrometer stays rigid.

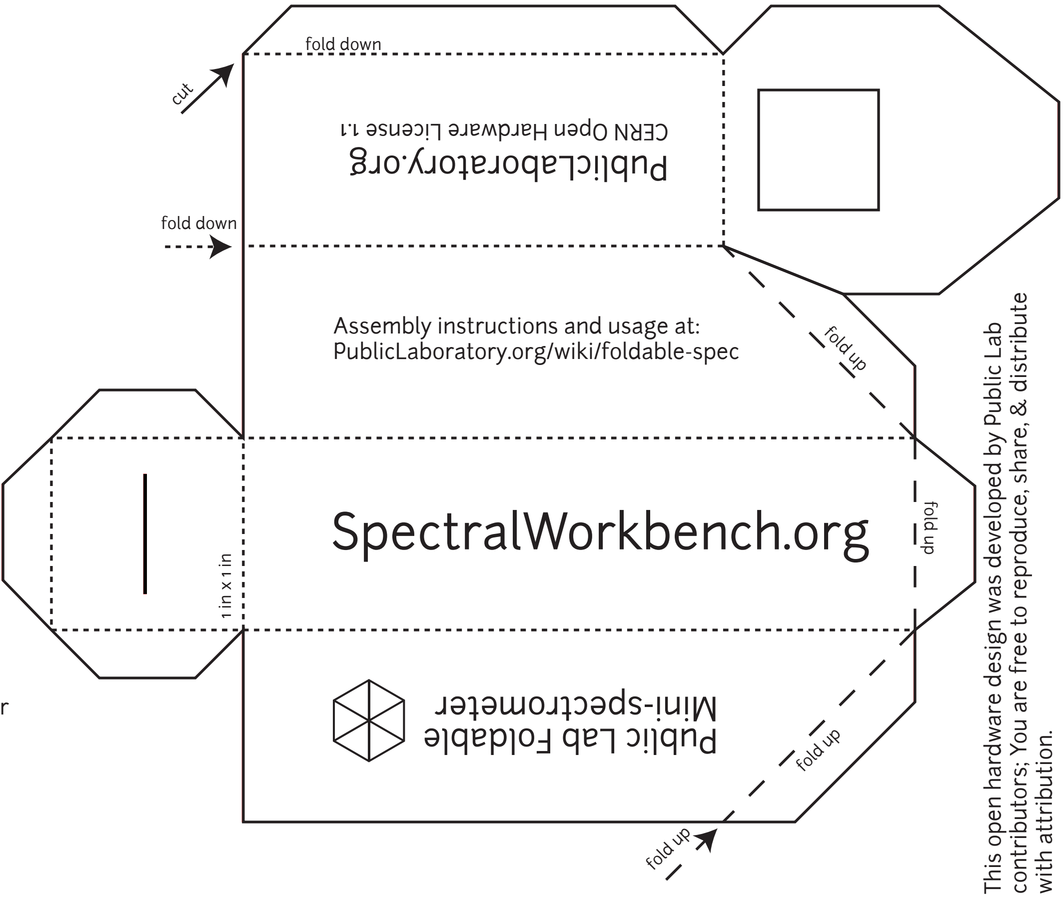




reading spectra

Every molecule emits only certain frequencies of light, and under the right conditions a spectrometer can detect these as rainbow bands. With two clear bands, the mercury in compact fluorescents makes calibration easy.

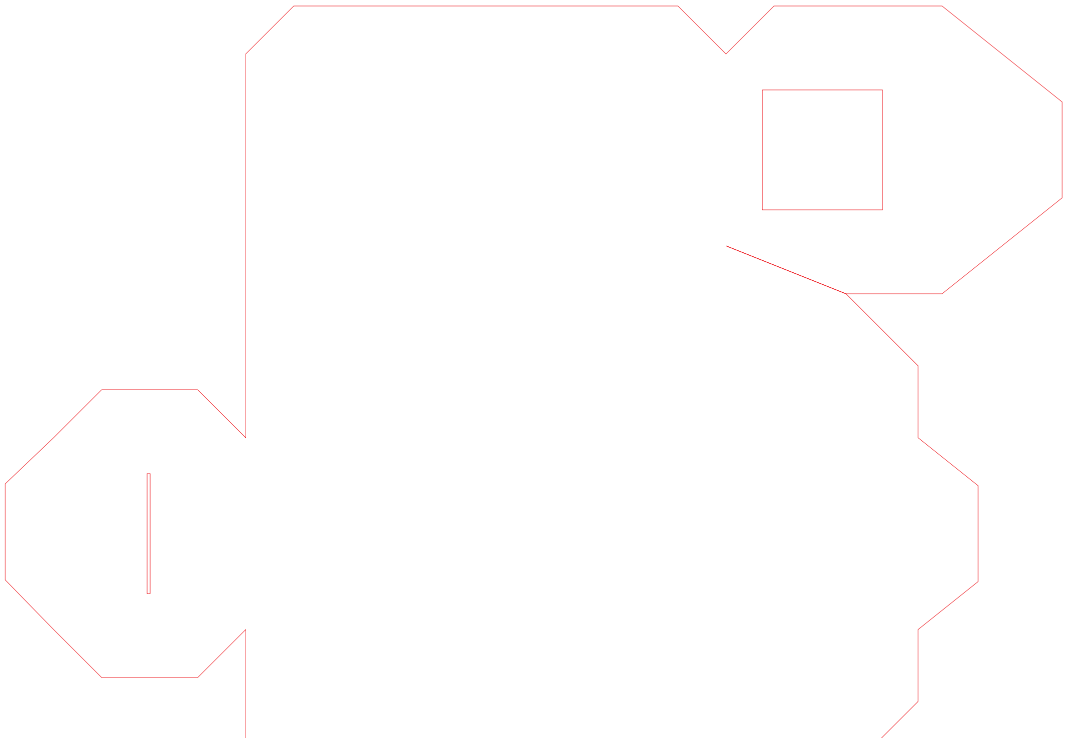




Join up, calibrate, & share spectra

Go online to Spectralworkbench.org, follow the calibration instructions, and you'll be ready to upload calibrated spectra!

Don't forget to share and publish your research as Research Notes on Publiclaboratory.org, and ask questions through the Public Laboratory Spectrometry mailing list.



Recreating the Lycurgus Cup: Nanoparticle “Stained Glass”

Background

Composite materials are materials made of at least two distinct substances that have been combined in order to create new properties that the original materials alone wouldn’t have. Nanocomposites are composites in which one of the constituent substances is present at a grain size so small that it is measured in nanometers. In this activity you will be teaming up with another lab group who synthesized a different nanoparticle than you and you will be creating a polymer nanocomposite to try and mimic the properties of the Lycurgus cup.

The Lycurgus cup is a nanocomposite of gold and silver nanoparticles, infused into mineral glass with other ions. You will be trying to create the same effects in a white, water soluble polymer called polyvinyl alcohol (PVA)

Planning

You will need to devise a plan for how to create the effect using your nanoparticles and salt. For clues, read the handout about the Lycurgus cup given to you or found online at http://www.arne-lueker.de/Objects/work/Surface%20Plamons/lycurgus.pdf . Read the section entitled “The Colour of the Cup” very carefully. Take notes on any information given that you think is relevant to recreating the effect.

Present your plan, along with any calculations that you have done, to your teacher for approval before proceeding.

Setting up Your “Stained Glass”

You can create a faux stained glass look using a sheet of Plexiglas and “liquid leading” from the craft store. Just trace the design that you want onto the sheet of Plexiglas with a black marker and go over it with the “liquid leading”. Allow it 30min to dry before working with it. Here’s an example of an intricate design. You will want to keep your design simple because of time and material constraints.

Plan to keep track of which nanoparticle Sol you place in which compartment. It will allow you to create different combinations of silver/gold/salt and try it, recording your results.

Creating the PVA Polymer Solution

Once you've decided on a plan with your groupmates for recreating the Lycurgus effect, you'll need to create a solution of the polymer to add you nanoparticles to. Polyvinyl alcohol is solution in water are high temperatures, but it requires patience and careful attention to come our right. Here are the steps:

1. Fill a 500mL beaker with 250mL of distilled water and place on a stirring hotplate.
2. Heat the water to just under boiling 88-90F. Do not allow the water to boil.
3. While waiting for your water to heat, mass out about 8 grams of PVA.
4. Once the water is heated, lightly sprinkle the polyvinyl alcohol into the water while stirring continuously. It's important that the polyvinyl alcohol be added lightly and slowly since each grain of polyvinyl alcohol must be individually "wetted" for it to go into solution. Remember, add the polyvinyl alcohol slowly while continuously stirring. Failure to stir during the addition of the polyvinyl alcohol will result in a gooey mass of wet polymer that sticks together, settles out and clings to the wall of the vessel.
5. Be very careful to monitor the temperature and not overheat, it will ruin your polymer!

Creating the "Stained Glass"

1. Using your plan discussed with your teacher, mix the appropriate quantities of silver nanoparticles, gold nanoparticles, and salt into small beakers of your warm PVA Solution and mix them in. You cannot take home you nanoparticle sols, so try different combinations of silver, gold, and salt for the different panes in your stained glass.
2. Using a dropper, drop your PVA/Nanoparticle solutions into the different panes of your "stained glass". Keep a chart of what combinations are in what pane so that you can evaluate your results when it dries!
3. Allow to dry overnight or longer, until water has evaporated to give a dry nanocomposite.

The Lycurgus Cup – A Roman Nanotechnology

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Introduction

The Lycurgus Cup (fig 1) represents one of the outstanding achievements of the ancient glass industry. This late Roman cut glass vessel is extraordinary in several respects, firstly in the method of fabrication and the exceptional workmanship involved and secondly in terms of the unusual optical effects displayed by the glass.

The Lycurgus Cup is one of a class of Roman vessels known as *cage cups* or *diatreta*, where the decoration is in openwork which stands proud from the body of the vessel, to which it is linked by shanks or bridges Typically these openwork "cages" comprise a lattice of linked circles, but a small number have figurative designs, although none of these is as elaborate or as well preserved as the Lycurgus Cup. Cage cups are generally dated to the fourth century A.D. and have been found across the Roman Empire, but the number recovered is small, and probably only in the region of 50-100 examples are known [1, 2]. They are among the most technically sophisticated glass objects produced before the modern era.

The openwork decoration of the Lycurgus Cup comprises a mythological frieze depicting the legend of King Lycurgus from the sixth book of Homer's Iliad. The figures, carved in deep relief, show the triumph of Dionysus over Lycurgus. However it is not only the cut-work design of the Cup that shows the high levels of skill involved in its production. The glass of the cup is dichroic; in direct light it resembles jade with an opaque greenish-yellow tone, but when light shines through the glass (transmitted light) it turns to a translucent ruby colour (Fig 1a and b).

The cup was acquired by the British Museum from Lord Rothschild in 1958 (with the aid of a contribution from the National Art Collection Fund) [3]. The mythological scenes on the cup depict the death of Lycurgus, King of the Edoni in Thrace at the hands of Dionysus and his followers. A man of violent temper, Lycurgus attacked Dionysus and one of his

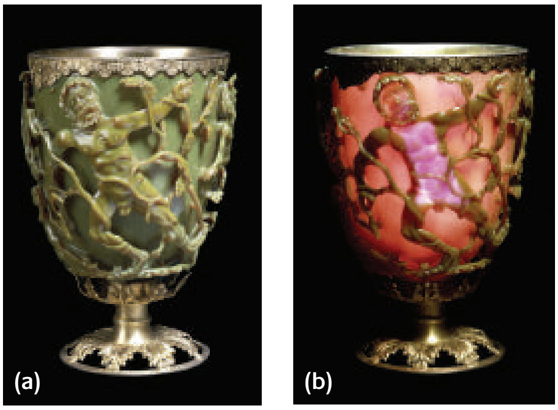
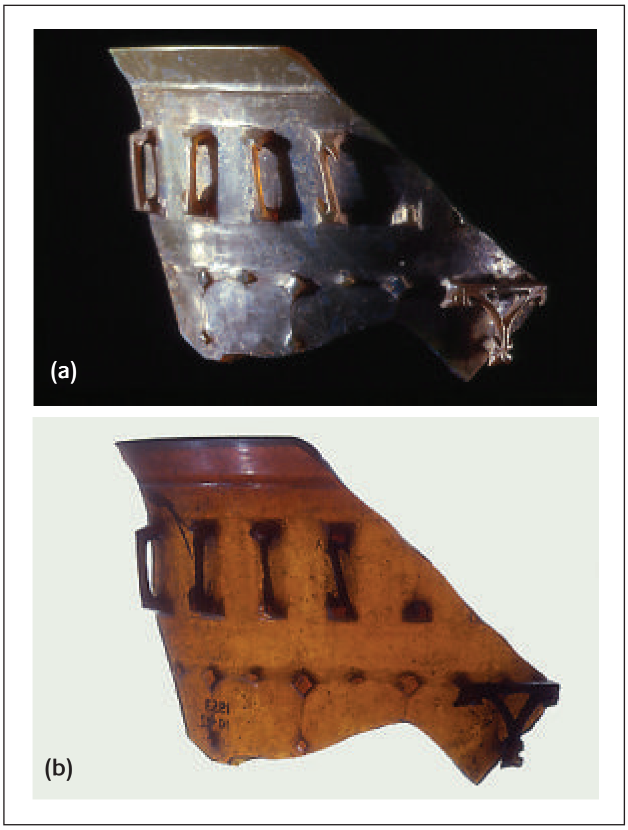


Figure 1 (a and b)
The Lycurgus Cup *1958,1202.1 in reflected (a) and transmitted (b) light. Scene showing Lycurgus being enmeshed by Ambrosia, now transformed into a vine-shoot. Department of Prehistory and Europe, The British Museum. Height: 16.5 cm (with modern metal mounts), diameter: 13.2 cm. © The Trustees of the British Museum*

Figure 2
The Lycurgus Cup *1958,1202.1, scene showing Dionysus instructing his followers to destroy Lycurgus. © The Trustees of the British Museum*

Figure 3 (a and b)
Fragment of diatretum *1953,1022.2 (h. 6.5 cm; d. 8 cm) in reflected (a) and transmitted (b) light. Department of Greek and Roman Antiquities, The British Museum. © The Trustees of the British Museum*



maenads, Ambrosia. Ambrosia called out to Mother Earth, who transformed her into a vine. She then coiled herself about the king, and held him captive. The cup shows this moment when Lycurgus is enmeshed in vines by the metamorphosing nymph Ambrosia, while Dionysus with his thyrsos and panther (Fig 2), a Pan and a satyr torment him for his evil behaviour. It has been thought that the theme of this myth - the triumph of Dionysus over Lycurgus - might have been chosen to refer to a contemporary political event, the defeat of the emperor Licinius (reigned AD 308-24) by Constantine in AD 324.

No precise parallels of this depiction of the myth exist but a number of versions of Dionysiac theme, related artistically or iconographically to the Cup, are known – in mosaic decoration, sculpture, coins and other decorated vessels [4]. According to Harden, the depictions that are perhaps the closest in terms of the drama of the scene are the Lycurgus and Ambrosia group in the centre of the frieze on the 2nd century Borghese sarcophagus (now in the Villa Taverna at Frascati) and the mosaic decoration in the apse of the *triclinium* of the 4th century Villa Romana del Casale at Piazza Armerina in Sicily.

The Lycurgus Cup is first mentioned in print in 1845 and is thought to have been acquired by the Rothschild family shortly afterwards, but the early history of the cup is unknown (as is the find spot) [5, 6]. However, no detailed study of the Cup was undertaken until 1950 when it was examined, at the request of Lord Rothschild, by Harden and Toynbee, resulting in their definitive article in *Archaeologia* in 1959. Because of the highly unusual colour and optical properties of the piece, there was initially some debate over whether the Cup was indeed glass as it seemed impossible, with the technical knowledge of ancient glass-working at the time, to produce such an effect. However, although noting that it exhibited a number of curious phenomena, Dr G. F. Claringbull, Keeper of the Department of Mineralogy in the British Museum (Natural History) concluded that it was made of glass (rather than opal or jade) [7], a result that was later confirmed in 1959 by X-ray diffraction [8].

Although now lost, due to breakage at some point in the past, the cup must originally have had an openwork base and may have had a taller rim [9]. The current silver-gilt foot with open-work vine leaves and the rim mount of leaf ornament are thought to date to the eighteenth or nineteenth centuries. On stylistic grounds, and also from the dates of comparative pieces (some of which are associated with more easily dated objects), the Cup has been dated to the 4th century AD. Harden and Toynbee suggested that it is probably of Italian manufacture, although they considered an Alexandrian origin also possible.

The colour of the Cup

The most remarkable aspect of the Cup is its colour. Only a handful of other ancient glasses, all of them Roman, change colour this way [10]; several of these are *diatreta,* with the more typical geometric decoration, but tend to show a less spectacular colour change (see Fig 3 a and b). It is therefore likely that the Lycurgus Cup was a special commission produced by a workshop which already made highly specialised and expensive glass products.

When the glass first came to scholarly attention in the 1950s the base, which had itself been added sometime in the early modern period to cover or repair earlier damage, was removed and some loose glass fragments from the original base were found (one showing signs of decoration but the other two being amorphous). Following preliminary study at the British Museum, including qualitative spectrographic analysis, the British Museum sent a sample in 1959 to the research laboratories of the General Electric Company Ltd (GEC) at Wembley for more detailed micro-analysis to try to determine the colorant [11]. Even at this stage, B.S. Cooper at GEC noted that the presence of trace quantities of gold, silver and other elements in the glass might be responsible for the complex colour and scattering effects of the glass and suggests that the colour may arise from "a combination of the "physical optical" colouration of colloidal metal in the glass plus, possibly, some pigmentation from metal combinations" [12].

Chemical analysis at GEC showed the glass to be of the soda-lime-silica type, similar to most other Roman glass (and to modern window and bottle glass) [13], containing in addition about 0.5% of manganese [14, 15]. In addition, a number of trace elements including silver and gold make up the final 1%. It was further suggested that the unique optical characteristics of the glass might be connected with the presence in the glass of colloidal gold. It was also noted that "to obtain the colouring constituents in the state necessary to give the remarkable glass its special qualities a critical combination of conditions was required during manufacture. These would be associated with the composition, including the presence of minor constituents, time and temperature of founding, chemical conditions during founding, and subsequent heat treatment. It is perhaps not altogether surprising that no other example of a glass having such unusual properties has come to light" [16]. Note that at that time, researchers were unaware of the handful of other examples of Roman dichroic glass that have since been recognised.

In the continuing quest to understand the remarkable colour effect, in 1962 a sample was sent to Dr Robert Brill of the Corning Museum of Glass, along with a sample of the diatretum shown in Fig 3a and b [17]. Work carried out by Brill, latterly in collaboration with GEC, on the Lycurgus Cup and diatretum samples (and on another example of dichroic glass) as well as on experimental glass melts confirmed that the dichroism was linked to the presence of minute amounts of gold (about 40 ppm) and silver (about 300 ppm) in the glass [18, 19]. However, simply adding traces of gold and silver to glass would not produce these unique optical properties and the critical factor was believed to be to be the formation of minute submicroscopic crystals or *colloids* of the metals. Colloidal systems can give rise to light scattering phenomena that result in dichroic effects. It was suggested that both the gold and silver contributed to the colour, the gold component being mainly responsible for the reddish transmission and the silver for the greenish reflection.

The work of Brill and GEC suggested that glass containing minute amounts of gold and silver had been heat treated, using suitable reducing agents, to produce colloidal metallic particles within the glass which resulted in the green-red dichroic effects. The colours produced in such a process would have depended upon the precise colloidal concentration and the particle diameter and are highly dependent on the proportions and oxidation states of certain elements, the time and temperature of heating and probably the atmosphere during heating [20].

Using the then available technology, Brill was unable to demonstrate unequivocally the presence of metallic particles. The relative contributions of silver and gold to the colourant effect, and whether the inferred metal colloids were a gold-silver alloy or separate particles of silver and gold, were unclear. Therefore, in the late 1980s, a further small fragment of the Cup was subjected to examination by Barber and Freestone [21]. Analytical transmission electron microscopy revealed the presence of minute particles of metal, typically 50-100 nm in diameter (see Fig 4). X-ray analysis showed that these nanoparticles are silver-gold alloy, with a ratio of silver to gold of about 7:3, containing in addition about 10% copper. The identification of silver-gold alloy particles confirms the earlier inference that the dichroic effect is caused by colloidal metal. In addition to these metallic particles, the glass was shown to contain numerous small particles (15-100 nm) that were shown to be particles of sodium chloride (see Fig 5); the chlorine probably derived from the mineral salts used to supply the alkali during the glass manufacture [22].

Of interest is the high gold to silver ratio of the alloy particles in the glass (c. 3:7) relative to the gold:silver (Au:Ag) ratio in the glass as a whole (c. 1:7). This is a reflection of the relative reduction potentials of Ag^+ and Au^+ and indicates that a substantial proportion of the silver remained dissolved in the silicate matrix after precipitation of the alloy particles. Recent work by Wagner and co-workers indicates that gold dissolves in glass in the monovalent form [23]. The reduction of previously dissolved silver and gold, during heat-treatment of the glass, will have caused the fine dispersion of silver-gold nanoparticles responsible for the colour. A key agent likely to have been involved in the redox reaction that reduced the silver and gold is the polyvalent element antimony, which is present in the glass at around 0.3%. Antimony was commonly added to glass in the Roman period, as both an oxidising agent (decolourant) and as an opacifier.

The fine particles of sodium chloride observed (fig. 5) are likely to have exsolved from the glass during the heat-treatment that caused the crystallisation of the alloy particles, but as they are colourless and their refractive index close to that of soda-lime-silica glass, their direct contribution to the

Figure 4
Transmission electron microscopy (TEM) image of a silver-gold alloy particle within the glass of the Lycurgus Cup [21]. © The Trustees of the British Museum.

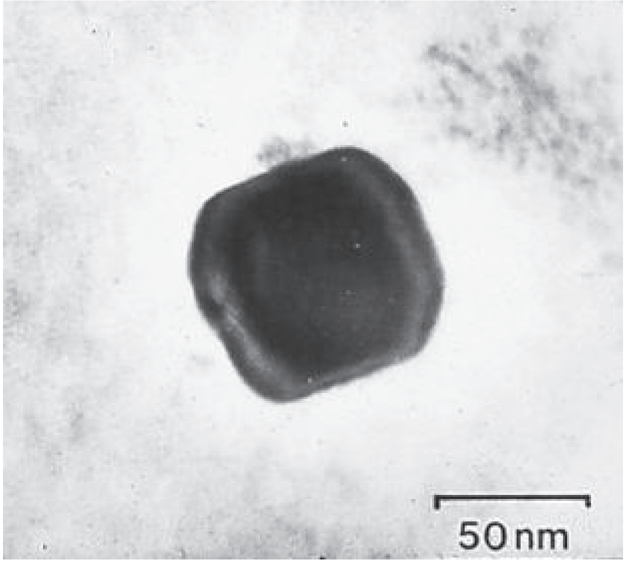


Figure 5
TEM image of sodium chloride particles within the glass of the Lycurgus Cup [21]. © The Trustees of the British Museum

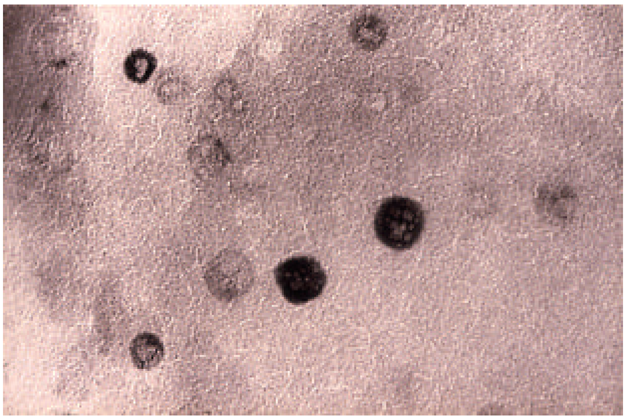


Figure 6 (a and b)
Glass blank made at the Corning Glassworks as a replica of the blank for the Lycurgus Cup in reflected (a) and transmitted (b) light . © The Trustees of the British Museum

colour of the glass is likely to have been minimal. However, halide additions have been found to promote the development of colour in gold ruby glasses [24] so it is possible that the sodium chloride in the glass indirectly contributed to its colour.

Fabrication of the Cup

The Cup and other cut cage vessels are generally considered to have been made by cutting and grinding the open work decoration out of a thick-walled blank of cast or blown glass, leaving small glass bridges linking the cutwork to the vessel [25]. It is believed that glass-makers (*vitrearii*) who made blanks were different from the glass cutters (*diatretarii*) who decorated and finished them. In their article Harden and Toynbee dismiss the view that the cage was carved from a separate blank and later joined to the inner vessel and cite Fremersdorf's article of 1930 as giving the best account of the manufacturing process for such vessels [26]. They also suggest that the hollows and borings behind the figures on the interior of the cup (discussed below) would also argue against the decorated Cup having been mould-blown. The Corning Glassworks produced a replica of the blank in the 1960s and this gives an impression of the nature of the original blank, which must have had walls about 15 mm thick (see Fig 6 a and b).

A number of replication studies have been based on this approach and, following a detailed examination of the surface of the Cup using low power microscopy, Scott suggested in 1995 that the Lycurgus Cup had been cut and polished using rotary wheels ranging from 6 to 12 mm in diameter [27-28]. However, more recently Lierke has suggested that many current assumptions about early glass working techniques are incorrect. In particular she has suggested that diatreta such as the Lycurgus Cup were not formed by cold cutting of glass blanks but by moulding [29-31].

This debate and recent research at the British Museum on the carving techniques of early semi-precious stones prompted an investigation of the cutting technique of the Lycurgus Cup at the Museum. The results of this study are summarised here but will be published in full elsewhere. The fragment of openwork (vine stem) found when the base of the Cup was removed was examined for traces of tool marks with a binocular microscope (see Fig 7) and a scanning electron microscope. The methodology adopted was based on that originally

Figure 7

Macroscopic photography of the cut-work fragment from the Lycurgus Cup in reflected light. © The Trustees of the British Museum

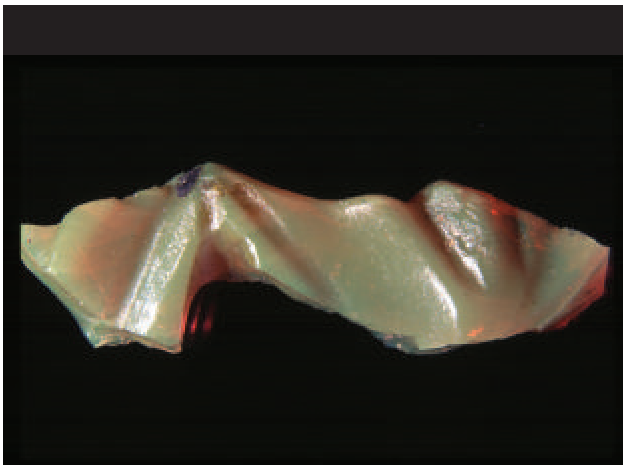


Figure 8

Backscattered electron image taken in the scanning electron microscope of the cut-work fragment from the Lycurgus Cup, showing the back surface of the fragment and the crescent-shaped cuts on the side, suggestive of rotary abrasion and polishing. © The Trustees of the British Museum

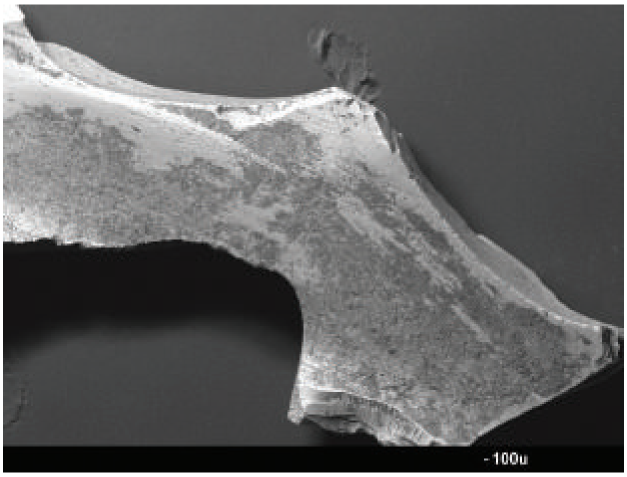
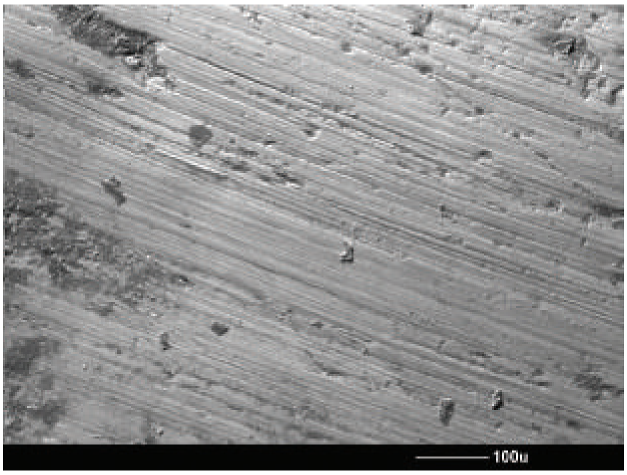


Figure 9

Backscattered electron image taken in the scanning electron microscope of the cut-work fragment from the Lycurgus Cup, showing coarse and fine abrasion striations on the back of the fragment. © The Trustees of the British Museum



developed by Sax, Meeks and Collon to investigate methods of stone engraving in the ancient world [32].

In the ancient Classical world, decorative gemstones of this type would have usually been worked using rotary methods of abrasion. Copper, bronze or iron wheels would have been attached to the end of a spindle, mounted on a lathe and rotated with a bow drill. Drills, both solid and tubular, as well as non-rotary saws and files were also used. Metal tools are too soft to have working surfaces themselves. They would have been charged with abrasive slurry, made by mixing a fine-grained abrasive sand, such as quartz or emery (corundum), with water or oil. These tools were then applied to wear away or 'cut' the stone [33]. Pliny indicates that Roman lapidaries used slivers of diamond to cut hard stones [34], but it seems likely that diamond abrasive would have only occasionally been available.

Examination of the open-work glass fragment showed that faint tool marks remain on most of the surfaces. The tool marks provide extensive evidence for mechanical abrasion and polishing not only on the outer surface but also on the sides and underneath the fragment. The sides of crescent-shaped cuts through the glass suggest the use of rotary abrasion and polishing (see Fig 8). In contrast, the front and the back of the open work appear to have been worked with non-rotary files and abrasives. The evidence for the mechanical removal of glass from the undercut back area of the fragment suggests that cutting and grinding rather than moulding of soft glass was the method of producing the lattice design (see Fig 9). The very highly polished surfaces of the fragment, once thought to have been fire polished, seems to have been produced purely by mechanical means as groups of regular fine parallel striations can be seen.

The skill of the craftsman consisted not only in the cutting of such an intricate design in such a fragile material, but also in the design and layout of the figures, and the advantage taken of the colour effects. For example, the body of Lycurgus is cut from an area of the glass which is a slightly different colour from the rest; as shown in figs 1a & b it is more violet in transmitted light and more yellow in reflection. In addition the glass inside the Cup and behind the bodies of the figures, which are not completely undercut, has been hollowed or bored out. This would have allowed similar amounts of light to pass through the bodies and the adjacent walls of the vessel so that the colour change was seen to maximum advantage [35].

The context of the Cup

Before the first century BC, glass had been a relatively uncommon material, and glass vessels were made in strong and often opaque colours. From the late first century BC, however, the new technique of glass blowing caused a revolution – colourless or weak blue-green vessels became widely used over a much wider cross-section of society. The mature Roman glass industry operated on a massive scale.

Glass was made in Egypt and Palestine in large tank furnaces which melted many tonnes of sand and soda at a time, and was distributed as raw lumps across the Empire where it could be remelted and made into artefacts. An illustration of the scale of glassmaking is provided by the Baths of Caracella, a major public building dating to the early third century A.D., which used some 350 tonnes of glass in wall and vault mosaics and windows [36, 37].

The Lycurgus Cup and the related vessels must be seen in the context of such a long-lived large-scale production of glass. The small number of cage cups represents a minute fraction of the total amount of glass in circulation at the time, and those showing so-called "dichroic" colour changes are a small fraction of this group. A limited number of other Roman-period glasses appear to have been coloured by gold, e.g. certain pinks in *opus sectile* panels from the Mediterranean region. Even the colours of the other dichroic glasses do not replicate the Lycurgus effect exactly. For example, the cage cup fragment shown in figure 3a and b is dichroic from opalescent buff on the surface to a clear brown in transmitted light. This vessel has a high silver content (2270 ppm) and only 13 ppm gold [36], so that the colourant effect is likely to be due to nanoparticles that are largely silver.

The Lycurgus Cup is therefore made of a very rare glass, and this glass seems to have been saved for a very rare type of vessel – a figurative cage cup. The execution of the openwork was carried out in a very skilful manner and must surely have been the work of a master lapidary. Even using modern power-driven tools, this type of vessel takes a great deal of time to complete [37-40]. Unlike the majority of glass of its time, the Cup, with its unique colour and decoration, must have been highly valued and intended for some special purpose. Remarkably, Whitehouse has drawn attention to a reference in the ancient literature which might well describe the Cup, or a similar vessel [41]. In his life of the third century pretender Saturninus, Vopiscus, who wrote in the early fourth century A.D., reports a letter supposedly written by Hadrian to his brother-in-law Severianus in Rome "I have sent you parti-coloured cups that change colour, presented to me by the priest of a temple. They are specially dedicated to you and my sister. I would like you to use them at banquets on feast days." Here then, is clear evidence that vessels that change colour were being made in the early fourth century (Vopiscus had seen them) and that they were prestigious items, worthy as gifts from the emperor to his close relatives. Furthermore, they were used on special occasions, on feast days. Whitehouse goes on to speculate that the change in colour from green to red symbolises the ripening of the grape, and that the depictions of vines on the Cup, as well as Dionysus, the Roman god of wine triumphing over Lycurgus, are strong evidence in support of this. Thus the Cup may have been specially intended for use at banquets dedicated to Dionysus.

The colour of the glass is therefore likely to be the reason for the creation of the Cup as it is seen, and is what provides its unique character. However, our understanding of the production of this glass is unclear. It seems very likely that, in the Roman period, the workshops which produced the "base" uncoloured glass, those that coloured the glass and those that carried out the cutting, were separate. Coloured opaque glasses were widely used in mosaics at this time, and it is likely that they were produced by a limited number of glass workshops which specialised in the colouring process, then sold on to mosaicists in the form of cakes, which could be broken up into the desired size. We can speculate that a colouring workshop produced one or more batches of glass coloured with gold and silver, recognised their importance, and sold them on to lapidary shops for cutting, perhaps in the form of blanks resembling that in Figs 6a and b. As some other cage cups are also coloured or have coloured cages, in blues, greens and yellows, it is possible that the workshop that made the Lycurgus glass was also supplying glass to the lapidaries who cut these.

It is clear that the colouring of glass using gold and silver was far from routine and something of a hit and miss affair. There were a large number of factors to control, including the overall concentration of the metals, their distribution and the time and temperature at which the glass was heat-treated [42]. It seems that not even the absolute and relative concentrations of gold and silver were easily controlled, let alone the distribution and growth of particles. Gold and silver concentrations vary widely between the few examples known [43], and even the colour of the Lycurgus blank was not homogeneous (see above). It is quite likely that the glassmakers were unaware that gold was the critical colourant, as most of these glasses are richer in silver. To introduce gold as a component of a gold-silver alloy (electrum) would make sense, as it would have allowed a more even distribution of the gold in solution. The addition of metals or metal oxides to colour glass was familiar to Roman glassmakers; for example, opaque red and brown glasses were produced by the addition of copper. Freestone et al. have speculated that the oxidised by-products of metallurgical processes ("dross", "slag" etc) were sometimes acquired to colour glass, and that this might explain how the "Lycurgus effect" was discovered [44]. It would also explain the relatively high levels of copper and lead oxides which are also present in the glass. However, there are a number of other possibilities which allow for the chance "discovery" of gold ruby, including accidents in the production of glasses with gold leaf decoration.

However the colouration of glass by gold was discovered, it appears that replicating gold ruby was a challenge to the Roman glassmaker; the technology was very restricted and does not appear to have outlasted the fourth century. While the production of red glass using gold is mentioned in medieval Islamic writings, examples of such glass have yet to be confirmed. Although the red "stained" glass of medieval church windows is sometimes suggested to be gold ruby, the colourant has been found to be copper in all cases so far analysed. The production of gold ruby on anything like a routine basis does not appear to have taken place until the seventeenth century in Europe, a discovery often credited to Johann Kunckel, a German glassmaker and chemist [45].

Conclusion

The Lycurgus Cup demonstrates a short-lived technology developed in the fourth century A.D. by Roman glass-workers. They discovered that glass could be coloured red and unusual colour change effects generated by the addition of a precious metal bearing material when the glass was molten. We now understand that these effects are due to the development of nanoparticles in the glass. However, the inability to control the colourant process meant that relatively few glasses of this type were produced, and even fewer survive. The Cup is the outstanding example of this technology in every respect – its outstanding cut work and red-green dichroism render it a unique record.

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3 Harden D.B., Hellenkemper H., Painter K. and Whitehouse D. (1987) *Glass of the Caesars*, Olivetti, Milan, pp. 245-249 (catalogue entry 139)

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13 SiO_2 73.5%; Na_2O 13.0; K_2O 0.9; CaO 6.0; MgO 2.0; Al_2O_3 2.9; B_2O_3 0.1; MnO 0.5 (last 1% suggested to include traces of Fe, Ti, Ag, Au, Sb, Pb, Sn, Ba, Sr)

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